A new generation of effective core potentials

Correlation consistent effective core potentials (ccECPs)

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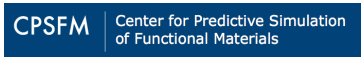

ccECPs in a few slides

Features:

- Many-body constructions are inherited for many-body use (e.g. beyond mean-field).
- Semi-local gaussian expansions with a minimal number of parameters (great for gaussian-based codes).
- Eliminated Coulomb singularities resulting in finite smooth potential functions for any size of core spaces (great for periodic codes with resulting in low-cutoff of plane waves).

Semi-local averaged relativistic effective potential V^{AREP}

$$V_i^{\mathrm{AREP}} = \underbrace{V_L(r_i)}_{\text{Local potential}} + \underbrace{\sum_{\ell=0}^{\ell_{\max}=L-1} \left(V_\ell(r_i) - V_L(r_i)\right) \times \sum_{m=-\ell}^{\ell} |\ell m\rangle\langle \ell m|}_{\text{Non-local potential}},$$

Local Potential: $V_L(r_i) = \underbrace{-\frac{Z_{\mathrm{eff}}}{r}\left(1 - e^{\alpha r^2}\right) + \alpha Z_{\mathrm{eff}} r e^{-\beta r^2}}_{\text{Coulomb singularity cancellation}} + \underbrace{\sum_{i=1} \gamma_i e^{-\delta_i r^2}}_{\text{Smoothing terms}}$

Non-local Potentials: $V_\ell(r_i) - V_L(r_i) = \sum_{k=1} \beta_{\ell k} r^{n_{\ell k}-2} e^{-\alpha_{\ell k} r^2}$

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Si AREP ccECP replaces
10 inner core electrons

local potential
n_lk  exponent coefficient
1     5.168316 4.000000
3     8.861690 20.673264
2     3.933474 -14.818174



non-local s channel
n_lk  alpha_lk      beta_lk
2     9.447023 14.832760
2     2.553812 26.349664

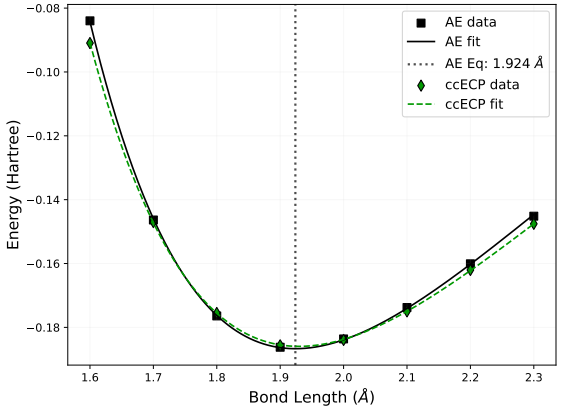
non-local p channel
n_lk  alpha_lk      beta_lk
2     3.660001 7.621400
2     1.903653 10.331583
```

Accuracy validation for ccECPs

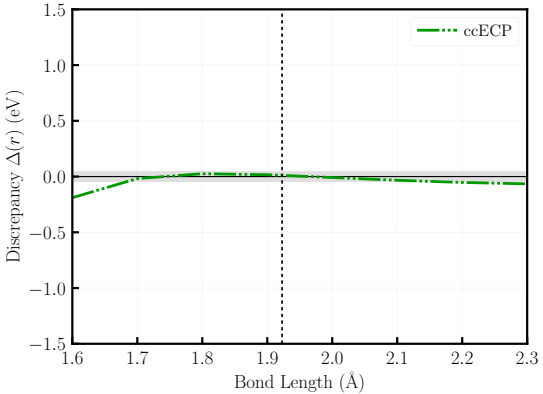
- Validated against **CCSD(T)** for precise spectra (neutral atom, IP, EA, excitations).
- Stress tested in various bonding environments using molecular binding curves across non-equilibrium geometries, ensuring **chemical accuracy** (1 kcal/mol $\approx$ 0.043 eV).
- Quantify the associated locality and fixed-node biases in DMC.
- Determine energy cutoffs for plane-wave codes using the UPF forms:
  - Main Group Elements (large core): $\approx$ 60 Ry
  - Main Group Elements (small core): $\approx$ 200 Ry
  - Transition Metals: $\approx$ 350 Ry
  - Lanthanides: $\approx$ 400 Ry

PbO molecule binding curve and discrepancy, all-el vs ccECP

(Pb: core[[Xe]$4f^{14}5d^{10}$], valence $6s^26p^2$)



(a) Comparison of Morse potential fits for PbO: AE vs ccECP.



(b) Binding energy discrepancies for PbO molecule.

Generalization for spin-orbit interactions

- Semi-local, fully spin-orbit relativistic ECP (SOREP):

$$V_i^{\mathrm{SOREP}} = \underbrace{V_i^{\mathrm{AREP}}}_{\text{Averaged relativistic effective potential}} + \underbrace{V_i^{\mathrm{SO}}}_{\text{Spin-orbit terms}} ,$$

where:

- V_i^{AREP}: Captures all relativistic effects with averaged spin-orbit coupling (acts on ordinary spatial orbitals).
- V_i^{SO}: Captures relativistic splitting (acts on 2-comp. spinors).

Currently Available Elements on Pseudopotential Library (https://pseudopotentiallibrary.org/)

- Currently completed: 67 elements (~ 60% of the periodic table).

$$\underbrace{12}_{s\text{-block}} + \underbrace{25}_{p\text{-block}} + \underbrace{25}_{d\text{-block}} + \underbrace{5}_{f\text{-block}} = 67$$

E.g. Si ccECP on pseudopotential library

- Multiple core choice
- Format support for quantum chemistry codes.
- Optimized **(aug)-cc-p(C)VnZ Gaussian basis sets**.
- **Semi-local** formats (including radial grid-based ".xml" used in QMCPACK)
- **Kleinman-Bylander** ".upf" version for plane-wave codes.
  - ".rpt" contains relevant information about the conversion and transferability.

Download directly through the website or using command-line
wget http://pseudopotentiallibrary.org/recipes/element/ccECP/element.file.format

Silicon

ccECP

ccECP from Chandler Bennett et al. Journal of Chemical Physics 149, 104108 (2018)

Si.aug-cc-pV5Z.gamess
Si.aug-cc-pV5Z.gaussian
Si.aug-cc-pV5Z.molpro
Si.aug-cc-pV5Z.nwchem
Si.aug-cc-pV6Z.gamess
Si.aug-cc-pV6Z.gaussian
Si.aug-cc-pV6Z.molpro
Si.aug-cc-pV6Z.nwchem
Si.aug-cc-pVDZ.gamess
Si.aug-cc-pVDZ.gaussian
Si.aug-cc-pVDZ.molpro
Si.aug-cc-pVDZ.nwchem
Si.aug-cc-pVQZ.gamess
Si.aug-cc-pVQZ.gaussian
Si.aug-cc-pVQZ.molpro
Si.aug-cc-pVQZ.nwchem
Si.aug-cc-pVTZ.gamess
Si.aug-cc-pVTZ.gaussian
Si.aug-cc-pVTZ.molpro
Si.aug-cc-pVTZ.nwchem
Si.cc-pV5Z.gamess
Si.cc-pV5Z.gaussian
Si.cc-pV5Z.molpro
Si.cc-pV5Z.nwchem
Si.cc-pV6Z.gamess
Si.cc-pV6Z.gaussian
Si.cc-pV6Z.molpro
Si.cc-pV6Z.nwchem
Si.cc-pVDZ.gamess
Si.cc-pVDZ.gaussian
Si.cc-pVDZ.molpro
Si.cc-pVDZ.nwchem
Si.cc-pVQZ.gamess
Si.cc-pVQZ.gaussian
Si.cc-pVQZ.molpro
Si.cc-pVQZ.nwchem
Si.cc-pVTZ.gamess
Si.cc-pVTZ.gaussian
Si.cc-pVTZ.molpro
Si.cc-pVTZ.nwchem
Si.ccECP.gamess
Si.ccECP.gaussian
Si.ccECP.molpro
Si.ccECP.nwchem
Si.ccECP.rpt
Si.ccECP.upf
Si.ccECP.xml

ccECP_He_core

ccECP from Chandler Bennett et al. Journal of Chemical Physics 149, 104108 (2018)

Si.aug-cc-pCV5Z.gamess
Si.aug-cc-pCV5Z.gaussian
Si.aug-cc-pCV5Z.molpro
Si.aug-cc-pCV5Z.nwchem
Si.aug-cc-pCVDZ.gamess
Si.aug-cc-pCVDZ.gaussian
Si.aug-cc-pCVDZ.molpro
Si.aug-cc-pCVDZ.nwchem
Si.aug-cc-pCVQZ.gamess
Si.aug-cc-pCVQZ.gaussian
Si.aug-cc-pCVQZ.molpro
Si.aug-cc-pCVQZ.nwchem
Si.aug-cc-pCVTZ.gamess
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Si.aug-cc-pCVTZ.molpro
Si.aug-cc-pCVTZ.nwchem
Si.aug-cc-pV5Z.gamess
Si.aug-cc-pV5Z.gaussian
Si.aug-cc-pV5Z.molpro
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Si.aug-cc-pVTZ.gaussian
Si.aug-cc-pVTZ.molpro
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Si.cc-pCV5Z.molpro
Si.cc-pCV5Z.nwchem
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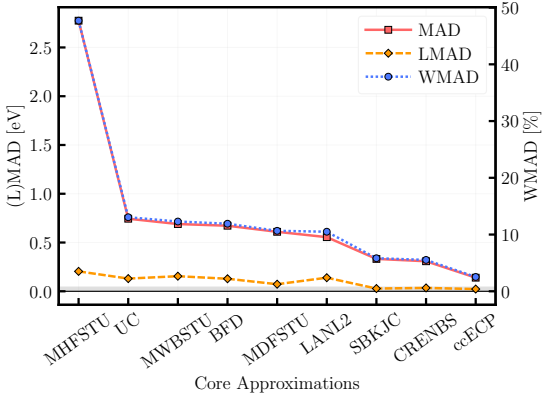
Si.cc-pCVQZ.gaussian
Si.cc-pCVQZ.molpro
Si.cc-pCVQZ.nwchem
Si.cc-pCVTZ.gamess
Si.cc-pCVTZ.gaussian

ccECPs library and literature

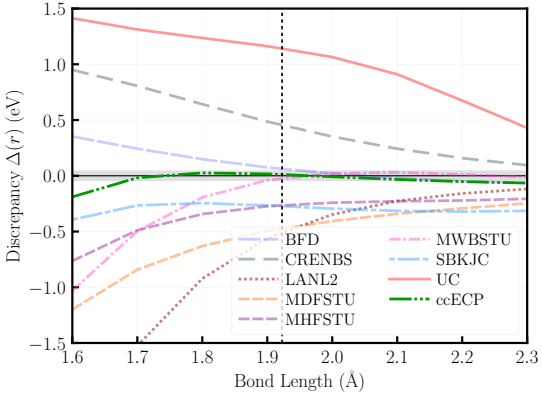
- Available at pseudopotentiallibrary.org:
- Papers:
  - Lanthanides, heavy 5*s*, 6*s*, 5*p*, 6*p* and 4*d* arXiv:2505.18100 (2025)
  - Lanthanides, heavy 4*d* and 5*d*: Journal of Chemical Physics 160 084302 (2024)
  - 3*d* ccECP-soft: J. Chem. Phys. 157, 174307 (2022)
  - Heavy 4*d*, 5*d*, 6*s*, and 6*p*: Journal of Chemical Physics 157 054101 (2022)
  - 4*s*, 4*p* and 1st row: Journal of Chemical Physics 151, 144110 (2019)
  - 3*d* transition metals: Journal of Chemical Physics 149, 134108 (2018)
  - 2nd row: Journal of Chemical Physics 149, 104108 (2018)
  - 1st and 2nd row: Journal of Chemical Physics 147, 224106 (2017)

$6p$: Pb with [[Xe]$4f^{14}5d^{10}$] (4 valence e^-: $6s^26p^2$)

- Energy cutoff for plane-wave calculations 40 Ry.



(a) Atomic Spectra Benchmarks



(b) Binding energy discrepancies for PbO molecule.