

# Correlation Consistent ECPs and QMCPACK

## QMCPACK User Meeting

### Oak Ridge National Laboratories. Oak Ridge, TN

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Center for Predictive Simulation  
of Functional Materials



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National Laboratory

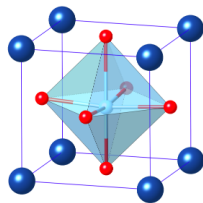
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 **OAK RIDGE**  
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 **Sandia**  
National  
Laboratories

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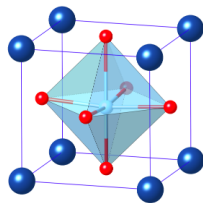
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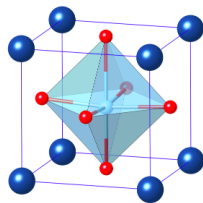


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- Many-body construction. Constructed from relativistic *many-body* spectra leading to the reproduction of *nearly exact* many-body properties.

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We envision constructing a new generation of pseudopotentials that are highly accurate and isospectral to the original many-body Hamiltonian:

- Many-body construction. Constructed from relativistic *many-body* spectra leading to the reproduction of *nearly exact* many-body properties.
- Reliable and universal. Tested and validated in many-body framework. Usable in both mean-field and many-body methods (in the spirit of the original all-electron  $H$ )

## ECP Parametrization

We choose a semi-local parametrization for the ECPs.

$$H_{\text{val}} = \sum_i [T_i^{\text{kin}} + V_i^{\text{pp}}] + \sum_{i < j} \frac{1}{r_{ij}}$$

where

$$V_i^{\text{pp}} = V_{\text{loc}}(r_i) + \sum_{\ell=0} V_{\ell}(r_i) |\ell m\rangle \langle \ell m|, \quad V_{\ell}(r) = \sum_{k=1} \beta_{\ell k} e^{-\alpha_{\ell k} r^2}$$

and the local channel is finite at the origin

$$V_{\text{loc}}(r) = -\frac{Z_{\text{eff}}}{r} \left(1 - e^{-\alpha r^2}\right) + \alpha Z_{\text{eff}} r e^{-\beta r^2} + \sum_{k=1} \gamma_k e^{-\delta_k r^2}$$

# Many-body spectra and norm-conservation

- Total Objective Function:

$\mathcal{O}^2 = \omega_0 \mathcal{E}^2 + \omega_1 \mathcal{N}^2$ , where  $\omega_0, \omega_1$  are tunable weights

- CCSD(T) energy consistency:

$\mathcal{E}^2 = \sum_s (\Delta E_s^{\text{ECP}} - \Delta E_s^{\text{AE}})^2$ , note that  $\Delta E_s^{\text{AE}}$  agrees with experiment to  $\leq 0.03$  eV

- Norm-conservation:

$\mathcal{N}^2 = \sum_\ell (N_\ell^{\text{ECP}} - N_\ell^{\text{AE}})^2 + (V_\ell^{\text{ECP}} - V_\ell^{\text{AE}})^2 + (S_\ell^{\text{ECP}} - S_\ell^{\text{AE}})^2 + (\epsilon_\ell^{\text{ECP}} - \epsilon_\ell^{\text{AE}})^2$   
where

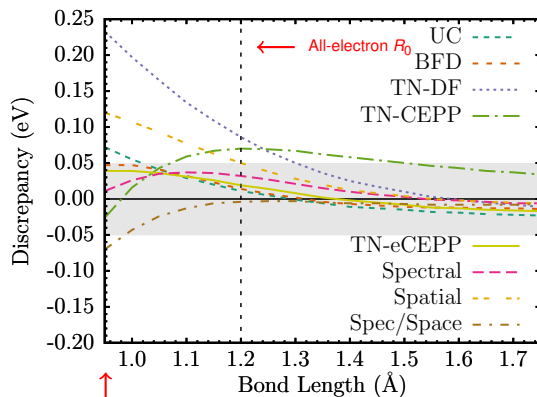
$N_\ell$ : norm inside cutoff radius,  $V_\ell, S_\ell, \epsilon_\ell$ : value, derivative, eigenvalue of the orbital

# Discrepancies from AE atomic spectrum & CCSD(T) binding curve:

## O Atomic Spectrum (eV)

Core Approx.	$\Delta IP(I)$	$\Delta EA$	MAD
UC	-0.0142	-0.0017	0.0865
BFD	-0.0438	-0.0105	0.3275
TN-DF	-0.0436	-0.0092	0.2669
TN-CEPP	-0.0192	-0.0259	0.1442
TN-eCEPP	-0.0053	0.0083	0.1434
Spectral	-0.0058	-0.0044	0.0078
Spatial	-0.0118	0.0012	0.1303
Spec/Space	0.0083	0.0036	0.0192

## O<sub>2</sub>(<sup>3</sup> $\Sigma_g$ )



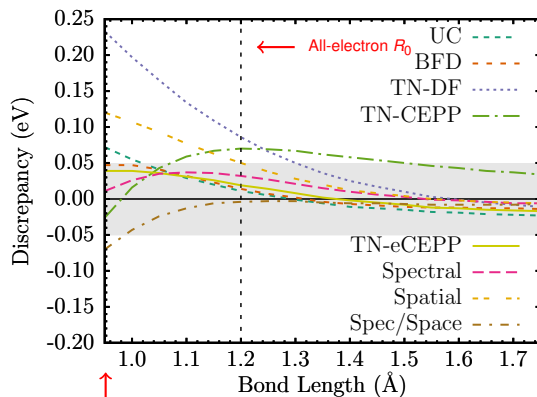
Near Dissociation Threshold

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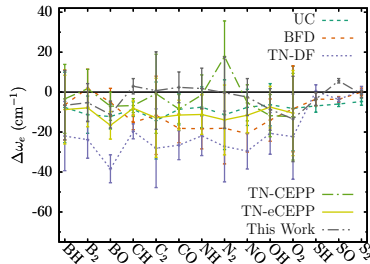
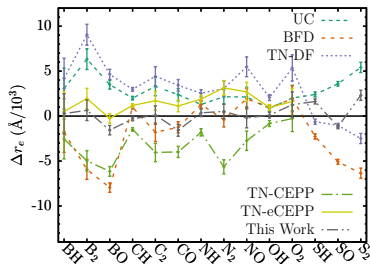
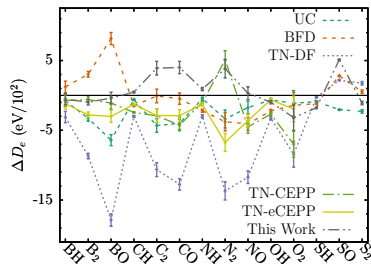
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Near Dissociation Threshold



# Transferability Testing



MAD	UC	BFD	TN-DF	TN-CEPP	TN-eCEPP	This Work
$D_e$ (eV/10 <sup>2</sup> )	<b>2.0(2)</b>	6.9(2)	2.3(2)	2.9(3)	2.6(3)	<b>2.0(2)</b>
$r_e$ (Å/10 <sup>3</sup> )	2.9(3)	2.8(3)	3.7(3)	3.1(3)	1.5(3)	<b>0.9(3)</b>
$\omega_e$ (cm <sup>-1</sup> )	9(3)	10(3)	20(3)	7(4)	11(4)	<b>5(3)</b>
$D_{diss}$ (eV/10 <sup>2</sup> )	13.10	19.96	11.75	20.94	7.79	<b>5.75</b>

**AE Reference:** RCCSD(T) correlating *all* electrons

**UC:** is a uncorrelated Ne-core RCCSD(T)

**BFD:** Burkatzki-Filippi-Dolg DHF ECPs for QMC

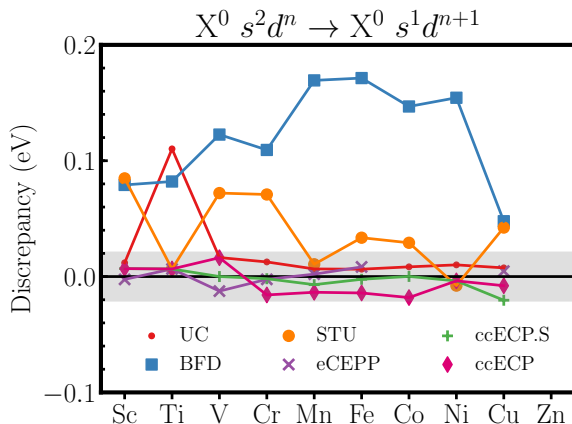
**STU:** Stuttgart group DHF ECPs

**TN17:** Trail-Needs correlated ECPs for QMC

**Our ccECP:** Our correlation-consistent ECP

**Discrepancy:**

$$(E_s^{\text{ECP}} - E_{\text{GS}}^{\text{ECP}}) - (E_s^{\text{AE}} - E_{\text{GS}}^{\text{AE}})$$



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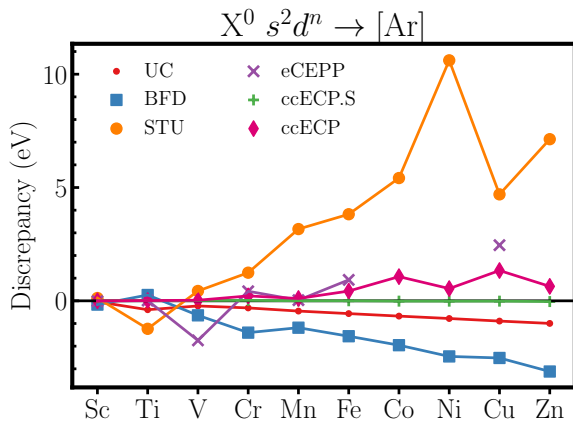
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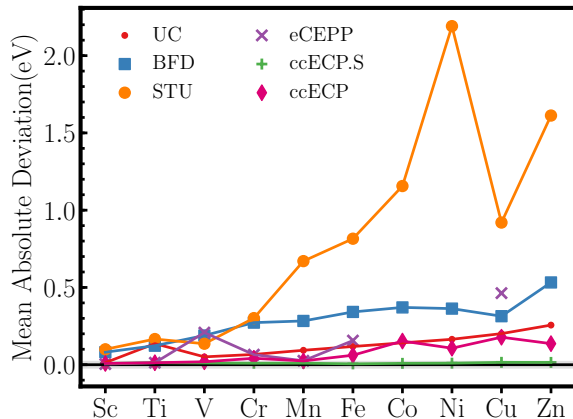


## Example Spectrum (Ni)

[Ar] 3d <sup>8</sup> 4s <sup>2</sup>	<sup>3</sup> F	[Ar] 3d <sup>5</sup>	<sup>6</sup> S
[Ar] 3d <sup>9</sup> 4s <sup>1</sup>	<sup>3</sup> D	[Ar] 3d <sup>4</sup>	<sup>5</sup> D
[Ar] 3d <sup>10</sup>	<sup>1</sup> S	[Ar] 3d <sup>3</sup>	<sup>4</sup> F
[Ar] 3d <sup>8</sup> 4s <sup>1</sup>	<sup>4</sup> F	[Ar] 3d <sup>2</sup>	<sup>3</sup> F
[Ar] 3d <sup>9</sup>	<sup>2</sup> D	[Ar] 3d <sup>1</sup>	<sup>2</sup> D
[Ar] 3d <sup>8</sup>	<sup>3</sup> F	[Ar]	<sup>1</sup> S
[Ar] 3d <sup>7</sup>	<sup>4</sup> F	[Ne] 3s <sup>2</sup>	<sup>1</sup> S
[Ar] 3d <sup>6</sup>	<sup>5</sup> D	[Ar] 3d <sup>9</sup> 4s <sup>2</sup>	<sup>2</sup> D

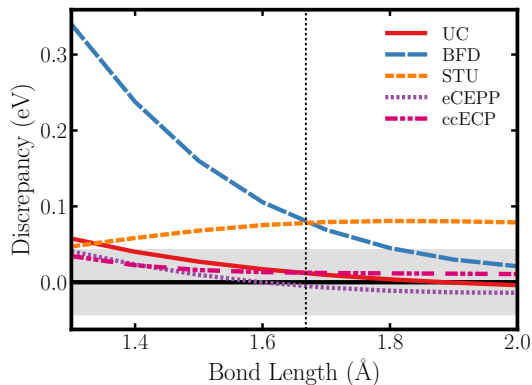
## Mean Absolute Deviation:

$$\frac{1}{N} \sum_{s=1}^N |(E_s^{\text{PP}} - E_{\text{GS}}^{\text{PP}}) - (E_s^{\text{AE}} - E_{\text{GS}}^{\text{AE}})|$$

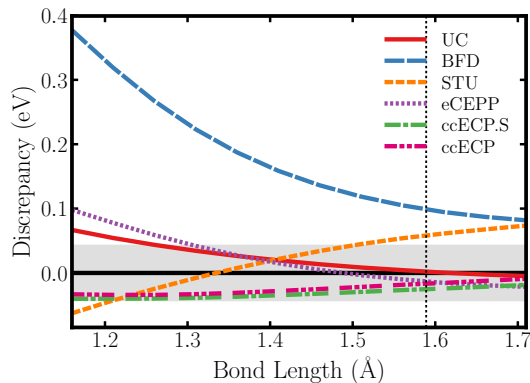


# Monoxides

## ScO binding curve discrepancies



## VO binding curve discrepancies



KB projectors for *some* atoms are available, will update as they become available

Create an issue on the [GitHub site](#) or contact the developers of the potential you are interested in.

## ccECP format

$$V_{\ell}(r) = \sum_{k=1}^{N_{\ell}} \beta_k r^{n_k-2} e^{-\alpha_k r^2}$$

$$\left. \begin{array}{ccc} Z_{\text{eff}} & L+1 & \\ N_0 & \dots & N_L \\ n_1 & \alpha_1 & \beta_1 \\ \vdots & \vdots & \vdots \\ n_{N_0} & \alpha_{N_0} & \beta_{N_0} \end{array} \right\} \ell = 0$$

$$\left. \begin{array}{ccc} n_1 & \alpha_1 & \beta_1 \\ \vdots & \vdots & \vdots \\ n_{N_L} & \alpha_{N_L} & \beta_{N_L} \end{array} \right\} \ell = L$$

## Carbon Example

```

4 2
1 3
2 7.76079 52.13345
1 14.43502 4.00000
3 8.39889 57.74008
2 7.38188 -25.81955

```

## Pseudopotential Library

A community website for pseudopotentials/effective core potentials developed for high accuracy correlated many-body methods such as quantum Monte Carlo and quantum chemistry.

H																	He																							
Li	Be											B	C	N	O	F	Ne																							
Na	Mg											Al	Si	P	S	Cl	Ar																							
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br																								
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I																								
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At																								
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mn	Nd	Pm																								
																	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu									
																	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mn	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

## Carbon

C.ccECP →

cCEPP	eCEPP	CEPP
cCEPP from Chandler Bennett et al. <i>Journal of Chemical Physics</i> 147, 224106 (2017).	eCEPP from J. R. Trail and R. J. Needs <i>Journal of Chemical Physics</i> 146, 204107 (2017).	CEPP from J. R. Trail and R. J. Needs <i>Journal of Chemical Physics</i> 142, 064110 (2015).
C.cc-pVTZ.nwchem C.ccECP.xml C.ccECP.gamess C.ccECF C.cc-pVQZ.gamess C.cc-pVTZ.gamess C.cc-pV5Z.gamess C.cc-pVDZ.gamess C.cc-pVDZ.nwchem C.cc-pV5Z.nwchem C.ccECF.nwchem C.cc-pVQZ.nwchem	aug-cc-pVTZ-eCEPP.dat_C C.cpp.casino C.data C.awfn C.cpp.molpro pp_eCEPP_C aug-cc-pVTZ_eCEPP.dat_C aug-cc-pVQZ_eCEPP.dat_C aug-cc-pVDZ_eCEPP.dat_C	C.data C.awfn pp_gamess_C C_cpp.data

# Available Quantum Chemistry Formats

For each ccECP, we include a variety of basis sets and pseudopotential formats for various codes, including cc-pVnZ and aug-cc-pVnZ basis sets, with  $n \in \{D, T, Q, 5\}$ .

Basis/ECP formats included for each code QMCPACK interfaces to

**GAMESS**: Basis sets and pseudopotential format

e.g. [C.cc-pVTZ.gamess](#) & [C.ccECP.gamess](#)

**QUANTUM PACKAGE**: Uses GAMESS file formats

e.g. [C.cc-pVTZ.gamess](#) & [C.ccECP.gamess](#)

**PYSCF**: Parses NWCHEM formats

e.g. [C.cc-pVTZ.nwchem](#) & [C.ccECP.nwchem](#)

**QMCPACK**: Uses qmcpack xml format

e.g. [C.ccECP.xml](#)



# PySCF Example: Catom.py

```
#!/usr/bin/env python
```

```
from pyscf import gto, scf, dft  
from urllib import urlretrieve  
from PyscfToQmcpack import savetoqmcpack  
import os
```

```
#Set the current working directory  
cwd = os.getcwd()
```

# PySCF Example: Catom.py

```
#Obtain basis and ECP files from pseudopotentiallibrary.org
atom = "C"
pptype = "ccECP"
bastype= "cc-pVTZ"
pplib = "http://pseudopotentiallibrary.org/recipes"
basfile="{0}.{1}.nwchem".format(atom,bastype)
ecpfile="{0}.{1}.nwchem".format(atom,pptype)
xmlfile="{0}.{1}.xml".format(atom,pptype) #grab qmcpack xml file for
urlretrieve("{0}/{1}/{2}/{3}".format(pplib,atom,pptype,basfile),
            filename=basfile)
urlretrieve("{0}/{1}/{2}/{3}".format(pplib,atom,pptype,ecpfile),
            filename=ecpfile)
urlretrieve("{0}/{1}/{2}/{3}".format(pplib,atom,pptype,xmlfile),
            filename=xmlfile)
```

# PySCF Example: Catom.py

```
#Initialize molecule object
mol = gto.Mole()
mol.atom = "{0} 0.0 0.0 0.0".format(atom)
with open(os.path.join(cwd,basfile)) as f:
    bas = f.read()
mol.basis = {atom: gto.basis.parse(bas)}
with open(os.path.join(cwd,ecpfile)) as f:
    ecp = f.read()
mol.ecp = {atom: gto.basis.parse_ecp(ecp)}
mol.spin = 2
mol.charge = 0
mol.build()
```

# PySCF Example: Catom.py

```
#run HF and PBE
hf = scf.ROHF(mol)
hf.kernel()
pbe = dft.ROKS(mol)
pbe.xc = 'pbe'
pbe.kernel()

savetoqmcpack(mol,hf,title='{}.hf'.format(atom))
savetoqmcpack(mol,pbe,title='{}.pbe'.format(atom))
```

# Using ccECPs for solid state

- If using gaussian basis sets, i.e. (PySCF), our potentials can be used as is, as shown previously.
- Using PBC, basis sets may need to be altered and/or reoptimized entirely. e.g. Diffuse functions can cause linear dependency issues, to fix add: `cell.drop_exponent=0.1` in pySCF to the cell object
- If basis is problematic, contractions for occupied orbitals need to be tailored to the ECP. Often useful to use an ionized +1, +2 state to get contractions. Uncontracted primitives can come from existing solid-state basis sets. For inspiration, can use primitives from <http://www.crystal.unito.it/basis-sets.php> or <https://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html>

## Semi-local potential

$$\hat{V}_{\text{SL}} = \sum_{\ell m} |\ell m\rangle V_{\ell}(r) \langle \ell m|$$

## KB potential

$$\hat{V}_{\text{KB}} = V_{\text{local}}(r) + \sum_{\ell m} \frac{|\psi_{\ell m}^{\text{PS}} \delta V_{\ell}\rangle \langle \delta V_{\ell} \phi_{\ell m}^{\text{PS}}|}{\langle \phi_{\ell m}^{\text{PS}} | \delta V_{\ell} | \phi_{\ell m}^{\text{PS}} \rangle}$$

**Ghost States:** Low energy states that have the wrong number of nodes. Can cause unphysical energies, difficulty, optimizing wave functions, unstable DMC, etc. (see Drummond, Trail, & Needs, PRB **94**, 165170 (2016)).

**Transferability:** Ability of a potential to perform the same as the reference.

We take our semi-local ccECPs to be an accurate representation of the AE Hamiltonian. Therefore, we need the KB version to be transferable with respect to the semi-local potential.

OPIUM is a norm-conserving pseudopotential generation tool to develop pseudopotentials for plane-wave codes like QE.

A modified version that can input gaussian parameterized semi-local potentials (ccECPs, Stuttgart, BFD, etc) has been used to generate the UPF files, and included some information about ghost states, transferability, recommended plane-wave cutoffs, in the .rpt file.

## Ghost States

### Carbon

ccECP

ccECP from Chandler Bennett et al.  
Journal of Chemical Physics 147,  
224106 (2017)

C.ccECP

C.ccECP.gamess

C.ccECP.xml

C.cc-pVSZ.gamess

C.cc-pVSZ.nwchem

C.cc-pVDZ.gamess

C.cc-pVDZ.nwchem

C.cc-pVQZ.gamess

C.cc-pVQZ.nwchem

C.cc-pVTZ.gamess

C.cc-pVTZ.nwchem

C.ccECP.nwchem

C.rpt

C.upf

```
### PS report #####
```

Orbital	Ghost
---------	-------

100	no
210	no

```
### NL/SL report #####
```

NL: Orbital	Filling	Eigenvalues [Ry]	Norm	Ghost
-------------	---------	------------------	------	-------

100	2.000	-1.8994061622	0.5269147933	no
210	1.000	-1.2463147015	0.5139289547	no

```
===== No ghosts in potential!!=====
```

```
E_tot = -9.9027869501 Ry
```

Information about existence of ghosts for the semi-local and non-local evaluation



## Suggested Cutoff

## Carbon

ccECP

ccECP from Chandler Bennett et al.  
*Journal of Chemical Physics* 147,  
224106 (2017)

C.ccECP  
 C.ccECP.gamess  
 C.ccECP.xml  
 C.cc-pV5Z.gamess  
 C.cc-pV5Z.nwchem  
 C.cc-pVDZ.gamess  
 C.cc-pVDZ.nwchem  
 C.cc-pVQZ.gamess  
 C.cc-pVQZ.nwchem  
 C.cc-pVTZ.gamess  
 C.cc-pVTZ.nwchem  
 C.ccECP.nwchem  
 C.rpt  
 C.upf

=== Ecut necessary for ~1 eV convergence error / electron ===		
	Ecut[Ry]	error [meV/e]
100	25	981.442
210	38	997.824
=== Ecut necessary for ~100 meV convergence error / electron ===		
	Ecut[Ry]	error [meV/e]
100	45	96.722
210	91	97.371
=== Ecut necessary for ~10 meV convergence error / electron ===		
	Ecut[Ry]	error [meV/e]
100	98	9.994
210	159	9.948
=== Ecut necessary for ~1 meV convergence error / electron ===		
	Ecut[Ry]	error [meV/e]
100	162	0.993
210	238	0.982

Suggested cutoffs for the projectors. Here,  $\sim 240$  Ry. Choose max from each atom!

## Transferability

### Carbon

ccECP  
 ccECP from Chandler Bennett et al.  
 Journal of Chemical Physics 147,  
 224106 (2017)  
 C.ccECP  
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 C.cc-pVDZ.nwchem  
 C.cc-pVQZ.gamess  
 C.cc-pVQZ.nwchem  
 C.cc-pVTZ.gamess  
 C.cc-pVTZ.nwchem  
 C.ccECP.nwchem  
 C.rpt  
 C.upf

### TC report #####

#### Comparison of total energies

Config	E_sl (Ry)	E_nl (Ry)	Delta (eV)
0	-9.902787	-9.902787	-0.000000
1	-10.700429	-10.700446	0.000233
2	-10.071747	-10.071751	0.000049
3	-9.442983	-9.442983	0.000000
4	-9.902787	-9.902787	-0.000000
5	-9.252319	-9.252325	0.000080
6	-8.604609	-8.604609	0.000000
7	-8.140843	-8.140878	0.000480
8	-7.490481	-7.490560	0.001082
9	-6.848954	-6.848954	0.000000
10	-4.613496	-4.613692	0.002665
11	-4.000547	-4.000547	0.000000

MAD (eV): 0.000382367

Transferability of projector wrt semi-local potential. Small errors, especially for low lying states

- Each ccECP that has been developed has a *.nwchem* & *.gamess* extension, which allows them to be used with GAMESS, PYSCF, and QUANTUM PACKAGE using the appropriate format.
- The number of UPF files is currently limited, but will be updated as they are generated and tested. For transition metals, a good alternative is to use the projectors from Jaron Krogel, listed under RRKJ\_PRB\_93\_075143 and TM\_PRB\_93\_075143.
- To proceed further, simply download the XML potential for QMCPACK and run the appropriate converter to generate the files (convert4qmc for QUANTUM PACKAGE, PYSCF, and GAMESS and pw2qmcpack for QUANTUM ESPRESSO and proceed with your QMC workflow.