

QMC Workshop 2021

Optimization of Pseudopotentials

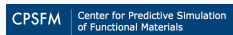
Week 6 / 9 November 2021

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https://github.com/QMCPACK/qmc_workshop_2021

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Conventional ECP Optimization Approaches

For a chosen subset S of atomic spectrum, generate relativistic all-electron (AE) reference states using HF (mean-field). Two main approaches are:

1. Energy-consistency of the atomic spectrum gaps:

$$\mathcal{E}_{\text{HF}}^2 = \sum_{i \in S} \left(\Delta E_{\text{HF}}^{\text{ECP}} - \Delta E_{\text{HF}}^{\text{AE}} \right)_i^2 \quad (1)$$

2. Shape-consistency:

$$\mathcal{N}^2 = \sum_{\ell} \left[\left(\epsilon_{\ell}^{\text{ECP}} - \epsilon_{\ell}^{\text{AE}} \right)^2 + \left(N_{\ell}^{\text{ECP}} - N_{\ell}^{\text{AE}} \right)^2 + \left(V_{\ell}^{\text{ECP}} - V_{\ell}^{\text{AE}} \right)^2 + \left(S_{\ell}^{\text{ECP}} - S_{\ell}^{\text{AE}} \right)^2 \right] \quad (2)$$

where ϵ_{ℓ} : eigenvalues, $N_{\ell}^{\text{AE}} = \int_0^{R_{\ell}} (r^{\ell+1} \phi_{\ell}^{\text{AE}}(r))^2 dr$, $V_{\ell}^{\text{AE}} = \phi_{\ell}^{\text{AE}}(R_{\ell})$, $S_{\ell}^{\text{AE}} = \frac{d}{dr} \phi_{\ell}^{\text{AE}}(r)|_{R_{\ell}}$, R_{ℓ} : cutoff radius ($r^{\frac{4}{5}} \phi_{\ell}^{\text{AE}}$).

A new approach: go beyond mean-field HF, and consider electron-electron correlations.

1. AE reference data: scalar relativistic, fully-correlated (CC, CV, VV) CCSD(T).
2. Many-body method is used:

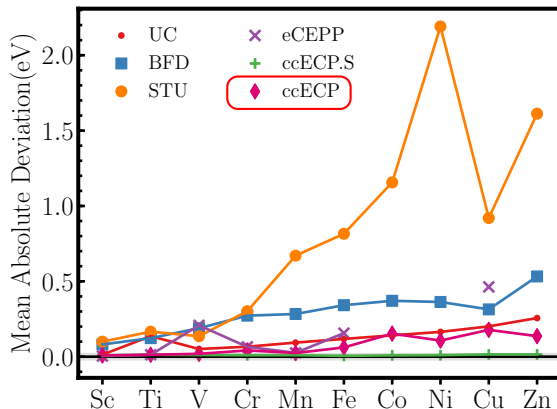
$$\mathcal{E}_{\text{CCSD(T)}}^2 = \sum_{i \in S} \left(\Delta E_{\text{CCSD(T)}}^{\text{ECP}} - \Delta E_{\text{CCSD(T)}}^{\text{AE}} \right)_i^2 + \omega \mathcal{N}^2 \quad (3)$$

3. Simple form parametrized with few Gaussians.
4. More emphasis on testing/transferability, especially on compressed XH and XO bond lengths.

Deviations between AE and ECP atomic spectrum energies

$$\text{MAD} = \frac{1}{N_s} \sum_{s=1}^{N_s} \left| \Delta E_s^{\text{ECP}} - \Delta E_s^{\text{AE}} \right| \quad (4)$$

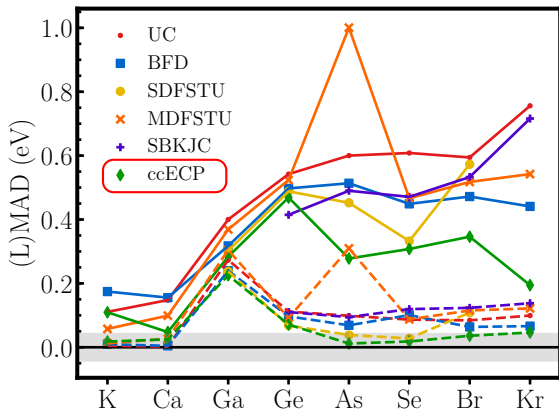
- Iso-spectrality with AE is met to a high-accuracy.
- Many states are included: neutral excitations, EA, IPs down to the bare core.
- ccECP shows significant improvement over older ECPs.



Annaberdiyev et al, J. Chem. Phys. 149, 134108 (2018) [2]

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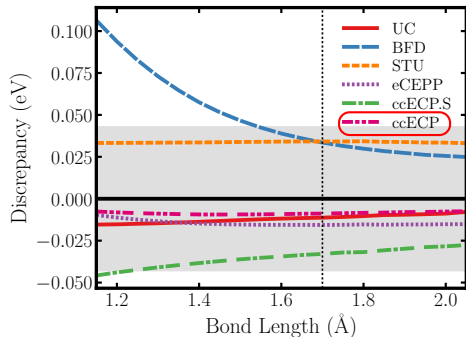
- Accurate in low-lying excitations (LMAD) and for large set of states (MAD).
- Better iso-spectrality in all ccECPs: H-Kr.
- Training data was optimized better. How does this carry to more complicated systems?



Wang et al, J. Chem. Phys. 151, 144110 (2019) [4]

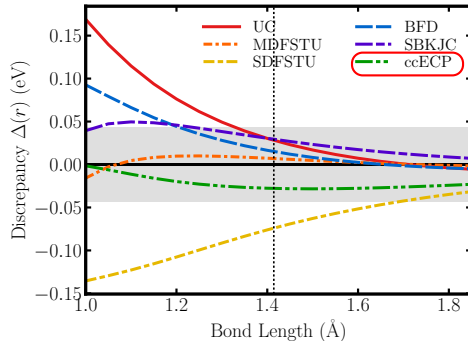
Discrepancy between AE and ECP monohydride binding energies (σ bonds)

VH molecule



Annaberdiyev et al, J. Chem. Phys. 149, 134108 (2018) [2]

BrH molecule

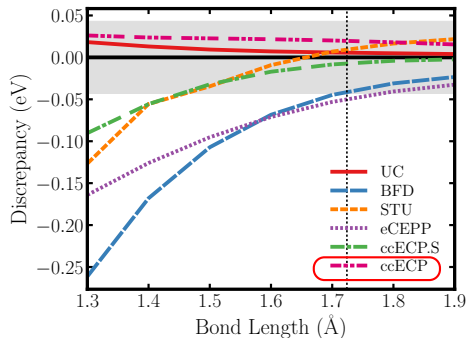


Wang et al, J. Chem. Phys. 151, 144110 (2019) [4]

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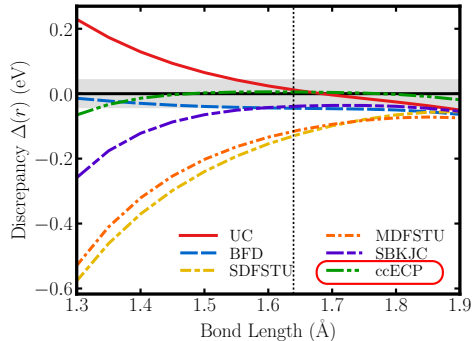
Discrepancy between AE and ECP monoxide binding energies (π bonds)

CuO molecule



Annaberdiyev et al, J. Chem. Phys. 149, 134108 (2018) [2]

SeO molecule

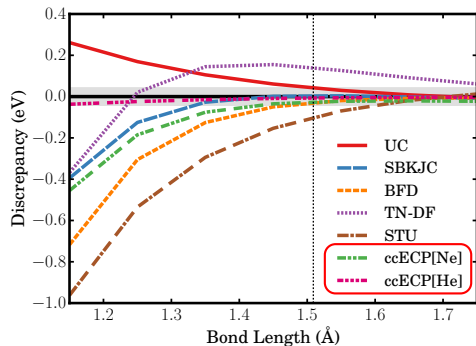


Wang et al, J. Chem. Phys. 151, 144110 (2019) [4]

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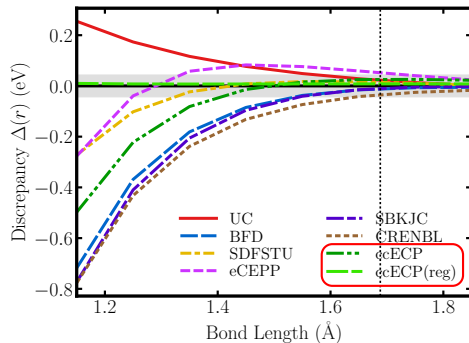
Various core sizes are available for ccECP

SiO molecule



Bennett et al, J. Chem. Phys. 149, 104108 (2018) [3]

LiO molecule



Wang et al, J. Chem. Phys. 151, 144110 (2019) [4]

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DMC singlet/triplet excitations for Si systems agree well with experiments.

TABLE IV. Si₂H₆ total energies (Ha) and vertical excitation gaps (eV) using various methods. Experimental geometry was used for this molecule.²²

	GS (¹ A _{1g})	EX (¹ E _{1u})	EX (³ A _{1g})		
Method	Total (hartree)	Total (hartree)	Gap (eV)	Total (hartree)	Gap (eV)
CISD/RHF ^a	-11.3287	-10.8183	13.889	-11.0825	6.699
CISD/CAS(14e ⁻ , 13o) ^b	-11.3400	-11.0623	7.557		
RCCSD(T)/RHF ^c	-11.3766(3)			-11.1308(5)	6.69(2)
CCSDT(Q)/RHF ^d	-11.3782(3)			-11.1336(5)	6.66(2)
DMC/RHF	-11.3708(2)	-11.0855(2)	7.763(8)	-11.1215(2)	6.784(8)
DMC/PBE ^e	-11.3725(2)	-11.0934(2)	7.595(8)	-11.1248(2)	6.740(8)
Lehtonen <i>et al.</i> ^f			7.61		
Experiment ⁴¹			7.6		≈6.7 ^g
Experiment ³⁹			7.56		

DMC IP and EA of variety of molecular systems were tested by an independent group.

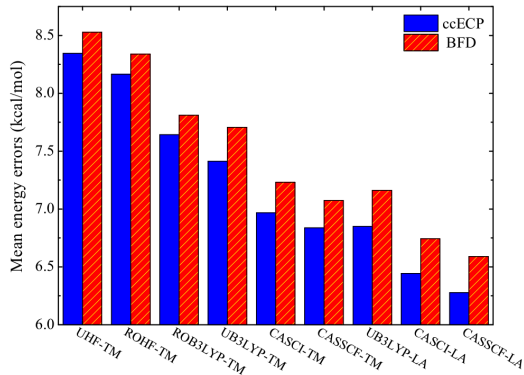


FIG. 5. Mean errors in DMC energies using ccECP and BFD potentials with different trial wave functions and nonlocal-treating strategies.

- The library is hosted on GitHub:
<https://github.com/QMCPACK/pseudopotentiallibrary>
- AREP ccECPs for H-Kr elements are available now.
- Heavier elements with SOC will be added later, attend Week-8 to learn how to run with SOREP.
- (aug)-cc-p(C)VnZ [$n = D - 6$] basis-sets are available.
- Commonly used formats are available: MOLPRO, GAMESS, NWChem, PYSCF.
- Also, UPF files are available for use in plane wave basis codes.

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	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
		Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu									
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

Copper

RRKJ_PRB_93_075143 Rappe-Rabe-Kaxiras-joannopoulos potential from J. T. Krogel et al. Physical Review B 93 075143 (2016) Cu.opt.upf Cu.opt.xml	TM_PRB_93_075143 Troullier-Martins potential from J. T. Krogel et al. Physical Review B 93 075143 (2016) Cu.tm.upf Cu.tm.xml	eCEPP eCEPP from J. R. Trail and R. J. Needs Journal of Chemical Physics 146, 204107 (2017) Cu.awfn Cu.data	ccECP ccECP from A. Annaberdiyev et al. Journal of Chemical Physics 149, 134108 (2018) Cu.cc-pCVTZ.gamess Cu.cc-pCVTZ.molpro
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Update workshop example files:

```
cd $HOME/qmc_workshop_2021  
git pull
```

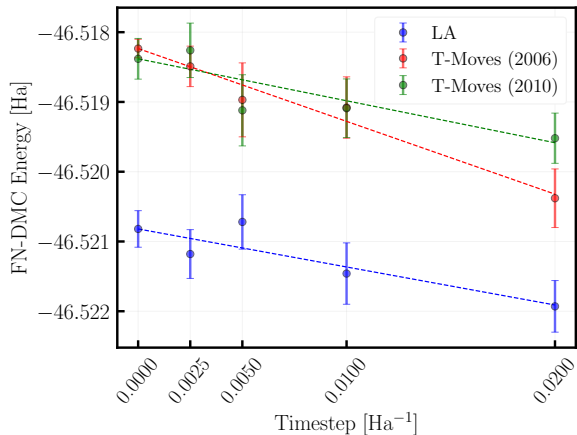
Enter week 6 example directory:

```
cd $HOME/qmc_workshop_2021/week6_ecps_and_observables/02_ccECP_slides_runs/
```

See Week 3 material for introduction to NEXUS.

(Walkthrough of input files here ...)

Sc atom results



Locality Treatment	Execution Time (min)
LA	18.3
T-Moves (2006)	21.0
T-Moves (2010)	26.6

Table 1: Comparison of execution times for various locality treatments. NERSC, 8 KNL nodes.

Table 17. Most Accurate Total Energies for ccECP[Ne] K–Zn Elements along with Fixed-Node DMC Energies with Single-Reference HF Trial Wave Functions^a

atom	state	“exact” (Ha)	DMC/HF (Ha)	ϵ (mHa)	η
K	(² S)	−28.25243(25)	−28.2394(2)	13.0(3)	4.1(1)
Ca	(¹ S)	−36.72897(46)	−36.7055(2)	23.5(5)	6.2(1)
Sc	(² D)	−46.55704(81)	−46.5202(4)	36.8(9)	8.4(2)
Ti	(³ F)	−58.09263(76)	−58.0458(2)	46.8(8)	9.6(2)
V	(⁴ F)	−71.44178(59)	−71.3829(2)	58.9(6)	10.8(1)
Cr	(⁷ S)	−86.64109(33)	−86.5876(2)	53.5(4)	9.03(7)
Mn	(⁶ S)	−103.8919(10)	−103.8260(3)	66(1)	10.2(2)
Fe	(⁵ D)	−123.38804(93)	−123.3100(3)	78(1)	10.5(1)
Co	(⁴ F)	−145.1541(10)	−145.0709(3)	83(1)	10.1(1)
Ni	(³ F)	−169.3912(12)	−169.2973(6)	94(1)	10.3(1)
Ni	(³ D)	−169.3932(12)	−169.3056(6)	88(1)	9.0(1)
Cu	(² S)	−196.4038(10)	−196.3178(3)	86(1)	8.1(1)
Zn	(¹ S)	−226.3699(18)	−226.2775(4)	92(2)	8.4(2)

Annaberdiev et al, J. Chem. Theory Comput. 2020, 16, 3, 1482–1502 [1]

Another reason to use T-Moves: Avoiding instabilities

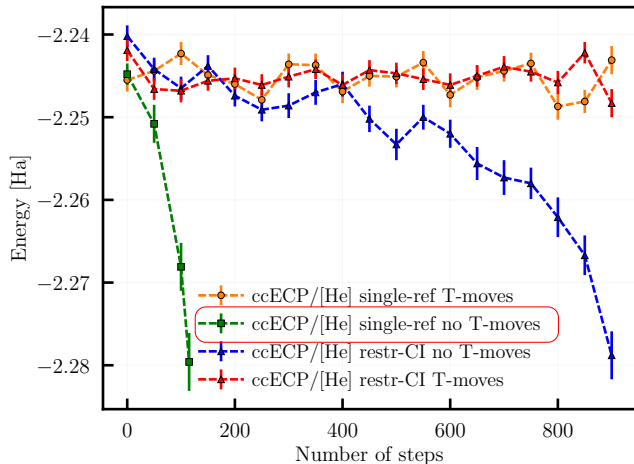


Figure: FNDMC energies vs number of steps (in time steps of 0.001 Ha^{-1}) for BeH_2 molecule. Be atom is represented by ccECP/[He].



A. Annaberdiyev, C. A. Melton, M. C. Bennett, G. Wang, and L. Mitas.

Accurate Atomic Correlation and Total Energies for Correlation Consistent Effective Core Potentials.

Journal of Chemical Theory and Computation, 16(3):1482–1502, Mar. 2020.



A. Annaberdiyev, G. Wang, C. A. Melton, M. C. Bennett, L. Shulenburger, and L. Mitas.

A new generation of effective core potentials from correlated calculations: 3d transition metal series.

The Journal of Chemical Physics, 149(13):134108, Oct. 2018.



M. C. Bennett, G. Wang, A. Annaberdiyev, C. A. Melton, L. Shulenburger, and L. Mitas.

A new generation of effective core potentials from correlated calculations: 2nd row elements.

The Journal of Chemical Physics, 149(10):104108, Sept. 2018.



G. Wang, A. Annaberdiyev, C. A. Melton, M. C. Bennett, L. Shulenburger, and L. Mitas.

A new generation of effective core potentials from correlated calculations: 4s and 4p main group elements and first row additions.

The Journal of Chemical Physics, 151(14):144110, Oct. 2019.



G. Wang, A. Annaberdiyev, and L. Mitas.

Binding and excitations in SixHy molecular systems using quantum Monte Carlo.

The Journal of Chemical Physics, 153(14):144303, Oct. 2020.



H. Zhou, A. Scemama, G. Wang, A. Annaberdiyev, B. Kincaid, M. Caffarel, and L. Mitas.

A quantum Monte Carlo study of systems with effective core potentials and node nonlinearities.

arXiv:2109.08653 [physics], Sept. 2021.



X. Zhou, H. Zhao, T. Wang, and F. Wang.

Diffusion quantum Monte Carlo calculations with a recent generation of effective core potentials for ionization potentials and electron affinities.

Physical Review A, 100(6):062502, Dec. 2019.