Correlation Consistent ECPs and QMCPACK

QMCPACK User Meeting
Oak Ridge National Laboratories. Oak Ridge, TN

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U.S. DEPARTMENT OF ENERGY | Office of Science

CPSFM | Center for Predictive Simulation of Functional Materials

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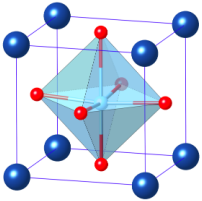
For accurate calculations of functional materials (e.g. perovskites), explicitly correlated methods like QMC need to be solving the *correct* Hamiltonian.



Effective Core Potentials (ECPs) are necessary in order to feasibly tackle large systems, include relativity, etc.

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

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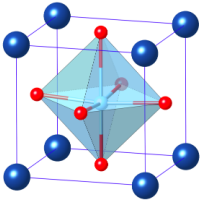

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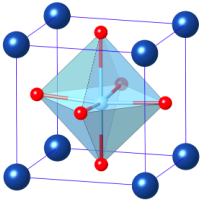

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→ Many-body construction. Constructed from relativistic *many-body* spectra leading to the reproduction of *nearly exact* many-body properties.

→ 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.

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

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

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

Many-body spectra and norm-conservation

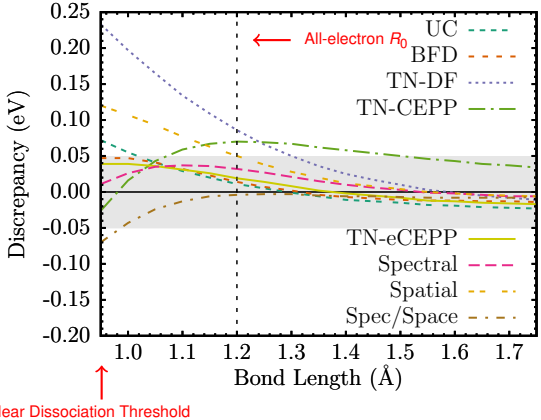
- Total Objective Function:
  $\mathcal{O}^2 = \omega_0 \mathcal{E}^2 + \omega_1 \mathcal{N}^2$, where ω_0, ω_1 are tunable weights
- CCSD(T) energy consistency:
  $\mathcal{E}^2 = \sum_s \left(\Delta E_s^{\mathrm{ECP}} - \Delta E_s^{\mathrm{AE}}\right)^2$, note that ΔE_s^{AE} agrees with experiment to ≤ 0.03 eV
- Norm-conservation:
  $\mathcal{N}^2 = \sum_\ell \left(N_\ell^{\mathrm{ECP}} - N_\ell^{\mathrm{AE}}\right)^2 + \left(V_\ell^{\mathrm{ECP}} - V_\ell^{\mathrm{AE}}\right)^2 + \left(S_\ell^{\mathrm{ECP}} - S_\ell^{\mathrm{AE}}\right)^2 + \left(\epsilon_\ell^{\mathrm{ECP}} - \epsilon_\ell^{\mathrm{AE}}\right)^2$
  where
  N_ℓ: 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.	ΔIP(I)	ΔEA	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

$O_2(^3\Sigma_g)$



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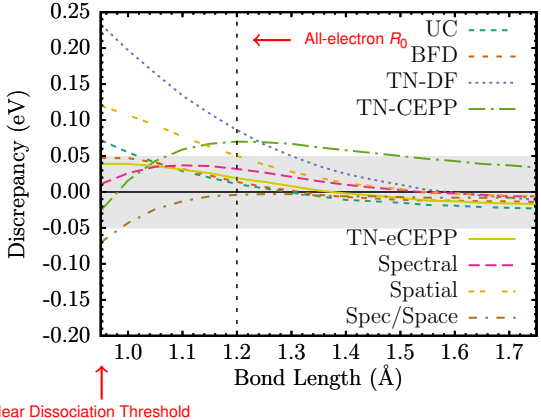
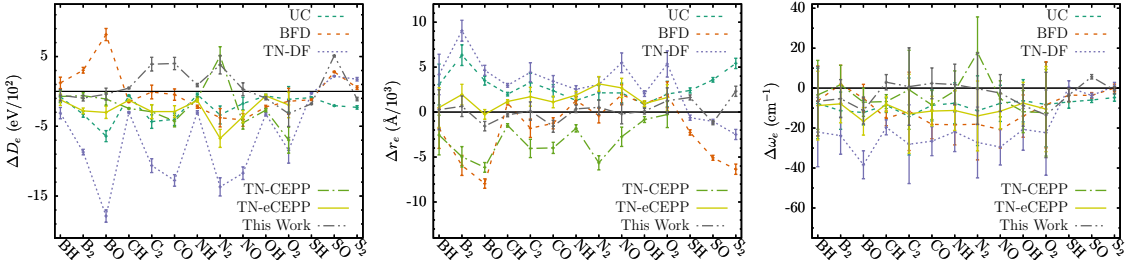


Transferability Testing



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

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

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

BFD: Burkatzki-Filippi-Dolg DHF ECPs for QMC

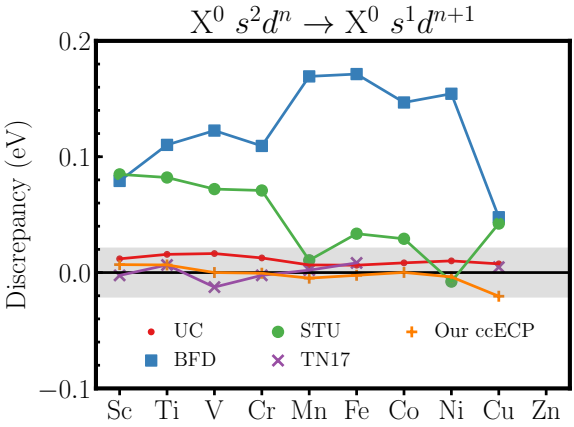
STU: Stuttgart group DHF ECPs

TN17: Trail-Needs correlated ECPs for QMC

Our ccECP: Our correlation-consistent ECP

Discrepancy:

$$\left(E_s^{\mathrm{ECP}} - E_{\mathrm{GS}}^{\mathrm{ECP}}\right) - \left(E_s^{\mathrm{AE}} - E_{\mathrm{GS}}^{\mathrm{AE}}\right)$$



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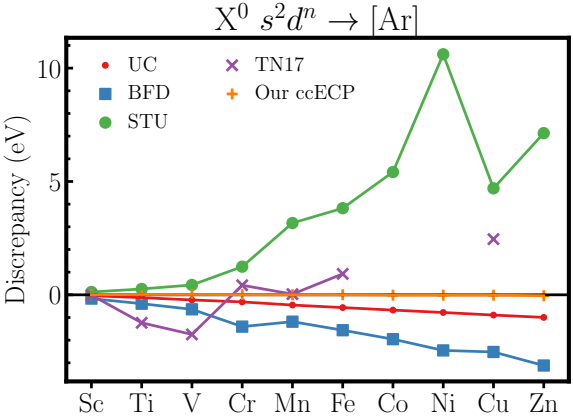
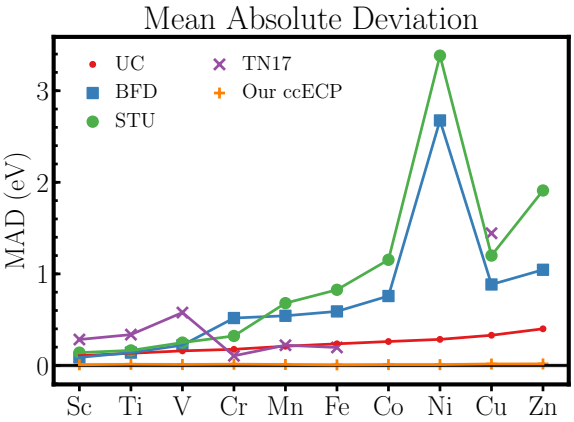


Example Spectrum (Ni)

[Ar] $3d^8 4s^2$	^3F	[Ar] $3d^5$	^6S
[Ar] $3d^9 4s^1$	^3D	[Ar] $3d^4$	^5D
[Ar] $3d^{10}$	^1S	[Ar] $3d^3$	^4F
[Ar] $3d^8 4s^1$	^4F	[Ar] $3d^2$	^3F
[Ar] $3d^9$	^2D	[Ar] $3d^1$	^2D
[Ar] $3d^8$	^3F	[Ar]	^1S
[Ar] $3d^7$	^4F	[Ne] $3s^2$	^1S
[Ar] $3d^6$	^5D	[Ar] $3d^9 4s^2$	^2D

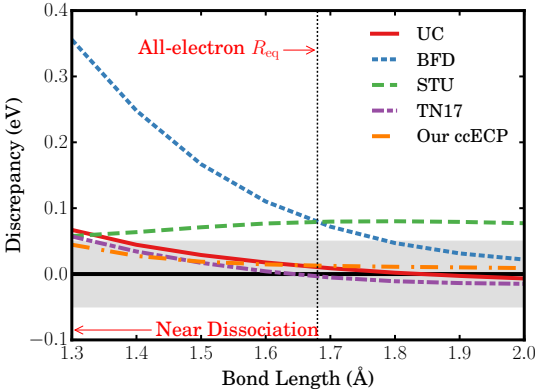


Mean Absolute Deviation:

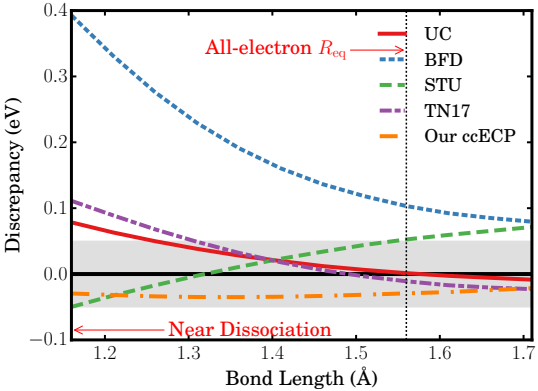
$$\frac{1}{N}\sum_{s=1}^{N}\left|\left(E_s^{\mathrm{PP}} - E_{\mathrm{GS}}^{\mathrm{PP}}\right) - \left(E_s^{\mathrm{AE}} - E_{GS}^{\mathrm{AE}}\right)\right|$$

Monoxides

ScO binding curve discrepancies



VO binding curve discrepancies



http://pseudopotentiallibrary.org

Updated as new correlated ECPs are developed

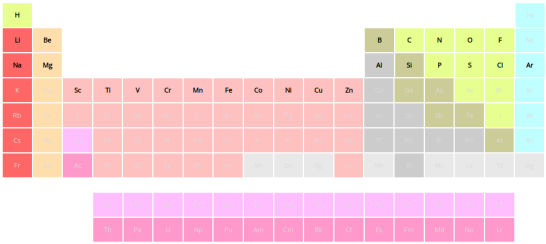
Anyone can contribute ECPs through `http://github.com/QMCPACK/pseudopotentiallibrary`

Soon will include completed table up through Kr

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

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.



Click an element above to view available recipes.

Available ECPs and pseudopotentials

- ccECPs from Abdulgani Annaberdiyev et al. Journal of Chemical Physics 149, 134108 (2018)
- ccECPs from Chandler Bennett et al. Journal of Chemical Physics 149, 104108 (2018)
- ccECPs from Chandler Bennett et al. Journal of Chemical Physics 147, 224106 (2017)
- eCEPPs from Trail and Needs Journal of Chemical Physics 146, 204107 (2017)
- RRKJ and TM based potentials from Krogel et al. Physical Review B 93, 075143 (2016)
- CEPPs from Trail and Needs Journal of Chemical Physics 142, 064110 (2015)

Help and feedback

Create an issue on the GitHub site or contact the developers of the potential you are interested in.

ccECP format

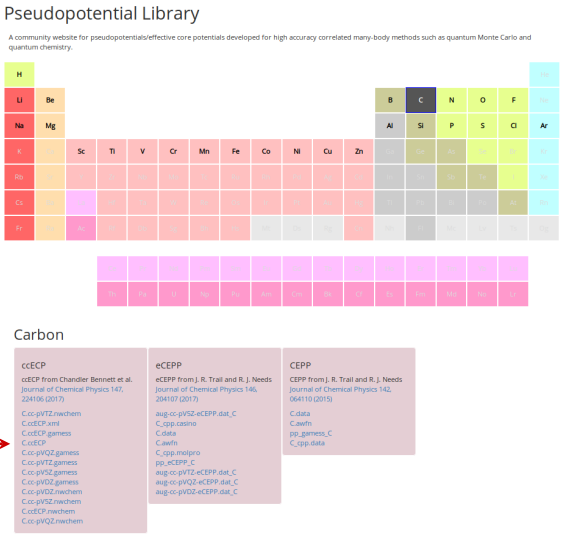
$$V_\ell(r) = \sum_{k=1}^{N_\ell} \beta_k r^{n_k - 2} e^{-\alpha_k r^2}$$

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

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
```

C.ccECP



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 $n \in \{\mathrm{D}, \mathrm{T}, \mathrm{Q}, 5\}$.

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

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

KB potential

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

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-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

```
### 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
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

```
### 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.