The concept and the form of DCACPs

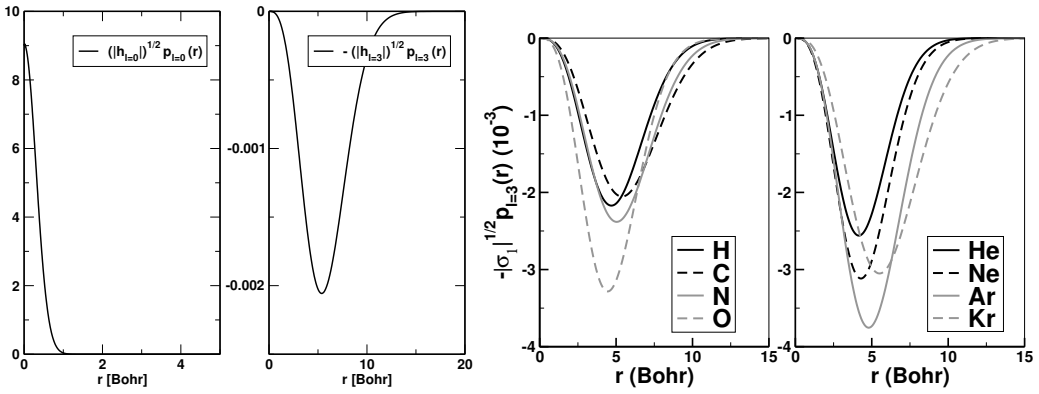
$$v_{\rm xc}^{\rm extended} = v_{\rm xc} + \sum_{\rm I} v_{\rm I}^{\rm DCACP}(\mathbf{r},\mathbf{r}')$$

$$v_{\rm I}^{\rm DCACP}(\mathbf{r},\mathbf{r}') \;=\; \sum_{m=-l}^{+l} Y_{lm}(\hat{\mathbf{r}}) p_l(r) \sigma_1 p_l(r') Y_{lm}^*(\hat{\mathbf{r}}')$$

with the projector,

$$p_l(r) \propto r^l \exp(-r^2/(2\sigma_2^2)).$$

$r = |\mathbf{r} - \mathbf{R}_{\rm I}|$ is the distance from position $\mathbf{R}_{\rm I}$ of nucleus I. $\hat{\mathbf{r}}$ is the unit vector in the direction of $\mathbf{r} - \mathbf{R}_{\rm I}$, and Y_{lm} denotes a spherical harmonic. The dispersion corrected atom centered potential (DCACP) has the same analytical form as the non-local part of the pseudopotentials of Goedecker *et al.* We found that only one projector is sufficient to reproduce the desired accuracy and, usually, a high angular momentum component ($l = 3$) is chosen.



(a) (b)

Figure 1: (a) s channel vs DCACP in the form shown in the legend, note the difference in the magnitude; (b)DCACPs complementing the BLYP functional for hydrogen, carbon, nitrogen, oxygen, and the rare gas atoms are shown in the form of -$|\sigma_1|^{1/2} p_{l=3}(r)$ where the projector $p_l(r)$ is proportional to $r^l \exp(-r^2/2\sigma_2^2)$.

Troullier-Martins format

Derivation

$$\hat{V}_{\text{ion}}^{\text{PP}}(r) = V_{\text{ion,local}}^{\text{PP}}(r) + \sum_l V_{\text{nonlocal},l}(r)\hat{P}_l$$

$V_{\text{ion,local}}^{\text{PP}}(r)$ is the local potential and $V_{\text{semi-local},l}(r)\hat{P}_l = \Delta V_l(r) = V_{\text{ion},l}^{\text{PP}}(r) - V_{\text{ion,local}}^{\text{PP}}(r)$ is the semi-local potential for the angular momentum component l. $\hat{P}_l$ projects out the lth angular momentum component from the wave function.

The semi-local form can be transformed into a nonlocal one using a procedure suggested by Kleinman and Bylander (KB):

$$V_{\text{nonlocal},l}^{\text{KB}}(\mathbf{r},\mathbf{r}') = \sum_{m=-l}^{l} Y_{lm}(\hat{\mathbf{r}}) \frac{|\Delta V_l(r)\,\phi_l(r)\rangle\,\langle\Delta V_l(r')\,\phi_l(r')|}{\langle\phi_l(r'')\,|\Delta V_l(r'')|\,\phi_l(r'')\rangle} Y_{lm}(\hat{\mathbf{r}}')$$

$$v^{\text{DCACP}}(\mathbf{r},\mathbf{r}') = \sum_{m=-l}^{l} Y_{lm}(\hat{\mathbf{r}})\, p_{l1}(r)\,\sigma_1 p_{l1}(r')\, Y_{lm}(\hat{\mathbf{r}}')$$

so...

$$p_{l1}(r)\,\sigma_1 p_{l1}(r') = \frac{|\Delta V_l(r)\,\phi_l(r)\rangle\,\langle\Delta V_l(r')\,\phi_l(r')|}{\langle\phi_l(r'')\,|\Delta V_l(r'')|\,\phi_l(r'')\rangle}$$

One choice: $\Delta V_l(r)$ is a constant; then

$$p_{l1}(r)\,\sigma_1 p_{l1}(r') = \phi_l(r)\,\frac{\Delta V_l}{\langle\phi_l(r'')\,|\phi_l(r'')\rangle}\phi_l(r')$$

Thus we can select

$$p_{l1}(r) = \phi_l(r)$$

$$\sigma_1 = \frac{\Delta V_l}{\langle\phi_l(r'')\,|\phi_l(r'')\rangle}$$

$$p_{l1}(r) = \frac{\sqrt{2}r^l \exp\left(-\frac{r^2}{2r_l^2}\right)}{r_l^{l+3/2}\sqrt{\Gamma(l+3/2)}}$$

Γ denotes the gamma function.

The projectors satisfy the normalization condition:

$$\int_0^\infty p_{l1}(r)\,p_{l1}(r)\,r^2 dr = 1$$

Implementation

We have to write in the Troullier-Martins pseudopotential file

- as the "wave function": $r\, p_{l1}$
- as the "potential":

$$\begin{aligned} &\sigma_1 \langle \phi_l |\, \phi_l \rangle + V_{\rm loc}\,(r) \\ &\quad \rightarrow \sigma_1 + V_{\rm loc}\,(r) \end{aligned}$$

DCACPs have been included in the f channel of Troullier-Martins pseudopotentials using the script 'DCACP2TM.sh'. The (angular momentum) channel assigned to be the local channel is tabluted in Table **??**. For other choices of local channel, one can generate via the 'DCACP2TM.sh' script (downloadable from http://lcbcpc21.epfl.ch/Research/dcacp.html).

functional	H	C	N	O
BLYP	p	d	d	p
BP	p	d	d	-
PBE	p	d	d	d

Table 1: The angular momentum chosen to be the local channel in the generation of DCACP-included Troullier-Martins pseudopotentials.

Example 1: DCACP_N_MT_BLYP.psp, N pseudopotential file with DCACP included in f channel

```
&POTENTIAL
   624
.89285714E-03  -6.7725706E+00  -2.0208424E+01  -1.6542135E+01  -1.6542740E+01
.90848214E-03  -6.7725706E+00  -2.0208424E+01  -1.6542135E+01  -1.6542740E+01
...

&WAVEFUNCTION
   624 CHANNELS=1
.89285714E-03   2.1376395E-04   9.6690717E-07   5.6480573E-11   2.1540102E-15
.90848214E-03   2.1750482E-04   1.0010450E-06   5.9497997E-11   2.3087953E-15
...
```

In the input file for the CPMD code, one should then specify:

```
&ATOM
*DCACP_N_MT_BLYP.psp KLEINMAN-BYLANDER
LMAX=F LOC=D
...
```

Example 2: DCACP_H_MT_BLYP.psp, H pseudopotential file with DCACP included in f channel

```
&POTENTIAL
   511
   .62500000E-02 -7.6586836E+00 -5.6929400E+00  0.0000000E+00 -5.6933456E+00
   .63593750E-02 -7.6586835E+00 -5.6929400E+00  0.0000000E+00 -5.6933456E+00
...

&WAVEFUNCTION
   511 CHANNELS=1
   .62500000E-02  3.0730264E-03  2.1382580E-05  0.0000000E+00  7.1658861E-12
   .63593750E-02  3.1268044E-03  2.2137519E-05  0.0000000E+00  7.6808191E-12
...
```

In the input file for CPMD code, one should specify:

```
 &ATOM
 *DCACP_H_MT_BLYP.psp KLEINMAN-BYLANDER
  LMAX=F LOC=P SKIP=D
  ...
```

When choosing the **LOC** and the **SKIP**, one should bear in mind that in the code CPMD, one can only **SKIP** ONE channel at a time. Please consult the keyword **SKIP** in the CPMD manual for further information (http://www.cpmd.org/manual/node46.html).