

# Pseudopotentials for Quantum Monte Carlo

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# The need for pseudopotentials

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

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

Solution:

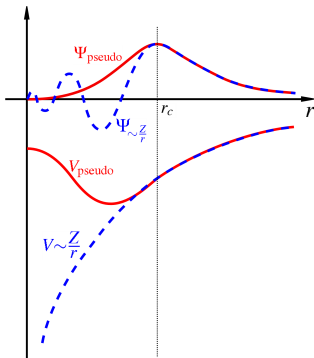
- Solution is to **remove core electrons** by replacing  $e - n$  Coulomb interaction with an effective core-valence electron interaction, a **pseudopotential**

# Constructing pseudopotentials

## 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  
→ eigenvalues same as all-electron orbitals  
→ orbitals same as all-electron orbitals for large  $r$

# Constructing pseudopotentials



- 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 a **pseudopotential** whose ground state is the **pseudo-orbital**

## Constructing pseudopotentials

- Reproduces **scattering properties** of atom (Lüders relation or norm conservation)
- 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

- 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  $\Psi = \hat{A}\{\Psi_{core}\Psi_{valence}\} \rightarrow$  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  $Z$

$\rightarrow$  Best to construct pseudopotentials from one-particle theories

# Pseudopotentials in QMC

- Can try DFT or HF pseudopotentials
- HF 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
- HF pseudopotentials are the best we have (for now)



# Pseudopotentials in QMC

## Implementation in VMC

- Must evaluate the expectation value of  $\hat{V}_{nl} = V_{loc} + \sum_l \Delta V_l(r_{il}) \hat{P}_l$  where  $\hat{P}_l$  projects out the  $l$ -th spherical harmonic component of the wave function
- At each  $\mathbf{R}$  the quantity  $\Psi^{-1}(\mathbf{R}) \sum_i \sum_l \Delta V_l(r_{il}) \hat{P}_l \Psi(\mathbf{R})$  is computed
- Integration of  $\Psi$  over the surface of sphere  $r_{il} \equiv \text{constant}$  for **each** electron

# Pseudopotentials in QMC

- 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

# Pseudopotentials in QMC

## Implementation in DMC

- Non-local operators problematic in DMC
- Must evaluate  $\hat{V}_{nl}\Phi$ , but  $\Phi$  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  
 $\Rightarrow$  PLA may make DMC non-variational.
- PLA introduce singularities in the local energies
- Other methods are available

## Core Polarization Potentials (CPP)

### 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 Uu	111 Uu	112 Uu	113 Uu	114 Uu	115 Uu	116 Uu	117 Uu	118 Uu
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://www.tcm.phy.cam.ac.uk/~mdt26/casino2\\_pseudopotentials.html](http://www.tcm.phy.cam.ac.uk/~mdt26/casino2_pseudopotentials.html)

# Pseudopotentials in CASINO

Fig.	Description	Representation	CASINO awfn.data	Further data
<a href="#"><u>1</u></a>	Dirac-Fock AREP <i>Trail &amp; Needs summary</i>	<a href="#"><u>Tabulated</u></a>	<ul style="list-style-type: none"> <li>□ <math>3s^2 3p^2</math> 3P (GS)</li> <li>□ <math>3s^2 3p^1</math> 5S</li> <li>□ <math>3s^2 3p^1 3d^1</math> 3F</li> </ul>	<a href="#"><u>Core-Polarization</u></a>
<a href="#"><u>2</u></a>	Dirac-Fock AREP <i>Trail &amp; Needs summary</i>	<a href="#"><u>GAUSSIAN</u></a> <a href="#"><u>CRYSTAL</u></a>		<a href="#"><u>Spin-Orbit Pseudopotential</u></a>
<a href="#"><u>3</u></a>	Dirac-Fock AREP <i>Trail &amp; Needs summary</i>	<a href="#"><u>GAMESS</u></a>		
<a href="#"><u>4</u></a>	Hartree-Fock <i>Trail &amp; Needs summary</i>	<a href="#"><u>Tabulated</u></a>	<ul style="list-style-type: none"> <li>□ <math>3s^2 3p^2</math> 3P (GS)</li> <li>□ <math>3s^2 3p^1</math> 5S</li> <li>□ <math>3s^2 3p^1 3d^1</math> 3F</li> </ul>	<a href="#"><u>Core-Polarization</u></a>
<a href="#"><u>5</u></a>	Hartree-Fock <i>Trail &amp; Needs summary</i>	<a href="#"><u>GAUSSIAN</u></a> <a href="#"><u>CRYSTAL</u></a>		
<a href="#"><u>6</u></a>	Hartree-Fock <i>Trail &amp; Needs summary</i>	<a href="#"><u>GAMESS</u></a>		
<a href="#"><u>7</u></a>	Softer DF AREP <i>Trail &amp; Needs summary</i>	<a href="#"><u>Tabulated</u></a>	<ul style="list-style-type: none"> <li>□ <math>3s^2 3p^2</math> 3P (GS)</li> <li>□ <math>3s^2 3p^1</math> 5S</li> <li>□ <math>3s^2 3p^1 3d^1</math> 3F</li> </ul>	<a href="#"><u>Core-Polarization</u></a>

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

# Pseudopotentials in CASINO

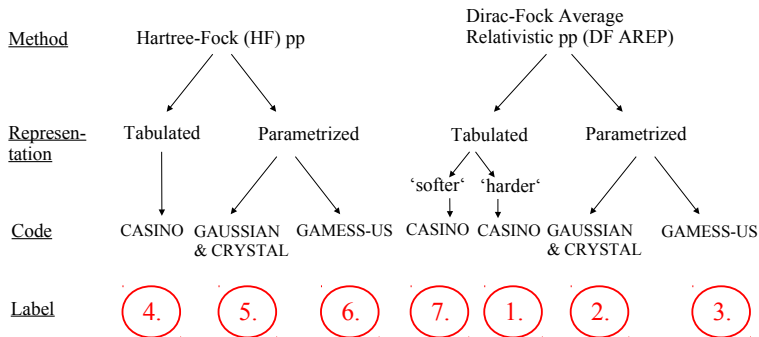
Information provided by [links](#)

- 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

## 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

# Pseudopotentials in CASINO

## 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 **necessary** for many packages
- GAUSSIAN, CRYSTAL, GAMESS for these packages and more.
- Format conversion routines in CASINO/utils/pseudo\_converters
- Consistency - If we use DF for GAMESS, should use DF ppot 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** untested so you must 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 this is your research interest

# 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 1-st row transition metals
- Problem is solvable by changing local potential from  $d$  to  $s$  or  $p$ 
  - see CASINO/utis/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)