

# Pseudopotentials for QMC

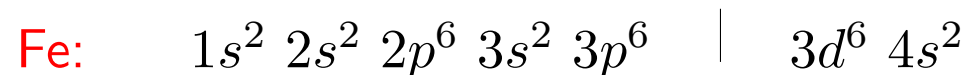
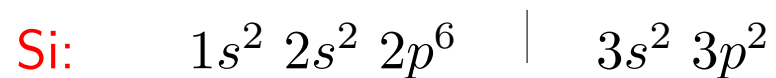
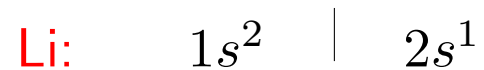
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QMC in the Apuan Alps, Vallico Sotto, Italy, July 2010

# Core-valence partition

Assign orbitals to core or valence



Partition is also in energy and space

# Density matrix approach of Acioli and Ceperley

“Pseudopotentials from correlated wave functions”

Acioli and Ceperley, J Chem Phys 100, 8169 (1994)

$$\rho(\mathbf{r}, \mathbf{r}') = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N$$

Write in terms of eigenvectors and eigenfunctions of  $\rho(\mathbf{r}, \mathbf{r}')$

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{\infty} n_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') \quad 0 \leq n_i \leq 2$$

Norm-conservation

$$\rho(\mathbf{r}, \mathbf{r}') = \rho^{\text{PS}}(\mathbf{r}, \mathbf{r}') \quad r, r' \geq r_c$$

Need accurate all-electron wave function for atom

Helium:  $\rho^{\text{PS}}(\mathbf{r}, \mathbf{r}')$  only correct when both electrons are outside  $r_c$

# Pseudopotentials with local DFT

All-electron orbitals  $\phi_l^{\text{AE}}(r)$  eigenvalues  $\epsilon_l^{\text{AE}}$   
Pseudo orbitals  $\phi_l^{\text{PS}}(r)$  eigenvalues  $\epsilon_l^{\text{PS}}$

For valence electrons insist that:

$$\begin{aligned}\epsilon_l^{\text{PS}} &= \epsilon_l^{\text{AE}} \\ \phi_l^{\text{PS}}(r) &= \phi_l^{\text{AE}}(r) \quad r > r_c\end{aligned}$$

$$\begin{aligned}\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V^{\text{AE}} \right] \phi_l^{\text{AE}} &= \epsilon_l^{\text{AE}} \phi_l^{\text{AE}} \\ \left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l^{\text{PS}} \right] \phi_l^{\text{PS}} &= \epsilon_l^{\text{PS}} \phi_l^{\text{PS}}\end{aligned}$$

Must therefore have  $V_l^{\text{PS}}(r) = V^{\text{AE}}(r) \quad r > r_c$

Use norm conservation and smoothness for  $\phi_l^{\text{PS}}(r < r_c)$ , invert SE for  $V_l^{\text{PS}}$

# Pseudopotentials within Hartree-Fock theory

Similar to local DFT – with a twist!

Exchange interaction is very long ranged

Inverting the Schrödinger equation in local DFT gives

$$V_l^{\text{PS}} \simeq -\frac{Z_{\text{ion}}}{r} \quad r \rightarrow \infty$$

but in Hartree-Fock theory get

$$V_l^{\text{PS}} \simeq A - \frac{Z_{\text{ion}} + B}{r} + \mathcal{O}(r^{-2}) \quad r \rightarrow \infty$$

Trail and Needs, J Chem Phys 122, 014112 (2005)

Total energy not defined for an extended system

Can apparently deal with the problem without much loss of accuracy

# Pseudopotentials from fitting to excitation energies

Don't need to invert the Schrödinger equation to make a pseudopotential

Can fit to excitation energies obtained from:

- (1) Hartree-Fock theory
- (2) A correlated theory
- (3) Experiment

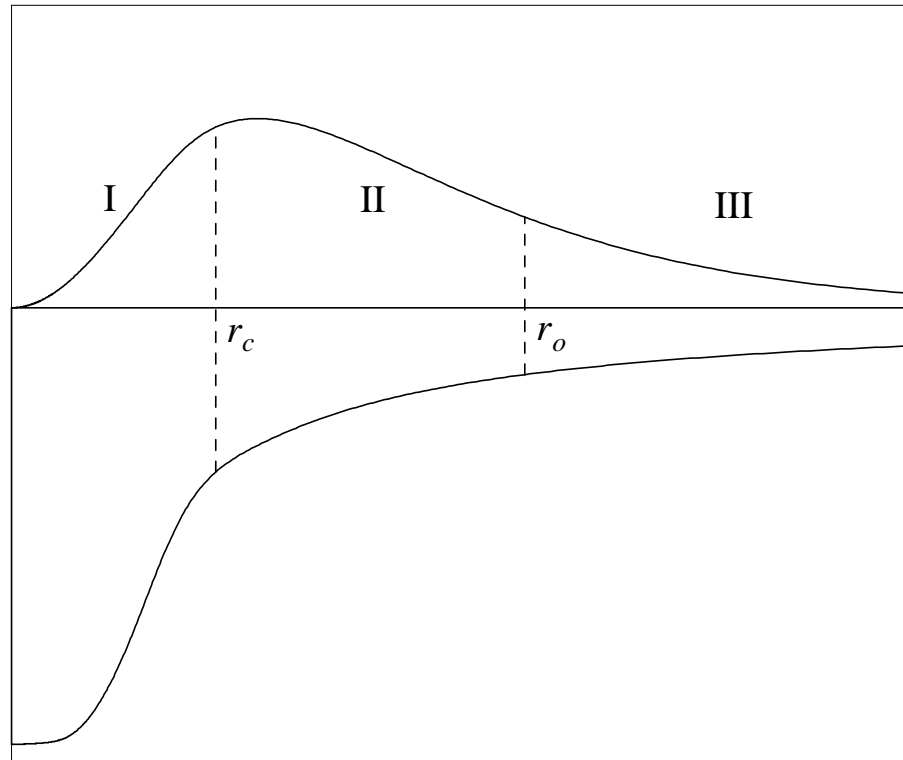
Issue: excitation energies may be very large

Lowest excitation energy of H is  $1s \rightarrow 2s$  which costs  $\sim 8$  eV

Could fit to correlated energies with a perturbing potential

# Empirical Pseudopotential I

Lee, Kent, Towler, Needs, and Rajagopal, Phys Rev B 62, 13347 (2000)



$$\phi^{\text{III}}(r) \propto W_{x, l+1/2} \left( \frac{2Z_{\text{ion}}r}{x} \right) \quad , \quad x = \frac{Z_{\text{ion}}}{\sqrt{2\epsilon}}$$

$W \equiv$  Whittaker function of the second kind

# Empirical Pseudopotential II

Consider single electrons outside of the core in  $s$ ,  $p$ , or  $d$  levels

$$V_{\text{III}}^{\text{PS}}(r) = -\frac{Z_{\text{ion}}}{r}$$

For  $r_c > r < r_0$  take

$$V_{\text{II}}^{\text{PS}}(r) = -\frac{Z_{\text{ion}}}{r} - \frac{\alpha}{2r^4}$$

Energy  $\epsilon_l$  to remove the electron available experimentally for most atoms

Get charge density norms for each orbital from DFT

Make corrections to the energies  $\epsilon_l$  (roughly -0.05 eV for Si) and norms (roughly 0.002 electrons for Si) to allow for fact that  $\epsilon_l$  come from 3+ ions



## Empirical Pseudopotential III

Integrate Schrödinger equation at energy  $\epsilon_l$  from  $r_o$  to  $r_c$  to get  $\phi_{II}(r)$

Si atom:  $r_{cs} = 1.75$  a.u.,  $r_{cp} = 1.80$  a.u.,  $r_{cd} = 2.0$  a.u.,  $r_0 = 20.17$  a.u.

Invert Schrödinger equation to get  $\phi_I(r)$  and hence  $V_I^{PS}(r)$  as in DFT

Gave best results in atomic excitation tests, also good results in recent solid state calculations of silicon in diamond and  $\beta$ -tin structures

Problems? Need a more accurate potential in region II

Current level of testing insufficient

# Testing HF pseudopotentials

Test two sets of pseudos:

Trail and Needs, J Chem Phys 122, 174109 (2005)

Burkatzki, Filippi, Dolg, J Chem Phys 126, 234105 (2007)

55 molecules of the G2 set with the CRYSTAL code

Atoms: H, Li, Be, C, N, O, F, Na, Si, P, S, Cl

Max number of atoms in a molecule = 8

Gaussian basis sets optimised for each molecule

Normally 17 basis functions per atom, sometimes have to reduce a bit

Compare spherical atoms from CRYSTAL from integrating HF on a grid:

MAD = 0.0012 eV per atom

Compare atomisation energies with all-electron HF of O'Neill and Gill Mol Phys 103, 763 (2005)

MAD (Trail and Needs) = 0.26 eV per molecule

MAD (Burkatzki, Filippi, Dolg) = 0.24 eV per molecule

(NB, THESE ARE NOT FINISHED YET)

The molecules are almost all overbound

Conclusion !\*&(?!+)\*(\*@!?!@:¿ @