



the
abdus salam
international centre for theoretical physics

ICTP 40th Anniversary

SMR 1595 - 10

Joint DEMOCRITOS - ICTP School on
CONTINUUM QUANTUM MONTE CARLO METHODS
12 - 23 January 2004

TUTORIAL ON PSEUDOPOTENTIALS

Stefano de GIRONCOLI
SISSA and INFN DEMOCRITOS
Trieste, Italy

These are preliminary lecture notes, intended only for distribution to participants.

PSEUDOPOTENTIALS

Stefano de Gironcoli

SISSA and INFN-DEMOCRITOS

CORE and VALENCE electrons

- In atoms, the least bound (valence) electrons determine the chemical (low energy) properties in molecules and condensed phases
- Inner (core) electrons are strongly bound to the nucleus and are largely unaffected by changes in chemical environment
- Valence electrons avoid core region (due to electrostatic repulsion and Pauli principle)
- Core/Valence separation is not always clear cut (as for instance for 3d electrons in Cu, Zn, Ga, ...)

valence electron energy scale $\sim 1-10$ eV

core electron energy scale $\sim Z^2 R_{yd}$; $1 R_{yd} = 13,6$ eV

PERIODIC TABLE OF THE ELEMENTS

Table of Radioactive Isotopes

Ae 227(22y) β^-	Cd 115(43d) β^-	Fe 55(2.6y) β^- 59(45d) β^-	La 140(40.2h) β^-	Po 210(138.4d) α 209(103y) α	Sr 90(28y) β^- 89(51d) β^- 85(64d) β^-
Ag 110(24d) β^- 111(7.5d) β^-	Ce 141(32d) β^- 143(33h) β^- 144(28.5d) β^-	Fm 255(20h) α	Lu 176(10 ¹⁰ y) β^- 177(6.8d) β^-	Pr 143(13.8d) β^-	Ta 182(115d) β^-
Am 241(4.9h) α 242(16.0h) α 243(8000y) α	Cf 246(35h) α 249(300y) α 251(800y) α	Ge 72(14.1h) β^-	Md 256(90m) α	Pu 242(3.8 × 10 ⁴ y) α 241(13.5y) α 239(24300y) α	Tb 160(73d) β^-
As 76(26.7h) β^- 77(39h) β^-	Cl 36(3 × 10 ⁶ y) β^-	Ga 71(111d) β^-	Nd 147(11.1d) β^-	Ra 226(1620y) α	Te 127(9.3h) β^-
At 210(8.3h) α 211(7.2h) α	Co 58(71d) β^- 60(5.27y) β^-	H 3(12.3y) β^-	Ni 63(125y) β^- 59(8 × 10 ⁴ y) α	Rb 86(18.6d) β^-	Th 232(1.4 × 10 ¹⁰ y) α 228(1.91y) α
Au 198(2.69d) β^-	Cr 51(27d) β^-	He 18(145d) β^-	Np 237(2.2 × 10 ⁶ y) α 239(2.33d) α	Rn 222(3.82d) α	Tl 204(3.81y) α 208(3.05y) α
Ba 131(12d) β^- 133(7.2y) β^-	Cs 134(2.0y) β^- 135(3 × 10 ⁸ y) β^- 137(30y) β^-	Hf 181(45d) β^-	Os 191(15d) β^-	S 32(88d) β^-	U 238(4.5 × 10 ⁹ y) α 234(2.5 × 10 ⁴ y) α 235(7.1 × 10 ⁸ y) α 233(1.6 × 10 ⁵ y) α
Bi 210(5d) β^-	Cu 64(12.8h) β^- 65(3.05y) β^-	In 114(50d) β^-	P 32(14.2d) β^-	Sb 122(2.8d) β^- 124(60d) β^-	W 185(75d) β^- Y 90(64h) β^-
Bk 245(4.9d) α 249(314d) α	Er 253(20d) α 254(1y) α	Ir 192(74.4d) β^-	Pa 231(34000y) α	Sc 46(84d) β^-	Xe 136(10 ²¹ y) β^-
Br 82(36h) β^-	Eu 154(16y) β^- 155(1.3y) β^-	K 40(10 ¹⁰ y) β^- 42(12.4h) β^-	Pd 103(17d) β^-	Se 75(120d) β^-	Zn 65(24.5d) β^-
C 14(5700y) β^-			Pm 147(2.6y) β^-	Sm 153(47h) β^- 145(340d) β^-	Zr 95(2.1 × 10 ¹¹ y) α 93(9 × 10 ¹⁰ y) α

Naturally occurring radioactive isotopes are indicated by a blue mass number. Half lives are in parentheses where s, m, h, d and y stand for seconds, minutes, hours, days and years respectively. The symbols describing the mode of decay and resulting radiation are defined as follows:

- α alpha particle
- β^- beta particle
- β^+ positron
- K K-electron capture
- L L-electron capture
- SF spontaneous fission
- γ gamma ray
- e⁻ internal electron conversion

GROUP IA

1	1.00797
1	1
-237.2	
-239.2	
0.071	
H	
1 ⁺	
Hydrogen	

IIA

4	9.0122
2	2
2770	
1277	
1.85	
Li	
1 ⁺ 2 ⁺	
Lithium	

IIA

4	9.0122
2	2
2770	
1277	
1.85	
Be	
1 ⁺ 2 ⁺	
Beryllium	

IIA

11	22.9898
1	1
892	
97.8	
0.97	
Na	
[Ne]3s ¹	
Sodium	

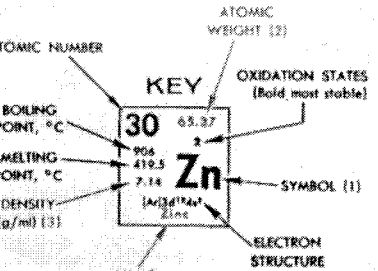
IIA

12	24.312
2	2
1107	
650	
1.74	
Mg	
[Ne]3s ²	
Magnesium	

IIIB IVB VB VIB VIIIB VIII IB IIB

19 39.102	20 40.08	21 44.956	22 47.90	23 50.942	24 51.996	25 54.938	26 55.847	27 58.933	28 58.71	29 63.54	30 65.37	31 69.72	32 72.59	33 74.922	34 78.96	35 79.904	36 83.80
760	1440	3730	3360	3450	2565	2150	3000	2900	3730	2905	906	2237	2830	613	685	98	-152
63.7	838	1839	1668	1900	1875	1245	1536	1498	1433	1083	419.3	29.8	237.4	817	21.7	-7.2	-132.2
0.86	1.55	5.0	4.51	6.1	7.19	7.43	7.86	8.9	8.9	8.96	7.14	5.91	5.32	5.72	4.79	3.12	2.6
[Ar]4s ¹	[Ar]4s ²	[Ar]3d ¹ 4s ²	[Ar]3d ² 4s ²	[Ar]3d ³ 4s ²	[Ar]3d ⁴ 4s ²	[Ar]3d ⁵ 4s ²	[Ar]3d ⁶ 4s ²	[Ar]3d ⁷ 4s ²	[Ar]3d ⁸ 4s ²	[Ar]3d ⁹ 4s ¹	[Ar]3d ¹⁰ 4s ²	[Ar]3d ¹⁰ 4s ² 4p ¹	[Ar]3d ¹⁰ 4s ² 4p ²	[Ar]3d ¹⁰ 4s ² 4p ³	[Ar]3d ¹⁰ 4s ² 4p ⁴	[Ar]3d ¹⁰ 4s ² 4p ⁵	[Ar]3d ¹⁰ 4s ² 4p ⁶
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton

5 10.811	6 12.01115	7 14.0067	8 15.9994	9 18.9984	10 20.183
1	2	3	4	5	6
4830	24.2	-195.8	53.5, 4.2	-183	-2
-218	-219.4	-1.14	-188.2	-1	-246
2.34	2.16	0.81	1.505	1.30	-248.6
1s ² 2s ² 2p ¹	1s ² 2s ² 2p ²	1s ² 2s ² 2p ²	1s ² 2s ² 2p ²	1s ² 2s ² 2p ²	1s ² 2s ² 2p ²
B	C	N	O	F	Ne
Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
13 26.9815	14 28.086	15 30.9738	16 32.064	17 35.453	18 39.948
2450	2680	2800	444.6	-34.7	-185.8
660	1410	44.2	119.0	-101.0	-189.4
2.70	2.33	1.82	2.07	1.36	1.40
1s ² 3s ² 3p ¹	1s ² 3s ² 3p ²	1s ² 3s ² 3p ³	1s ² 3s ² 3p ⁴	1s ² 3s ² 3p ⁵	1s ² 3s ² 3p ⁶
Al	Si	P	S	Cl	Ar
Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon



- NOTES:
- (1) Black — solid.
Red — gas.
Blue — liquid.
Outline — synthetically prepared.
 - (2) Based upon carbon — 12. () indicates most stable or best known isotope.
 - (3) Values for gaseous elements are for liquids at the boiling point.

SARGENT-WELCH Ing. A. RASTELLI e C.

SARGENT-WELCH SCIENTIFIC COMPANY

ROMA - VIA S. MARTINO DELLA BATTAGLIA, 31
MILANO - VIA CASTEL MORRONO, 18 • PALERMO - VIA G. PUCCINI, 74/76
NAPOLI - VIA COSTANTINOPOLI, 27

Copyright 1963
Copyright 1964
Copyright 1965
Copyright 1966

Cost of a QMC atomic/molecular calculation

[Ceperley, J. Stat. Phys. 43 815 (1986); Hammond, Reynolds and Lester, JCP 87 1130 (1987)]

$$\text{CPU} \propto M Z^3$$

← cost for updating determinant wfc
↑ number of configuration sampled

$$\sigma^2 \approx \frac{E^2}{M} \rightarrow \text{fluctuation of the integrand}$$

↑ desired accuracy (\sim constant across the periodic table)

$$M \propto E^2 \sim E \Delta E + \tau^{-1} \Delta E$$

total energy $\propto Z^2$ correlation energy $\propto Z^{1.5}$ time step of walkers $\tau \sim \Delta R^2 \propto \frac{1}{Z^2}$

$$\text{CPU} \propto Z^{5.5} \div Z^{6.5}$$

a very bad scaling, primarily determined by
core electron properties: $\Delta R \propto \frac{1}{Z}$, $E \propto Z^2$

Pseudopotentials remove core electrons from the problem

$$H = \sum_v \left(-\frac{\hbar^2}{2m} \nabla_v^2 + \sum_I V_I^{PS}(r_v - R_I) \right) + \frac{1}{2} \sum_{\substack{v, v' \\ v \neq v'}} \frac{e^2}{|r_v - r_{v'}|} + \sum_{\substack{I, J \\ I \neq J}} \frac{Z_I^{eff} Z_J^{eff} e^2}{|R_I - R_J|}$$

where $V_I^{PS}(r - R_I) \approx -\frac{e^2 Z_I^{eff}}{|r - R_I|}$ outside core region

with $Z_I^{eff} = Z_I - N_I^{core}$

Z^{eff} remain bound across the periodic table

$$CPU \propto (Z^{eff})^{3.5}$$

Pseudopotentials in DFT or HF

[Hamann, Schlüter and Chiang, PRL 63, 1494 (1979)]

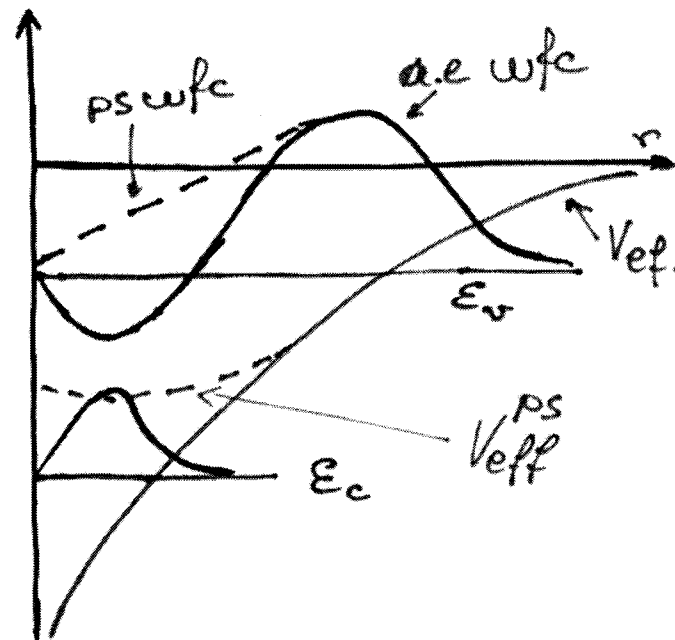
$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \underbrace{V_{\text{ext}} + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + V_{xc}[\rho]}_{V_{\text{eff}}} \right] \varphi_i(r) = \epsilon_i \varphi_i$$

$i = c, v$

$$\rho = \rho_c + \rho_v$$

$$\left\{ \begin{array}{l} V_{\text{ext}} + e^2 \int \frac{\rho_c(r')}{|r-r'|} d^3r' + V_{xc}[\rho_c] \\ \text{orthogonality to core states} \end{array} \right\} \rightarrow V^{\text{PS}}$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \underbrace{V^{\text{PS}} + e^2 \int \frac{\rho_v(r')}{|r-r'|} d^3r' + V_{xc}[\rho_v]}_{V_{\text{eff}}^{\text{PS}}} \right] \varphi_v^{\text{PS}}(r) = \epsilon_v \varphi_v^{\text{PS}}$$



- Single particle radial pseudowfc for valence states are nodeless and agree with all-electron wfc outside core region
- Pseudo wfc are not anymore orthogonal to core states that have been removed from the problem.

- A repulsive contribution to the pseudopotential
the effect of orthogonality to core electrons
- Different angular momenta \leftrightarrow different core states

V^{ps} is a non-local operator

$$V^{ps} = \sum_{l=0}^{\infty} V_e^{ps}(l|r) \hat{P}_e^l = V_{loc}^{ps}(l|r) + \sum_{l=0}^{l_{max}} \Delta V_{NL,e}^{ps}(l|r) \hat{P}_e^l$$

$$\hat{P}_e^l(r, r') = \sum_{m=-l}^l Y_{lm}(r) Y_{lm}^*(r')$$

$$V_{loc}^{ps}(l|r) \sim -e^2 \frac{Z_{eff}}{|r|} \quad \text{for } r \rightarrow \infty$$

$$\Delta V_{NL,e}^{ps} = 0 \quad \text{for } r > r_c$$

Pseudopotential transferability

[Hamann, Schlüter and Chiang, PRL 43 1494 (1979)]

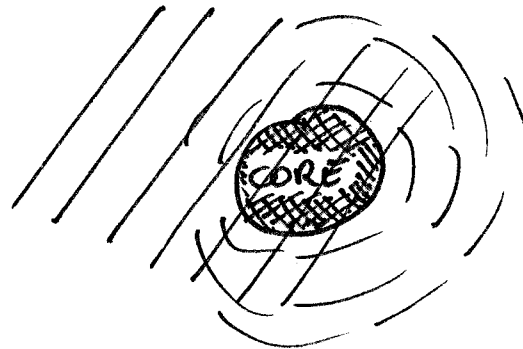
- $\epsilon_v^{AE} = \epsilon_v^{PS}$

- $\psi_v^{AE}(r) = \psi_v^{PS}(r)$ for $r > r_c$

- $\int_0^R |\psi_v^{AE}(r)|^2 r^2 dr = \int_0^R |\psi_v^{PS}(r)|^2 r^2 dr \quad \forall R > r_c$ Norm Conservation
interatomic electrostatics
is correct

- scattering properties of AE^- and PS atoms agree to linear order for electrons around the reference $\epsilon_v^{AE} = \epsilon_v^{PS}$

$$\left. \frac{d \ln \psi(r)}{d\epsilon} \right|_{\epsilon = \epsilon^{AE}} = \left. \frac{d \ln \psi(r)}{d\epsilon} \right|_{\epsilon = \epsilon^{PS}}$$



Pseudopotential generation

- Choose an energy functional (HF, LDA, GGA, ...)
- Solve all-electron self-consistent single particle Sch. eq. for the atom
 V^{SCF}, ψ_i
- Remove ψ_{core} , smooth $\psi_{valence}$ (keeping NORM conservation)
- Invert (for all relevant ang. momenta) pseudo Sch. eq.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{SCF}^{PS} \right] \psi_{valence} = E \psi_{valence} \rightarrow V_{SCF}^{PS} = \frac{-\frac{\hbar^2}{2m} \nabla^2 \psi_{val} - E_{val} \psi_{val}}{\psi_{val}}$$

- Unscreen the potential to obtain the bare pseudopotential to be used in molecular/solid applications

$$V_{bare}^{PS} = V_{SCF}^{PS} - e^2 \int \frac{\rho_{val}^{PS}(r')}{|r-r'|} d^3r' - V_{xc}[\rho_{val}^{PS}]$$

The result depends on the energy functional used

It is in general not consistent to use a pseudopotential generated within a given scheme in another one

IN PRACTICE: HF pseudopotentials give better results when used in QMC than LDA ones

Pseudopotentials from correlated WFC's

(Acidri, and Ceperley JCP 100, 8169 (1994))

the response of an atom to an external perturbation can be calculated from its density matrices

$$\rho^{(P)}(r_1, r_2 \dots r_P; r'_1, r'_2, \dots r'_P) = \binom{N}{P} \int d^3r_{P+1} \dots d^3r_N \psi^*(r_1, r_2 \dots r_P, r_{P+1}, \dots r_N) \times \psi(r'_1, r'_2 \dots r'_P, r_{P+1}, \dots r_N)$$

Also for correlated wfe transferability is linked to norm conservation

$$V_{AE} = -\frac{e^2 Z}{r} \rightarrow V_{PS} \quad \Rightarrow \quad \psi_{AE} \rightarrow \psi_{PS}$$

$$\rho_{AE}^{(N)}(r, r') = \rho_{PS}^{(N)}(r, r') \quad \text{for } r, r' > r_c \quad \text{Norm conservation}$$

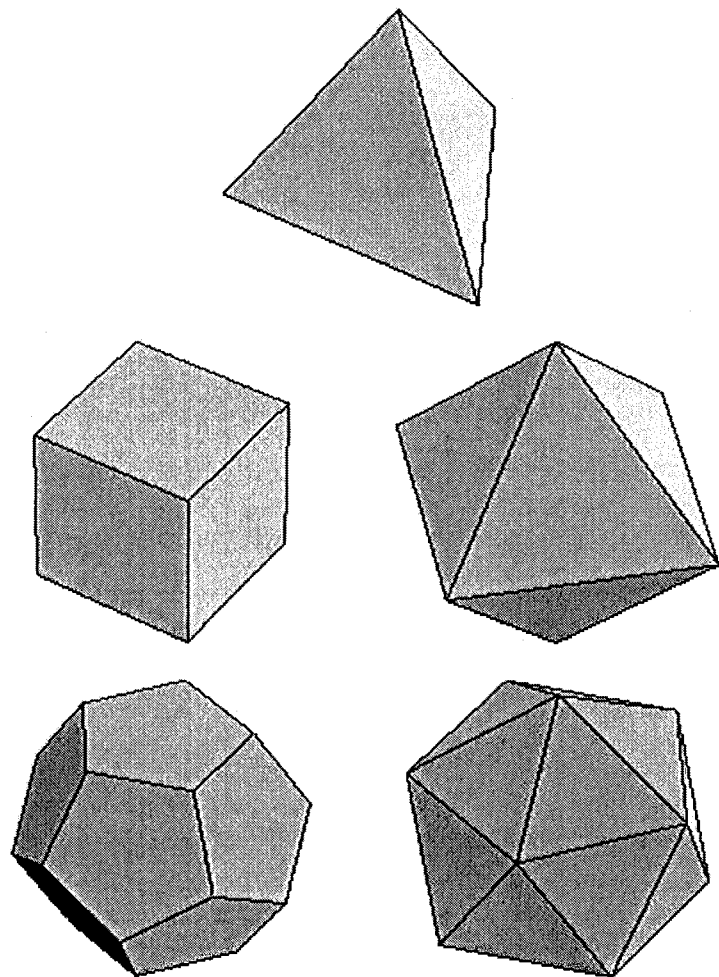
- Natural orb. b's agree beyond r_c thus ensuring good representation of the main effects due to changes in the environment
- Hopefully also higher order density matrices agree beyond r_c
- So far, a correlated pseudopotential has been generated only for Li

Pseudopotentials in VMC

$$E(R) = \frac{H\psi_T}{\psi_T} = \frac{-\sum_i \nabla_i^2 \psi_T}{\psi_T} + \frac{\sum_i V_{loc} \psi_T}{\psi_T} + \frac{\sum_i V_{NL} \psi_T}{\psi_T} + \frac{V_{ee} \psi_T}{\psi_T}$$

$$\frac{V_{NL} \psi_T}{\psi_T} = \sum_i \sum_l V_{NL,l}^{ps}(r_i) \frac{\sum_{m=-l}^l Y_{em}(\vec{r}_i) \int d\Omega_i Y_{em}^*(\vec{r}'_i) \psi_T(r_1, \dots, r'_i, \dots, r_N)}{\psi_T(r_1, \dots, r_i, \dots, r_N)}$$

$$\int d\Omega_i: Y_{em}^*(\hat{r}_i) f(r_i) \cong \sum_{k=1}^{N_p} w_k Y_{em}^*(\hat{r}_k) f(r_k)$$



N_p	Group	l_{exact}
4	Tetrahedron	2
6	Octahedron	3
12	Icosahedron	5
18	Octahedron	5
26	Octahedron	7
32	Icosahedron	9
50	Octahedron	11
134	Octahedron	23

with random orientation of the axes
the estimate of the integral is unbiased

Pseudopotentials in DMC

(Mitas, Shirley, and Ceperley)

JCP 95, 3467 (1991)

$$-\frac{\partial \phi(R,t)}{\partial t} = (H_{VAL} - E_T) \phi$$

where $H_{VAL} = \frac{1}{2} \sum_i \nabla_i^2 + V_{loc} + V_{NL} + V_{ee}$
 $= H_{loc} + V_{NL}$

$$f(R,t) = \psi_T(R) \phi(R,t)$$

$$-\frac{\partial f}{\partial t} = \underbrace{-\frac{1}{2} \sum_i \nabla_i^2 f}_{\text{diffusion}} + \underbrace{\sum_i \nabla_i \cdot (f \nabla_i \ln \psi_T)}_{\text{drift}} + \underbrace{\frac{(H_{loc} - E_T) \psi_T}{\psi_T} \cdot f}_{\text{local branching}} + \underbrace{\frac{V_{NL} \phi}{\phi} \cdot f}_{\substack{\text{non local} \\ \text{branching} \\ \text{sign problem}}}$$

$$-\frac{\partial f}{\partial t} = -\frac{1}{2} \sum_i \nabla_i^2 f + \sum_i \nabla_i \cdot (f \nabla_i \ln \psi_T) + \frac{(H_{VAL} - E_T) \psi_T}{\psi_T} \cdot f + \left(\frac{V_{NL} \phi}{\phi} - \frac{V_{NL} \psi_T}{\psi_T} \right) f$$

\swarrow local branching with $V_{loc} \rightarrow V_{loc} + \frac{V_{NL} \psi_T}{\psi_T}$
 \searrow locality approximation

- it can be shown that the error involved in the locality approximation is second order in the quality of the trial wavefunction (not an upper bound)

Summary

- Pseudopotentials make possible QMC calculations for all elements
- Use of DFT/HF pseudopotentials in QMC is not fully consistent but only for Li a pseudopotential has been generated from correlated wfc
- Use of pseudopotentials is straightforward in VMC
- For DMC the locality approximation is needed with error $\propto \delta\psi^2$