Pseudopotential (ECP) Development, Roadmap and Requests

ABSTRACT
This document is intended to collect the current activities of the pseudopotential (ECP) development effort within the CMS, to collect ideas about what has been done, what is being worked on, pain points and requests for new potentials

CURRENT STATUS
Current ECPs covering developed by NCSU cover the first three rows of the periodic table. Papers concerning their construction are found`? ? ? ?` in the literature. They were constructed to have good transferrability and to be as iso-spectral as possible with all electron correlated calculations. They are available at www.pseudopotentiallibrary.org. They also include gaussian style basis sets for use in quantum chemistry style calculations.

There are a number of outstanding issues to address

- Projectors are available for most ECPs for use in Kleinman-Bylander plane wave DFT codes. These may currently be hard and their transferrability is not guaranteed.
- The format for including spin-orbit terms as been defined, but currently there are no ECPs available that use this.
- Transferrability data is not readily available outside of papers for the ECPs, furthermore it is difficult to assess trade-offs when trying to look for something like a potential with a lower cutoff or smaller / more amenable basis set.

REQUESTS
such and such is hard. Please make element x for reason y

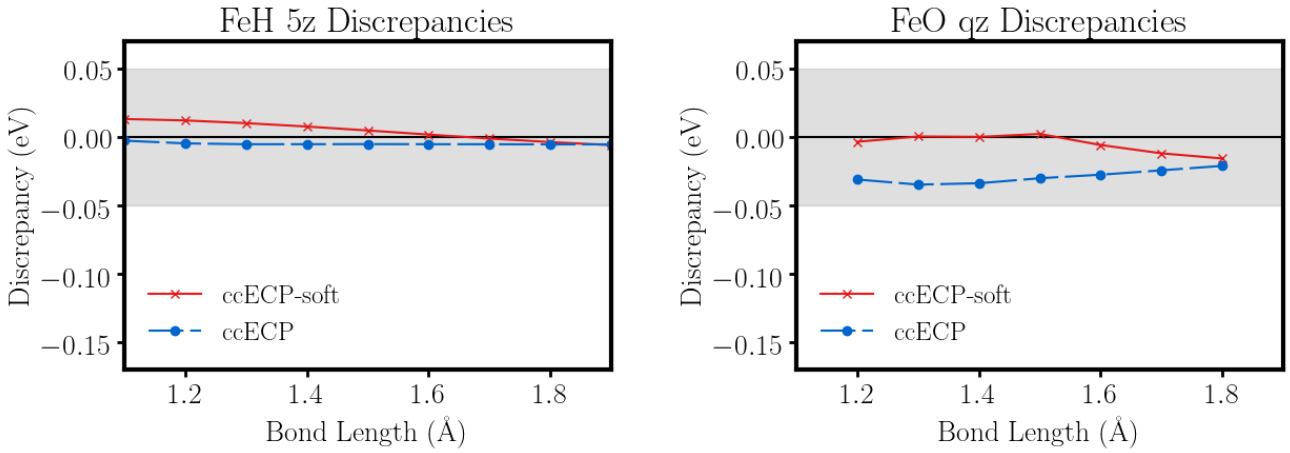
CURRENT WORK
So and so is doing element x

1 IRON

I generated another softer ECP for Fe in the same scheme as ccECPs, labeled as ccECP-soft. The KE cutoff is about 700 Ry. Below is the atomic gaps and molecular transferability test. Original published ccECP is included there as comparison too.

The Fe ccECP-soft parameter is give below and can also be downloaded under ./ccECP-soft-param/ directory:

16 3
2 2 4
2 8.9890516 13.9428916
2 14.963588 189.50111
2 9.9838449 25.8036121
2 14.979791 95.801262
1 12.000794 16.0
3 9.9968683 192.012710
2 9.4029511 -110.30045
2 5.9990706 2.59183990



(a) FeH 5Z binding curve discrepancies

(b) FeO QZ binding curve discrepancies

Figure 1. Binding energy discrepancies for (a) FeH 5Z and (b) FeO QZ molecules with regard to CCSD(T). The shaded region indicates the band of chemical accuracy. The dashed vertical line represents the equilibrium geometry.

Table 1. Fe gaps and relative errors for various ECPs. All values in eV

States and Symmetry		AE	ccECP	ccECP-soft
[Ar] $3d^7 4s^2$ EA	^4F	-0.0579872	-0.005436	-0.003053
[Ar] $3d^7 4s^1$	^5F	0.88855	-0.014150	-0.021149
[Ar] $3d^8$	^3F	4.15711	-0.017024	-0.019415
[Ar] $3d^6 4s^1$	^6D	7.88583	-0.016111	-0.034720
[Ar] $3d^7$	^4F	8.16252	-0.002125	-0.044298
[Ar] $3d^6$ 2nd Ion	^5D	24.0909	0.013863	-0.041475
[Ar] $3d^5$ 3rd Ion	^5S	54.6615	0.021912	0.005008
MAD			0.012946	0.024160

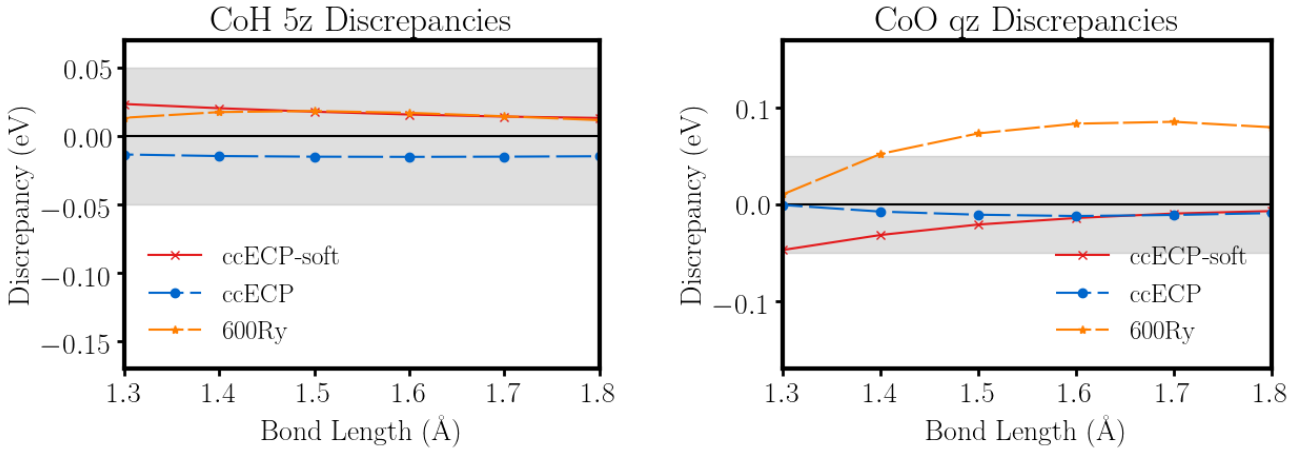
2 COBALT

The KE cutoff of ccECP-soft Co is about 700 Ry. Below is the atomic gaps and molecular transferability test. Original published ccECP is included there as comparison too.

Note that here I have an ECP labeled as 600Ry, this is generated by Cody using Opium package from Troullier-Martins method fitting from original ccECPs. It is a numerical ECP but I fit it into Gaussian and test it in atomic gaps and molecules. The fit is not perfect and can not represent the full accuracy of it.

The Co ccECP-soft parameter is give below and can also be downloaded under ./ccECP-soft-param/ directory:

```
17 3
2 2 4
2 10.013765 15.836729
2 15.026211 172.58644
2 7.9885909 15.3494954
2 14.997586 90.995647
1 12.003882 17.0
3 10.005064 204.06599
2 9.4548033 -117.74448
2 6.0069244 2.85018517
```



(a) CoH 5Z binding curve discrepancies

(b) CoO QZ binding curve discrepancies

Figure 2. Binding energy discrepancies for (a) CoH 5Z and (b) CoO QZ molecules with regard to CCSD(T). The shaded region indicates the band of chemical accuracy.

Table 2. Co gaps and relative errors for various ECPs. All values in eV

States and Symmetry		AE	ccECP	ccECP-soft	600Ry
[Ar] $3d^8 4s^2$ EA	^3F	-0.648825	-0.011727	0.023771	0.017302
[Ar] $3d^8 4s^1$	^4F	0.404998	-0.018725	0.010404	-0.022794
[Ar] $3d^9$	^2D	3.29022	-0.028436	0.018581	0.053097
[Ar] $3d^7 4s^1$	^5F	8.2851	-0.014988	-0.025523	-0.006439
[Ar] $3d^8$	^3F	7.85217	-0.013046	-0.004582	-0.038360
[Ar] $3d^7$ 2nd Ion	^4F	24.9596	0.005217	-0.024421	0.062209
[Ar] $3d^6$ 3rd Ion	^5D	58.4749	0.009923	-0.040255	0.461901
MAD			0.014580	0.021077	0.094586