

Correlation consistent effective core potentials: recent developments

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Effective Core Potentials (ECP)

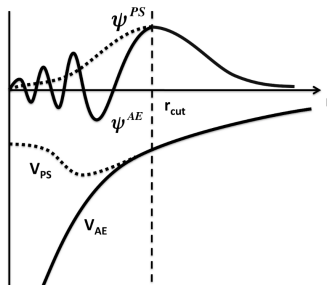
AE calculations are expensive:

QMC : $O(Z^{5.5 \sim 6.5})$

CISD : $O(Z^6)$

CCSD(T) : $O(Z^7)$

- Deep inner core electrons are largely inert in most cases, hence they can be treated as a 'background'.
- Replace the inner-shell electrons with effective potentials.
- Core choices: break by primary quantum number n for most, and special l -based constructions for lanthanides.



Schematic of how an ECP mimics the Coulomb potential and the effect on wavefunction compared to the all-electron case.

Correlation consistent effective core potential(ccECP)

$$SOREP \text{ ccECP} = AREP \text{ ccECP} + SO \text{ terms}$$

$$V_{ECP}(r_i) = V_{loc}(r_i) + \sum_{l=0}^{l_{max}} V_l(r_i) \sum_m |lm\rangle \langle lm| \quad (1)$$

SO represents spin-orbit and AREP is averaged relativistic effective potential.

- **Many-body construction**. High accuracy at the coupled-cluster level.
- **Spin-orbit terms** are provided for heavier elements for research on novel properties of materials.
- **Accuracy and transferability** are tested at atomic and molecular levels.
- Providing **plane-wave and semi-local Gaussian** forms.

Overview of developments

- Created competitive ECPs that are adapted for use in planewave codes.
- Developed a number of ccECPs for heavy transition metals and main group elements.
- Developed a few new 4f ccECPs that break into the lanthanide block.

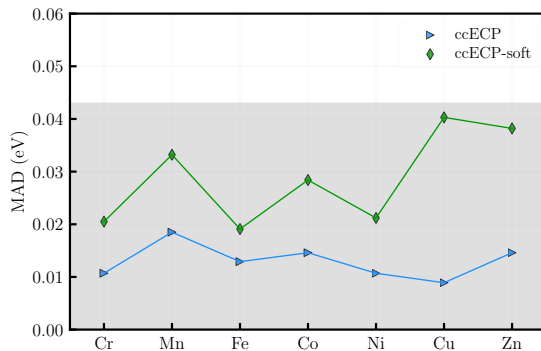
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Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		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	Md	No	Lr		

Haihan Zhou et al. J. Chem. Phys. (accepted, expected publication early 2024)
 Benjamin Kincaid et al. J. Chem. Phys. 157, 174307 (2022)
 Guangming Wang et al. J. Chem. Phys. 157 054101 (2022)
 Guangming Wang et al. J. Chem. Phys. 151, 144110 (2019)
 Abdulgani Annaberdiyev et al. J. Chem. Phys. 149, 134108 (2018)

Soft 3d spectrum performance and MADs

$$\text{MAD} = \frac{1}{N} \sum_{s=1}^N |\Delta E_s^{\text{ECP}} - \Delta E_s^{\text{AE}}| \quad (2)$$

- The states tested range from low-lying excitations to +4 or +5 ionized states
- For every state coupled cluster was run to test the ECP for correlation energy
- ccECP-soft MADs lay within chemical accuracy for all elements in this set.



B. Kincaid et al, JCP, 2022

Soft 3d performance in molecular binding

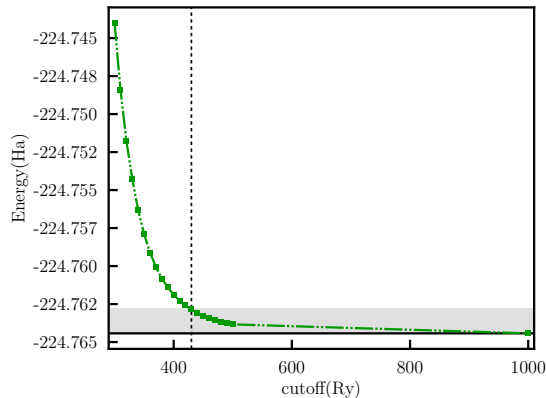
- MAD of binding parameters for various core approximations w.r.t. all electron correlated data for late 3d transition metals.
- All parameters obtained using Morse potential fit
- Dissociation energy D_e , equilibrium bond length r_e , vibrational frequency ω_e and discrepancy of binding energy at dissociation bond length D_{diss}

TABLE II: Mean absolute deviations of binding parameters for various core approximations with respect to AE correlated data for related hydride and oxide molecules. All parameters were obtained using Morse potential fit. The parameters shown are dissociation energy D_e , equilibrium bond length r_e , vibrational frequency ω_e and binding energy discrepancy at dissociation for compressed bond length D_{diss} .

	D_e (eV)	r_e (Å)	ω_e (cm ⁻¹)	D_{diss} (eV)
ccECP	0.0119(50)	0.0008(17)	2.8(5.5)	0.015(47)
ccECP-soft	0.0174(50)	0.0012(17)	4.6(5.5)	0.023(47)

TMO solidstate performance and cutoffs

- Using QE we verified the performance of the softened ccECPs at smaller cutoffs
- We first calculated a reference “converged” energy at a large cutoff (2000 Ry)
- We then performed the same calculation only altering the cutoff over the range 300 Ry to 500 Ry
- The energy is considered converged when the discrepancy drops below 1 meV/valence electron



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Figure: FeO

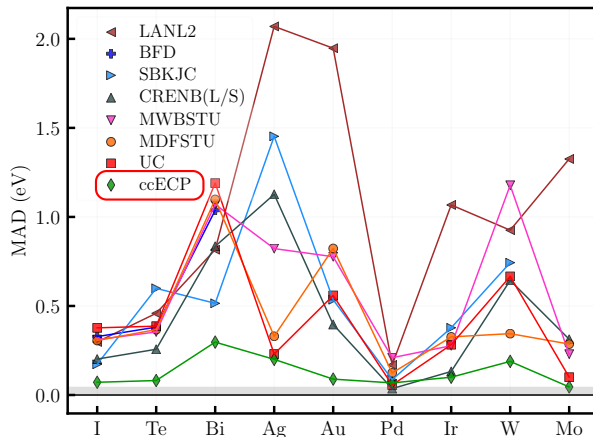
TMO cutoffs comparison

TMO	ccECP-soft(Ry)	ccECP(Ry)
FeO	430	1140
CuO	390	1500
ZnO	390	1315

TABLE XXIII: Summarizing table for FeO, CuO and ZnO comparing the cutoffs for the ccECP-soft and ccECP pseudopotentials. The old standard ccECPs generally triple the cutoff of the softened versions, leading to a much higher computational cost in this particular application.

Atomic Spectrum MADs for selected heavy elements

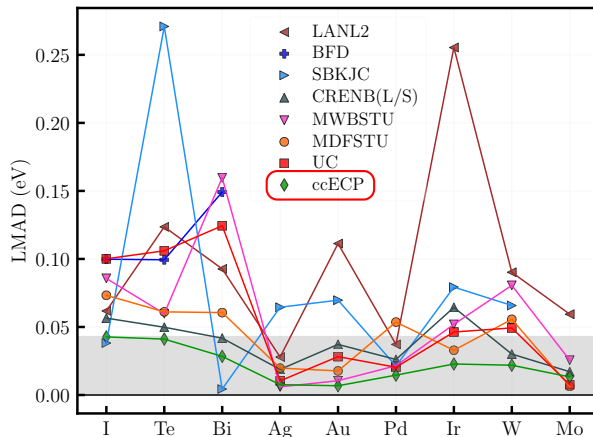
- Discrepancies with AE CCSD(T) excitations.
- ccECPs show significant improvement over other ECPs
- ccECPs also show overall improvement in accuracy when compared to UC(uncorrelated core).



G. Wang et al, JCP, 2022

Atomic Spectrum L-MADs for selected heavy elements

- Low-lying state discrepancies with AE CCSD(T) excitations.
- The states considered are the first excited, electron affinity, first ionization potential(IP), and second IP.
- All discrepancies fall below the chemical accuracy threshold when looking specifically at the low-lying states.

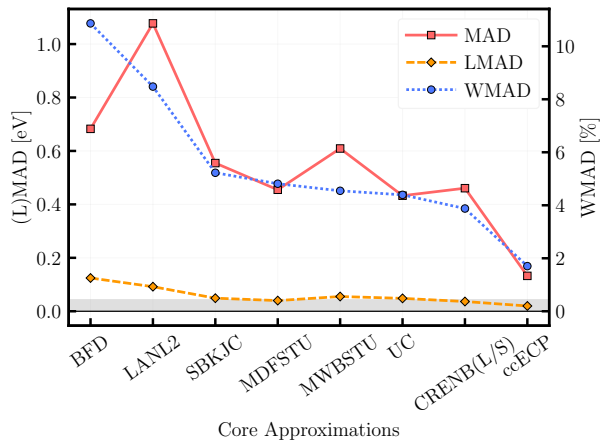


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Complete summary of (L/W)MADs for selected heavy elements

$$\text{WMAD} = \frac{1}{N} \sum_i^N \frac{100\%}{\sqrt{|\Delta E_i^{\text{AE}}|}} \left| \Delta E_i^{\text{ECP}} - \Delta E_i^{\text{AE}} \right|. \quad (3)$$

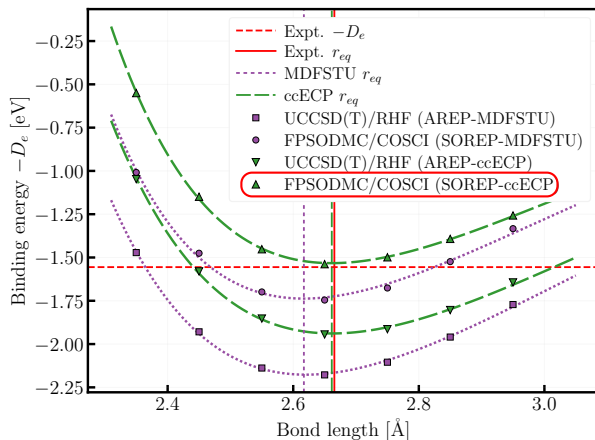
- ccECPs clearly improve on average all MADs accross the elements in the project.
- No other ECP table is as accurate.



Spin orbit performance in molecular binding at fixed phase DMC level

- In the I_2 dimer, spin orbit greatly improves the agreement with experiment.
- The inclusion of spin orbit moves the binding energy to very close to experimental values.

G. Wang et al, JCP 2022



Performance for molecular parameters: heavy elements

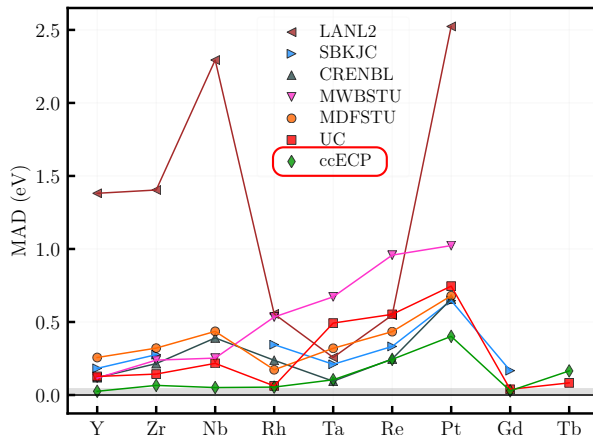
- MAD of binding parameters for various core approximations w.r.t. all electron correlated data for selected heavy transition metals.
- All parameters obtained using Morse potential fit
- Dissociation energy D_e , equilibrium bond length r_e , vibrational frequency ω_e and discrepancy of binding energy at dissociation bond length D_{diss}

TABLE XV: Mean absolute deviations of binding parameters for various core approximations with respect to AE correlated data for I, Te, Ag, Pd, Mo, Bi, Au, Ir, W related molecules. All parameters were obtained using Morse potential fit. The parameters shown are dissociation energy D_e , equilibrium bond length r_e , vibrational frequency ω_e and binding energy discrepancy at dissociation bond length D_{diss} .

	$D_e(\text{eV})$	$r_e(\text{\AA})$	$\omega_e(\text{cm}^{-1})$	$D_{diss}(\text{eV})$
BFD	0.078(6)	0.018(1)	22(3)	0.41(5)
CRENBL(S)	0.115(5)	0.0183(9)	26(3)	0.40(4)
LANL2	0.118(5)	0.0122(9)	16(3)	0.36(4)
MDFSTU	0.096(5)	0.0094(9)	10(3)	0.24(4)
MWBSTU	0.050(5)	0.0056(9)	10(3)	0.10(4)
SBKJC	0.089(4)	0.0120(8)	19(2)	0.30(4)
UC	0.040(5)	0.0104(9)	13(3)	0.19(4)
ccECP	0.018(5)	0.0022(9)	6(3)	0.07(4)

Atomic Spectrum MADs for heavy and f-elements

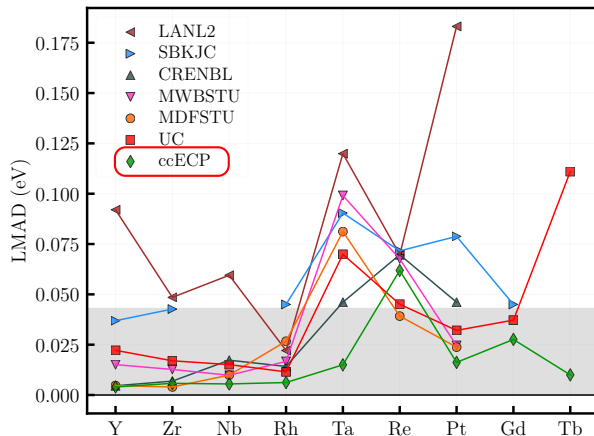
- Discrepancies when compared with AE CCSD(T) excitations.
- ccECPs also show moderate improvement when compared with UC, especially in the case of the 4f elements.
- There were a number of compromises that had to be made when constructing the 4f ccECPs.



GM Wang et al, JCP, 2022; Haihan Zhou et al, upcoming; A Annaberdiyev et al,

Atomic Spectrum LMADs for heavy and f-elements

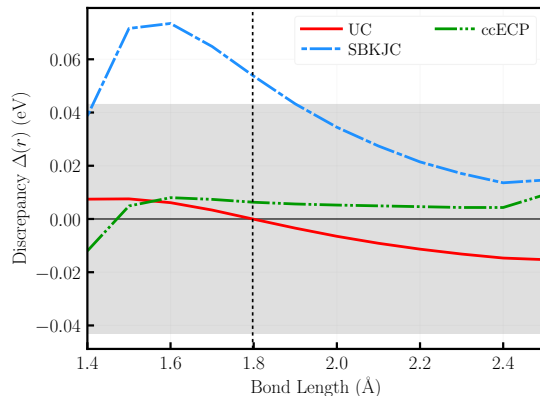
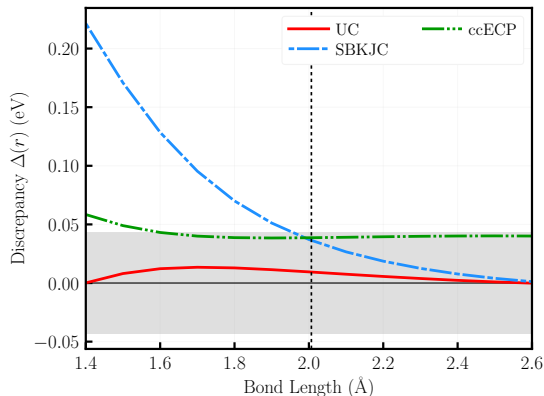
- Atomic spectra accuracy are improved in both low-lying excitations (LMAD) also for large set of states (MAD).
- The states considered are the first excited, the electron affinity, first IP, and second IP.
- Lathanides:** core choice: $[Kr]4d^{10}$
Tb, and Gd exhibit special difficulties in ECP construction due to stronger correlations and f-electron shell in valence space.



H. Zhou et al, upcoming; A. Annaberdiyev et al, arXiv.2302.01903

Gadolinium molecular binding curve discrepancies

GdH₃ and GdO discrepancies using an uncontracted aug-cc-pwCVTZ.



H. Zhou et al, upcoming

Performance for molecular parameters: *f*-elements

- MAD of binding parameters for various core approximations w.r.t. all electron correlated data for selected 4*d* transition metals.
- All parameters obtained using Morse potential fit
- Dissociation energy D_e , equilibrium bond length r_e , vibrational frequency ω_e and discrepancy of binding energy at dissociation bond length D_{diss}

TABLE IV: Mean absolute deviations of molecular binding parameters for various core approximations with respect to AE data for 4*d* selected heavy-element groups, Y, Zr, Nb, and Rh related molecules. All parameters were obtained using Morse potential fit. The parameters shown are dissociation energy D_e , equilibrium bond length r_e , vibrational frequency ω_e and binding energy discrepancy at dissociation bond length D_{diss} .

	D_e (eV)	r_e (Å)	ω_e (cm ⁻¹)	D_{diss} (eV)
UC	0.02(1)	0.002(2)	4(7)	0.05(8)
CRENBL	0.02(1)	0.001(2)	2(7)	0.03(8)
LANL2	0.05(1)	0.003(2)	6(7)	0.06(8)
MDFSTU	0.03(1)	0.002(2)	4(7)	0.05(8)
MWBSTU	0.01(1)	0.001(2)	3(7)	0.03(8)
SBKJC	0.03(1)	0.004(2)	10(7)	0.05(7)
ccECP	0.01(1)	0.002(2)	3(7)	0.03(8)

Conclusions

- New ccECP-soft versions for elements: Cr, Mn, Co, Ni, Cu, and Zn
- Developed more ccECPs for heavy transition metals and two f-elements at the time of writing.
- These new ccECPs are available in various useful formats (Gaussian, UPF, Molpro, XML, etc.)
- For each element there are basis sets available in any quality from DZ to 5Z in a variety of commonly used formats.

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	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		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	Md	No	Lr		

- All current ccECPs and basis sets may be found at pseudopotentiallibrary.org
- All papers are published with JCP or are available on arXiv.