Pseudopotentials for correlated electronic systems

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Why do we need even more pseudopotentials?

- Ultrasoft pseudopotentials are not applicable in QMC or Quantum chemistry
- Well-established libraries provide DFT or HF pseudopotentials
- None are available constructed from explicitly correlated atoms & ions
- Assessment of pseudopotentials is often for atoms only
- Assessment of pseudopotentials usually excludes correlation effects

Pseudopotentials

- Removing inert core electrons is physically justified and successful
- Reduce computational cost *a lot*
- Removes singularity in the electron-ion potential (eg QMC)
- Pseudopotentials are not unique, so there are many to choose from

but there are problems ...

- Pseudopotential error is uncontrolled
- Underlying theory is a mean-field theory
- No many-body pseudopotential theory is available
- Limited available error data for pseudopotentials in CCSD(T) or QMC
- Failure for plane-wave calculations can be catastrophic - 'ghost states'

New correlated electron pseudopotential - CEPPs [1]

- Define pseudopotentials using pseudo-density matrix
- Make pseudopotentials from explicitly correlated atoms
- Generate for first row atoms
- Generate for 3d-transition metal atoms

  . . . and test their performance:
- Compare all-electron and pseudopotential results
- Measure accuracy for small molecules
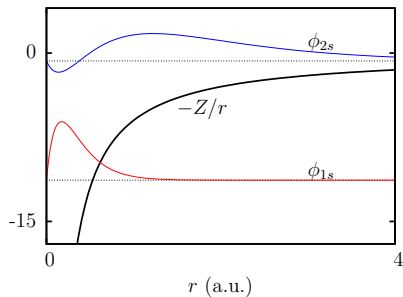- CCSD(T) for correlation of valence electrons
- Geometry, D_e, and ZPVE

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[1] Trail and Needs, J. Chem. Phys. 139 , 014101 (2013)
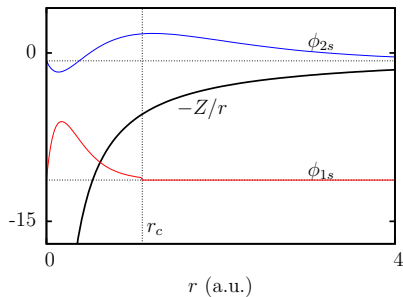
Mean-field pseudopotentials
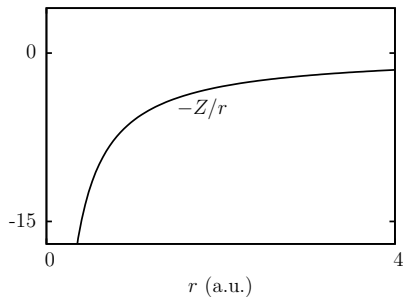
1) Coulomb potential and atomic number defines atom
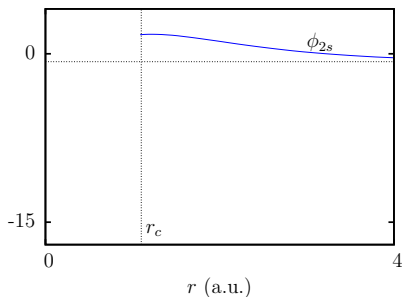
Mean-field pseudopotentials

2) Solve for one orbital per electron with mean-field theory

Mean-field pseudopotentials

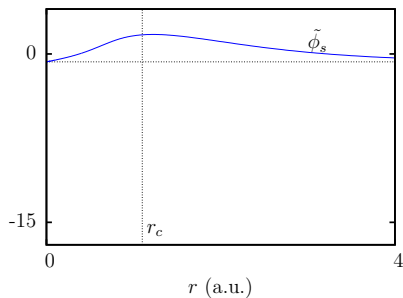3) Define a core region and contract core orbitals into core region

Mean-field pseudopotentials

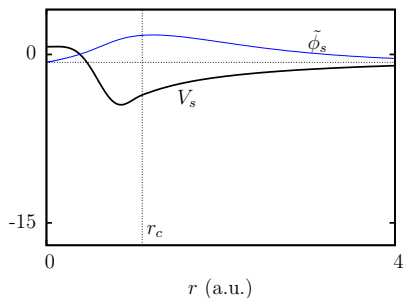4) Delete orbitals in core region, preserving orbitals outside

- This is norm-conservation as applied in mean-field theory

Mean-field pseudopotentials

5) Redefine valence orbitals in core region to provide a pseudo-atom

Mean-field pseudopotentials

6) Invert mean-field theory to make an effective potential

- Atomic GS with effective potential is the pseudo-atom
- Boundary conditions at $r = r_c$ reproduced exactly for GS atom
- Boundary conditions at $r = r_c$ approximately correct to 1st order
- Does not include variation of mean-field

Generalisation to Many-body wave functions

Generalisation to interacting electrons is non-trivial:

- Orbitals are not unique
- Many orbitals with partial occupation, or
- Wave functions not defined using orbitals
- Division into core and valence is unclear

  Approach is to:

- Define a pseudo-atom density-matrix from a multideterminant AE atom wave function
- Invert a SE to extract an effective potential - the Correlated Electron Pseudopotential (CEPP)

n-electron pseudo atom from a p-electron atom

AE many-body wave function p-electrons and n-valence electrons:

$$\Psi(\mathbf{r}_1 \ldots \mathbf{r}_p) = \sum_i w_i D_i(\mathbf{r}_1 \ldots \mathbf{r}_p)$$

$$\Gamma^n = \binom{p}{n} \int d\mathbf{r}_{n+1} \ldots \mathbf{r}_p \Gamma^p(\mathbf{r}_1 \ldots \mathbf{r}_n, \mathbf{r}_{n+1} \ldots \mathbf{r}_p; \mathbf{r}'_1 \ldots \mathbf{r}'_n, \mathbf{r}_{n+1} \ldots \mathbf{r}_p)$$

- p-body density matrix $\Gamma^p = \Psi^* \Psi$
- n-body density matrix obtained by reduction

$$\Gamma^n_{pp} = \begin{cases} \Gamma_n & \forall\ |\mathbf{r}_i| > r_c \\ \Gamma_{model} & \text{otherwise} \end{cases}$$

Conserving density matrix outside of core is many-body equivalent of norm-conservation [2]

- Smooth at $r = r_c$
- Normalises to n-electrons

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[2] P.H.Acioli and D.M.Ceperly, J.Chem.Phys, **100**, 8169 (1994)

n-electron pseudo atom from a p-electron atom

- Γ_{model} cannot be equivalent to HF pseudopotential
- All orbitals contribute outside of core region

This can be fixed by using determinants constructed from Natural Orbitals (NOs):

- Eigenstates of 1st order density matrix $\{\psi_i, o_i\}$
- o_i closest to step-function of all orbitals choices
- Set largest $(p - n)$ o_i's as core orbitals
- Set core orbitals to zero outside of core region

$\Rightarrow$ Modified pseudo-density $\tilde{\Gamma}_{pp}^n$

   The norm-conserving HF pseudo-atom is included in this definition

n-electron pseudo atom from a *p*-electron atom

We go no further for the general *n*-valence electrons case:

- Definition of Γ_{model} is not trivial
- $\Gamma_{pp}^n \rightarrow V_{eff}$ inversion is non trivial
- V_{eff} is non-local over all space
- V_{eff} is *n*-body potential

Solution?

- $n = 1$ for pseudopotential construction - make them from ions
- Poor transferability between ionic states occurs for KS-DFT not HF
- View the single valence electrons as a probe to measure 1-body scattering properties of the core

1-electron pseudo-atom from a *p*-electron atom

1-electron pseudo-atom density:

$$\tilde{\rho} = \left\{ \begin{array}{ll} \sum_{i>n_c} o_i \psi_i^2 & r > r_c \\ \phi^2 & r \le r_c, \end{array} \right.$$
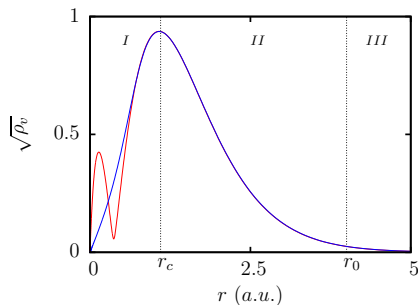
Model ϕ in the core region:

$$\phi = r^{l+1} \exp \left[\sum_{k=0}^{6} a_{2k} \, r^{2k} \right]$$

Parameters a_{2k} from:

- Normalisation
- Continuity of value and derivatives at r_c

Inversion of pseudo density

C^{+3} (^1S)

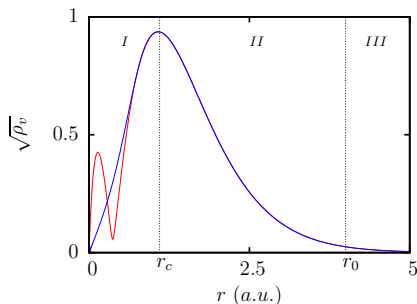Core regions *I*, region *II*, and asymptotic region *III*

- Region *III*: use asymptotic form for a polarizable ionic core

$$V_{III} = -\frac{Z_v}{r} - \frac{1}{2}\frac{\alpha}{r^4}$$

- Core charge $Z_v = Z - (p - n)$
- Dipole core polarizability α

Inversion of pseudo density

$$C^{+3} \; (^1S)$$

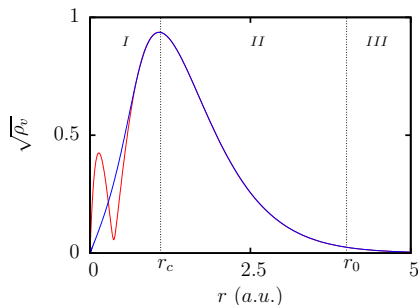Core regions *I*, region *II*, and asymptotic region *III*

- Region *II*: directly invert one-body Schrödinger equation

$$V_{II} = \frac{1}{2} \frac{1}{\rho^{1/2}} \frac{d^2 \rho^{1/2}}{dr^2} - \frac{1}{2} \frac{l(l+1)}{r^2} + \epsilon$$

- ϵ from continuity condition $V_{II}(r_0) = V_{III}(r_0)$

Inversion of pseudo density

C^{+3} (^1S)

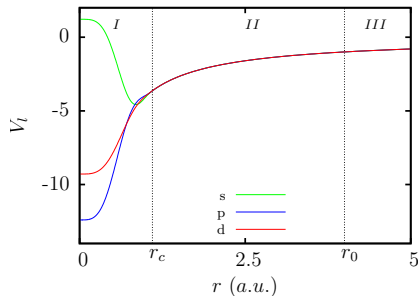Core regions *I*, region *II*, and asymptotic region *III*

- Region *I*: directly invert one-body Schrödinger equation

$$V_I = \frac{1}{2} \frac{1}{\phi} \frac{d^2\phi}{dr^2} - \frac{1}{2} \frac{l(l+1)}{r^2} + \epsilon$$

- ϵ as in region *II*

## Inversion of pseudo density

$$C^{+3} \; (^1S, ^1P, ^1D)$$

- NOs from multideterminant AE using ATSP2K
- Orbitals and determinant coefficients relaxed
- $(n - p)$ core orbitals fixed to neutral atom orbitals
- Channel L from ^1L state
- Breit-Pauli relativistic terms for transition metals

Active space defined using:

- 2 excitations, $(n, l) = (1 \ldots 7, 0 \ldots 6)$
- Channels s-d for 1st row atoms
- Channels s-f for 3d-transition metal atoms

Core Polarization Potential

- Core Polarization Potential (CPP) goes beyond 1-body pseudopotential semi-empirically
- $V_{eff} = [V_{cv} + V_e] + [V_{e-e} + V_{e-I} + V_{I-I}]$
- 1-body, 2-body and core-core interactions
- Example calculation [Müller and Meyer, 1983] for K_2 using pseudopotentials, CI, an CPP:
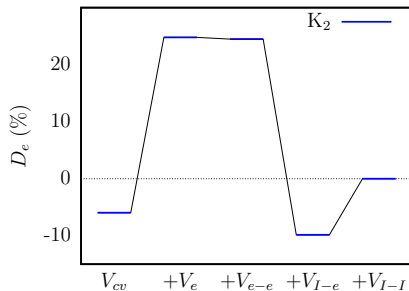
- CEPPs provides *ab initio* 1-body part $[V_{cv} + V_e]$
- Strong cancellation so keep CPP $[V_{e-e} + V_{e-I} + V_{I-I}]$
- Define $V_l^{CEPP} = V_l - V_e$
- Use V_l^{CEPP} with CPP

Parameterization

$$\tilde{V}_l^{CEPP} = \sum_{q=1}^{6} A_{ql} r^{n_{ql}} e^{-a_{ql} r^2} = \begin{cases} Z_v/r + V_{local}^{pp} & l = local \\ V_l^{pp} - V_{local}^{pp} & l \neq local \end{cases}$$

Penalty function (1):

$$\Sigma_1 = \langle \phi_l | \left[\tilde{\epsilon}_l | \tilde{\phi}_l \rangle \langle \tilde{\phi}_l | - \epsilon_l | \phi_l \rangle \langle \phi_l | \right]^2 | \phi_l \rangle$$

- (ϕ_l, ϵ_l) is 1-electron eigenstate for tabulated CEPP
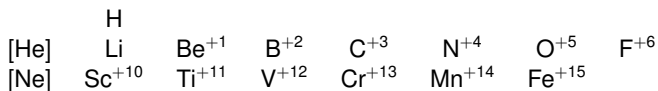- $(\tilde{\phi}_l, \tilde{\epsilon}_l)$ is 1-electron eigenstate for parameterized CEPP

Penalty function (2):

$$\Sigma_2 = \sum_{i=1}^{5} (\tilde{\epsilon}_{li} - \epsilon_{li})^2$$

- ϵ_{li} is energy for i^{th} state of tabulated CEPP
- $\tilde{\epsilon}_{li}$ is energy for i^{th} state of parameterized CEPP

CEPPs generated

Correlated MCHF 1st row ions and 3d-transition metal ions:

	H						
[He]	Li	Be^{+1}	B^{+2}	C^{+3}	N^{+4}	O^{+5}	F^{+6}
[Ne]	Sc^{+10}	Ti^{+11}	V^{+12}	Cr^{+13}	Mn^{+14}	Fe^{+15}	

CEPPs are:

- *ab initio* description of one-body part of core-electron interaction
- Parameterized pseudopotentials for use with CPPs
- CPPs contribute their many-body part only

Excitation energies for Li
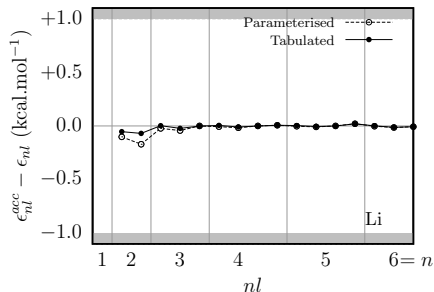
- Excitation energies compared with experiment
- Difference between CEPP energies and experiment
- Parameterization is successful
- Within chemical accuracy (< 0.1 kcal.mol^{-1})

Excitation energies for F^{+6}
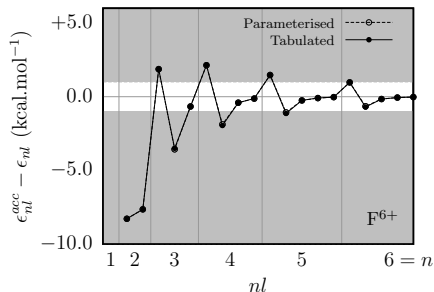
- Ion excitation energies compared with experiment
- Difference between CEPP and experiment
- Parameterization is successful
  For ionization energy:
- 3.2 kcal.mol^{-1} of 'error' from neutral atom core
- 4.3 kcal.mol^{-1} of 'error' from non-relativistic

Molecular properties

- CCSD(T) [Molpro] with CEPPs
- All-electron
- TNDF shape consistent HF pseudopotentials
- BFD energy consistent HF pseudopotentials

Quantities to evaluate and compare:

- Optimum geometries
- Dissociation energies (D_e)
- Zero-point vibrational energies (ZPVE)

CCSD(T):

- Uncontracted basis sets (aug-cc-pVnZ)
- State averaging for transition metal molecules when required
- Extrapolate to basis set limit for energies

Geometries: 1st row neutral G2 set
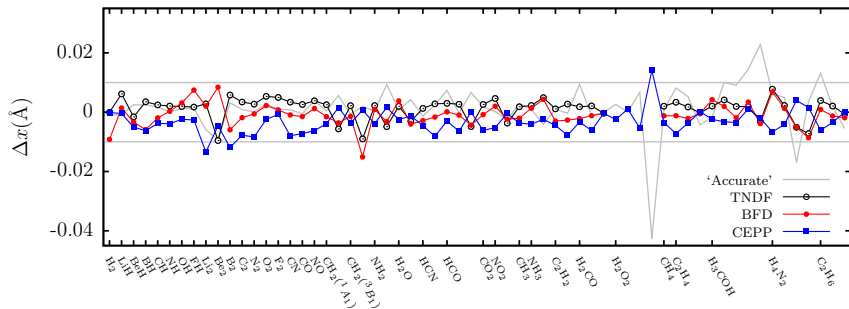
- Deviation from AE similar for TNDF, BFD, and CEPPs (MAD $\sim$ 0.004 Å)
- Almost all errors $<$ 0.01 Å
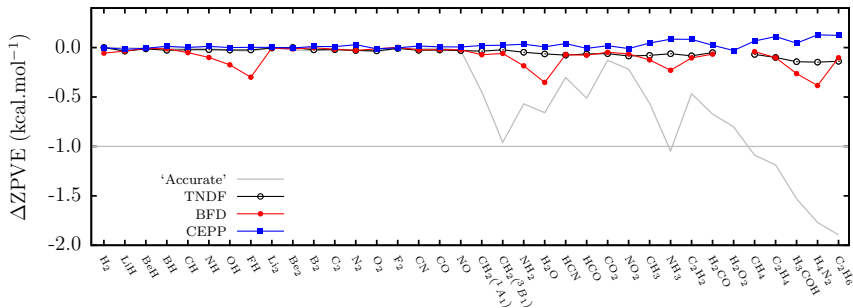- Deviation of AE from experiment is similar - MAD $\sim$ 0.005 Å

$\Rightarrow$ All approach chemical accuracy for optimum geometries

Dissociation energies: 1st row neutral G2 set
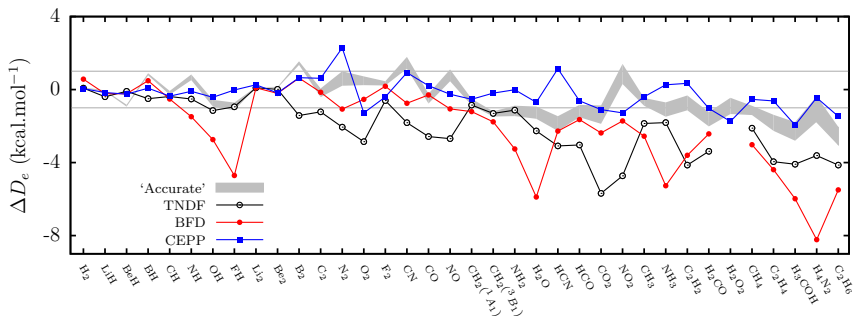
- CEPP MAD 0.6 kcal.mol^{-1}
- TNDF MAD 2.0 kcal.mol^{-1}
- BFD MAD 2.2 kcal.mol^{-1}

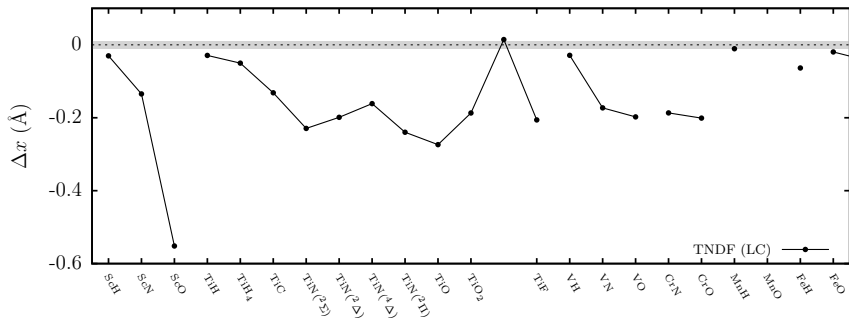$\Rightarrow$ CEPPs consistently and significantly more accurate than TNDF or BFD

ZPVEs: 1st row neutral G2 set

- Deviation from AE not significant for any potentials
- All errors < 0.13 kcal.mol^{-1}
- Deviation of AE from experiment is greater - anharmonic *H* bonds
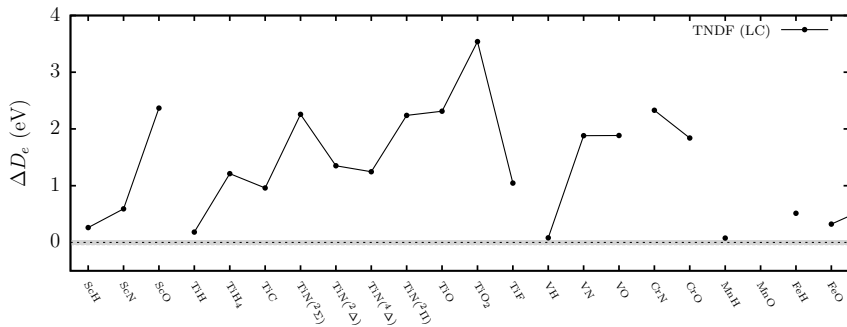
Geometries: 3d-transition metal molecules
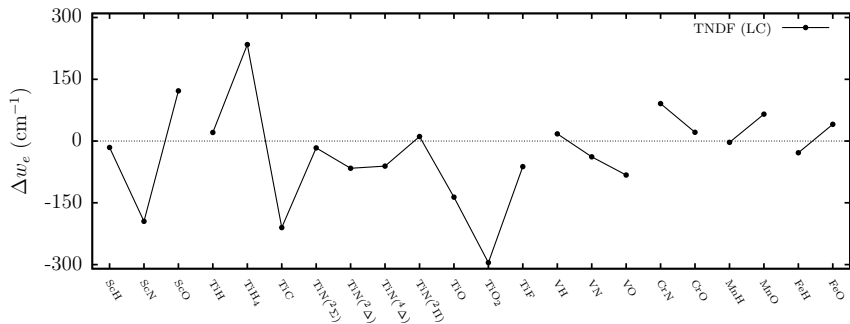
Large [Ar] core TNDF

Dissociation energies: 3d-transition metal molecules

Large [Ar]core TNDF

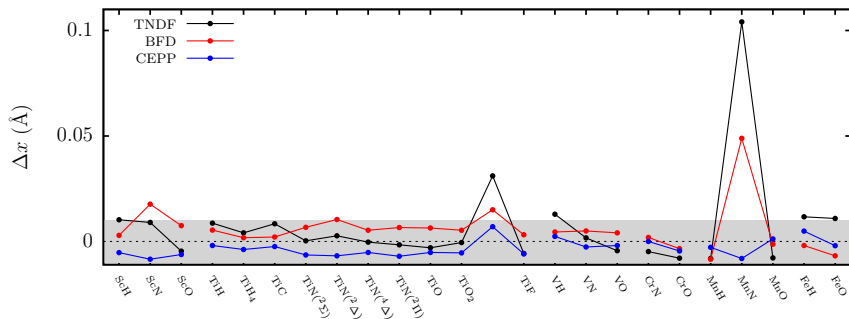## ZPVEs: 3d-transition metal molecules

Large [Ar] core TNDF
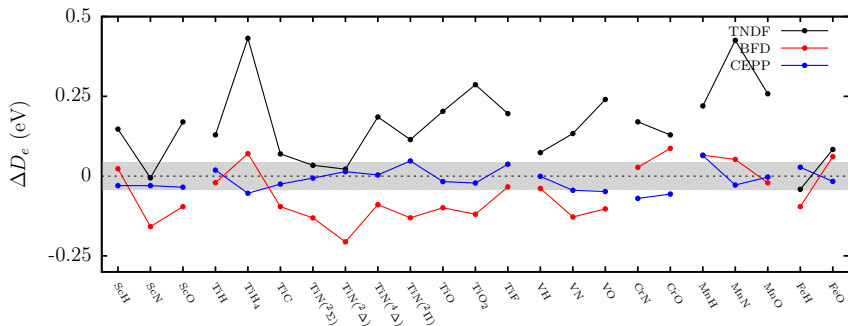
3d-transition metal molecules

- Better pseudopotentials and better testing required
- Small [Ne] cores required
- Include relativistic core effects
- Dipole core polarizability is available in the literature
- Examine Sc−Fe molecules where configurations available in literature

- Transition metal CEPPs from *very* ionised atoms: Sc^{+10} to Fe^{+15}
- Strong test of ion-molecule transferability

Geometries: 3d-transition metal molecules

- Deviation from AE least for CEPPs (MAD 0.004, 0.008, 0.011 Å for CEPP, BFD, TNDF)
- All CEPP errors < 0.01 Å
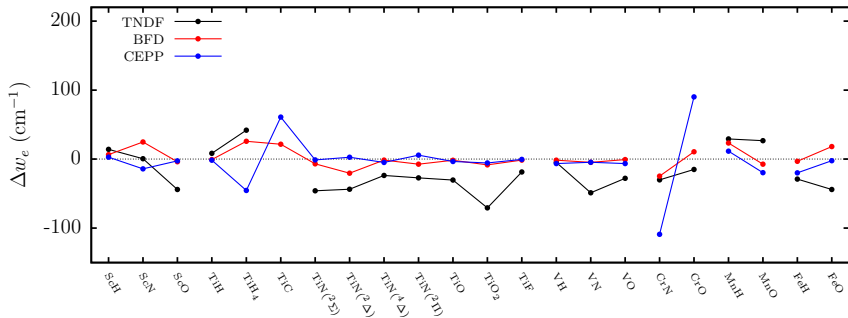- TiO_2 bond angle, and large TNDF, BFD error for MnN

Dissociation energies: 3d-transition metal molecules

- CEPP MAD 0.03 < 0.043 eV
- TNDF MAD 0.16 eV
- BFD MAD 0.09 eV

$\Rightarrow$ CEPPs consistently and significantly more accurate than TNDF or BFD

ZPVEs: 3d-transition metal molecules

- Deviation from AE not significant for any potentials
- All errors < 110 cm^{-1}
- CEPP MAD 20 cm^{-1}
- TNDF MAD 30 cm^{-1}
- BFD MAD 10 cm^{-1}

Conclusions

- CEPPs transfer well from *very* ionised atomic states to neutral states
- CEPPs are significantly more accurate than HF pseudopotentials for energies in explicitly correlated calculations
- CEPPs are accurate for a wide range of molecules
- CEPPs are accurate for strongly correlated and complex transition metal systems

Can we improve on this?

Maybe...

- Semi-empirical corrections for the small remaining error
- Take better account of the relativistic Hamiltonian
- Construct CEPPs from *n*-valence electron ions ($n > 1$) to provide *ab initio* e-e-I interactions