

The Towler Institute

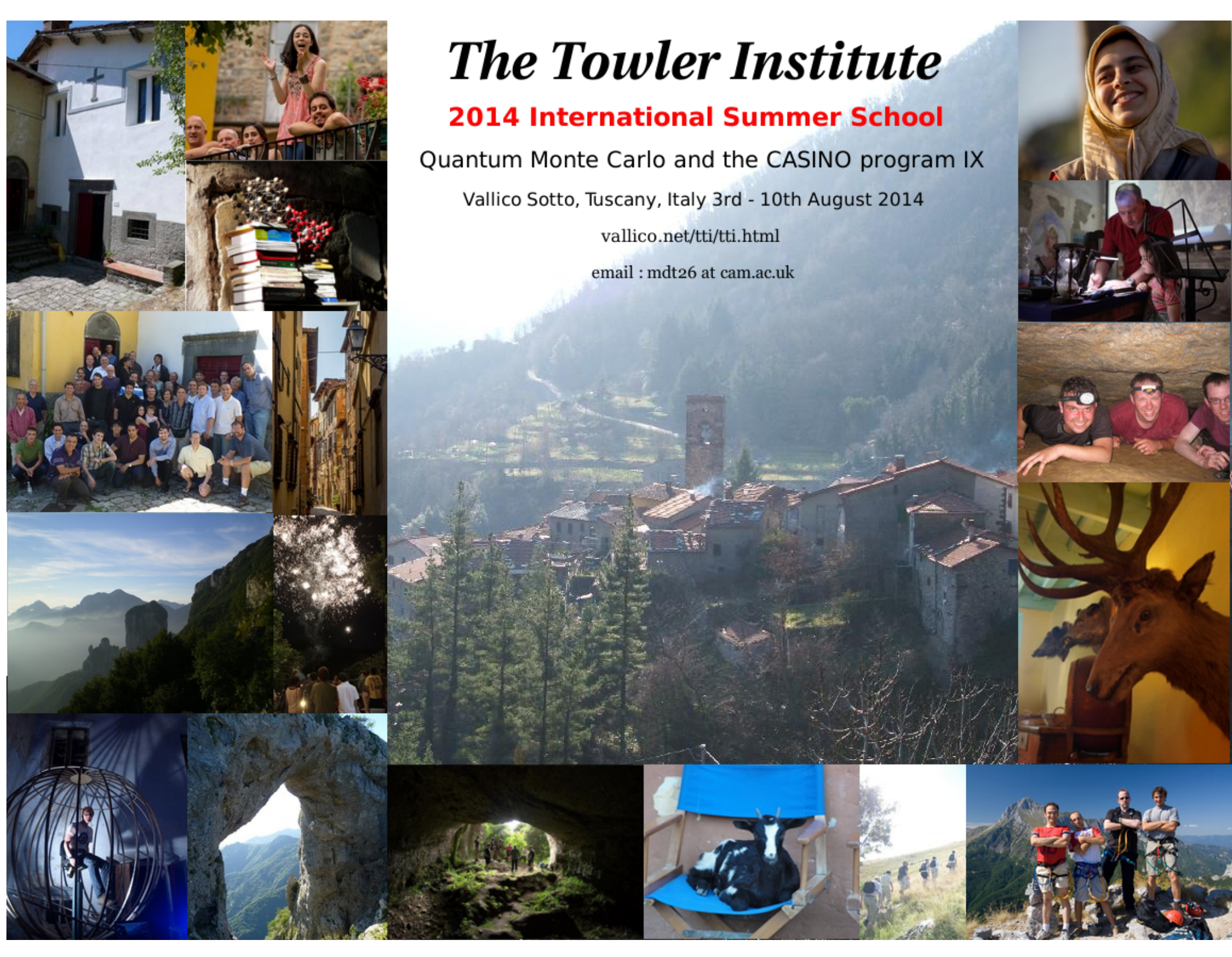
2014 International Summer School

Quantum Monte Carlo and the CASINO program IX

Vallico Sotto, Tuscany, Italy 3rd - 10th August 2014

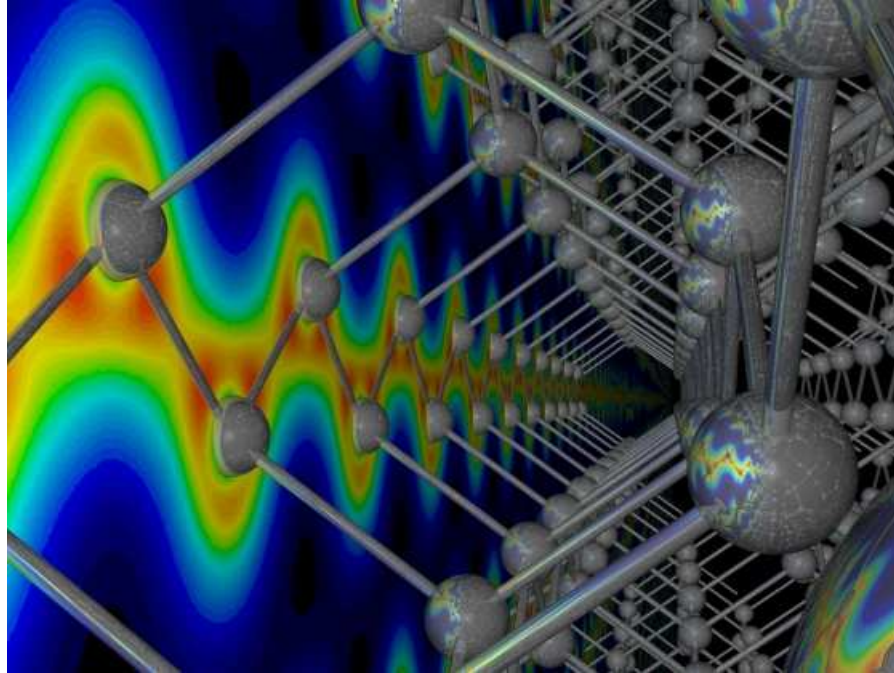
vallico.net/tti/tti.html

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Pseudopotentials for quantum Monte Carlo

A necessary evil



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The need for pseudopotentials

Introduction

“A pseudopotential is an attempt to replace the complicated effects of the motion of the core (i.e. non-valence) electrons of an atom and its nucleus with an effective potential, or pseudopotential, so that the Schrödinger equation contains a modified effective potential term instead of the Coulombic potential term for core electrons normally found in the Schrödinger equation. The pseudopotential approximation was first introduced by Hans Hellmann in the 1934.”

Used in our context e.g. in plane-wave DFT calculations, allowing the pseudo-wavefunctions to be described with far fewer Fourier modes and hence making plane-wave basis sets practical to use.

What about QMC?

QMC scales badly with atomic number - roughly $\propto Z^{4.5}$ (or possibly higher if you want to remove any residual timestep error).

- **Fluctuations** in $e - n$ potential energy lead to large variance.
- **Step size** must be smaller than minimum length scale of wave function ($\sim 1/Z$) for good DMC acceptance ratios, and this leads to significant **serial correlation**.

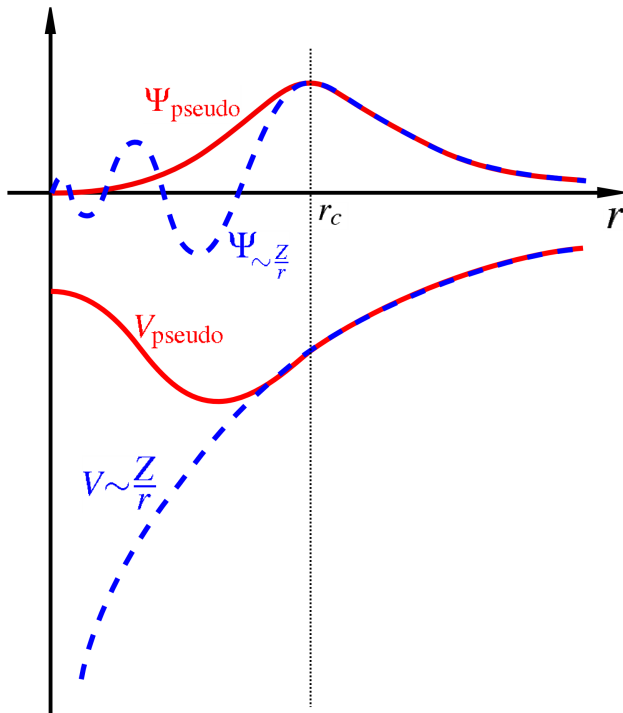
Solution:

- Solution is to **remove core electrons** by replacing $e - n$ Coulomb interaction with the effective core-valence electron interaction of a decent **pseudopotential**.

Constructing pseudopotentials

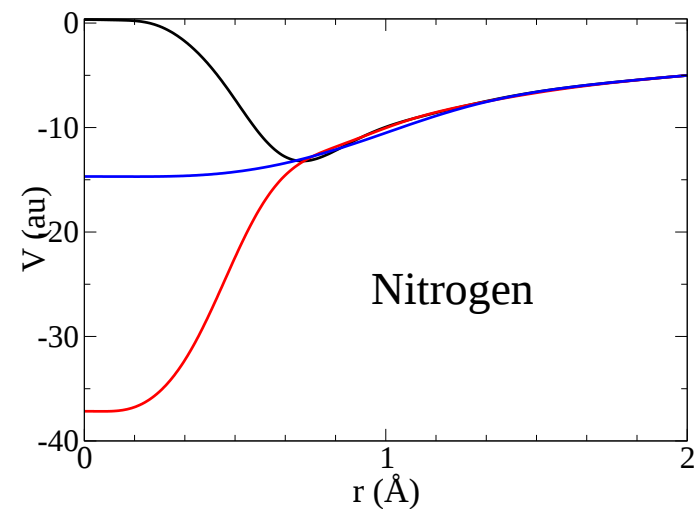
One-electron theory

- 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.
- The pseudopotential is different for each valence orbital.
 - pseudopotential depends on the **angular momentum**.
 - non-local
- Good pseudopotentials should:
 - be reasonably smooth.
 - behave as $-(Z - N_c)/r$ far from nucleus, where N_c is the number of removed core electrons.
 - have same eigenvalues as the all-electron orbitals.
 - have same orbitals as all-electron orbitals for large r .



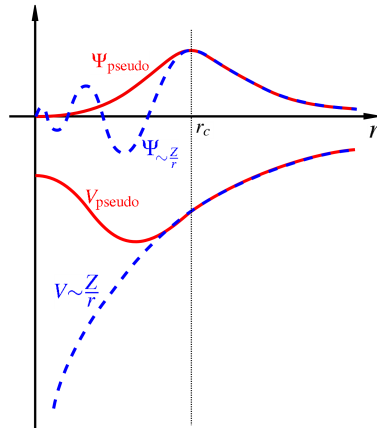
Notes:

- 'local' means that the potential depends only on one space position (like the Coulomb interaction).
- Space non-locality means that it depends on $\mathbf{r}$ and $\mathbf{r}'$, but this can be given a simplified picture.
- 'Semi-local' means the pseudopotential is expressed in terms of angular momentum dependence and not on $\mathbf{r}$ and $\mathbf{r}'$ separately. A truly non-local or 'separable' pseudopotential is defined to be non-local both in angular momentum and space coordinates.



Constructing pseudopotentials

One-electron theory



Recipe:

- Do an **all-electron atom** Hartree-Fock calculation.
- Ignore 'core' orbitals.
- Construct a **pseudo-orbital** that is different inside r_c .
- Invert the Hartree-Fock equations.
- Inversion gives **pseudopotential** whose ground state is the **pseudo-orbital**.

Details:

- Desirable to reproduce **scattering properties** of atom (requires *norm conservation*, i.e. we enforce condition that, inside the cut-off radius, norm of each pseudo-wavefunction identical to its corresponding all-electron wavefunction so they produce the same core charge).
- More than one potential: $V_s \neq V_p \neq V_d$
- Project out s , p , and d parts with a **projector operator** $\hat{P}_l$:

$$\begin{aligned}\hat{V}^{pp}\phi &= \sum_l V_l(r) \left[\sum_m \int Y_{lm}^*(\Omega') \phi(r, \Omega') d\Omega' \right] Y_{lm}(\Omega) \\ &= \sum_l V_l(r) \hat{P}_l \phi\end{aligned}$$

- Redo with V_d as local: $\hat{V}^{pp}\phi = V_d(r) + \sum_l [V_l(r) - V_d(r)] \hat{P}_l \phi$
- $\hat{V}^{pp}$ is a **one-body** potential and is a **non-local** potential.

Constructing pseudopotentials

One-electron theory

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

Many-body theory

- Core and valence are ill-defined concepts
- Different attempts to derive many-body pseudopotentials:
 - Approximate $\Psi = \hat{A}\{\Psi_{\text{core}}\Psi_{\text{valence}}\} \rightarrow$ no core-valence correlation, not much faster.
 - Generalise norm-conservation condition to many-body case $\rightarrow$ current research.
 - Pseudo-hamiltonians $\rightarrow$ inaccurate when transferred.
 - Use VMC for 'core' and DMC for 'valence' $\rightarrow$ does not change the scaling with atomic number.

Thus up to now usually considered best to construct pseudopotentials from one-particle theories.

But! John Trail and Richard Needs in Cambridge are working on '*correlated electron pseudopotentials*' which are now sufficiently well developed to be published:

J.R. Trail and R.J. Needs, *J. Chem. Phys.* **139**, 014101 (2013)

Abstract

"A scheme is developed for creating pseudopotentials for use in correlated-electron calculations. Pseudopotentials for the light elements H, Li, Be, B, C, N, O, and F, are reported, based on data from high-level quantum chemical calculations. Results obtained with these correlated electron pseudopotentials (CEPPs) are compared with data for atomic energy levels and the dissociation energies, molecular geometries, and zero-point vibrational energies of small molecules obtained from coupled cluster single double triple calculations with large basis sets. *The CEPPs give better results in correlated-electron calculations than Hartree-Fock-based pseudopotentials available in the literature.*"

Pseudopotentials in QMC

Choice of one-electron theory

- Can try DFT or Hartree-Fock pseudopotentials.
- Hartree-Fock seems to give systematically better results in QMC.
Why? DFT orbitals only represent **density** and are not components of a **many-body wave function**.
- Hartree-Fock neglects correlations, but in such a way that:
 - 1) Valence-valence correlation is done by QMC
 - 2) Core-core correlation is small and indirect
 - 3) Core-valence correlation is small
 - 4) Core-polarization potentials are available
- Hartree-Fock pseudopotentials are the best we have (for now).

Relativistic effects

- We can in fact go beyond this and approximately incorporate relativistic effects using Dirac-Fock theory → '**Dirac-Fock Average Relativistic Effective Potential (AREP)**'.
- Solving the Schrödinger equation with Dirac-Fock AREP pseudopotentials will result in the inclusion of scalar relativistic effects (i.e. mass polarization term, mass velocity term, Darwin terms, retardation terms, but not spin-orbit potentials).
- It is good to have HF pseudopotentials available as well since sometimes one wants to compare QMC results with experimental data where relativistic effects have been explicitly subtracted.

Pseudopotentials in QMC: 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
- At each $\mathbf{R}$ the quantity $\Psi^{-1}(\mathbf{R}) \sum_i \sum_l \Delta V_l(r_{iI}) \hat{P}_l \Psi(\mathbf{R})$ is computed
- Integration of Ψ over the surface of sphere $r_{iI} \equiv \text{constant}$ for **each** electron

Non-local integration:

- Integrate over sphere surfaces using *quadrature grids*.
- Number of points in grid set by **non_local_grid** parameter of input file.
- Integration error decreases with increasing **non_local_grid** value.
- Convergence with **non_local_grid** *should* be tested.

24x64:brutus% casinohelp non_local_grid

CASINO HELP SYSTEM

=====

NON_LOCAL_GRID selects the grid for non-local integration, ranging from coarse (low NON_LOCAL_GRID value) to fine (high NON_LOCAL_GRID value) to finer grids. The value is assumed to be the same for all atoms if it is controlled through this keyword; you can provide an override value of NON_LOCAL_GRID for particular atoms at the top of the corresponding pseudopotential file, where it is called NLRULE1. The following table gives the grid details:

+-----+			
NON_LOCAL_GRID	Exactly integrates l=...	No. points	
+-----+			
1	0	1	
2	2	4	
3	3	6	
4	5	12	
5	5	18	
6	7	26	
7	11	50	
+-----+			

Notice that NON_LOCAL_GRID=5 offers no theoretical advantage over NON_LOCAL_GRID=4, and is significantly more expensive (+50% points). We recommend that NON_LOCAL_GRID=5 not be used. The default value is NON_LOCAL_GRID=4 (this is also adopted if NON_LOCAL_GRID is given a negative value).

Pseudopotentials in QMC: implementation in DMC

- Non-local operators problematic in DMC.
- Must evaluate $\hat{V}_{nl}\Phi$, but Φ is unknown.
- Pseudopotential localization approximation (PLA): $\Phi^{-1}\hat{V}_{nl}\Phi \approx \Psi^{-1}\hat{V}_{nl}\Psi$
- PLA effective potential is many-body and local.
- Error incurred is proportional to square of error in trial wave function. However, the sign of the error is arbitrary.
⇒ PLA may make DMC non-variational.
- PLA introduce singularities in the local energies.
- Other methods are available:

```
24x64:brutus% casinohelp use_tmove
CASINO HELP SYSTEM
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```

DESCRIPTION

If USE_TMOVE is T then the Casula nonlocal pseudopotential scheme will be used in DMC. So-called 'T-moves' will be performed in order to give a DMC energy that is greater than or equal to the ground-state energy. This violates the detailed-balance principle at finite time steps, but greatly improves the stability of the DMC algorithm when nonlocal pseudopotentials are used. The advantages of T-moves are that they restore the variational principle and help to prevent population explosions; the disadvantages of T-moves are that the magnitude of the error due to the locality approximation is generally larger, although always positive, and the time-step bias is generally worse. [This latter problem is alleviated, to some extent, by using a symmetric branching factor (Casula 2010) as opposed to the asymmetric one suggested in his 2006 paper. This advice was implemented in CASINO in June 2014.]. A further disadvantage is that this option requires a truly enormous amount of memory in systems with large numbers of particles (seeing if this can be reduced remains a project). The default of USE_TMOVE is F and we tend *not* to use them unless we face stability issues. There are suggestions from some quarters that this is a bit harsh, and that using them should be the default. Further testing would clearly be helpful.

Core polarization potentials (CPP)

CPPs account for the polarization of the pseudo-ion cores by the fields of the other charged particles in the system. The polarization of the pseudo-ion cores by the fields of the valence electrons is a many-body effect which includes some of the core-valence correlation energy.

Derivation

- From electrostatic theory and an approximation
- A core J feels $\mathbf{E}$ due to cores, I , and electrons, i .

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

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

$$H_{CPP} = \sum_{iJ} V_e(\mathbf{r}_{iJ}) + \sum_{ijJ} V_{e-e}(\mathbf{r}_{iJ}, \mathbf{r}_{jJ}) + \sum_{iIJ} V_{e-n}(\mathbf{R}_{IJ}, \mathbf{r}_{iJ}) + \sum_{IJ} V_n(\mathbf{R}_{IJ})$$

- Potentials are many-body, local and $\propto 1/\text{distance}^4$

Core polarization potentials (CPP)

Results

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
7	87 Fr	88 Ra		103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 UUn	111 UUu	112 UUb	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

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

Pseudopotentials in CASINO

The CASINO pseudopotential library

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

All words **underlined in red** are links to further data.

Pseudopotentials in CASINO

The CASINO pseudopotential library

Fig.	Description	Representation	CASINO awfn.data	Further data
1	Dirac-Fock AREP Trail & Needs summary	Tabulated	☐ $3s^2 3p^2$ 3P (GS) ☐ $3s^2 3p^2$ 5S ☐ $3s^2 3p^3 3d^2$ 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	☐ $3s^2 3p^2$ 3P (GS) ☐ $3s^2 3p^2$ 5S ☐ $3s^2 3p^3 3d^2$ 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	☐ $3s^2 3p^2$ 3P (GS) ☐ $3s^2 3p^2$ 5S ☐ $3s^2 3p^3 3d^2$ 3F	Core-Polarization

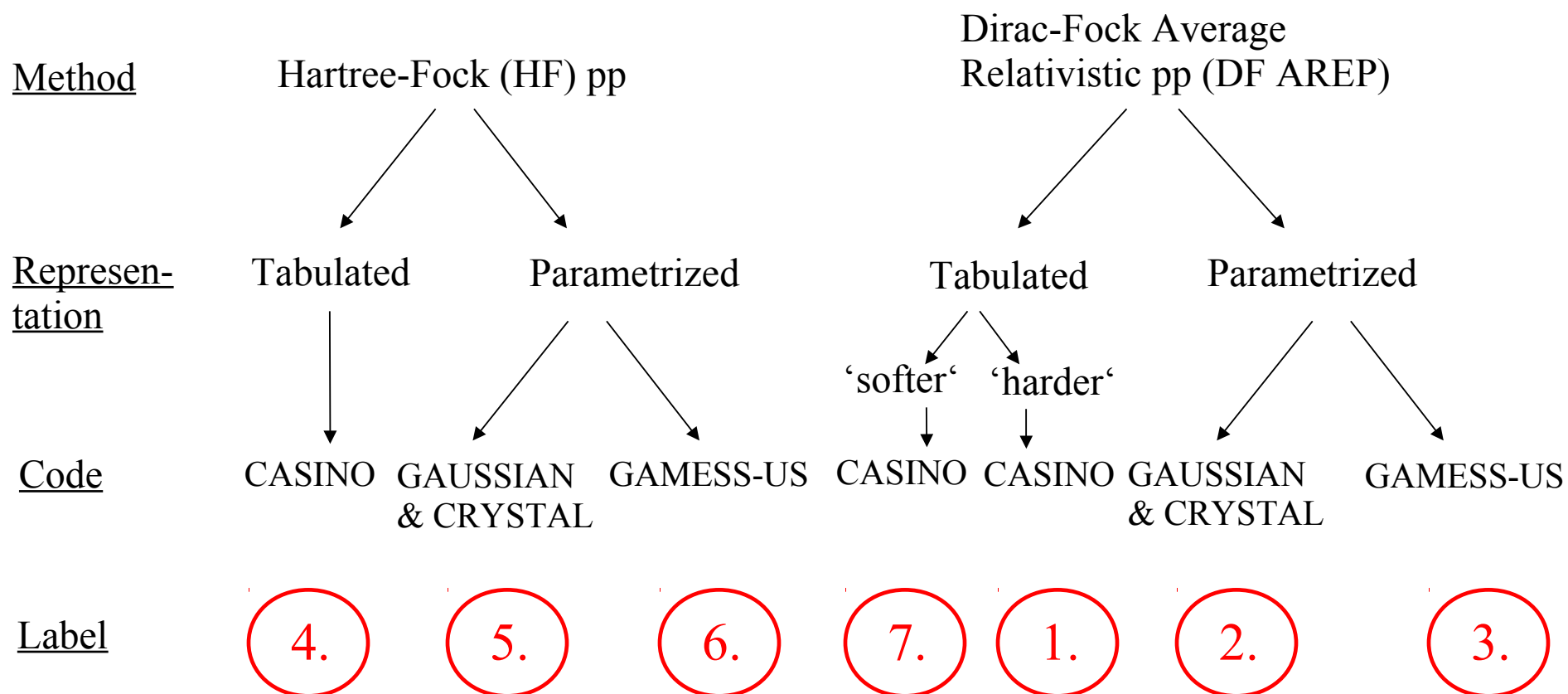
Information provided by these [links](#):

- Pseudopotential input files for other codes
- Pseudopotential plots
- Pseudopotential properties (total energies, etc)
- Atomic wave functions in CASINO format
- CPPs and spin-orbit potentials

Pseudopotentials in CASINO

Choosing a pseudopotential

Flow chart of the seven pseudopotentials



Pseudopotentials in CASINO

Which is best?

- Pseudopotentials are not unique.
→ There is no “best” pseudopotential.
- User must choose the most appropriate pseudopotential.
- It depends on what is being calculated.

Hartree-Fock or Dirac-Fock?

- Hartree-Fock includes no relativistic effects.
- Dirac-Fock includes some relativistic effects.

What results do you compare with?

- Compare with experiment → use DF pseudopotential.
- Compare with non-relativistic DFT → use HF pseudopotential.

Pseudopotentials in CASINO

Tabulated or parameterized

What code do you use to generate the trial wave function?

- Parameterisation is **neccessary** for many packages.
- GAUSSIAN, CRYSTAL, GAMESS for these packages and more.
- Format conversion routines in CASINO/Utils/pseudo_converters.
- Consistency - If we use Dirac-Fock for GAMESS, we should use Dirac-Fock pseudopotential for CASINO.

Use tabulated pseudopotentials if possible.

Pseudopotentials in CASINO

Core polarization potentials (CPPs)

- Used in addition to pseudopotentials.
- CPPs can only be included in CASINO and MOLPRO.
- **Should** make results more accurate.
- **BUT** largely untested so it's up to you to test them.

Spin-orbit (SO) potentials

- Used in addition to pseudopotentials to describe fine structure.
- Include fine structure effects.
- **Should** make results more accurate.
- **BUT** almost no packages use them.

Ignore CPP and SO unless your research is actually about this.

Pseudopotentials in CASINO

Plane-wave basis and ghost states

- Different projectors used for plane-wave-basis packages.
- Sometimes **ground state** of plane wave calculations are incorrect: **a ghost state**.
- Occurs often for first row transition metals.
- Problem is solvable by changing local potential from d to s or p
 - see CASINO/utills/pseudo_converters/NOTES.

Conclusions

Positive:

- Pseudopotentials **reduce** number of electrons.
- Pseudopotential make everything **smoother**
→ **more** samples so **higher** accuracy.

Negative:

- Uncontrolled but small error.
- One **must** choose carefully and check.

References:

- J.R. Trail and R.J. Needs, *J. Chem. Phys.* **122**, 174109 (2005)
J.R. Trail and R.J. Needs, *J. Chem. Phys.* **122**, 014112 (2005)
E.L. Shirley and R.M. Martin, *Phys. Rev. B* **47**, 15413 (1993)