On-the-fly pseudopotential generation in CASTEP

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A quick tutorial

Default CASTEP OTF pseudopotentials

Try the following:

```
somemachine:~/Work/RUNS/diamond cjp10$ cat diamond.cell
%BLOCK LATTICE_CART
0 1.77 1.77
1.77 0 1.77
1.77 1.77 0
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
     C    0.0000000000    0.0000000000    0.0000000000
     C    0.2500000000    0.2500000000    0.2500000000
%ENDBLOCK POSITIONS_FRAC

SYMMETRY_GENERATE

somemachine:~/Work/RUNS/diamond cjp10$ castep diamond
```

No other input files are needed. Near the start of the diamond.castep file you will see the following:

Atomic calculation performed for C: 1s2 2s2 2p2

Converged in 56 iterations to an ae energy of -1018.807 eV

```
    ============================================================
    | Pseudopotential Report - Date of generation 13-09-2006   |
    ------------------------------------------------------------
    | Element: C Ionic charge:  4.00 Level of theory: LDA      |
    |                                                          |
    |              Reference Electronic Structure              |
    |         Orbital            Occupation          Energy    |
    |           2s                 2.000            -0.501     |
    |           2p                 2.000            -0.199     |
    |                                                          |
    |              Pseudopotential Definition                  |
    |         Beta     l     e      Rc     scheme    norm      |
    |           1      0   -0.501  1.395     qc       0        |
    |           2      0    0.250  1.395     qc       0        |
    |           3      1   -0.199  1.395     qc       0        |
    |           4      1    0.250  1.395     qc       0        |
    |          loc     2    0.000  1.395     pn       0        |
    |                                                          |
    | Augmentation charge Rinner = 1.305                       |
    | Partial core correction Rc = 1.305                       |
    ------------------------------------------------------------
    | "2|1.4|1.4|1.3|6|10|12|20:21(qc=6)#[]"                   |
    ------------------------------------------------------------
    |      Author: Chris J. Pickard, Cambridge University      |
    ============================================================
```

Doing a self consistent calculation for the test configuration

Atomic calculation performed for C: 1s2 2s2 2p2

Converged in 56 iterations to an ae energy of -1018.807 eV

```
--------------------------------------
AE eigenvalue nl 10 =       -9.95226116
AE eigenvalue nl 20 =       -0.50140334
AE eigenvalue nl 21 =       -0.19918477
--------------------------------------
PS eigenvalue nl 20 =       -0.50139111
PS eigenvalue nl 21 =       -0.19916613
--------------------------------------
```

CASTEP has generated a pseudopotential using its internal definition for carbon, the recommended default, and done some limited testing. You can see that the eigenvalues of the pseudoatom match the corresponding ones of the all electron atom. Now lets do some more testing.

The definition string that CASTEP has used is displayed in the pseudopotential summary.

```
| Augmentation charge Rinner = 1.305                       |
| Partial core correction Rc = 1.305                       |
------------------------------------------------------------
| "2|1.4|1.4|1.3|6|10|12|20:21(qc=6)#[]"                   |  <-------- This line
------------------------------------------------------------
|       Author: Chris J. Pickard, Cambridge University     |
```

Getting more information

Extract this string (more about what it means later), and modify the diamond.cell file to include the following block:
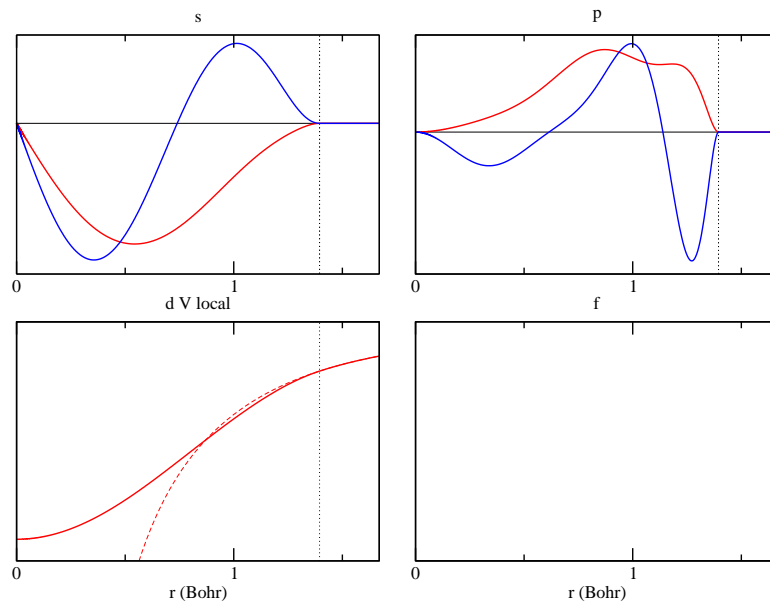
```
%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20:21(qc=6)[]
%ENDBLOCK SPECIES_POT
```

Removing the "#" activates full testing. Run the calculation again. This will cause some extra files to be output, which can be viewed with xmgrace.
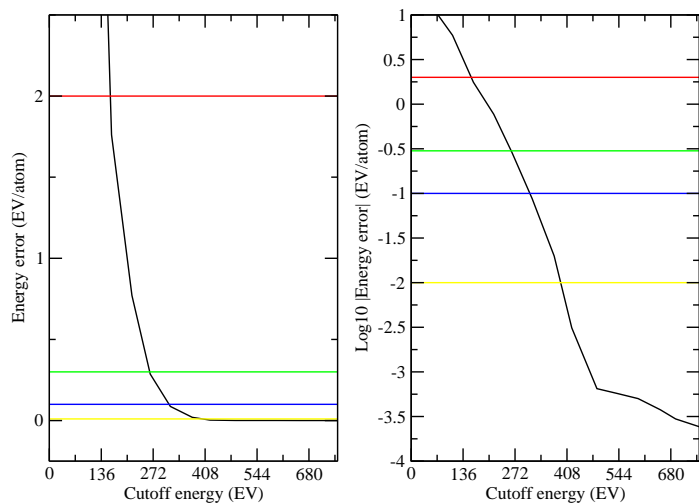
C_OTF.pwave - the all electron and pseudo partial waves:

3
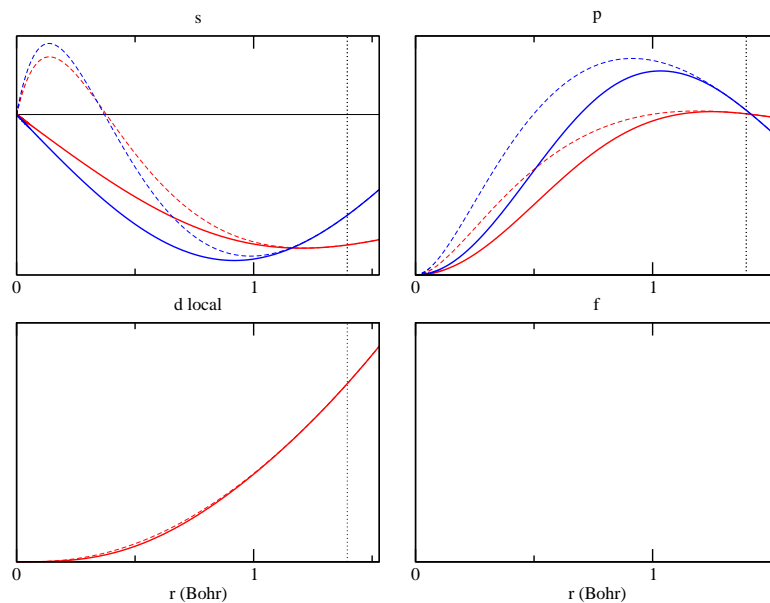
C_OTF.beta - the non-local projectors and local potential:

C_OTF.econv - the atomic convergence with cutoff:

You can see that the pseudopotential converges rapidly until about 500 eV. Note that for the q_c optimisation $q_c = 6$ and $6^2 * 13.6eV = 490eV$. You will also

notice that it is much better to look at cutoff convergence on a log plot.

Testing in another atomic configuration

It is possible to change the configuration in which the pseudopotential is tested. The square braces [] surround the modification to the default configuration that you want. The following moves an electron from 2s orbital to the 2p orbital.

```
%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20:21(qc=6)[2s1,2p3]
%ENDBLOCK SPECIES_POT
```

If you run again, you should get the following:

```
 Doing a self consistent calculation for the test configuration

 Atomic calculation performed for C: 1s2 2s1 2p3

 Converged in 44 iterations to an ae energy of -1010.565 eV


 -------------------------------------
 AE eigenvalue nl 10 =       -9.98304759
 AE eigenvalue nl 20 =       -0.51758214
 AE eigenvalue nl 21 =       -0.21406938
 -------------------------------------
 PS eigenvalue nl 20 =       -0.51701246
 PS eigenvalue nl 21 =       -0.21405887
 -------------------------------------
```

Note the small error in the pseudo eigenvalues.

Generating in another atomic configuration

It is possible to change the configuration in which the pseudopotential is generated. The curly braces {} surround the modification to the default configuration that you want. The following moves an electron from 2s orbital to the 2p orbital.

```
%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20:21{2s1,2p3}(qc=6)[2s1,2p3]
%ENDBLOCK SPECIES_POT
```

Atomic calculation performed for C: 1s2 2s1 2p3

Converged in 44 iterations to an ae energy of -1010.565 eV

Identity difference: 4.383367070873854E-004

```
============================================================
| Pseudopotential Report - Date of generation 13-09-2006   |
------------------------------------------------------------
| Element: C Ionic charge:  4.00 Level of theory: LDA      |
|                                                          |
|               Reference Electronic Structure             |
|         Orbital           Occupation          Energy     |
|           2s                1.000             -0.518     |
|           2p                3.000             -0.214     |
|                                                          |
|               Pseudopotential Definition                 |
|         Beta    l     e      Rc      scheme    norm      |
|           1     0   -0.518  1.395      qc       0        |
|           2     0    0.250  1.395      qc       0        |
|           3     1   -0.214  1.395      qc       0        |
|           4     1    0.250  1.395      qc       0        |
|          loc    2    0.000  1.395      pn       0        |
|                                                          |
| Augmentation charge Rinner = 1.305                       |
| Partial core correction Rc = 1.305                       |
------------------------------------------------------------
| "2|1.4|1.4|1.3|6|10|12|20:21{2s1,2p3}(qc=6)[2s1,2p3]"    |
------------------------------------------------------------
|       Author: Chris J. Pickard, Cambridge University     |
============================================================
```

Doing a self consistent calculation for the test configuration

Atomic calculation performed for C: 1s2 2s1 2p3

Converged in 44 iterations to an ae energy of -1010.565 eV

```
--------------------------------------
AE eigenvalue nl 10 =       -9.98304759
AE eigenvalue nl 20 =       -0.51758214
AE eigenvalue nl 21 =       -0.21406938
--------------------------------------
PS eigenvalue nl 20 =       -0.51757499
PS eigenvalue nl 21 =       -0.21405416
--------------------------------------
```

You can see that the pseudo-eigenvalues agree even better with the all electron ones if we test in the configuration in which it was generated.

What is the "identity difference"?

In the ultrasoft formalism $I = 1 + \sum_{nm} |\beta_n\rangle q_{nm} \langle\beta_m|$ is exactly true for the reference partial waves. At other energies it is only approximately true. The identity difference reported in diamond.castep gives an indication how well the identity operator is being described, and in some sense the transferability of the pseudopotential. The small the number the better. It will typically be worse if you have too few projectors. Using the following string:

```
%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20U:21U{2s1,2p3}(qc=6)[2s1,2p3]
%ENDBLOCK SPECIES_POT
```

the identity difference becomes worse:

```
 Identity difference:    3.029241718864615E-002
```

We have reduced the number of non-local projectors from two per channel to one. The portion of the string, 20U:21U, tells the code to place a single ultrasoft project (U) in the 2s (20) and 2p (21) channels. By default we use two, and the U labels are omited. The default is equivalent to 20UU:21UU, and more can be added, although it is possible to encounter linear dependence during the inversion of some important matrices.

Norm conserving pseudopotentials

Instead of using the U label for the ultrasoft channel, you can use N and generate a norm conserving pseudopotential. This will be harder (requiring a higher cutoff energy for convergence), but its transferability should be better with a single projector.

```
%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20N:21N{2s1,2p3}(qc=7)[2s1,2p3]
%ENDBLOCK SPECIES_POT
```

This results in a smaller identity difference:

```
 Identity difference:    6.321203331625732E-003
```

Note that the q_c has been increased to 7, leading to a harder potential. If you leave it as 6 the code will be unable to satisfy the norm constraint. Let's return to the neutral configuration.

```
%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20N:21N(qc=7)[]
%ENDBLOCK SPECIES_POT
```

The rest of the string

The first number (2 in this case) indicates that the local channel has been chosen to be d (l=2). The next number, 1.4, is the r_c for the local channel, and the next number is the r_c for the non-local channels. The 1.3 determines the r_{inner}, which is relevant for the pseudisation of the augmentation charge. The following three numbers have no impact on the generation of the pseudopotential, and set the COARSE, MEDIUM, and FINE levels of convergence. They are to be determined after testing the potential (although an estimate can be obtained from the C_OTF.econv file). Various other settings can be placed in the brackets. For example, (tm,nonlcc) tells the code to generate (my impression of) a Troullier-Martin pseudopotential, and not to include a non-linear core correction.

An exercise

Consider the following pseudopotential.

```
%BLOCK SPECIES_POT
C 1|1.4|6|10|12|20N:21L(tm,nonlcc)[]
%ENDBLOCK SPECIES_POT
```

It is possible to control all the core radii with a single number (in this case 1.4). For a norm conserving carbon pseudopotential it is also reasonable to ignore the d-channel, and instead choose the local channel to describe the p-channel. This is done by changing the first number to 1 (=l, p), and labelling the 21 with L instead of N. The Troullier-Martin scheme does not have an optimisation parameter, so this pseudopotential only has one free parameter: the core radius.

Investigate the properties of this pseudopotential as you change the core radius. Consider the plane wave convergence, and, for example, the change in the lattice parameter of diamond.