

An Example of Using CASTEP-NMR from the beginning

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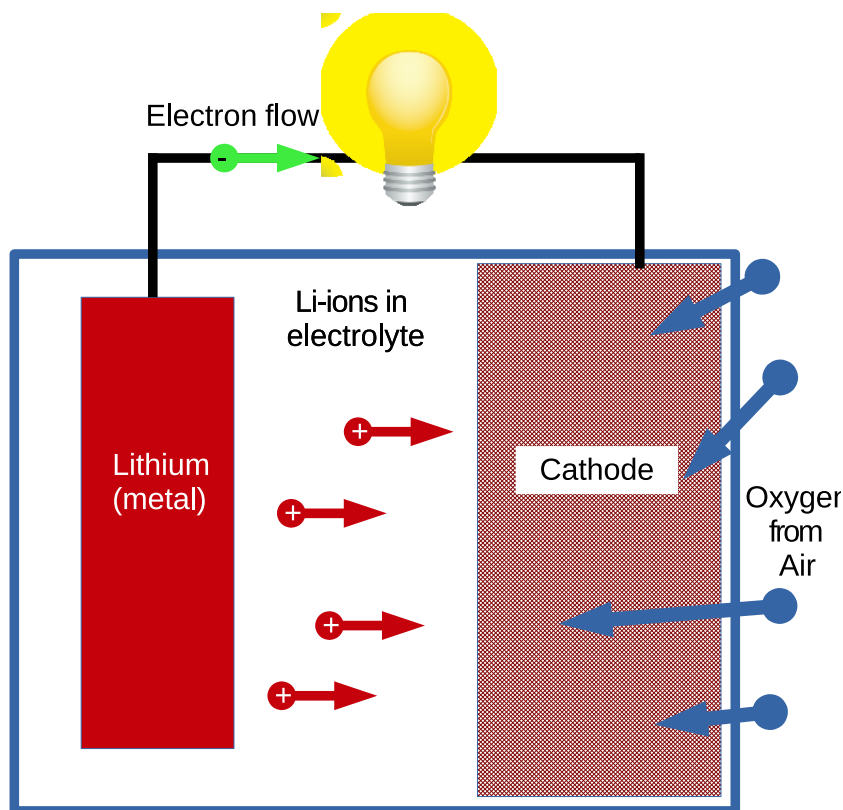


Figure 1: Lithium-Air Battery

1 Objective

A company has patented a new electrolyte for a lithium-air battery (LAB). LABs have the potential to revolutionise energy storage, due to their larger energy densities than conventional lithium-ion batteries. In their LAB, the anode is made from lithium metal, and the cathode relies on oxygen from the air to reduce the lithium ions.

However they have had a small incident. The battery cell exploded when charged quickly at a C/60 rate, (*i.e.* complete charge in 1 minute). Obviously the company would like to understand what went wrong. From one of the fragments of the LAB some substance was scraped off. The experimentalists have put this substance in an NMR spectrometer and found peaks at 45 part per million (ppm) for the ^{17}O isotropic chemical shift. They suspect that it could be either Li_2O_2 , the expected cathode phase, or more worryingly Li_2O , and the wonder electrolyte catastrophically degrades the cell on fast charge.

Your job is to find out which it is.

2 Introduction to CASTEP

2.1 CASTEP Overview

We begin with an overview of CASTEP. We assume that the reader has been introduced to the fundamentals of density-functional theory and the basic concepts of first-principles materials simulation, but has not used CASTEP or performed a magnetic resonance calculation before. CASTEP is a density-functional theory code based on the plane-wave pseudopotential method. The Kohn-Sham orbitals are expressed as a sum of plane-waves and, for computational efficiency, the ionic potential is described using a pseudopotential. CASTEP can not only find the electronic ground state of a crystal or molecule in a simulation cell obeying periodic boundary conditions, but will also calculate the forces on the ions, so that one may optimise the geometry of the given crystal structure, and/or perform molecular dynamics calculations. After finding the electronic ground state, one may obtain the electronic and phonon density of states, phonon and electronic dispersion (band structures), electronic charge density and Kohn-Sham eigenvalues and use these as a stepping stone to obtaining real experimental observables about the system, such as NMR chemical shifts, hyperfine parameters, electron-energy-loss, XANES, IR and Raman spectroscopies.

CASTEP calculations rely on two main input files. The `seedname.cell` which contains information about the simulation cell and the `seedname.param` file which contains information about how to perform the simulation, including the Hamiltonian to be used, and how it should be solved for the charge density.

Keywords can be of the type `keyword : value`. Or a block such as:

```
%BLOCK LATTICE_CART
3.0 0.0 0.0
0.0 3.0 0.0
0.0 0.0 3.0
%ENDBLOCK LATTICE_CART
```

which, in this case, creates a $3.0 \times 3.0 \times 3.0$ Å simulation cell.

You can always search for help, by using `castep -s <fragment of keyword>` to search for a fragment of a keyword, then `castep -h <keyword>` to get more information about it.

2.2 Obtaining the Electronic Ground State of Silicon

2.2.1 Inputs

It would be helpful to perform a couple of CASTEP examples before attempting to tackle the problem as posed in Section 1. So first, let us perform the simplest DFT calculation on crystalline silicon.

- Create a file called `Si2.cell` containing the text found in Appendix A. Note that a line beginning with an exclamation mark is a comment and ignored by CASTEP. They have been included as an aid to your understanding.
- Any keyword that is not clear can be investigated using `castep -h <keyword>`.

- Now also create the file `Si2.param` containing the text found in Appendix B.
- Run CASTEP by:

```
castep Si2
```

or, if you have the parallel version installed and want to run on 4 cores, using:

```
mpirun -np 4 castep Si2
```

N.B. Your CASTEP binary may go by a different name see Appendix D.

2.2.2 Outputs

When the calculation has completed you will have a `Si2.castep` output file. It is a good idea to familiarise yourself with this. In order, you will find:

- **CASTEP begins with its header.**
- **Information on the castep binary.** Also found using `castep -v` on the command line.
- **Generate a silicon pseudopotential *on-the-fly*.** Also written out to `Si_OTF.usp`.
- **Discussion of parallelisation strategy.**
- **Information about input keywords and any other defaults set.**
- **Information about the simulation cell, vectors and content.**
- **Details of the atomic species and pseudopotentials.** It has generated the silicon pseudopotential *on-the-fly*, if you had used a custom pseudopotential, the path to it would be shown here.
- **Details of the k-point grid and the number of k-points used.** To obey the `KPOINT_MP_SPACING` keyword, CASTEP is using a $4 \times 4 \times 4$ k-point grid. Due to the cell symmetry, it has reduced these 64 k-points to 10.
- **Details of the symmetry found.** In our case $Fd\bar{3}m$.
- **Any cell constraints applied to cell.** We have not added any. If we were doing high pressure calculations we might add pressure, and it would be reported here.
- **Memory estimate per process.** If this number is greater than the amount of memory you have per thread, then CASTEP may crash. Due to the way that modern compilers are designed, they will allocate memory on write *not on allocate*. This makes it very difficult for CASTEP to exit gracefully under these circumstances.

- **The main SCF loop obtaining the 0 K electron total energy.** In our case -340.969 eV per cell ¹.
- **Details of the forces on the atoms.** We do not have any forces on our atoms since, they are zero by symmetry.
- **The stress tensor and the pressure on the cell.** However, the cell vectors we have chosen are too small, and we do have some pressure, of around 0.5 GPa.
- **Muliken atomic and bond analysis.** This author does not have much time for this sort of analysis. The reported bond lengths can be useful though.
- **Details of parallel efficiency.**
- **End of calculation.**

2.2.3 Results You Can Trust

As a golden rule: all computational results are to be suspected until you have proven otherwise. We have made many assumptions when performing this calculation, and we cannot draw conclusions from the simulation until we can show that these assumptions do not change the result of the simulation. If we cannot eliminate them, we should at least be aware of the likely biases arising from these approximations.

You should now plot graphs of the 0 K energy and the pressure when changing:

- The basis set from 100 eV to 700 eV. If you pick a few values you can plot $\text{CUT_OFF_ENERGY}^{-1}$ and find the infinite basis set limit.
- The BZ sampling from $2\pi \times 0.1 \text{ \AA}^{-1}$ to $2\pi \times 0.03 \text{ \AA}^{-1}$. You may get jumps in your results as CASTEP converts these spacings to a grid with integer numbers of point in each direction. You might like to use `KPOINT_MP_GRID` instead. Use the help facility described in Section 2.1 to find out how.
- The exchange-correlation functional. You might like to try LDA and PBESOL and see how your convergence curves change.
- For the paranoid, you might like to playing with the Fourier transform grids. `GRID_SCALE` is set to the default of 1.75. It can be argued that 2.00 is a better value. `FINE_GRID_SCALE` is never less than `GRID_SCALE`, in some cases going beyond 2.00 can get you a more accurate answer.

2.3 Lattice Parameters of Silicon

You should now happy that the above calculation is giving the right DFT answer², and have an idea of what values must be set to get converged forces, energies and pressures.

¹It is worth wondering why you do not get exactly the same answer every time. Look up the `RAND_SEED` keyword.

²*N.B* That's not the same as the experimental answer! Or the right answer which is even more awkward to define.

You can see that lattice vectors we used were not quite right and there was some stress on the cell. We can find the 0 GPa lattice constant by performing a geometry optimisation calculation.

For this exercise we care about getting forces and stresses accurate, but not about the total energy. From the previous example you should know what values give you a converged pressure, so we can modify the input files with these values and also set **TASK: geometryoptimization** and now **add** to the bottom of the **Si2.param** file the lines found in Appendix C.

- What are the lattice parameters using the PBE functional?
- How does using the LDA functional change this?
- It has been argued that the PBEsol functional is best for obtaining the lattice parameter of solids – do you agree in the case of silicon?

3 GIPAW NMR Calculation with CASTEP

3.1 NMR Calculations

I have deliberately given you a real example, as I think it will be more interesting than just looking at the chemical shifts of a caffeine molecule³. It may be that the example is a little hard to get to full convergence on a laptop. I can certainly manage it with 6 cores of Intel(R) Xeon(R) CPU E5-2640 0 @ 2.50GHz interactively. But to be sure you're converged you may need to rerun the calculations during a coffee break or let them run overnight. It is always this way with calculations, a couple of hours to find something interesting, then may weeks convincing oneself that it is robust.

3.2 NMR Theory

GIPAW-NMR calculates, amongst other magnetic resonance parameters, the full chemical shielding tensor of a nucleus. Experimentalists generally report the isotropic part of this shielding tensor, σ_{iso} relative to another, reference material, that they have measured, σ_{ref} . This allows their results to be magnetic field independent, and groups with different sized magnets can compare results with ease. Hence they talk about the chemical shift δ_{iso} from some reference. Where $\delta_{\text{iso}} = \sigma_{\text{ref}} - \sigma_{\text{iso}}$.

Since we are working with oxygen, the simplest reference I can think of is low quartz SiO_2 ⁴. Low quartz SiO_2 has an experimental shift of $\delta_{\text{iso}} = 40.8$ ppm.

In this case we calculate a reference as: $\sigma_{\text{ref}}^{\text{calc}} = \delta_{\text{iso}}^{\text{expt}}(\text{SiO}_2) + \sigma_{\text{iso}}^{\text{calc}}(\text{SiO}_2)$ and we obtain the chemical shift of our sample from:

$$\delta_{\text{iso}}(\text{sample}) = \sigma_{\text{ref}}^{\text{calc}} - \sigma_{\text{iso}}^{\text{calc}}(\text{sample}) .$$

Hence we must perform calculations on three different structures.

³The keen or contrary could use <http://cactus.nci.nih.gov/translate/> to obtain a **pdb** file from the SMILES string for caffeine CN1C=NC2=C1C(=O)N(C)C(=O)N2C, or any other small pharmaceutical molecule. Then use the **pdb2cell** script (or **check2xsf**) to make a **cell** file.

⁴Isolated molecules would be another easy choice to calculate, but somewhat more difficult to obtain the commensurate experimental result.

3.3 Obtaining the Crystal Structures

First, we require the crystal structures of Li_2O_2 , Li_2O and SiO_2 . We could do with a “best guess” of these structures.⁵ These can be obtained from the Inorganic Crystal Structure Database (ICSD).

- Go to <http://icsd.cds.rsc.org/>, your IP address should be verified by the Royal society of Chemistry.
- Go to Basic Search and retrieve
- Composition : Li O
- Number of elements : 2 and press enter.
- You should now have all of the crystal structures of Li_xO_y since 1913.
- We’ll take the CaF_2 structure. So click the check-box to its left.
- Export data
- Enter a sensible seedname
- Click on single cif and save the cif file to your computer.
- You should have a Python program installed called `cif2cell` which will allow us to convert the cif file to a CASTEP cell file. The command is `cif2cell seedname.cif -p castep`
- You should now have a new cell file appear.

Whilst technically correct this new cell file is not in the same style as the ones you’ve been introduced to above. So you may decide to throw away everything other than the lattice vectors and the atomic positions. (N.B. It’s not necessary to add `symmetry_generate` since the cif file contains the symmetry operations explicitly)

3.4 NMR Calculations

Check the convergence parameters for accurate forces and geometry optimise.

Using these optimised cell parameters (*i.e.* those in the seed-out.cell), perform an NMR calculation, adding

```
TASK : magres
MAGRES_TASK : nmr
FIX_OCCUPANCY : true
```

⁵It is a matter of philosophy as to what is the *correct* structure. It is easy to argue that the approximations endured from using exchange correlation functionals means that DFT will under or over estimate the lattice constant. But in reality there will be zero-point energies, harmonic and anharmonic temperature effects, isotope and relativity effects *etc* also to be accounted for. Nevertheless, since experiment has its own problems, X-ray diffraction can rarely work out the positions of hydrogen atoms, whilst NMR can, it is limited to the local structure around the nucleus, a two-pronged attack of theory and experiment seems the only sensible approach.

to the parameters file.

Test the chemical shielding tensors' robustness to the usual convergence parameters.

Repeat for SiO_2 by downloading the low quartz polymorph from the ICSD, and finally Li_2O_2 .

You should now have the σ_{iso} for Li_2O , Li_2O_2 and SiO_2 . So using the formulae described in the NMR section calculate the chemical shifts and conclude which substance was found in the battery explosion.

4 Further Things to Try with CASTEP

- Band structure calculations (start from `castep -s SPECTRAL`).
- Phonon calculations, leading to Raman and IR spectroscopy (see ⁶).
- Density of Electronic States calculation, leading to low- and core-loss-EELS and optical spectra calculations. (With OPTADOS— see www.optados.org).

Appendices

A Si2.cell

```
! Example of two atoms of silicon
!
! The simulation cell lattice vectors in Angstrom
%BLOCK LATTICE_CART
2.73  2.73  0.00
2.73  0.00  2.73
0.00  2.73  2.73
%ENDBLOCK  LATTICE_CART

! The positions of the atoms within the simulation cell,
! as fractions of the above lattice vectors
%BLOCK POSITIONS_FRAC
Si 0.0      0.0      0.0
Si 0.25     0.25     0.25
%ENDBLOCK POSITIONS_FRAC

! Speed up the calculation by looking for the crystal
! symmetry of the underlying lattice
SYMMETRY_GENERATE

! Once we've found that symmetry, nudge any atoms that
! aren't quite in the right place
SNAP_TO_SYMMETRY
```

⁶http://www.tcm.phy.cam.ac.uk/castep/Phonons_Guide/Castep_Phonons.html

```

! Integrate the reciprocal space Brillouin Zone using a grid
! of points finer than 0.1*2*Pi per Angstrom
KPOINT_MP_SPACING 0.1

```

B Si2.param

```

! Tell CASTEP that we want to do a single SCF electronic
! minimisation
TASK                : singlepoint
! Using the GGA exchange-correlation functional PBE.
XC_FUNCTIONAL       : PBE
! The basis set should contain plane-waves up to this
! value
CUT_OFF_ENERGY      : 400 eV

! Speed up the calculation by not worrying about spin
! polarisation. We're not expecting it in 2 atoms of
! silicon anyway
SPIN_POLARIZED      : false

! Allow the occupancies of the state to change k-point
! per k-point and not just be 0 or 1. WARNING: for the
! NMR calculations later you MUST set this to TRUE as
! GIPAW-NMR will not work with metals
FIX_OCCUPANCY       : false

! Use the Density-Mixing scheme to find the ground state in
! the case of metals. (You can try EDFT instead, which is
! more robust, but much more expensive)
METALS_METHOD       : dm

! Whilst looking for the ground state we calculate some
! unoccupied bands in case, as the minimisation
! progresses, their energy's change.
! This is the percentage extra unoccupied bands we have
! beyond the occupied.
PERC_EXTRA_BANDS    : 40

! Stop if we haven't converged in this number of SCF loops
MAX_SCF_CYCLES      : 100

! It's useful to see the stresses and pressure of the cell.
CALCULATE_STRESS    : true

! These are here to keep the simulation fast. If you want
! to know more about them. Use the CASTEP help system
write_bib           : false
opt_strategy        : speed
page_wvfns          : 0

```

```
num_dump_cycles      : 0
backup_interval      : 0
finite_basis_corr    : 0
```

C Si2.param Geometry Optimisation

```
! Optimise the cell until the forces are less than 0.01 eV/Ang
GEOM_FORCE_TOL : 0.01
! Since the cell can change shape the number of plane waves that
! fit within it, can also change. Add and subtract plane waves in
! the calculation such that we always obey CUT_OFF_ENERGY
FIXED_NPW      : false
! Since we're finding a new cell structure, write it out in a .cell
! format. You should find it in Si2-out.cell
WRITE_CELL_STRUCTURE : true
! Use the low-memory BFGS method
GEOM_METHOD    : LBFGS
! If we haven't converged in GEOM_MAX_ITER iterations -- give up.
GEOM_MAX_ITER  : 100
```

D FAQs

D.1 Where do I find castep?

It should be installed. Perhaps the executable has a slightly different name? `castep.serial` for example.

D.2 How do I find out what my castep binary is called?

Type `castep` followed by TAB twice in succession:

```
15:08:01 apollo:~ $ castep
castep2cell castep2pdb castep2shx castep2xtl castep-openmpi-1.4
castep2cssr castep2shak castep2xsf castep2xyz
```

D.3 Where is the castep binary I am running?

Use `which`, *e.g.*

```
15:11:17 apollo:~ $ which castep-openmpi-1.4
/lsc/opt/CASTEP/castep-openmpi-1.4
```

D.4 What version of castep am I running?

Versions after 7.0.0 respond to the `-v` option. Versions before this still have it in the `seedname.castep` header.

D.5 How do I plot a graph?

Really!? Try `xmgrace` or `gnuplot`. Graph paper is not available on request.