Effective core potential, ECP

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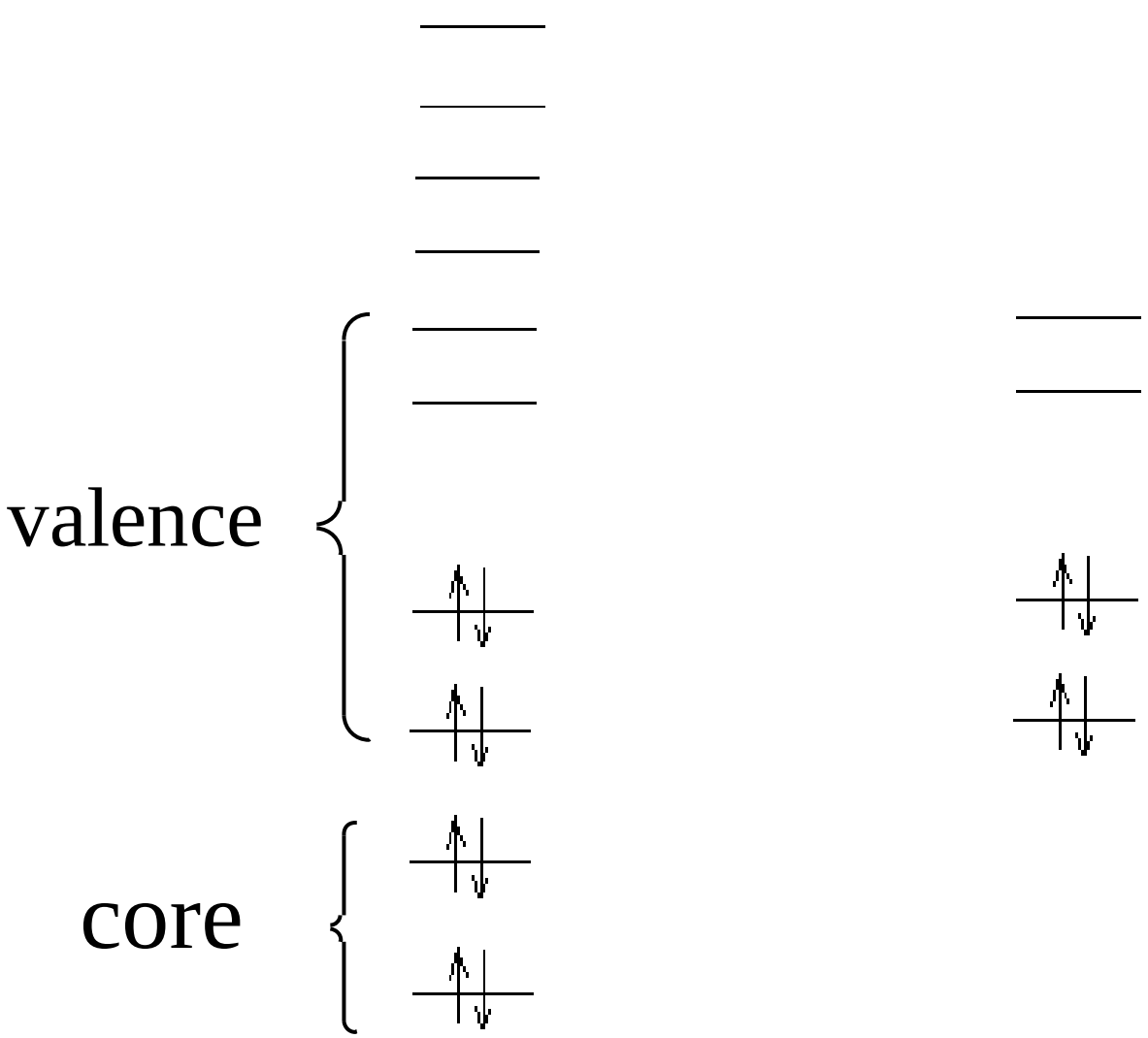
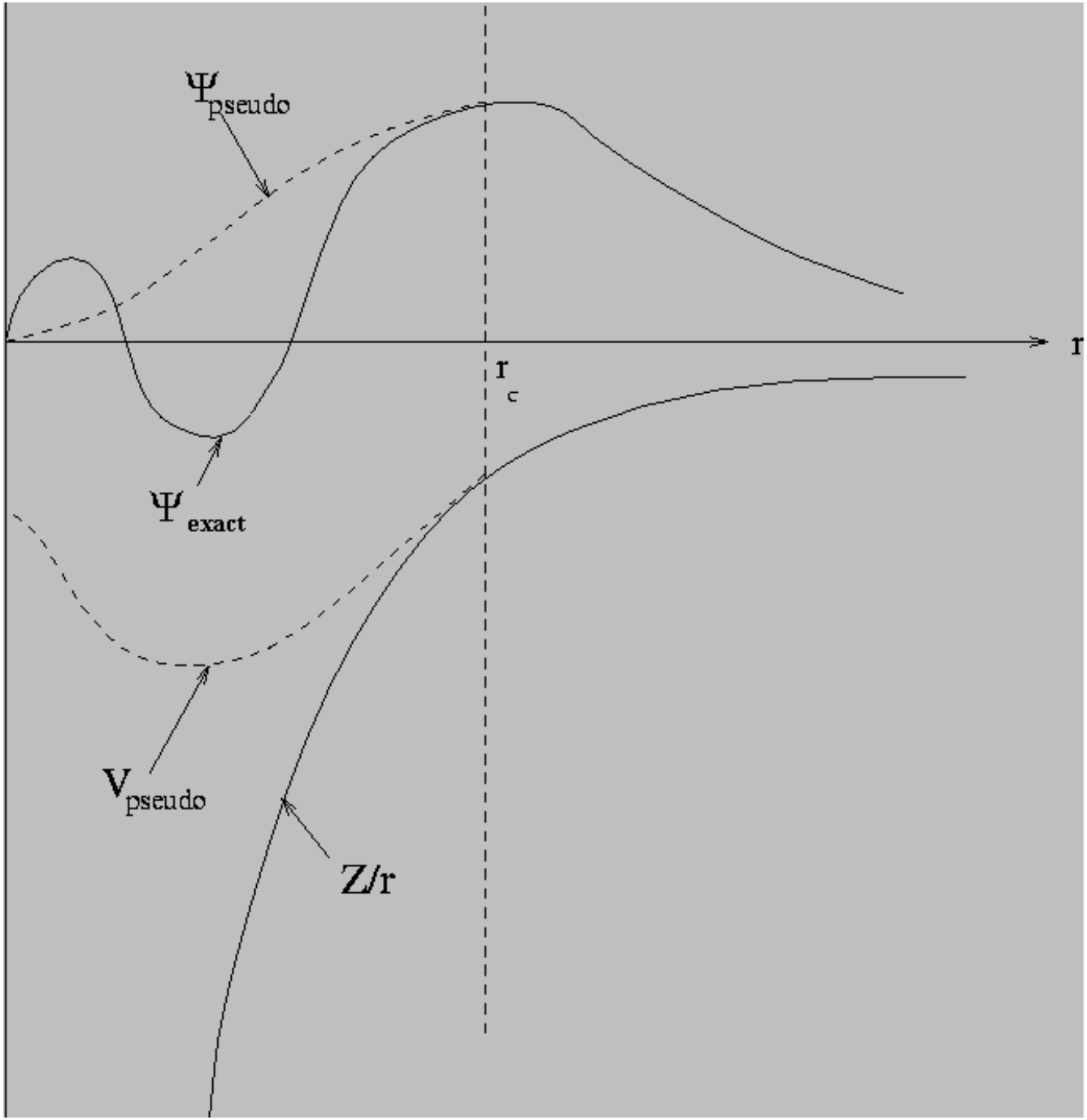
One electron energies of atoms

	ε(Cl)	ε(Cl)-ε(Cl^-)	ε(Sc)	ε(Sc)-ε(Sc^{+3})
1s	-104.88	0.38	-165.90	1.19
2s	-10.61	0.38	-19.08	1.22
2p	-8.07	0.38	-15.67	1.22
3s	-1.07	0.34	-2.57	1.15
3p	-0.51	0.36	-1.57	1.13


valence
core


Ψ_{pseudo}
r
r_c
Ψ_{exact}
V_{pseudo}
Z/r

Оператор псевдопотенциалу

Hartree-Fock equations

$$\left(-\frac{1}{2}\nabla^2 + V_{HF}\right)\varphi_i = \varepsilon_i \varphi_i, \qquad i = 1,...M$$

$$V_{HF} = V(r) + J(r) - K(r)$$

Hartree-Fock equations for pseudopotential

$$\left(-\frac{1}{2}\nabla^2 + V_{pp}\right)\varphi_i = \varepsilon_i \varphi_i, \qquad i = 1,...M$$

$$V_{pp} = V_{HF} + \rho A \rho$$

Псевдопотенціали

Huzinaga

$$V(r) = -\frac{Z}{r}\left(1 + \sum_i A_i e^{-\alpha_i r^2} + \sum_i B_i r e^{-\beta_i r^2}\right)$$

Soft-core

$$V_\ell(r,x) = \begin{cases} A_i(x) & r < R_e \\ -\dfrac{e}{r} & r > R_e \end{cases}$$

Hard-core

$$V_\ell(r,x) = -\frac{e}{r}\frac{B_\ell(x)}{r^2}$$

Pt Electronic shells

$[Pt]=[Xe]4f^{14}5d^{9}6s^{1}$

$[Xe]=[Kr]4d^{10}5s^{2}5p^{6}$

$[Kr]=[Ar]3d^{10}4s^{2}4p^{6}$

$[Ar]=[Ne]3s^{2}3p^{6}$

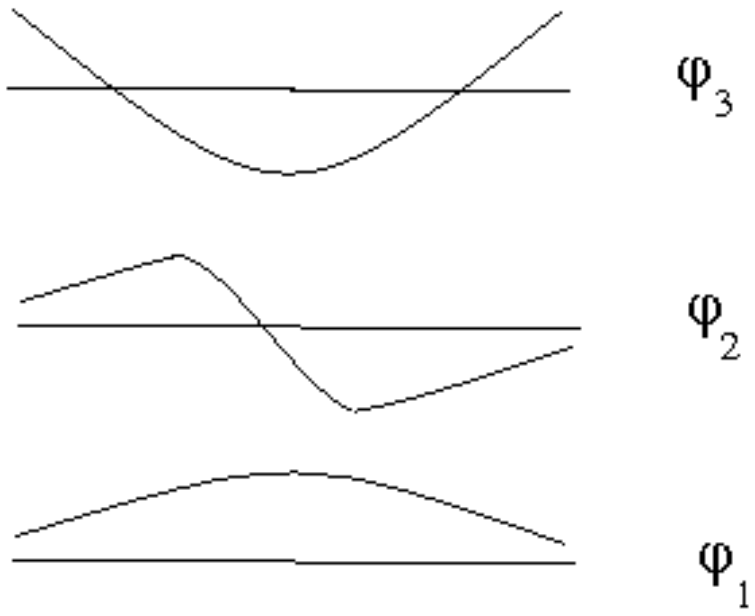
$[Ne]=[He]2s^{2}2p^{6}$

$[He]=1s^{2}$

Pt Valence shell: $5s^{2}5p^{6}5d^{9}6s^{1}$ 18 electrons

вузли

$$\Psi(r) = 0$$



Базиси ECP

Stevens-Basch-Krauss-Jasien-Cudari (SBKJC)
валентно-розщеплений (31G)
Аналог Lanl2DZ

Hay-Wadt (HW)
валентно-розщеплений (21G)

Базиси MCP

MCP-DZP, MCP-TZP

NaCL

ε (a.u)	HF (SBKJC)	HF (6-31G)
	core	(10 MO)
NaCl (S)	-0.9344	-0.9348
NaCl (Pz)	-0.3530	-0.3589
Cl(Px)	-0.3416	-0.3449
Cl(Py)	-0.3416	-0.3449