Correlated Electrons

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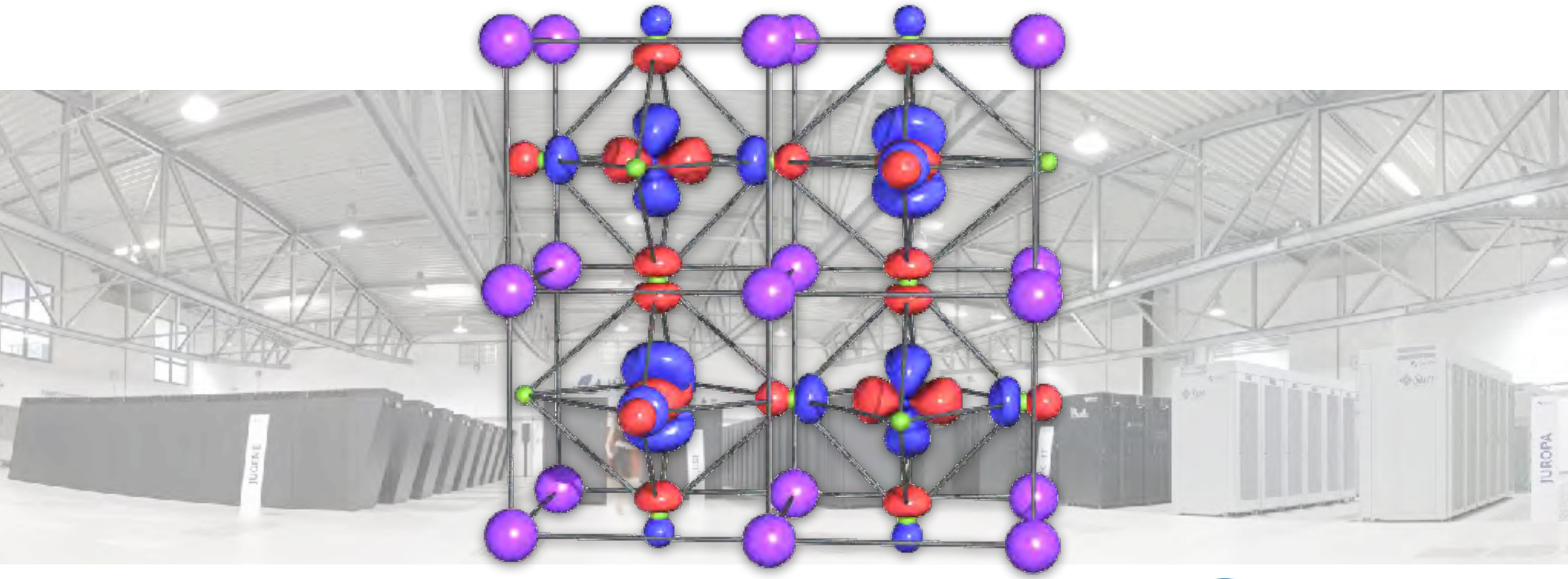


German Research School
for Simulation Sciences

outline

many-body physics for atoms

- self-consistent field methods
  - density matrices
  - exchange-correlation hole
  - density-functional theory
  - exercises: DFT code for atoms
- multiplets in open shells
  - second quantization
  - Hamiltonian matrix elements
  - angular momenta
  - diagonalizing the interaction
  - Hund's rules

www.cond-mat.de/teaching/correl

exercises

Correlated Electrons SS 2020, E. Koch

Exercise Sheet 1 due 16 April

prepare your solutions so you are ready to present them in class
if you cannot solve a problem, explain where you got stuck.

1. *atomic units*

Express the speed of light and the Bohr magneton in atomic units.
What unit of temperature do we have to choose to also make the numerical value of the Boltzmann constant to equal 1?

2. *magnetic moment*

From classical magnetostatics we know that the magnetic moment due to an electrical current density $\vec{j}_e$ is given by

$$\vec{m} = \frac{1}{2} \int \vec{r} \times \vec{j}_e \; d^3 r \; .$$

i. Given the quantum-mechanical probability current density

Lecture Notes

E. Pavarini, E. Koch,
F. Anders, M. Jarrell
Correlated Electrons:
From Models to Materials

- Exchange Mechanisms
- Multiplets in Transition Metal Ions
- Estimates of Model Parameter
- Crystal Field Theory, Tight-Binding

Autumn School on Correlated Electrons
www.cond-mat.de/events/correl.html

Übungsaufgabe

Gegeben:
Atome der Ordnungszahl Z_α an den Positionen R_α.
Lösen Sie

$$H = -\frac{\hbar^2}{2m}\sum_{j=1}^{N_e}\nabla_j^2 - \frac{1}{4\pi\epsilon_0}\sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \frac{1}{4\pi\epsilon_0}\sum_{j<k}^{N_e}\frac{e^2}{|r_j - r_k|} + \frac{1}{4\pi\epsilon_0}\sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.M.A. Dirac, *Proceedings of the Royal Society* **A123**, 714 (1929)

Theory of (almost) Everything

typical units

h = 6.626068 10^{-34} Js
m_{el} = 9.109382 10^{-31} kg
e = 1.602176 10^{-19} C

http://physics.nist.gov/cuu/Constants/index.html

$$E = \frac{\hbar^2 k^2}{2 m_{el}}$$

why use Å and eV?

E [in J] = 6.10 10^{-39} (k [in m^{-1}])^2

1 Å = 10^{-10} m
1 eV = 1.602176 10^{-19} J

E [in eV] = 3.81 (k [in $Å^{-1}$])^2

atomic units

$$
\begin{aligned}
\hbar &= 1.0546{\cdot}10^{-34}\ \mathrm{Js} && [ML^2T^{-1}] \\
m_e &= 9.1094{\cdot}10^{-31}\ \mathrm{kg} && [M] \\
e &= 1.6022{\cdot}10^{-19}\ \mathrm{C} && [Q] \\
4\pi\varepsilon_0 &= 1.1127{\cdot}10^{-10}\ \mathrm{F/m} && [M^{-1}L^{-3}T^2Q^2]
\end{aligned}
$$

http://physics.nist.gov/cuu

H. Shull and G.G. Hall, Nature **184**, 1559 (1959)

solve

$$
\begin{aligned}
\hbar &= 1\, a_0^2 m_e / t_0 \\
m_e &= 1\, m_e \\
e &= 1\, e \\
4\pi\varepsilon_0 &= 1\, t_0^2 e^2 / a_0^3 m_e
\end{aligned}
$$

to obtain

$$
\begin{aligned}
1\,\text{a.u. length} &= a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \approx 5.2918{\cdot}10^{-11}\ \mathrm{m} \\
1\,\text{a.u. mass} &= m_e = \phantom{\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}} \approx 9.1095{\cdot}10^{-31}\ \mathrm{kg} \\
1\,\text{a.u. time} &= t_0 = \frac{(4\pi\varepsilon_0)^2\hbar^3}{m_e e^4} \approx 2.4189{\cdot}10^{-17}\ \mathrm{s} \\
1\,\text{a.u. charge} &= e = \phantom{\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}} \approx 1.6022{\cdot}10^{-19}\ \mathrm{C}
\end{aligned}
$$

Übungsaufgabe

Gegeben:
Atome der Ordnungszahl Z_α an den Positionen R_α.
Lösen Sie

$$H = -\frac{\hbar^2}{2m}\sum_{j=1}^{N_e}\nabla_j^2 - \frac{1}{4\pi\epsilon_0}\sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \frac{1}{4\pi\epsilon_0}\sum_{j<k}^{N_e}\frac{e^2}{|r_j - r_k|} + \frac{1}{4\pi\epsilon_0}\sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

$$H = \frac{1}{2}\sum_{j=1}^{N_e}\nabla_j^2 - \sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{j<k}^{N_e}\frac{1}{|r_j - r_k|} + \sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}$$

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.M.A. Dirac, *Proceedings of the Royal Society* **A123**, 714 (1929)

Theory of (almost) Everything

More is Different

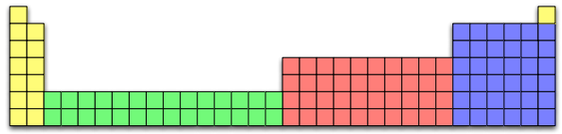
… the reductionist hypothesis does not by any means imply a ``constructionist'' one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe.

Sometimes, as in the case of superconductivity, the new symmetry — now called broken symmetry because the original symmetry is no longer evident — may be of an entirely unexpected kind and extremely difficult to visualize. In the case of superconductivity, 30 years elapsed between the time when physicists were in possession of every fundamental law necessary for explaining it and the time when it was actually done.

Thus with increasing complication at each stage, we go up the hierarchy of the sciences. We expect to encounter fascinating and, I believe, very fundamental questions at each stage in fitting together less complicated pieces into the more complicated system and understanding the the basically new types of behavior which can result.

P.W. Anderson: More is Different, *Science* **177**, 393 (1972)

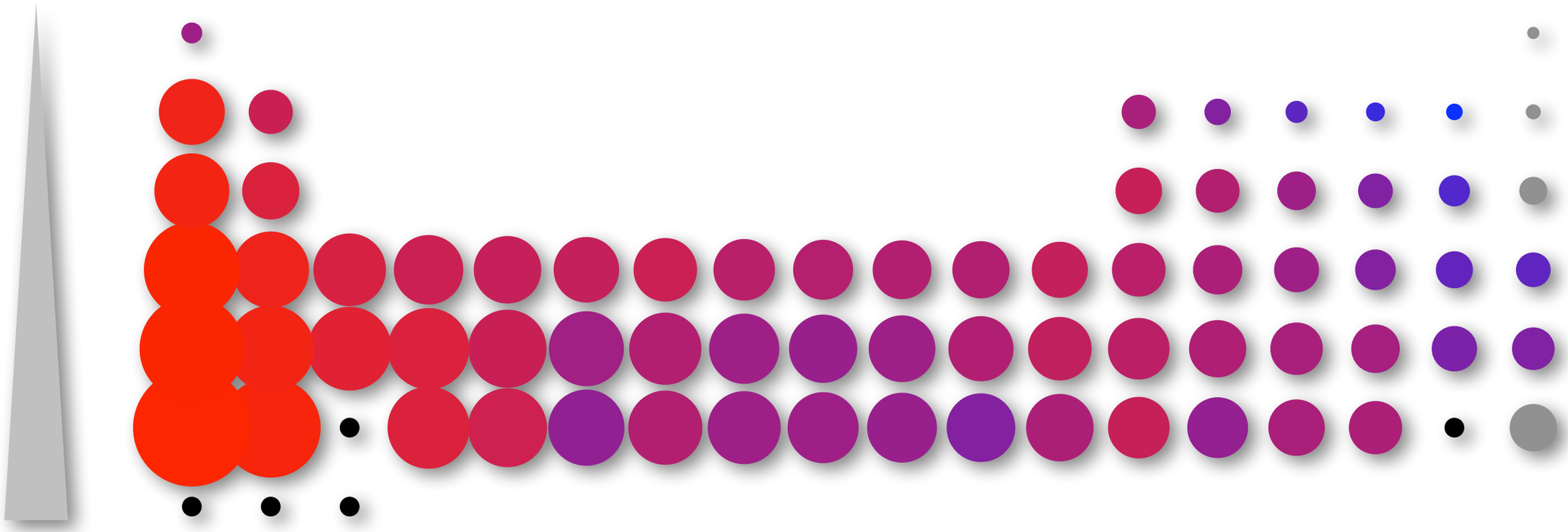
periodic table



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt									

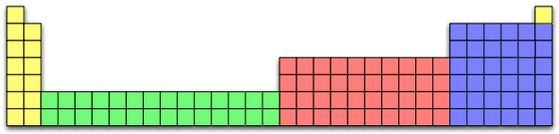
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

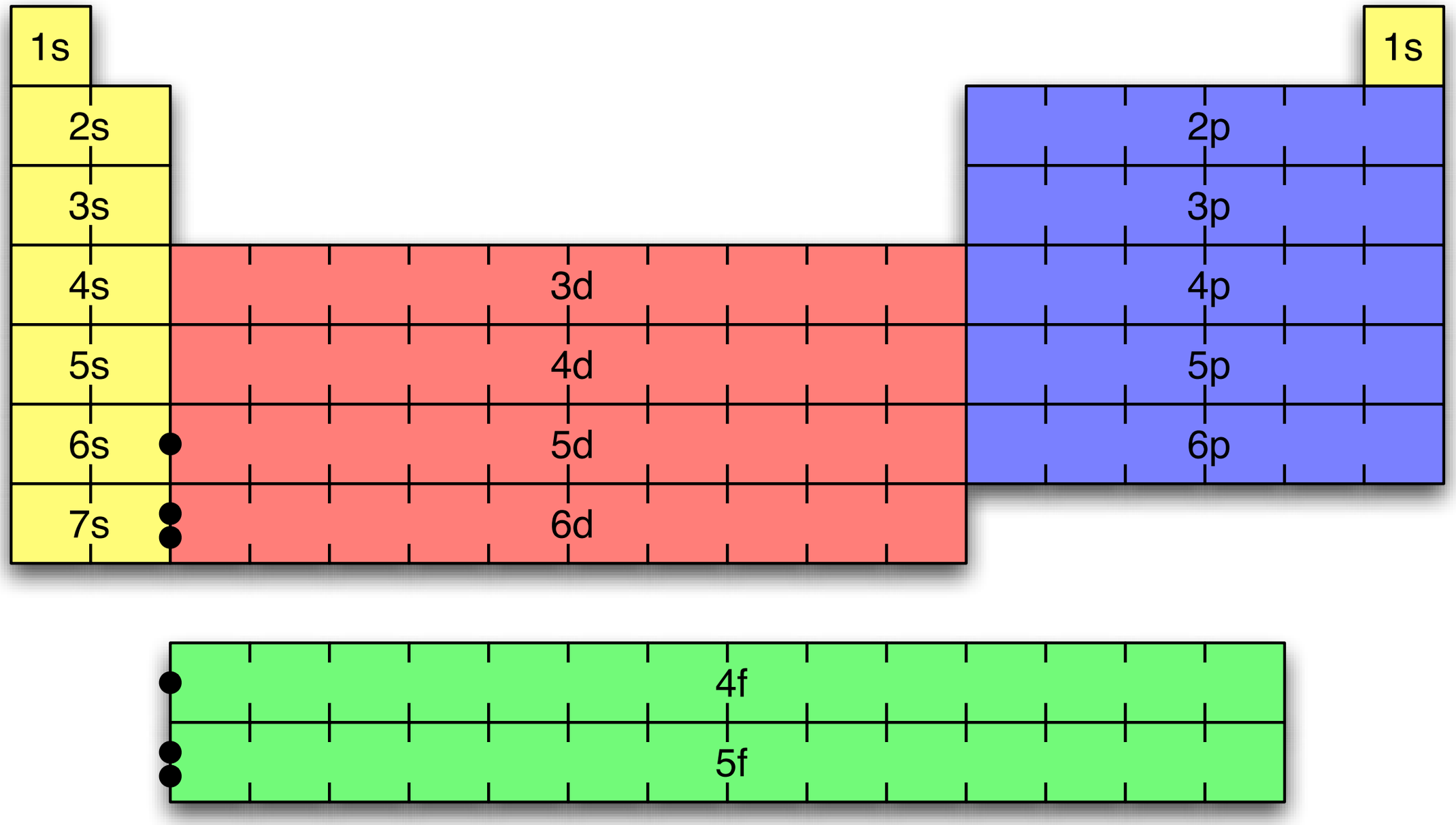
atomic radii



E. Clementi, D.L.Raimondi, and W.P. Reinhardt
J. Chem. Phys. **47**, 1300 (1967)

periodic table





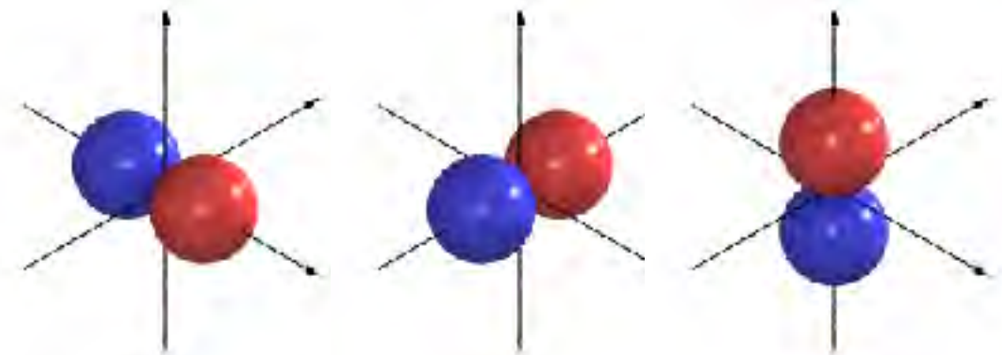
real harmonics

$$s \qquad Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$p_z \qquad Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$p_x \qquad \sqrt{\frac{1}{2}}\left(Y_{1,-1} - Y_{1,1}\right) = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$$

$$p_y \qquad \sqrt{\frac{1}{2}}i\left(Y_{1,-1} + Y_{1,1}\right) = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$$



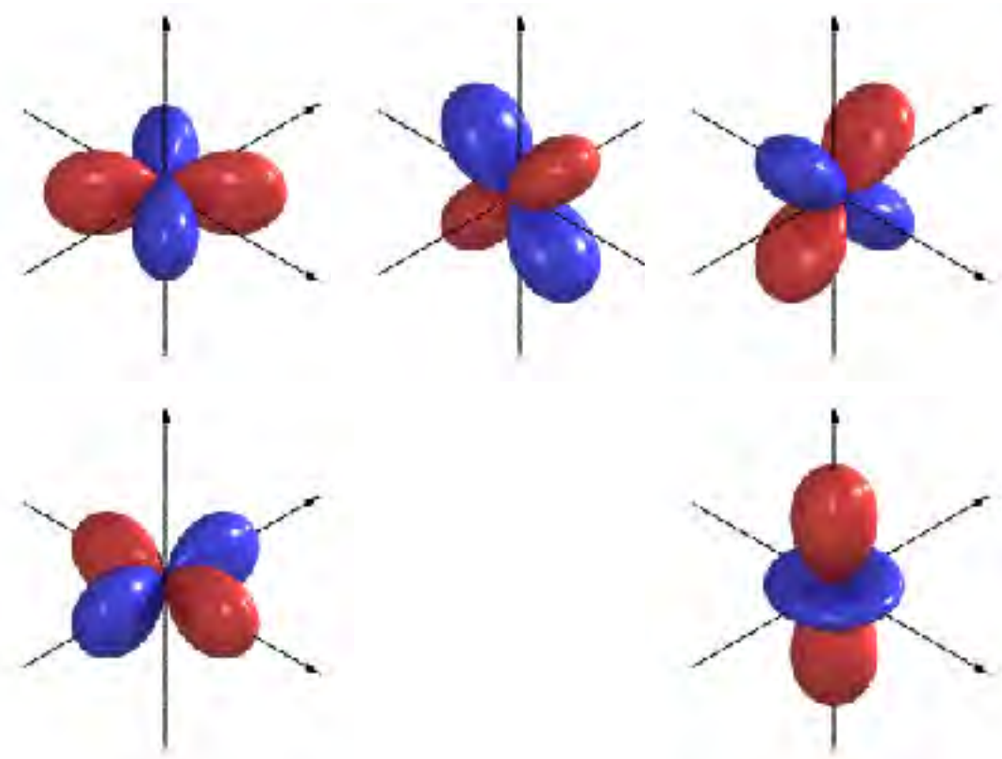
$$d_{3z^2-1} \qquad Y_{2,0} = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

$$d_{zx} \qquad \sqrt{\frac{1}{2}}\left(Y_{2,-1} - Y_{2,1}\right) = \sqrt{\frac{15}{16\pi}}\sin 2\theta\cos\phi$$

$$d_{yz} \qquad \sqrt{\frac{1}{2}}i\left(Y_{2,-1} + Y_{2,1}\right) = \sqrt{\frac{15}{16\pi}}\sin 2\theta\sin\phi$$

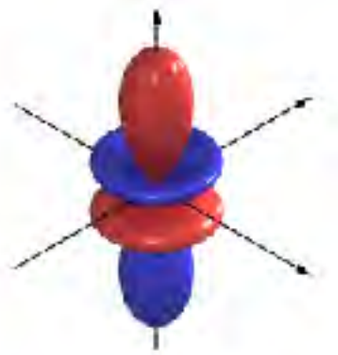
$$d_{x^2-y^2} \qquad \sqrt{\frac{1}{2}}\left(Y_{2,-2} + Y_{2,2}\right) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi$$

$$d_{xy} \qquad \sqrt{\frac{1}{2}}i\left(Y_{2,-2} - Y_{2,2}\right) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi$$



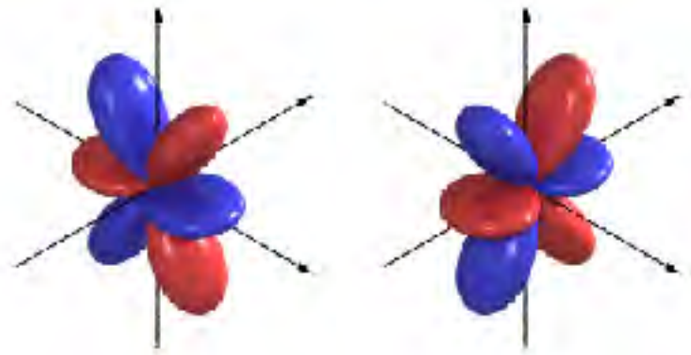
real harmonics

$$f_{z(5z^2-3)} \qquad Y_{3,0} \qquad = \qquad \sqrt{\tfrac{7}{16\pi}}\left(5\cos^2\theta - 3\right)\cos\theta$$



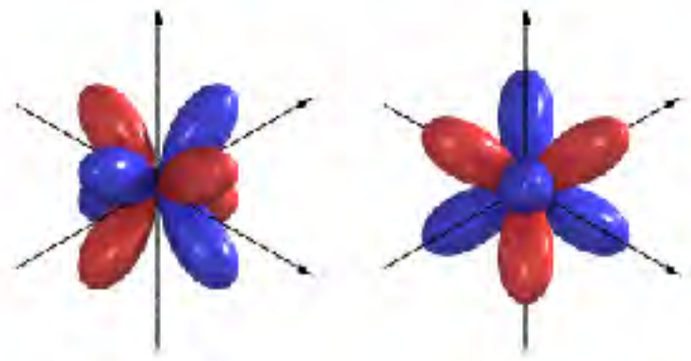
$$f_{x(5z^2-1)} \qquad \sqrt{\tfrac{1}{2}}\left(Y_{3,-1} - Y_{3,1}\right) = \sqrt{\tfrac{21}{32\pi}}\left(5\cos^2\theta - 1\right)\sin\theta\cos\phi$$

$$f_{y(5z^2-1)} \qquad \sqrt{\tfrac{1}{2}}\,i\left(Y_{3,-1} + Y_{3,1}\right) = \sqrt{\tfrac{21}{32\pi}}\left(5\cos^2\theta - 1\right)\sin\theta\sin\phi$$



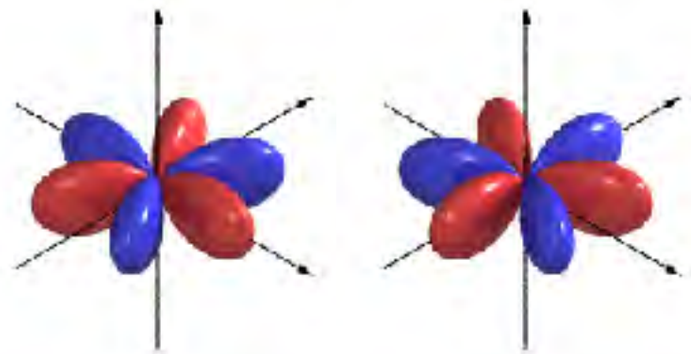
$$f_{z(x^2-y^2)} \qquad \sqrt{\tfrac{1}{2}}\left(Y_{3,-2} + Y_{3,2}\right) = \qquad \sqrt{\tfrac{105}{16\pi}}\cos\theta\sin^2\theta\cos 2\phi$$

$$f_{xyz} \qquad \sqrt{\tfrac{1}{2}}\,i\left(Y_{3,-2} - Y_{3,2}\right) = \qquad \sqrt{\tfrac{105}{16\pi}}\cos\theta\sin^2\theta\sin 2\phi$$

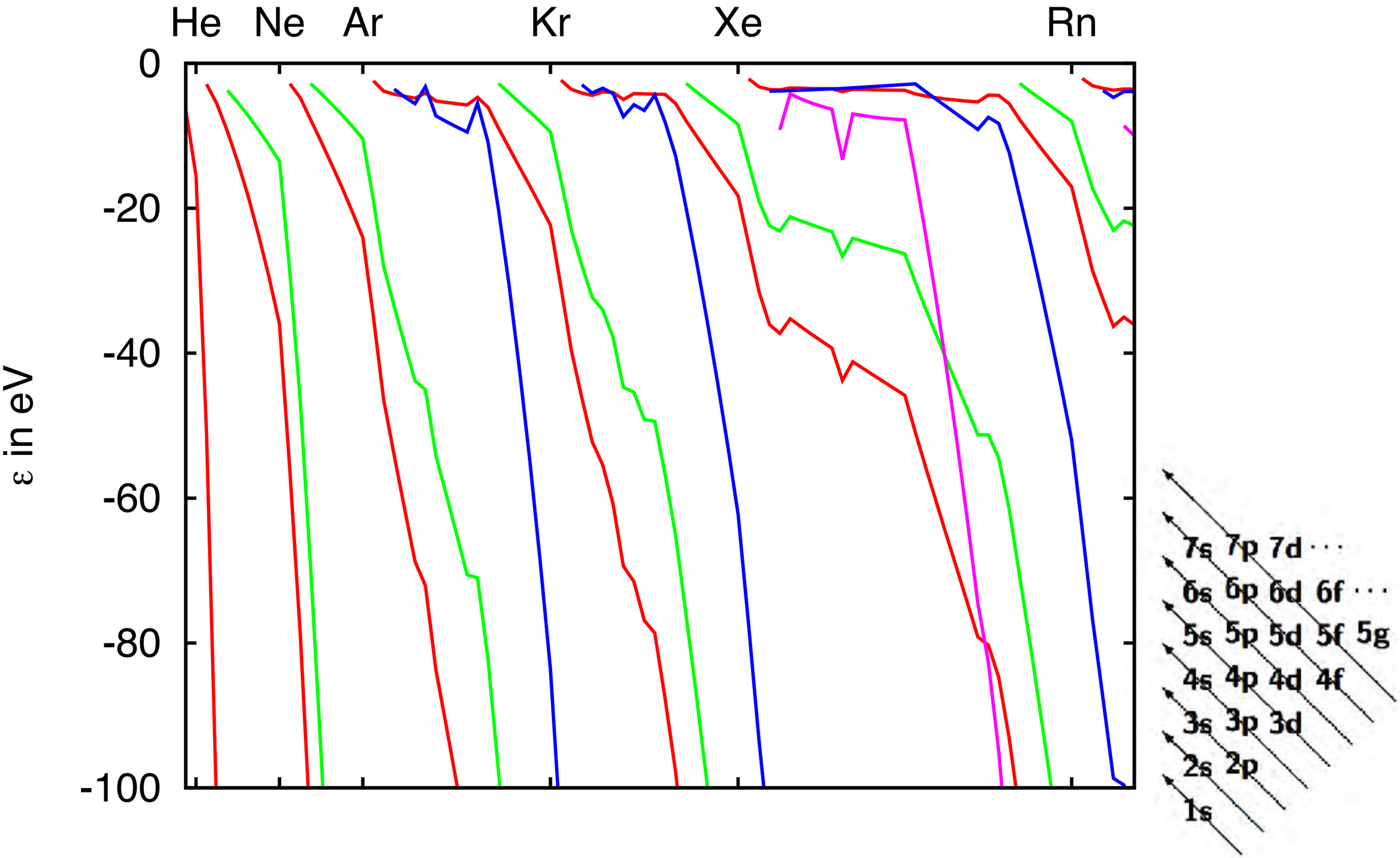


$$f_{x(x^2-3y^2)} \qquad \sqrt{\tfrac{1}{2}}\left(Y_{3,-3} - Y_{3,3}\right) = \qquad \sqrt{\tfrac{35}{32\pi}}\sin^3\theta\cos 3\phi$$

$$f_{y(3x^2-y^2)} \qquad \sqrt{\tfrac{1}{2}}\,i\left(Y_{3,-3} + Y_{3,3}\right) = \qquad \sqrt{\tfrac{35}{32\pi}}\sin^3\theta\sin 3\phi$$



atom in spherical mean-field approximation



Version History - Disclaimer

Atomic Reference Data for Electronic Structure Calculations

Data Sets

[Atomic Reference Data for Electronic Structure Calculations]

Contains total energies and orbital eigenvalues for the atoms hydrogen through uranium, as computed in several standard variants of density-functional theory.

1. Documentation
2. Access data through periodic table interface
3. Retrieve original data files
4. Results for all elements in pictorial form

Related links

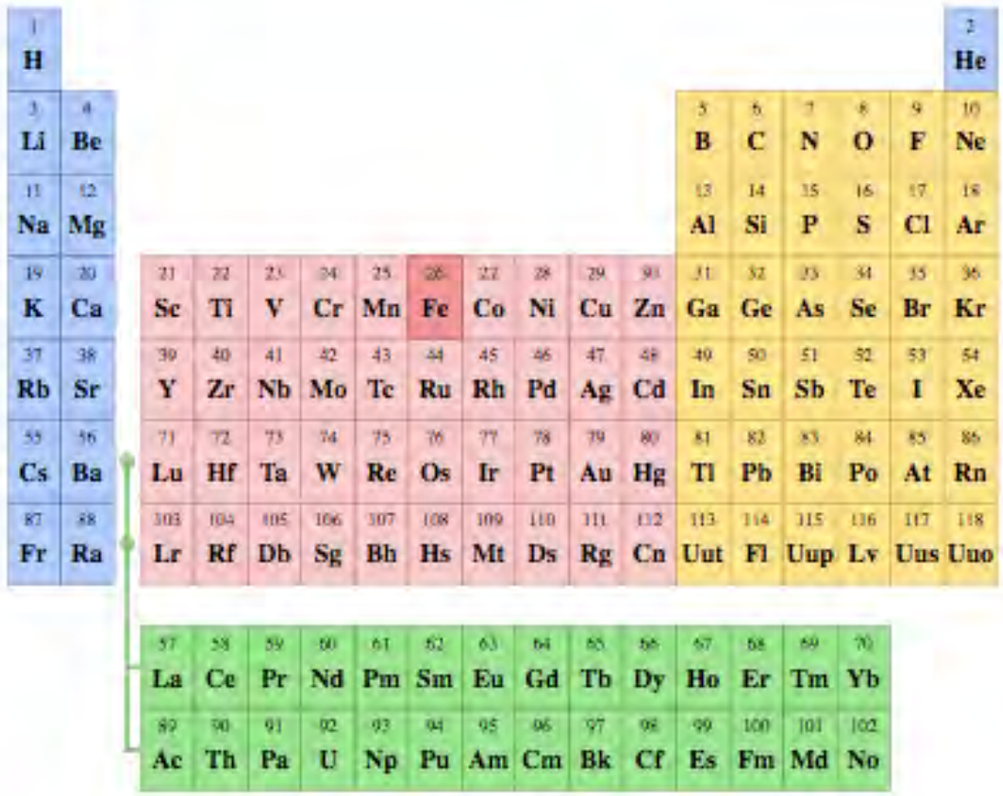
GAMS Guide to Available Mathematical Software
PADE NIST Parallel Applications Development Environment

Physical Reference Data
Physical Measurement Laboratory
Inquiries or comments: charles.clark@nist.gov
Online: August 1997 - **Last update:** April 2003

http://www.cond-mat.de/sims/multiplet/

cond-mat.de

Calculations of atomic multiplets across the periodic table



26

Fe

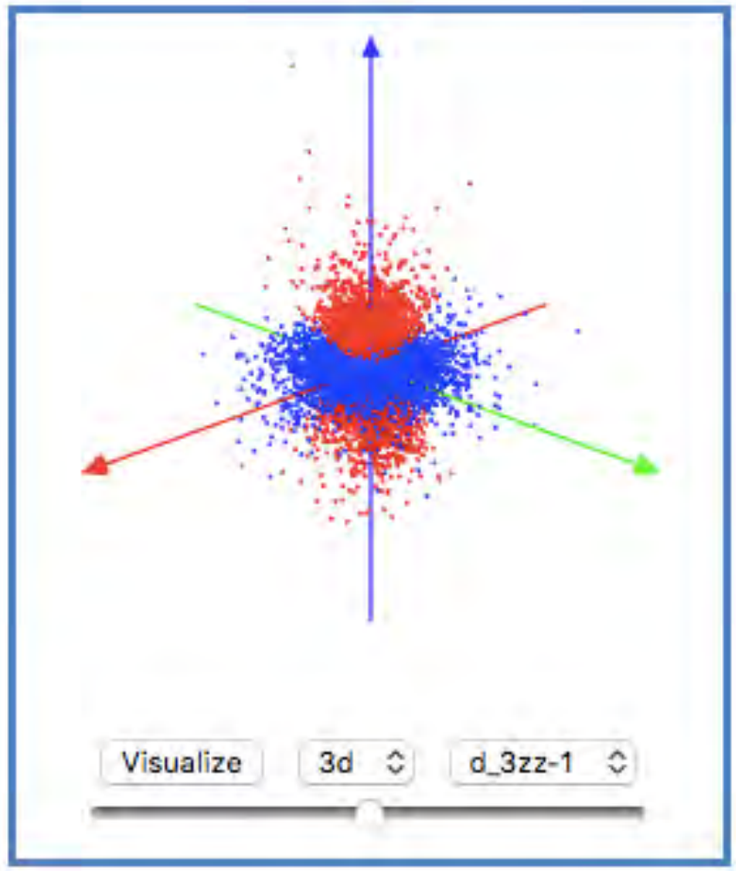
Iron

55.845

[Ar] 4s2 3d6

Default Configuration:

Realistic



Self-consistent field computation

Self-consistent iterations

Converge total energy to 4 digits

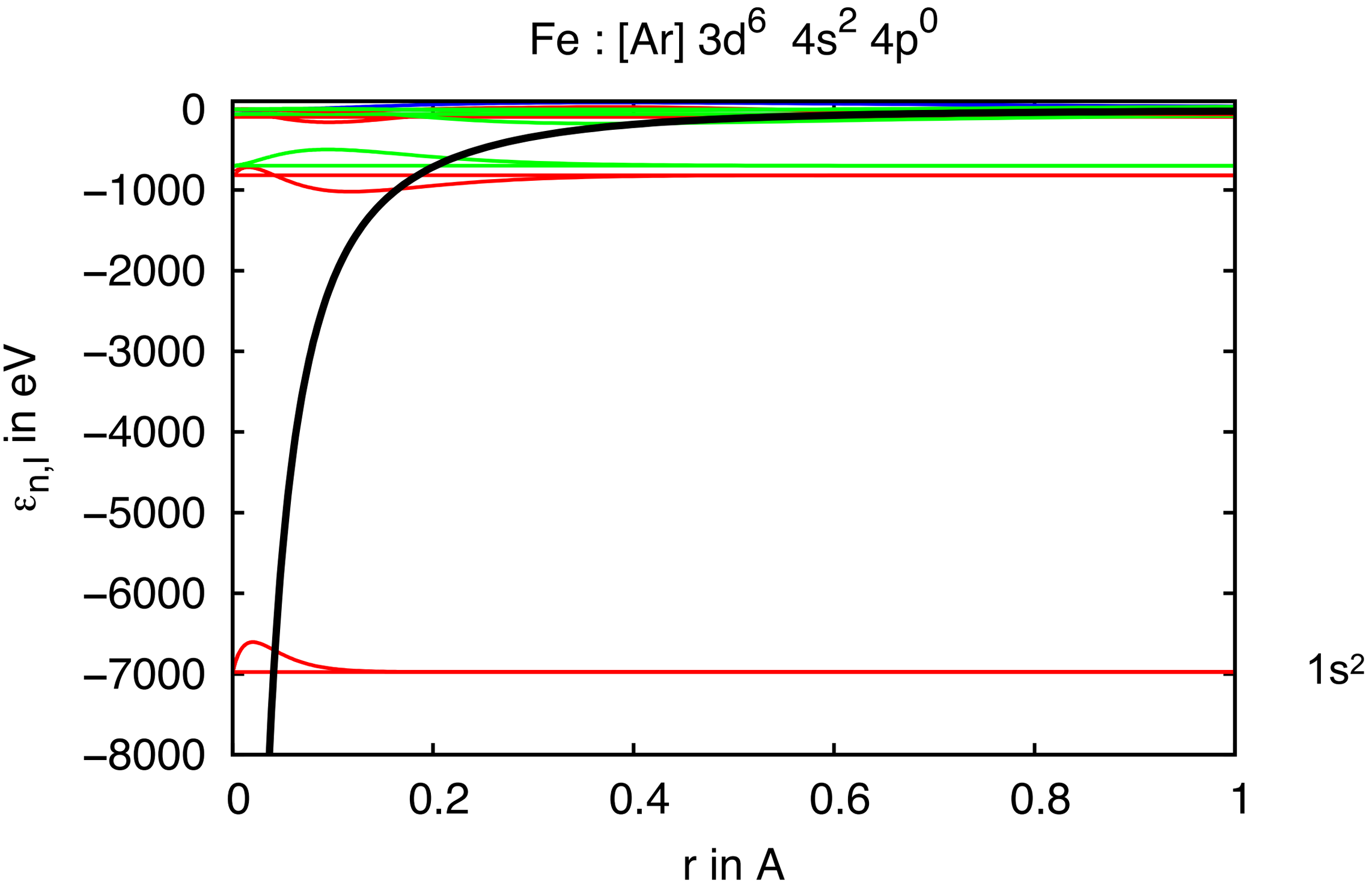
```
iter = 13, converge = 0.0295
iter = 14, converge = 0.0107
iter = 15, converge = 0.0056
```

Units

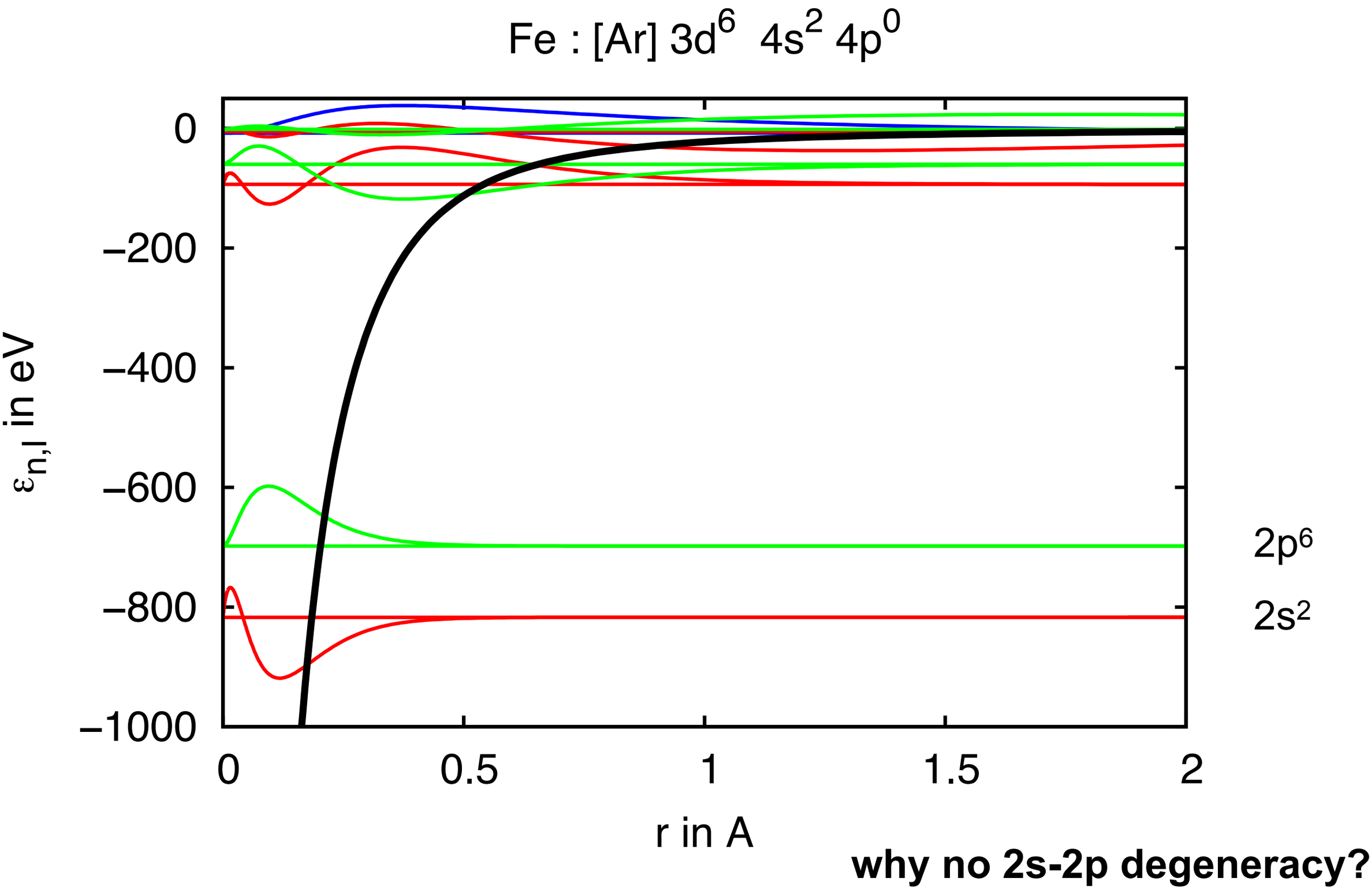
Distance unit Bohr radius Energy unit Hartree

Wave function plots

atom in spherical mean-field approximation

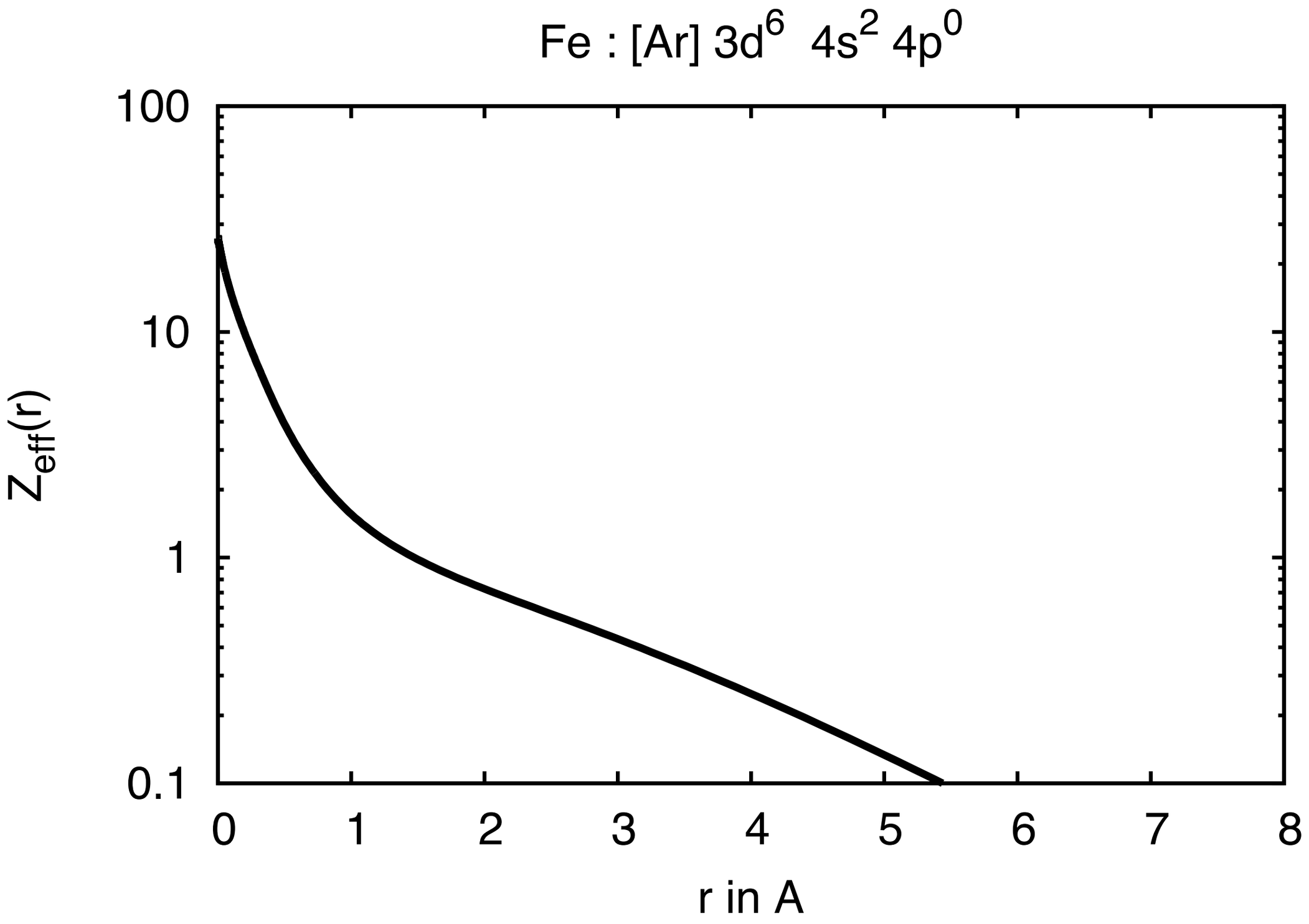


atom in spherical mean-field approximation

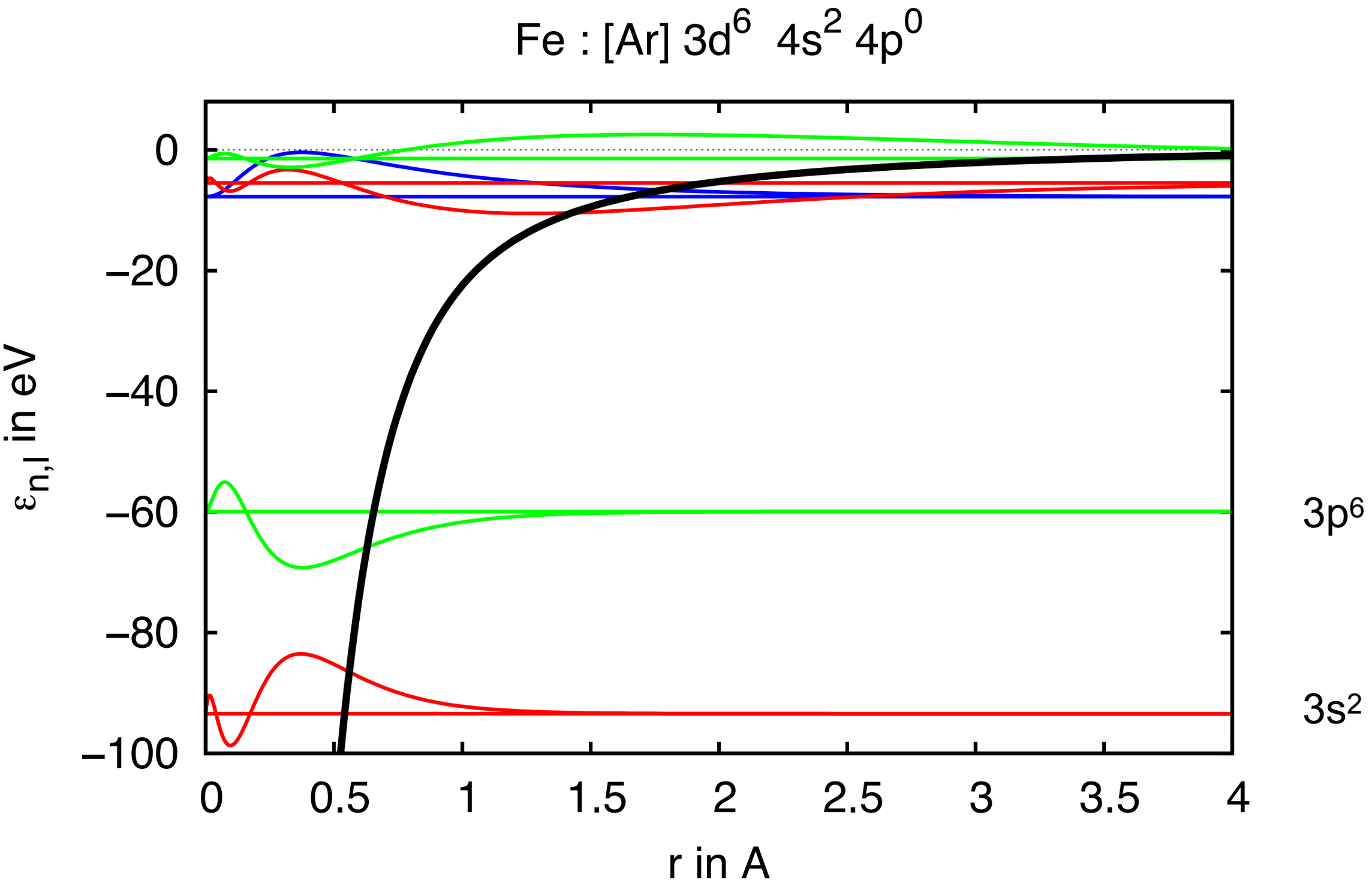


why no 2s-2p degeneracy?

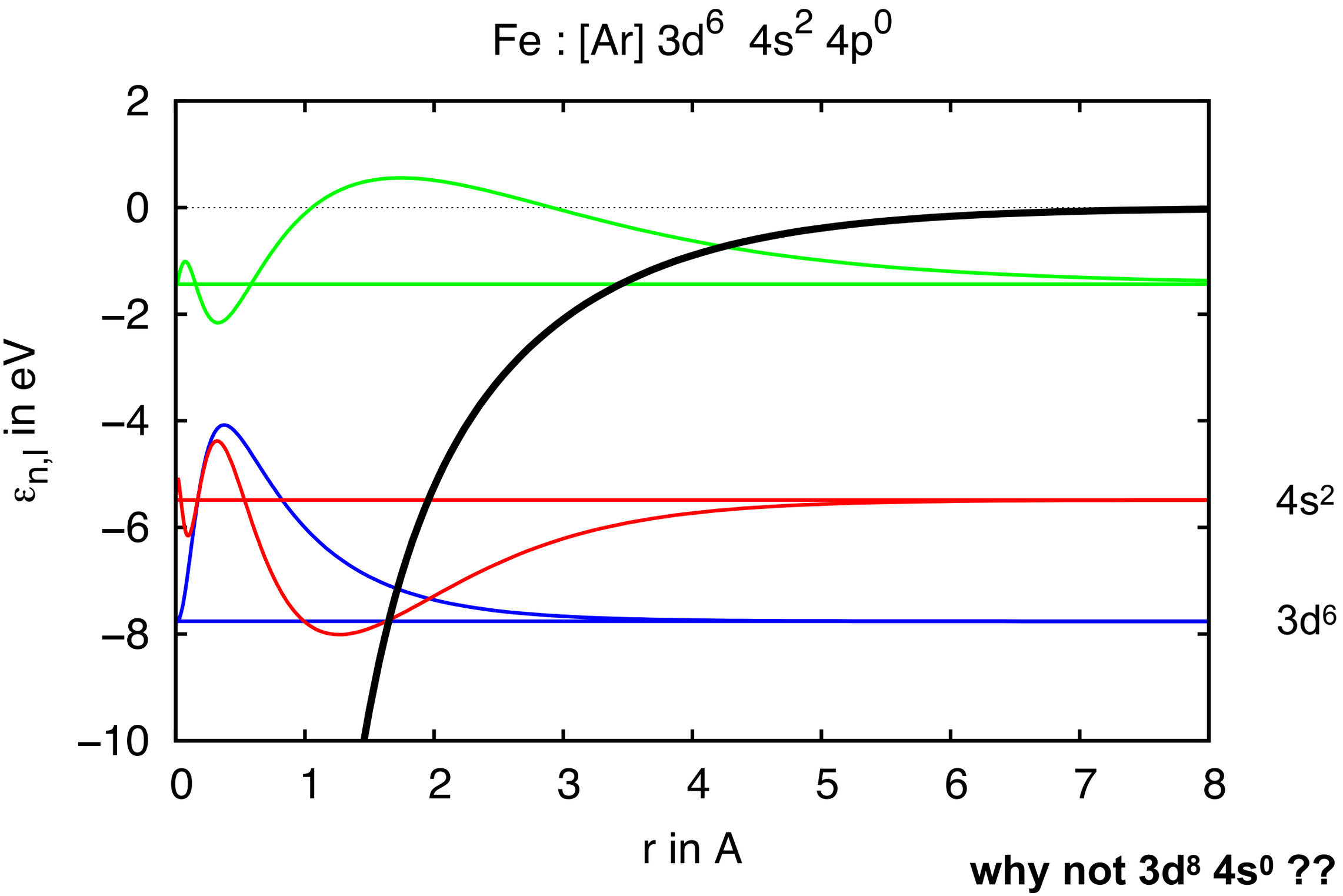
atom in spherical mean-field approximation



atom in spherical mean-field approximation

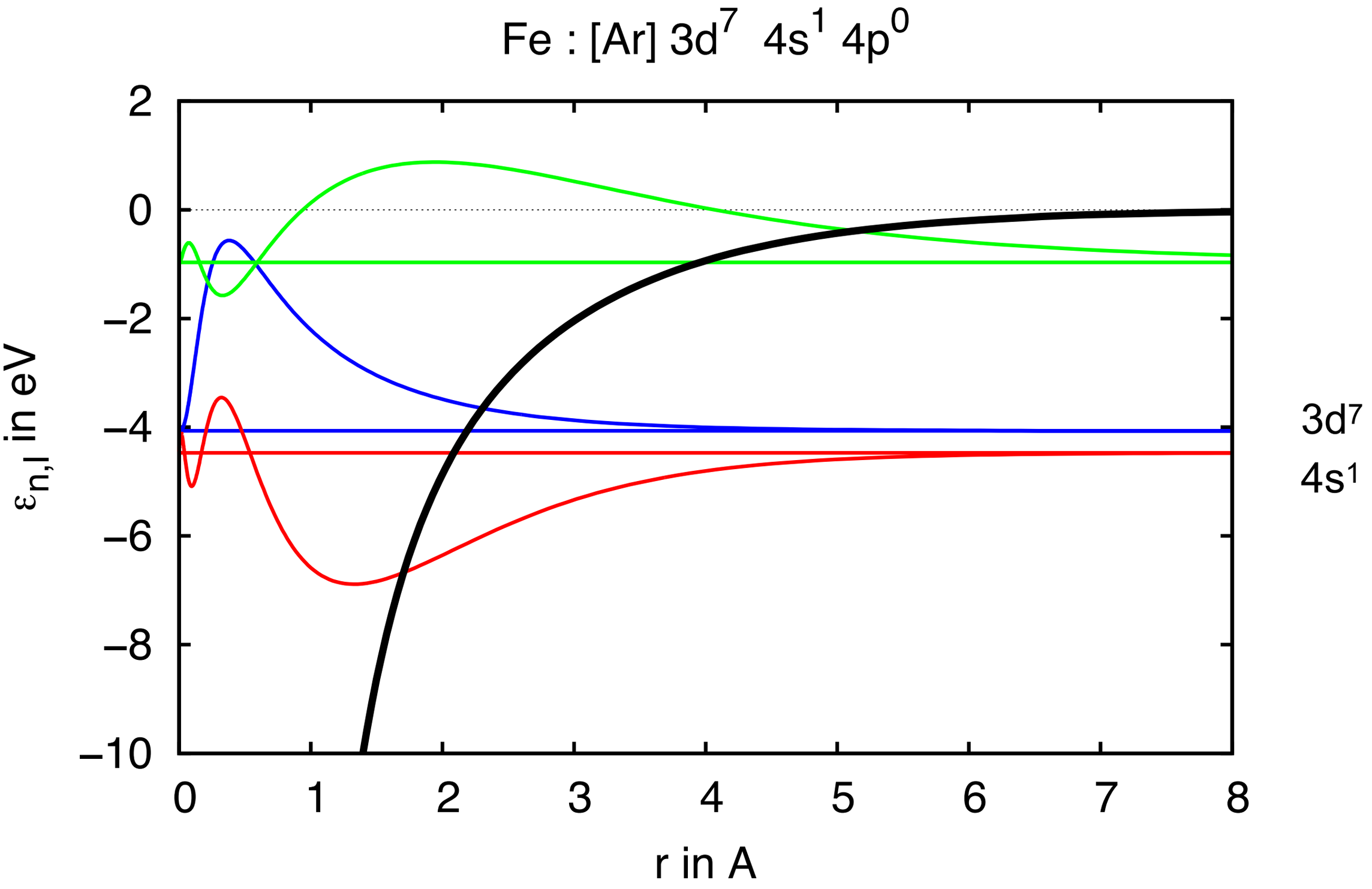


atom in spherical mean-field approximation

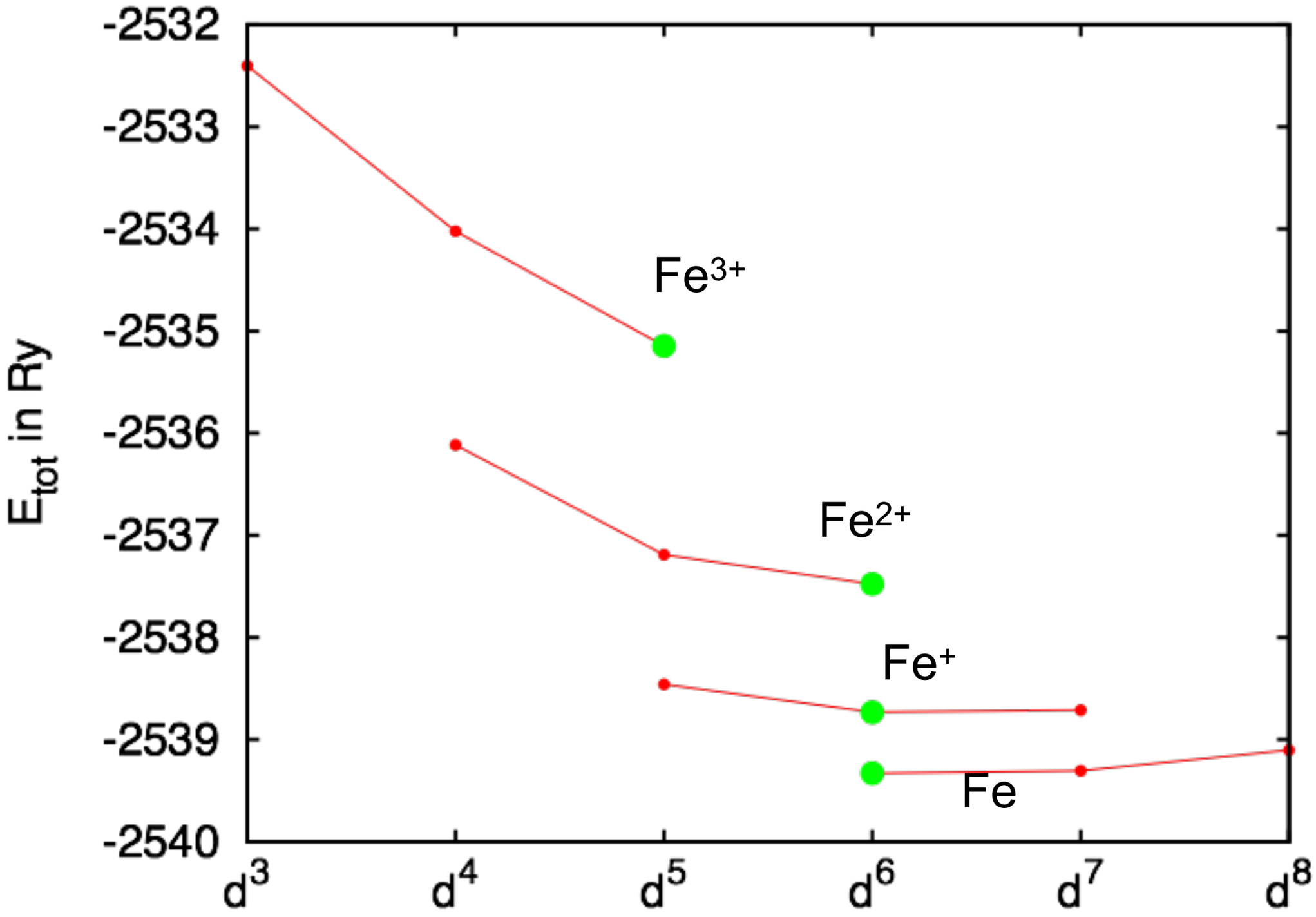


why not $3d^8\ 4s^0$??

atom in spherical mean-field approximation



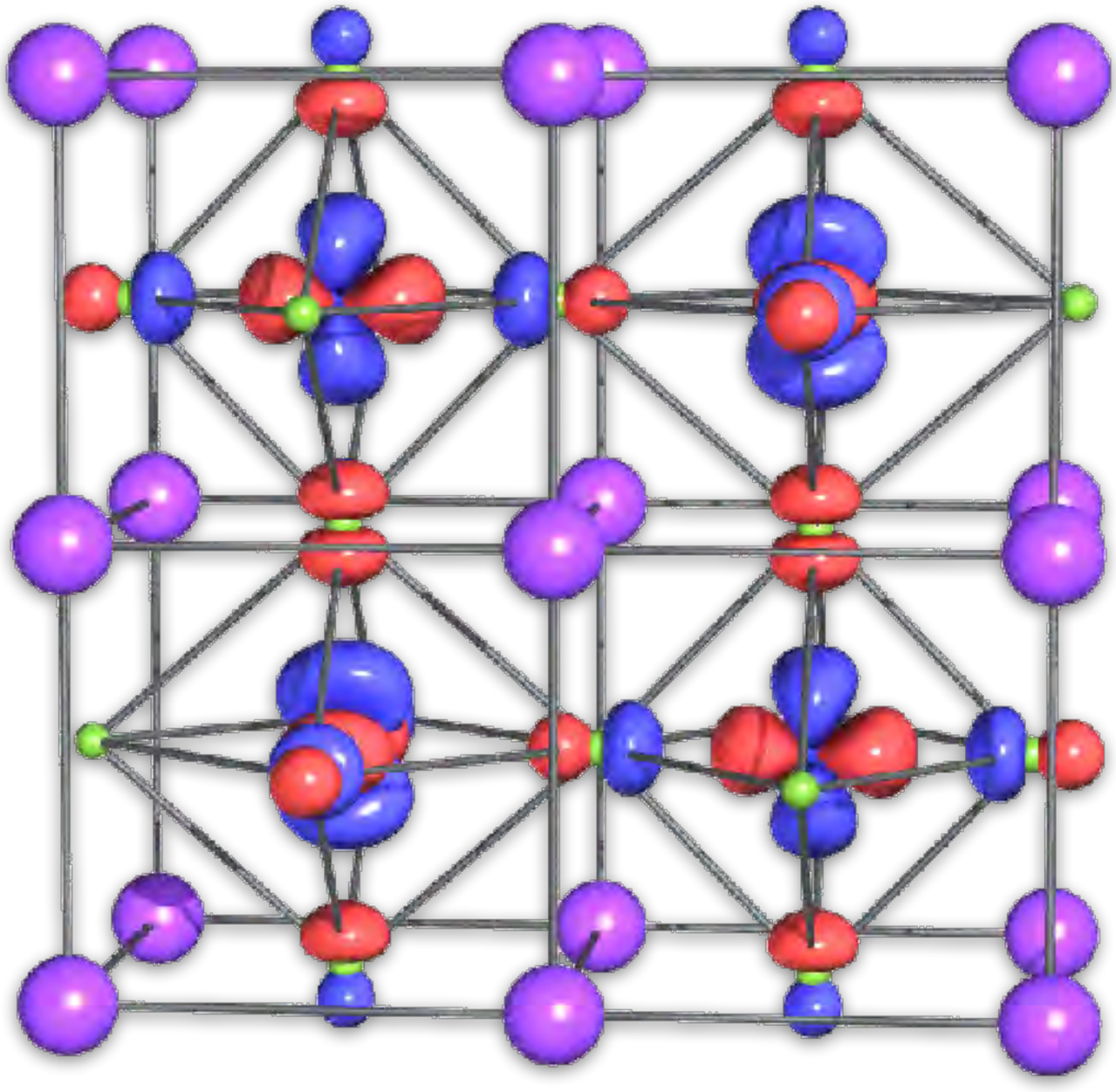
total energy



tools: pse

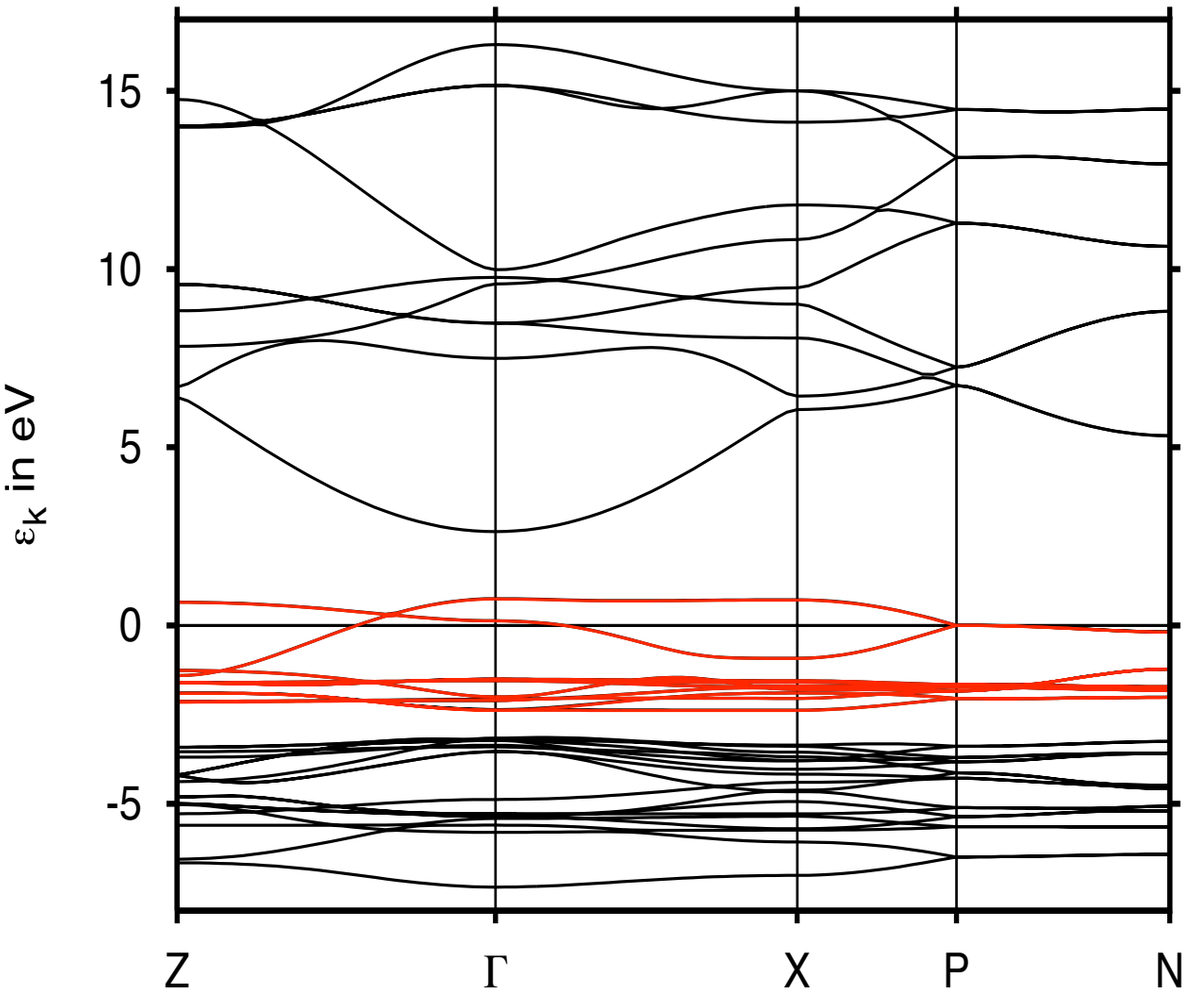
```
#!/bin/bash
if [ "$1" == "" ]
then
cat << EOF
1 2 3a La/Ac                          4a5a6a7a8a8a8a1a2a3 4 5 6 7 8
H                                                                 He
LiBe                                                   B C N O F Ne
NaMg                                                   AlSiP S ClAr
K CaSc                                TiV CrMnFeCoNiCuZnGaGeAsSeBrKr
RbSrY                                 ZrNbMoTcRuThPdAgCdInSnSbTeI Xe
CsBaLaCePrNdPmSmEuGdTbDyHoErTmYbLuHfTaW ReOsIrPtAuHgTlPbBiPoAtRn
FrRaAcThPaU NpPuAmCmBkCfEsFmMdNoLr
usage: pse [nuclear charge | element name | element symbol ]
EOF
exit
fi

for pattern in $@
do
grep -iw “ $pattern “ << EOF
  1 Hydrogen     Wasserstoff   H   1s1
  2 Helium                     He  1s2
  3 Lithium                    Li  [He] 2s1
  4 Beryllium                  Be  [He] 2s2
  5 Bor                        B   [He] 2s2 2p1
  6 Carbon       Kohlenstoff   C   [He] 2s2 2p2
```

crystals

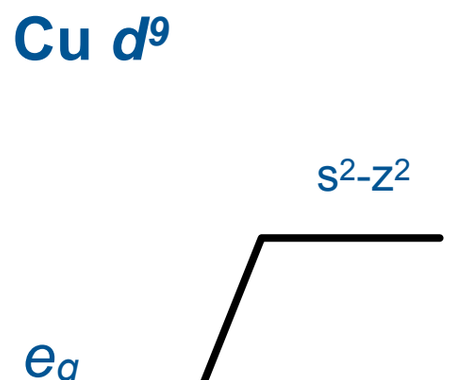


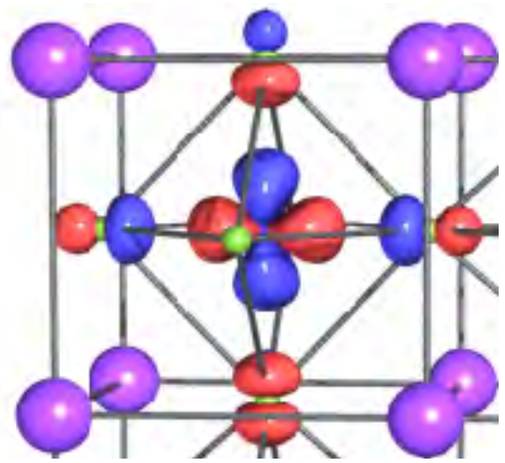
$KCuF_3$: orbital-ordering

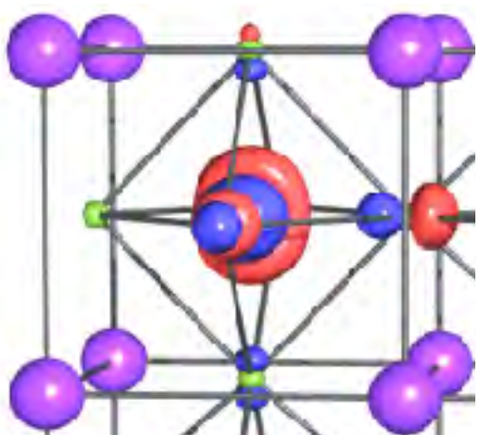
d-bands; e_g orbitals



orbital ordering







k-space vs real space

$$H = -\frac{\hbar^2}{2m}\sum_{j=1}^{N_e}\nabla_j^2 - \frac{1}{4\pi\epsilon_0}\sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \frac{1}{4\pi\epsilon_0}\sum_{j<k}^{N_e}\frac{e^2}{|r_j - r_k|} + \frac{1}{4\pi\epsilon_0}\sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

single-electron terms diagonal in *k*-space (band structure)

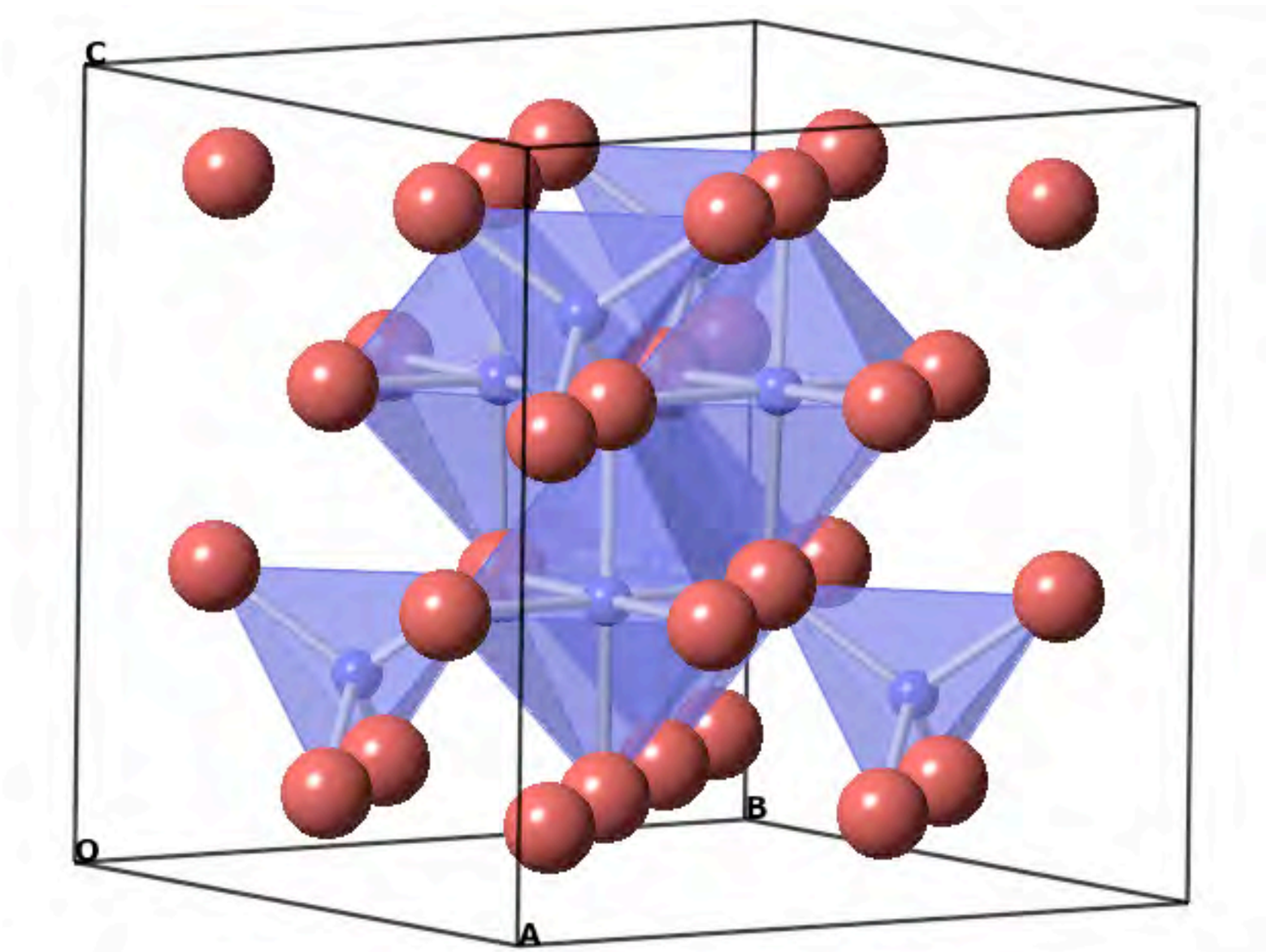
interaction terms diagonal in real (configuration) space

intinerant vs. localized

magnetite Fe_3O_4

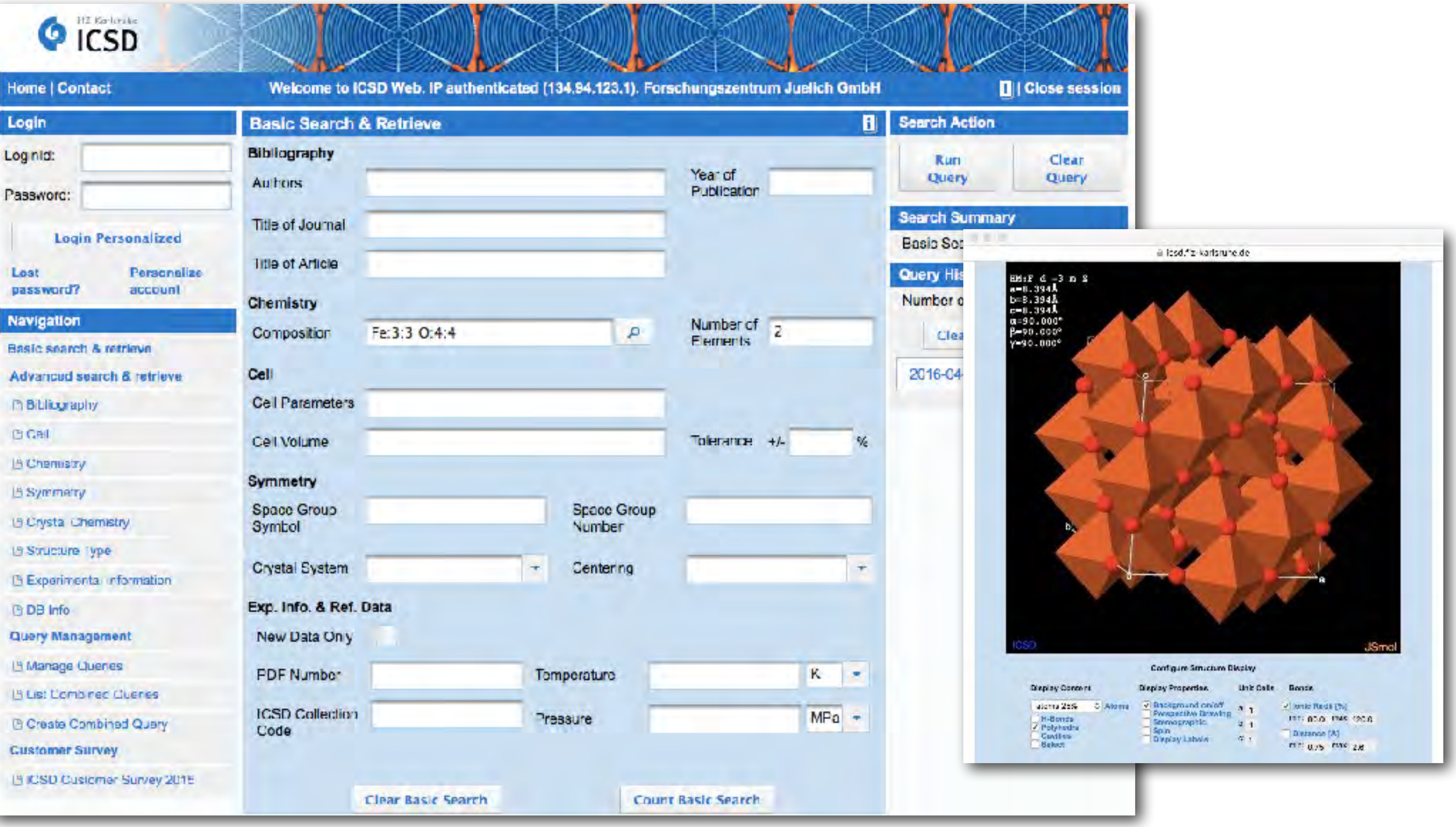
spinel structure AB_2O_4:
O on fcc sites
Fe in tetrahedral (1) and octahedral (2) sites

8 f.u. per unit cell
space group Fd-3m

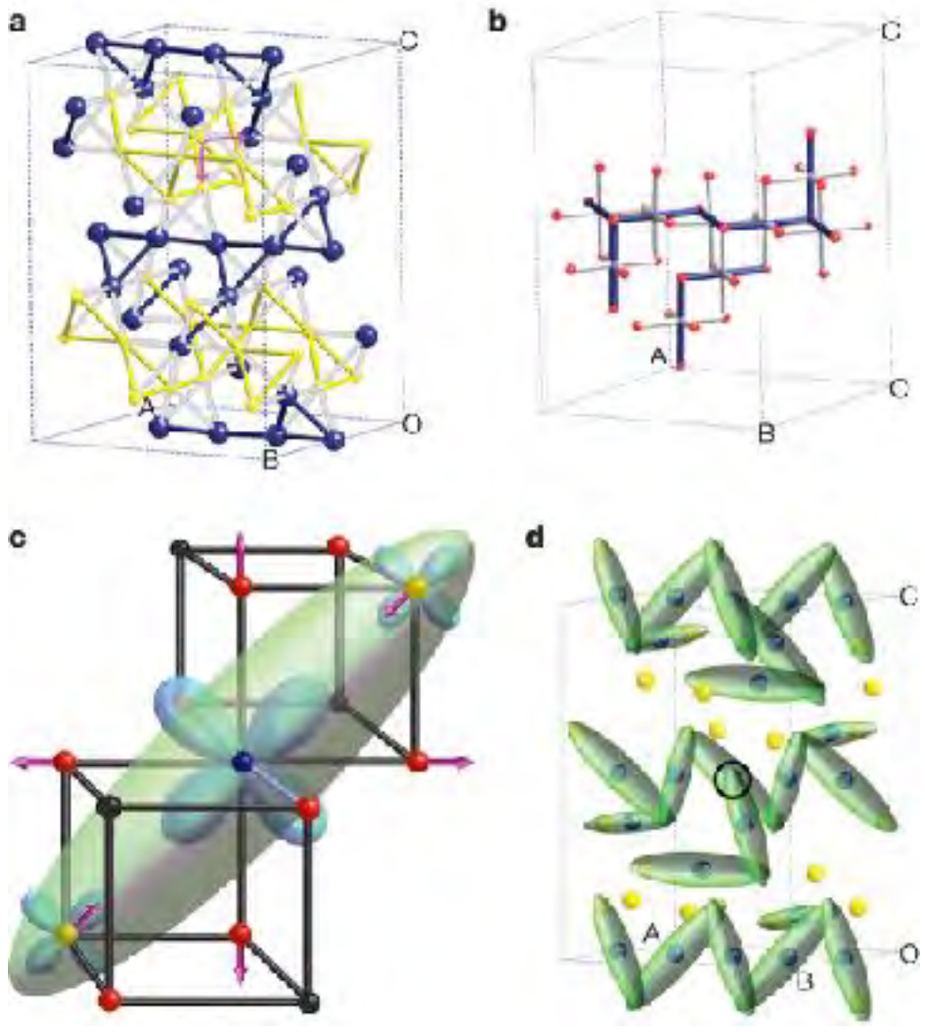


Inorganic Crystal Structure Database

http://icsd.fiz-karlsruhe.de



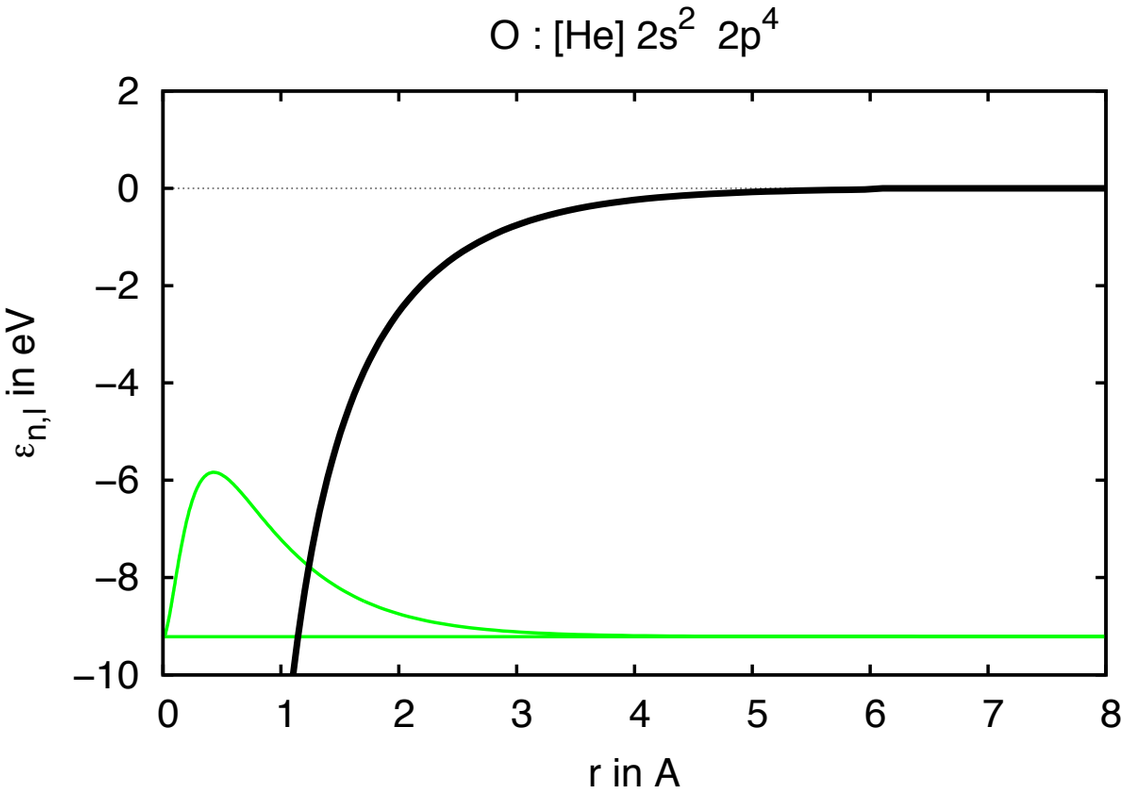
Charge, orbital and trimeron order in the low-temperature magnetite structure.

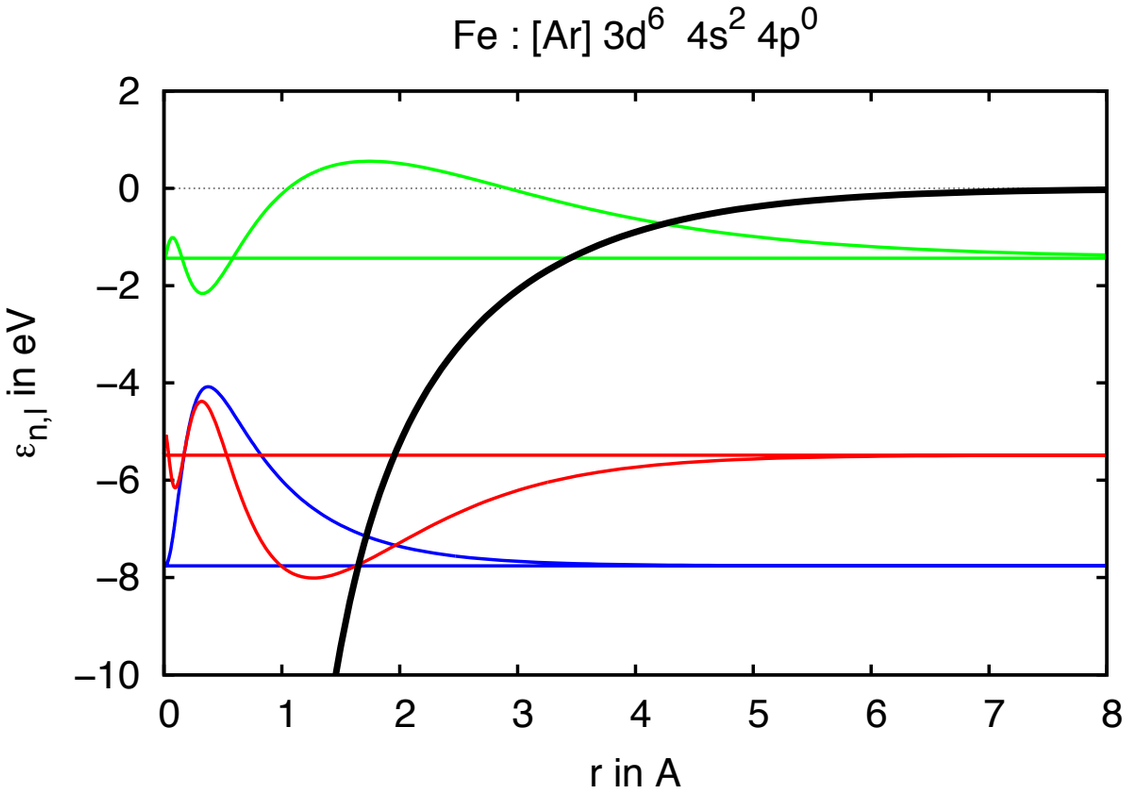


MS Senn *et al*. *Nature* **481**, 173 (2012) doi:10.1038/nature10704

nature

oxydation states

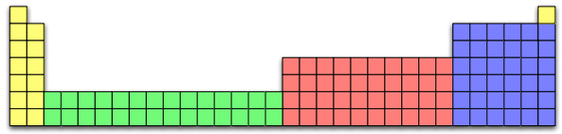




O^{2-} : [He] $2s^2$ $2p^6$ = [Ar]

Fe^{2+} : [Ar] $3d^6$
Fe^{3+} : [Ar] $3d^5$

typical charge states



+1 +2 -2 -1

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt									

transition metals

alkali metals

alkaline-earths

pnictogens

chalcogens

halogens

noble gasses

ionic radii