



the
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Joint DEMOCRITOS - ICTP School on
CONTINUUM QUANTUM MONTE CARLO METHODS
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TUTORIAL ON PSEUDOPOTENTIALS

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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(130y) 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(11.5d) β^-
Am 241(4.9h) α 242(16.0h) α 243(8000y) α	Cf 246(35h) α 249(360y) α 251(800y) α	Ge 72(14.1h) β^-	Md 256(90m) α	Pu 242(3.8 × 10 ⁴ y) α 241(13y) α 239(24300y) α	Tb 160(73d) β^-
As 76(26.7h) β^- 77(39h) β^-	Cl 36(3 × 10 ¹⁰ 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 251(90y) α	Er 253(20d) α 254(1y) α	Ir 192(74.4d) β^-	Pa 231(34000y) α	Sc 46(84d) β^-	Xe 136(16.9h) β^-
Br 82(36h) β^-	Ee 154(1.6y) β^- 155(1.8y) β^-	K 40(10 ¹⁰ y) β^- 42(12.4h) β^-	Pd 103(17d) β^- Pm 147(2.6y) β^-	Se 75(120d) β^-	Zn 65(24.5d) β^- Zr 95(65.5d) β^- 93(9 × 10 ¹⁰ y) β^-

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
-237.2 -239.2	1
0.071	H
1 ⁺	Hydrogen

IIA

4	9.0122
2770	2
1277	Be
1.85	Beryllium

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

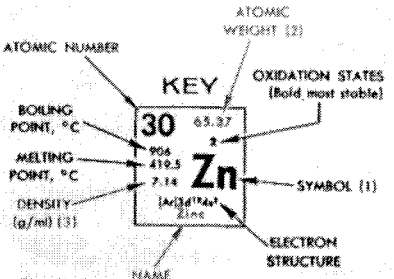
12	24.312
1107 450	2
0.97	Mg
[Ne]3s ²	Magnesium

IIIB IVB VB VIB VIIB 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 79.909	36 83.80
760 63.7 0.86	1440 938 1.55	3730 1839 3.0	3360 1668 4.51	3450 1900 6.1	2565 1875 7.19	2150 1245 7.43	3000 1536 7.86	2900 1498 8.9	3730 1433 8.9	2905 1083 8.96	906 419.3 7.14	2337 228 5.91	2830 937.4 5.32	613 817 5.72	685 217 4.79	98 312 3.12	-152 -182.2 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 ²	[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
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
—	4830 3729	24.2 -210	58.5, 4.2 -218	-183 -219.4	-188.2 -248.6
2.34	2.26	0.81	1.14	1.505	1.30
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
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 660 2.70	2680 1410 1.97	2800 44.2 2.39	32.064 119.0 2.07	35.453 -101.0 1.36	-185.8 -189.4 1.40
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
Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon

87 (223)	88 (226)	89 (227)	104	58 140.12	59 140.907	60 144.24	61 (147)	62 150.35	63 151.96	64 157.25	65 158.924	66 162.50	67 164.930	68 167.26	69 168.934	70 173.04	71 174.97
1271	700	1050		3448 795 6.67	3127 935 6.77	3027 1024 7.00	(1027)	1900 1072 7.34	1439 926 5.26	3000 1312 7.89	2900 1356 8.27	2600 1407 8.54	2690 1461 8.80	2900 1497 9.05	1727 824 6.99	1427 824 6.99	3327 1652 9.84
[Rn]7s ¹	[Rn]7s ²	[Rn]7s ²		[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴ 5d ² 6s ²	[Xe]4f ¹⁴ 5d ³ 6s ²	[Xe]4f ¹⁴ 5d ⁴ 6s ²	[Xe]4f ¹⁴ 5d ⁵ 6s ²	[Xe]4f ¹⁴ 5d ⁶ 6s ²	[Xe]4f ¹⁴ 5d ⁷ 6s ²	[Xe]4f ¹⁴ 5d ⁸ 6s ²	[Xe]4f ¹⁴ 5d ⁹ 6s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
Francium	Radium	Actinium		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu



- 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

TABLE OF PERIODIC PROPERTIES OF THE ELEMENTS

Percent Ionic Character of a Single Chemical Bond

Difference in electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
Percent ionic character %	0.3	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

GROUP IA

H	1.0
Li	0.98
Na	0.93
K	0.82
Rb	0.72
Cs	0.65

IIA

Be	1.5
Mg	1.31
Ca	1.00
Sr	0.95
Ba	0.89
Ra	0.82

Sc	1.3
Ti	1.5
V	1.6
Cr	1.6
Mn	1.5
Fe	1.5
Co	1.5
Ni	1.5
Cu	1.5
Zn	1.5

Sub-Atomic Particles

Symbol	Electron	Positron	Proton	Neutron	Photon	Neutrino	Meson	Hyperon																								
Mass*	1	1	1836.12	1838.68	γ	1	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	10 ⁻³⁰	
Charge**	-1	+1	+1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Spin	1/2	1/2	1/2	1/2	1	1/2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Magnetic Moment	1.00 n.m.	1.00 n.m.	2.791 n.m.	1.913 n.m.	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mean Life (sec.)	stable	stable	stable	1.11 × 10 ⁸	stable	stable	2.22 × 10 ⁻¹⁶	4.254 × 10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶
Decay Modes				β ⁺ β ⁻			γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ

IIIB

IVB

VB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

VIB

IIIA

B	2.0
Al	1.5
Ga	1.6
In	1.7
Tl	1.8

IVA

C	2.5
Si	1.9
Ge	2.0
Sn	2.1
Pb	2.2

VA

N	3.0
P	2.1
As	2.2
Sb	2.3
Bi	2.4

VIA

O	3.5
S	2.5
Se	2.6
Te	2.7
Po	2.8

VIIA

F	4.0
Cl	3.0
Br	3.1
I	3.2
At	3.3

VIIIA

Ne	4.0
Ar	3.0
Kr	3.1
Xe	3.2
Rn	3.3

Fr	0.7
Ra	0.9
Ac	1.1

Ce	1.1
Pr	1.2
Nd	1.3
Pm	1.4
Sm	1.5
Eu	1.6
Gd	1.7
Tb	1.8
Dy	1.9
Ho	2.0
Er	2.1
Tm	2.2
Yb	2.3
Lu	2.4

Th	1.3
Pa	1.4
U	1.5
Np	1.6
Pu	1.7
Am	1.8
Cm	1.9
Bk	2.0
Cf	2.1
Es	2.2
Fm	2.3
Md	2.4
No	2.5
Lr	2.6

KEY

Zn

COVALENT RADIUS, Å

ATOMIC RADIUS, Å (7)

IONIC RADIUS, Å (6)

ATOMIC VOLUME, m³/mol

FIRST IONIZATION ENERGY (kcal/g-mole)

SPECIFIC HEAT (cal/g°C)

THERMAL CONDUCTANCE (cal/cm²/cm²/sec [3])

CRYSTAL STRUCTURE (2)

ACID-BASE PROPERTIES (1)

ELECTRONEGATIVITY (Pauling's)

HEAT OF VAPORIZATION (k-cal/g-atom)

HEAT OF FUSION (k-cal/g-atom)

ELECTRICAL CONDUCTANCE (5) (microhms)⁻¹

NOTES:

- (1) For representative oxides (higher valence) of group. Oxide is acidic if color is red, basic if color is blue and amphoteric if both colors are shown. Intensity of color indicates relative strength.
- (2) Cubic, face centered; cubic, body centered; diamond; cubic; hexagonal; rhombohedral; tetragonal; orthorhombic; monoclinic.
- (3) At room temperature. (4) At boiling point. (5) From 0° to 20°C.
- (6) Ionic (crystal) radii for coordination number 6.
- (7) Metallic radii for coordination number of 12.

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, *PR* 43, 1494 (1979)]

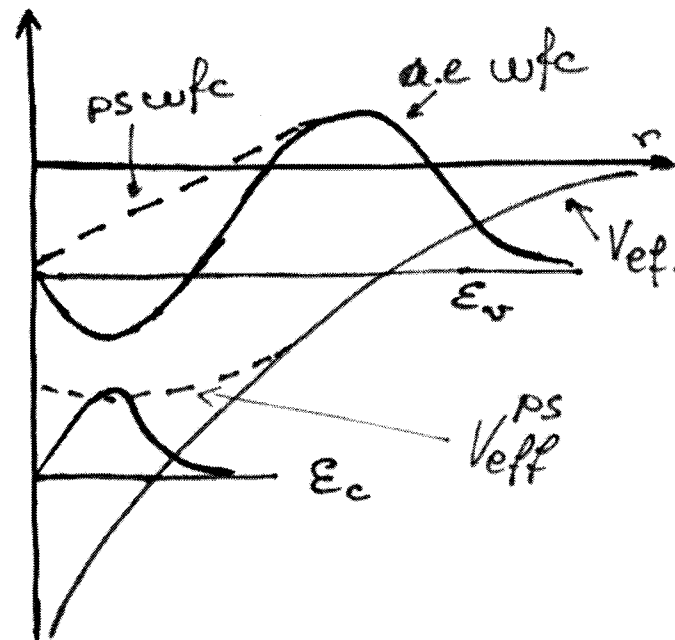
$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \underbrace{V_{\text{ext}} + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + V_{\text{xc}}[\rho]}_{V_{\text{eff}}} \right] \varphi_i(r) = \epsilon_i \varphi_i$$

$i = c, v$

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

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

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



- 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)]

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

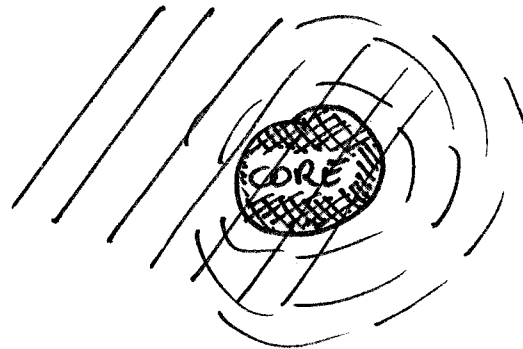
- $\psi_v^{AE}(r) = \psi_v^{PS}(r)$ for $r > r_c$

- $\int_0^R |\psi_v^{AE}(r)|^2 r^2 dr = \int_0^R |\psi_v^{PS}(r)|^2 r^2 dr \quad \forall R > r_c$

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. bts 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

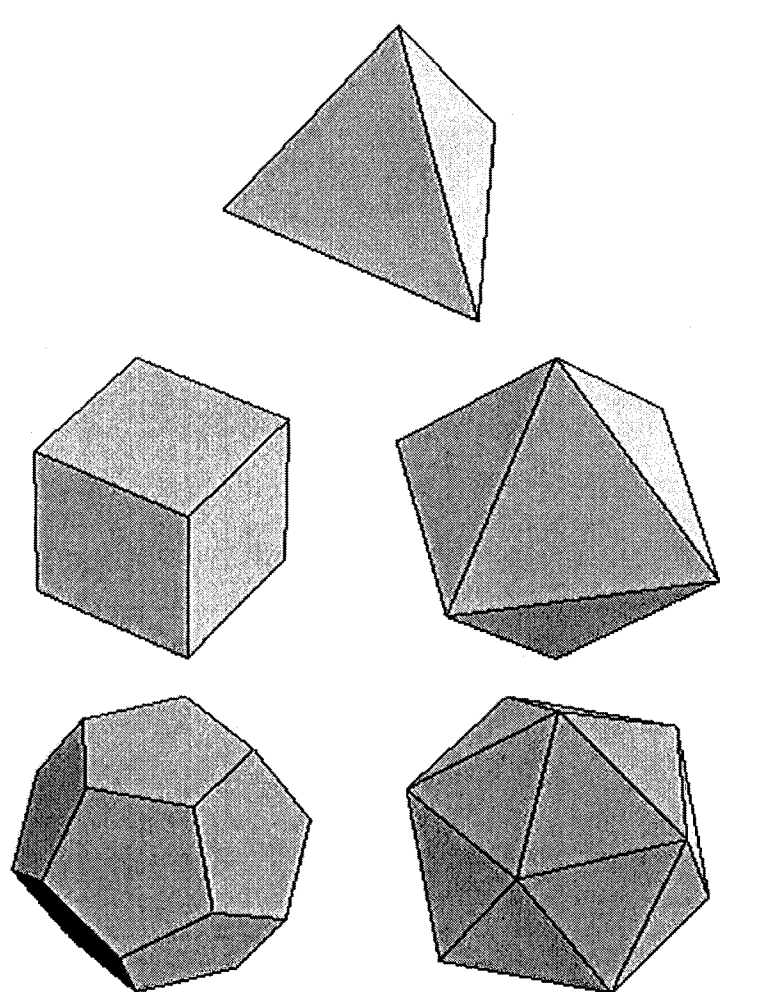
Pseudopotentials in VMC

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

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

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

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 $\propto \delta\psi^2$