Pseudopotentials for Quantum Monte Carlo

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25 March 2015

The need for pseudopotentials

QMC scales badly with atomic number, $\propto Z^{4.5}$

- Fluctuations in $e-n$ potential energy
  $\rightarrow$ large variance
- Step size must be smaller than minimum length scale of wave function ($\sim 1/Z$) for good DMC acceptance ratios
  $\rightarrow$ serial correlation

Solution:

- Solution is to remove core electrons by replacing $e-n$ Coulomb interaction with an effective core-valence electron interaction, a pseudopotential

Constructing pseudopotentials in one-electron theory

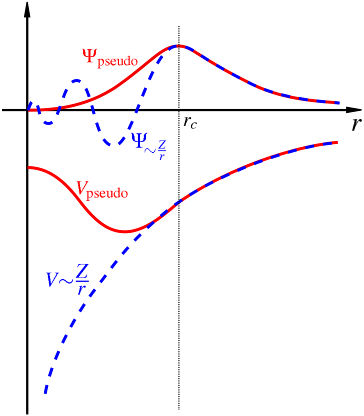
- Electrons deep in energy are classified as core electrons
- Electrons shallow in energy are classified as valence electrons
- Core electrons are considered inert and removed
- In compensation, valence electrons feel the pseudopotential
- Pseudopotential depends on angular momentum of each valence orbital → non-locality
- Good pseudopotentials should:
  - be reasonably **smooth**
  - behave as $-(Z-N_c)/r$ far from nucleus
  - have **same eigenvalues** as all-electron orbitals
  - have **same orbitals** as all-electron orbitals **for large** r
  - reproduce **scattering properties** of atom (Lüders relation/norm conservation)

Constructing pseudopotentials: core/valence separation

Example: Silicon atom one-electron(LDA-DFT) energy levels are

nl	Occ.	Eigenvalue (Ha)	
3p	2	-0.153526025	Valence
3s	2	-0.398313865	
2p	6	-3.514381690	Core
2s	2	-5.074463805	
1s	2	-65.184556915	

Constructing pseudopotentials in Hartree-Fock theory



- Do **all-electron atom** Hartree-Fock calculation
- Ignore ‘core’ orbitals
- Construct **pseudo-orbital** differing from orbital $r < r_c$
- Inverting Hartree-Fock equations gives **pseudopotential**, whose ground state is the **pseudo-orbital**

Constructing pseudopotentials with many-body theory

- Core and valence are ill-defined concepts
- Different attempts to derive pseudopotentials within many-body theory:
    - Approximate $\Psi = \hat{A}\{\Psi_{core}\Psi_{valence}\}$ → no core-valence correlation, not much faster
    - Use VMC for ‘core’ and DMC for ‘valence’ → does not change the scaling with Z
    - Pseudo-hamiltonians → innacurate when transfered
    - Generalise norm-conservation condition to many-body case

So far, best to use pseudopotentials constructed from one-particle theories.

Correlated electron pseudopotentials (CEPPs)

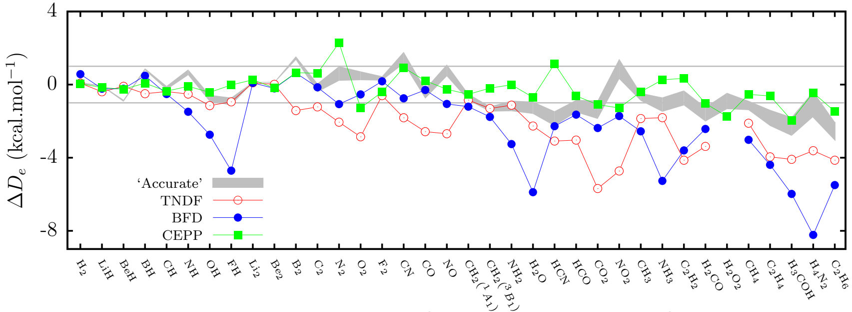
New pseudopotentials are available that are constructed to include correlation[1]:

- Pseudopotential from multideterminant atomic calculations
- Generalise norm conservation to the many-body case
- Construct CEPPs from ions with one valence electron
- Available for Li-F and Sc-Fe
- Constructed from Li^{+0} to F^{+6} (He core)
- Constructed from Sc^{+10} to Fe^{+15} (Ne core)

[1]: J.R. Trail and R.J. Needs J. Chem. Phys. 139, 014101 (2013); 142, 064110 (2015).

Correlated electron pseudopotentials (CEPPs)

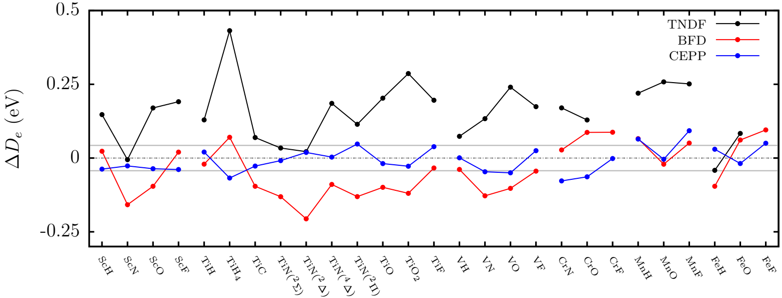
1^{st} row: CCSD(T) error in molecule dissociation energies



- TNDF are HF pseudopotentials (from CASINO website)
- BFD are alternative HF pseudopotentials
- CEPPs average error is $\sim 1/8$ of error with HF pseudopotentials

Correlated electron pseudopotentials (CEPPs)

3d-transition metals: CCSD(T) error in molecule dissociation energies



- TNDF are HF pseudopotentials (from CASINO website)
- BFD are alternative HF pseudopotentials
- CEPPs average error is $\sim 1/4$ of error with HF pseudopotentials

Correlated electron pseudopotentials (CEPPs)

CEPPs are still not included in the CASINO pseudopotential library, and are available only by direct request at the moment.

We will ignore the existence of CEPPs for the rest of this lecture (most of the contents are applicable to them in any case), and will focus on pseudopotentials from one-electron theories.

Implementation in VMC

- Must evaluate the expectation value of

$$\hat{V}_{nl} = V_{loc} + \sum_l \Delta V_l(r_{iI})\hat{P}_l$$

  where $\hat{P}_l$ projects out the l-th spherical harmonic component of the wave function
- I.e., for each configuration $\mathbf{R}$ one needs to evaluate

$$\Psi(\mathbf{R}) \left[\sum_I \sum_i \sum_l \Delta V_l(r_{iI})\hat{P}_l \right] \Psi(\mathbf{R}) \qquad (1)$$

- This involves the integration of Ψ over the surface of the sphere r_{iI}=constant for **each** electron and core

Implementation in VMC

- Integrate over sphere surfaces using **quadrature grids**
- Grid resolution set by `NON_LOCAL_GRID` parameter of input file
- Integration error decreases as `NON_LOCAL_GRID` value increases
- Convergence with `NON_LOCAL_GRID` **should** be tested

Implementation in DMC

- **Non-local** operators problematic in DMC
- Must evaluate $\hat{V}_{nl}\Phi$, but Φ is unkown
- **Pseudopotential localization approximation** (PLA):
  - PLA: $\Phi^{-1}\hat{V}_{nl}\Phi \approx \Psi^{-1}\hat{V}_{nl}\Psi$
  - PLA effective potential is **many-body** and **local**
  - PLA error is $\propto |\Psi - \Phi|^2$ with arbitrary sign
  - PLA makes DMC non-variational
  - PLA introduces singularities in the local energies
- **Alternatives** to PLA exist, but are costly

Derivation of core-polarization potentials (CPPs)

- An **approximation** from **electrostatic theory**
- Jth core feels electric field due to other cores and electrons:

$$\mathbf{E} = -\sum_{I \neq J} Z_I \frac{\mathbf{R_I} - \mathbf{R_J}}{|\mathbf{R_I} - \mathbf{R_J}|^3} + \sum_i \frac{\mathbf{r}_i - \mathbf{R_J}}{|\mathbf{r}_i - \mathbf{R_J}|^3}$$

- $\mathbf{E}$ polarizes core J by $\mathbf{P} = \alpha_J \mathbf{E}$, so $E_P = -1/2\alpha_J \mathbf{E} \cdot \mathbf{E}$
- Add up energy of **all** cores, and add to Hamiltonian

$$\begin{aligned} H_{CPP} \quad = \quad & \sum_{iJ} V_e(\mathbf{r}_i - \mathbf{R_J}) + \sum_{ii'J} V_{e-e}(\mathbf{r}_i - \mathbf{R_J}, \mathbf{r}_{i'} - \mathbf{R_J}) \\ & + \sum_{iIJ} V_{e-I}(\mathbf{R_I} - \mathbf{R_J}, \mathbf{r}_i - \mathbf{R_J}) + \sum_{IJ} V_{I-I}(\mathbf{R_I} - \mathbf{R_J}) \end{aligned}$$

- CPPs are **many-body**, **local** and $\propto 1/r^4$

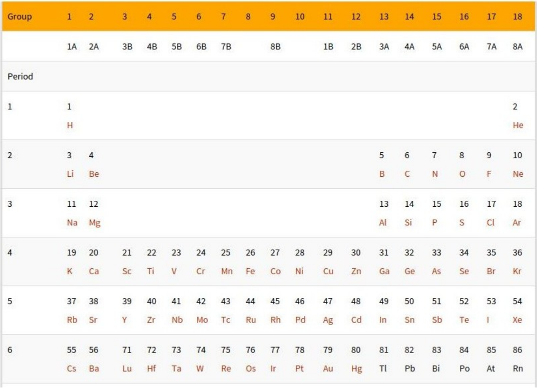
Results using CPPs

Energies (eV) for excitations of a Si atom:

	$3s^2 3p^2 \rightarrow 3s^1 3p^3$	$3s^2 3p^1 \rightarrow 3s^1 3p^2$	$3s^2 \rightarrow 3s^1 3p^1$
LDA	3.827(10)	4.994(10)	6.232(16)
HF	3.909(13)	5.096(9)	6.363(15)
HF+CPP	4.052(10)	5.264(9)	6.571(6)
DF	3.955(13)	5.146(9)	6.434(7)
DF+CPP	4.069(9)	5.297(9)	6.578(6)
Exp.	4.11	5.30	6.56

Pseudopotentials in CASINO

CASINO pseudopotential library



Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1A	2A	3B	4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A	7A	8A
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

http://vallico.net/casinoqmc/pplib/

Pseudopotentials in CASINO

CASINO pseudopotential library ⟩ click on Si

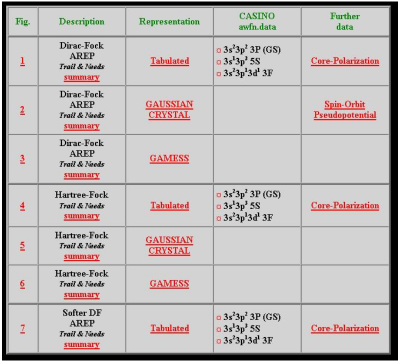


Fig.	Description	Representation	CASINO awfn.data	Further data
1	Dirac-Fock AREP *Trail & Needs* summary	Tabulated	¤ $3s^23p^2$ 3P (GS) ¤ $3s^13p^3$ 5S ¤ $3s^23p^13d^1$ 3F	Core-Polarization
2	Dirac-Fock AREP *Trail & Needs* summary	GAUSSIAN CRYSTAL		Spin-Orbit Pseudopotential
3	Dirac-Fock AREP *Trail & Needs* summary	GAMESS		
4	Hartree-Fock *Trail & Needs* summary	Tabulated	¤ $3s^23p^2$ 3P (GS) ¤ $3s^13p^3$ 5S ¤ $3s^23p^13d^1$ 3F	Core-Polarization
5	Hartree-Fock *Trail & Needs* summary	GAUSSIAN CRYSTAL		
6	Hartree-Fock *Trail & Needs* summary	GAMESS		
7	Softer DF AREP *Trail & Needs* summary	Tabulated	¤ $3s^23p^2$ 3P (GS) ¤ $3s^13p^3$ 5S ¤ $3s^23p^13d^1$ 3F	Core-Polarization

Links lead to further data

* AREP ≡ "average relativistic effective pseudopotential"

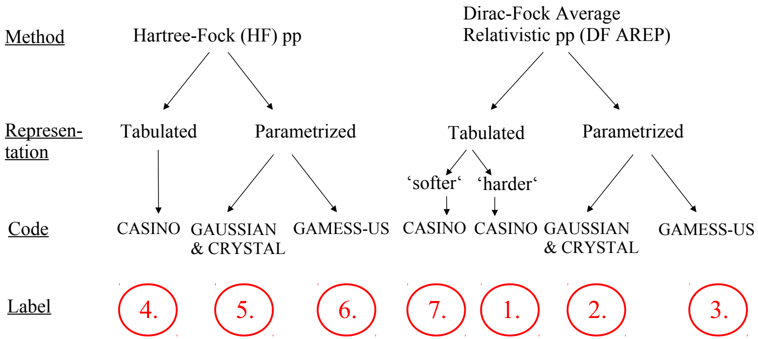
Pseudopotentials in CASINO

Information provided by links:

- Pseudopotentials formatted for different software packages
- Pseudopotential plots
- Pseudopotential properties (total energies, etc.)
- Atomic wave functions in CASINO format
- CPPs and spin-orbit potentials

Pseudopotentials in CASINO

Flow chart of the seven pseudopotentials



Method	Hartree-Fock (HF) pp			Dirac-Fock Average Relativistic pp (DF AREP)			
Representation	Tabulated	Parametrized		Tabulated		Parametrized	
				‘softer‘	‘harder‘		
Code	CASINO	GAUSSIAN & CRYSTAL	GAMESS-US	CASINO	CASINO	GAUSSIAN & CRYSTAL	GAMESS-US
Label	4.	5.	6.	7.	1.	2.	3.

Which is best?

- Pseudopotentials are not unique

There is no best pseudopotential

- User must choose the most appropriate pseudopotential
- **Consistency is key**: if we use DF pseudopotential for, e.g., GAMESS, should use DF pseudopotential for CASINO
- Precise choice depends on calculation details

DFT or HF?

- HF pseudopotentials seems to give systematically better results in QMC
- DFT pseudopotentials include the effect of electronic correlations, while Hartree-Fock neglects them
- Having the pseudopotential **not** include the effect of electronic correlation makes sense:
  1) Valence-valence correlation is done by QMC
  2) Core-valence correlation is small
  3) Core-core correlation is small and indirect
- Core-polarization potentials are available to address 2) and 3)

HF pseudopotentials are usually the safer choice

Hartree-Fock or Dirac-Fock?

- Hartree-Fock includes **no** relativistic effects
- Dirac-Fock includes **some** relativistic effects
- If the results are to be compared with:
  - **experiment** → use **DF** pseudopotential
  - **non-relativistic theory** → use **HF** pseudopotential

Tabulated or parametrized?

Choice depends on wave-function generating code

- Parametrized form needed by many software packages GAUSSIAN, CRYSTAL, GAMESS, etc
- Format conversion routines in `CASINO/utils/pseudo_converters`

Use tabulated pseudopotentials if possible

Should I use additions?

Core polarization potentials (CPPs)

- CPPs can only be included in CASINO and MOLPRO
- Should make results more accurate
- BUT untested so you must test them

Spin-Orbit (SO) potentials

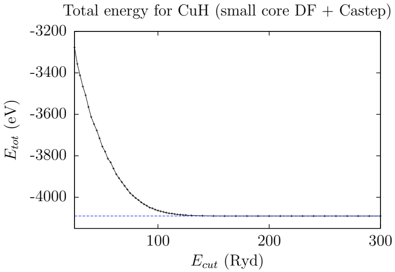
- Include fine structure effects
- Should make results more accurate
- BUT almost no software packages use them

Ignore CPP and SO unless this is your research interest

Plane wave basis and ghost states

- Plane-wave pseudopotential generation may intoduce a spurious eigenstate whose eigenvalue is in the range of those of the valence states
- These are called ghost states and render a pseudopotential useless
- Occurs often for $3d$ transition metals
- Problem is often solvable by changing local potential from d to s or p – see `CASINO/utils/pseudo_converters/NOTES`

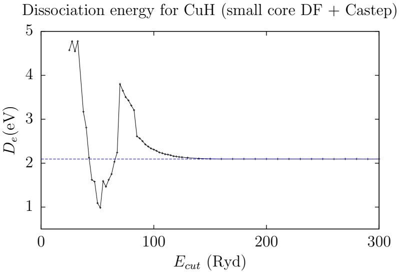
Ghost states for pseudopotentials in CASTEP



Convergence of total energy with size of plane-wave basis for CuH molecule

- Monotonically approaches limit, and **looks** correct
- This is not enough to be sure the ground state is correct

Ghost states for pseudopotentials in CASTEP



Convergence of dissociation energy with size of plane-wave basis for CuH molecule

- Problem:
    - Discontinuous due to ghost states below 140 Ry
    - Small regions can falsely appear to be converged
- Pre-QMC plane-wave basis calculations must consider:
    - A sufficiently large range of basis set sizes
    - Energy differences

Summary

Positive:

- Pseudopotentials reduce number of electrons
- Pseudopotential make everything smoother
  → fewer samples required for fixed statistical accuracy

Negative:

- PLA is uncontrolled (but small) error
- One must choose carefully and check

References:
HF pseudopotentials J.R. Trail and R.J. Needs, J. Chem. Phys. 122, 174109 (2005); 122, 014112 (2005)
CPPs E.L. Shirley and R.M. Martin, Phys. Rev. B 47, 15413 (1993)
CEPPs J.R. Trail and R.J. Needs, J. Chem. Phys. 139, 014101 (2013); 142, 064110 (2015)