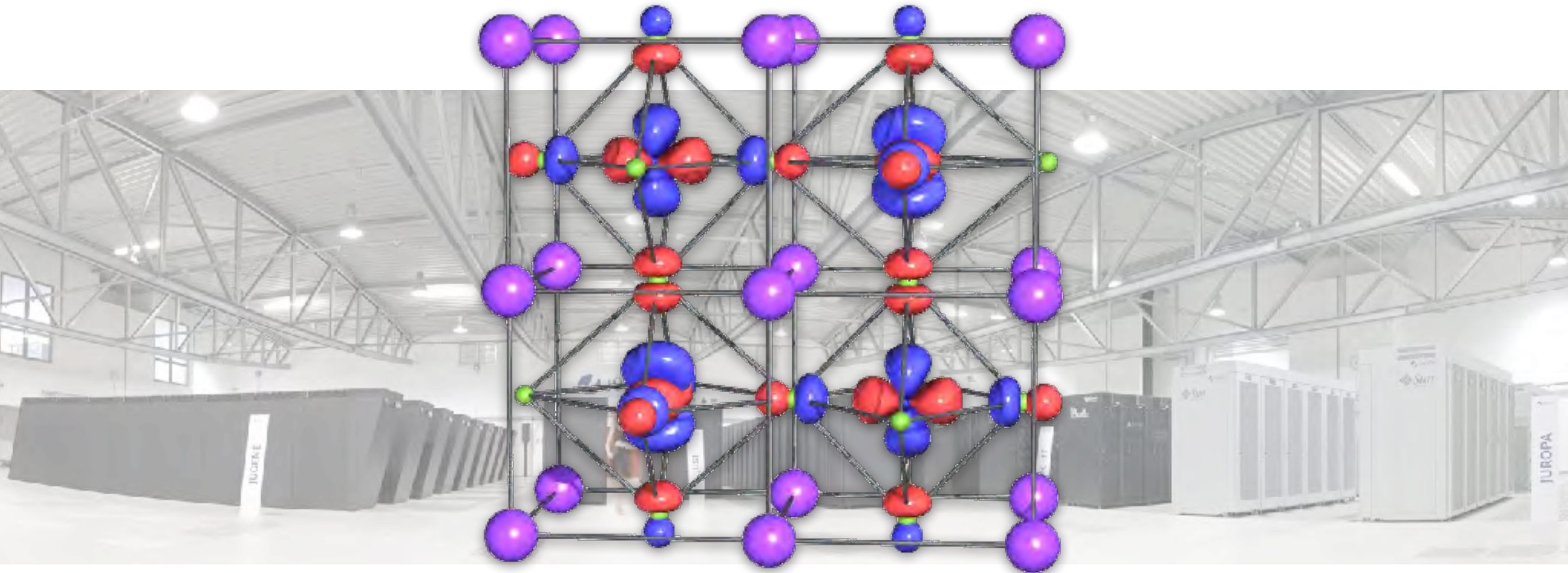


# Correlated Electrons

Erik Koch

Computational Materials Science  
German Research School for Simulation Sciences



German Research School  
for Simulation Sciences

# outline

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## **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](http://www.cond-mat.de/teaching/correl)

# exercises

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Correlated Electrons

SS 2020, E. Koch

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## 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?

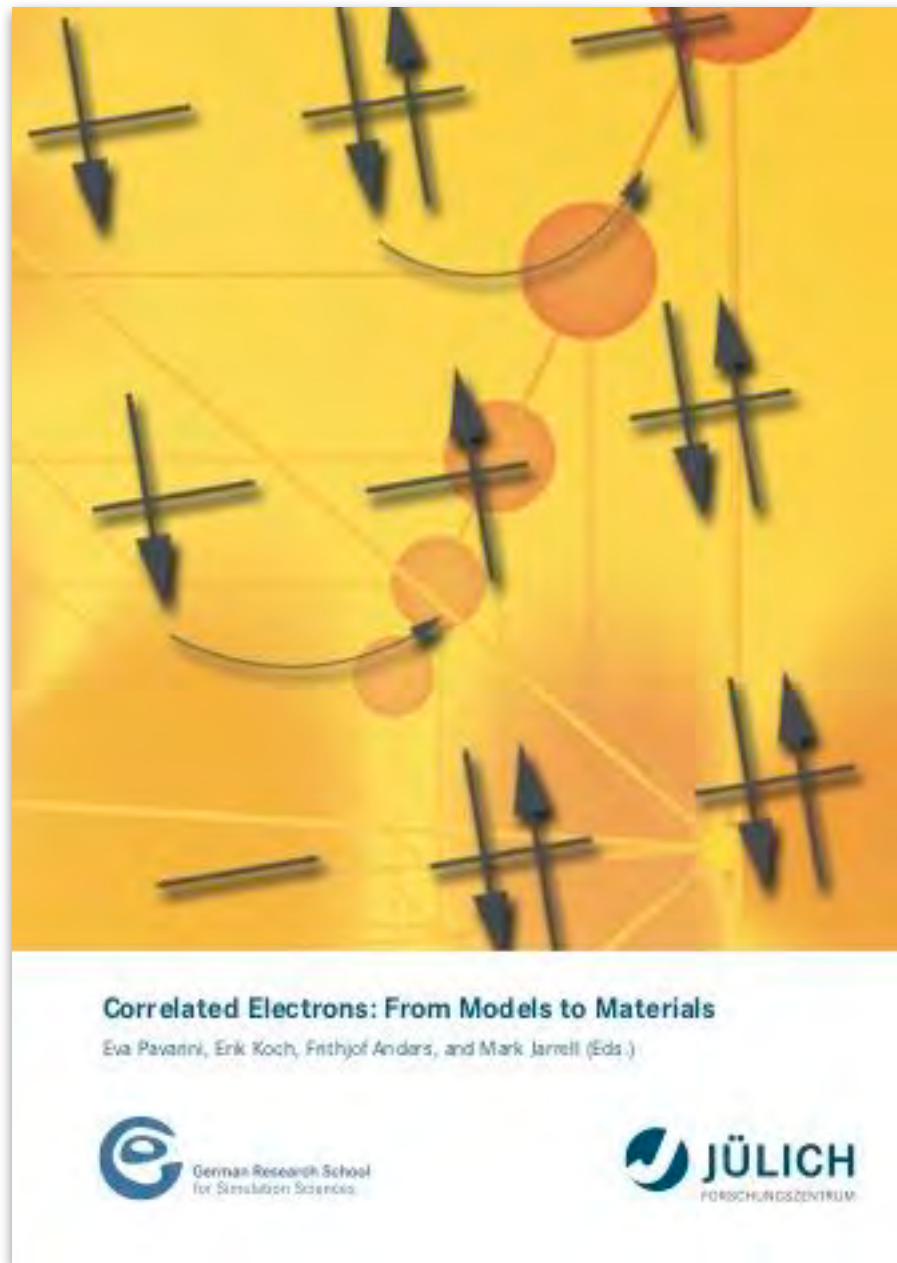
### 2. *magnetic moment*

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

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

- 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](http://www.cond-mat.de/events/correl.html)



# Übungsaufgabe

Gegeben:

Atome der Ordnungszahl  $Z_\alpha$  an den Positionen  $R_\alpha$ .

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

---

$$\begin{aligned}h &= 6.626068 \cdot 10^{-34} \text{ Js} \\m_{\text{el}} &= 9.109382 \cdot 10^{-31} \text{ kg} \\e &= 1.602176 \cdot 10^{-19} \text{ C}\end{aligned}$$

why use Å and eV?

$$\begin{aligned}1 \text{ Å} &= 10^{-10} \text{ m} \\1 \text{ eV} &= 1.602176 \cdot 10^{-19} \text{ J}\end{aligned}$$

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

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

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

$$E [\text{in eV}] = 3.81 (k [\text{in Å}^{-1}])^2$$

# atomic units

---

$$\hbar = 1.0546 \cdot 10^{-34} \text{ Js} \quad [ML^2T^{-1}]$$

$$m_e = 9.1094 \cdot 10^{-31} \text{ kg} \quad [M]$$

$$e = 1.6022 \cdot 10^{-19} \text{ C} \quad [Q]$$

$$4\pi\epsilon_0 = 1.1127 \cdot 10^{-10} \text{ F/m} \quad [M^{-1}L^{-3}T^2Q^2]$$

<http://physics.nist.gov/cuu>

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

$$\begin{array}{lll} & \hbar & = 1 \ a_0^2 m_e / t_0 \\ \text{solve} & m_e & = 1 \ m_e \\ & e & = 1 \ e \\ & 4\pi\epsilon_0 & = 1 \ t_0^2 e^2 / a_0^3 m_e \end{array} \quad \text{to obtain}$$

$$1 \text{ a.u. length} = a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 5.2918 \cdot 10^{-11} \text{ m}$$

$$1 \text{ a.u. mass} = m_e \approx 9.1095 \cdot 10^{-31} \text{ kg}$$

$$1 \text{ a.u. time} = t_0 = \frac{(4\pi\epsilon_0)^2 \hbar^3}{m_e e^4} \approx 2.4189 \cdot 10^{-17} \text{ s}$$

$$1 \text{ a.u. charge} = e \approx 1.6022 \cdot 10^{-19} \text{ C}$$

# Übungsaufgabe

Gegeben:

Atome der Ordnungszahl  $Z_\alpha$  an den Positionen  $R_\alpha$ .

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**



# More is Different

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... 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.

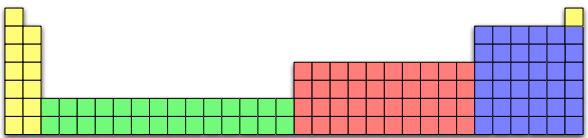
Sometimes, as in the case of superconductivity, the new symmetry — now called broken symmetry because the original symmetry is no longer evident — may be of an entirely unexpected kind and extremely difficult to visualize. In the case of superconductivity, 30 years elapsed between the time when physicists 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)



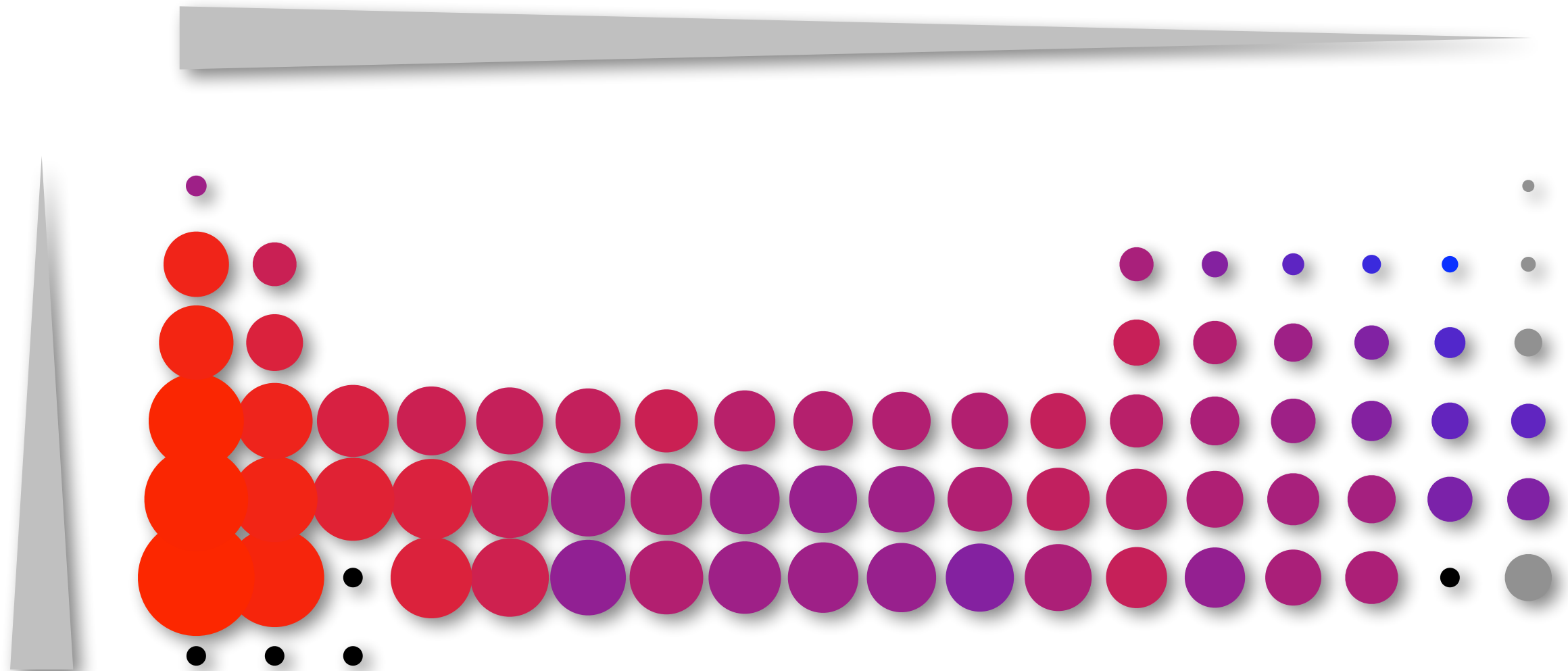
# periodic table



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)





A simplified periodic table diagram. The first period consists of two yellow blocks. The second period consists of a green block (groups 1-10) and a red block (groups 11-18). The third period consists of a green block (groups 1-10) and a blue block (groups 1-10 of the next period). The blue block is positioned to the right of the red block, indicating a continuation of the periodic table.

The diagram illustrates the filling order of atomic orbitals. The orbitals are arranged in a grid where rows represent the principal quantum number  $n$  and columns represent the subshell type. The orbitals are color-coded: yellow for s, red for d, blue for p, and green for f. The number of orbitals in each subshell is indicated by the number of vertical lines in the grid. The filling order is shown by black dots placed in the orbitals, following the Aufbau principle.

Subshell	Orbitals	Electron Capacity	Filling Order
1s	1	2	1
2s	1	2	2
2p	3	6	3, 4, 5
3s	1	2	6
3d	5	10	7, 8, 9, 10, 11
4s	1	2	12
4p	3	6	13, 14, 15
4d	5	10	16, 17, 18, 19, 20
5s	1	2	21
5p	3	6	22, 23, 24
5d	5	10	25, 26, 27, 28, 29
6s	1	2	30
6p	3	6	31, 32, 33
6d	5	10	34, 35, 36, 37, 38
7s	1	2	39
7p	3	6	40, 41, 42
7d	5	10	43, 44, 45, 46, 47
7f	7	14	48, 49, 50, 51, 52, 53, 54



# real harmonics

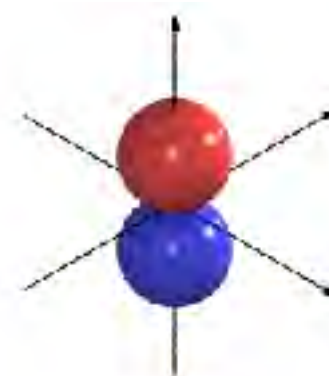
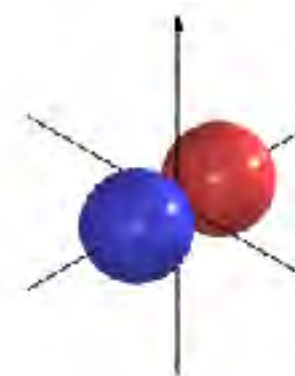
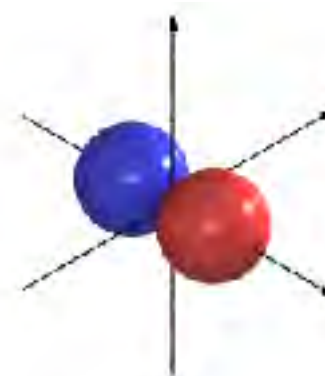
$$s \quad Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$



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

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

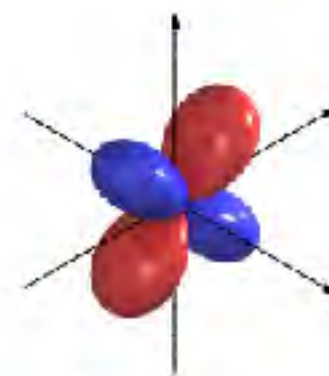
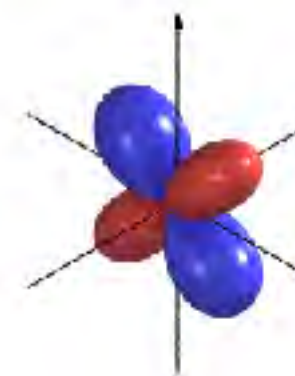
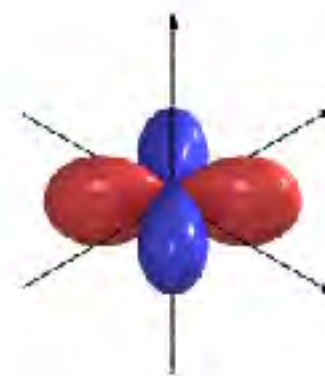
$$p_y \quad \sqrt{\frac{1}{2}} i (Y_{1,-1} + Y_{1,1}) = \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi$$



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

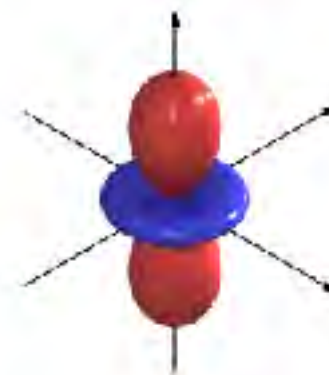
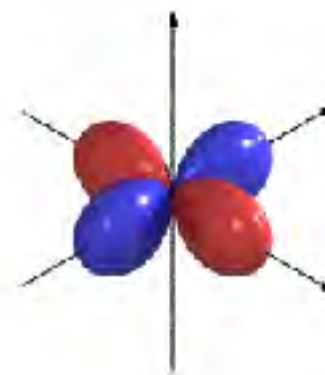
$$d_{zx} \quad \sqrt{\frac{1}{2}} (Y_{2,-1} - Y_{2,1}) = \sqrt{\frac{15}{16\pi}} \sin 2\theta \cos \phi$$

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



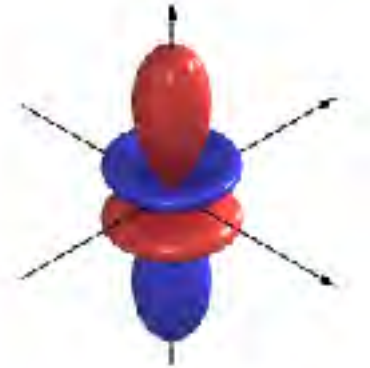
$$d_{x^2-y^2} \quad \sqrt{\frac{1}{2}} (Y_{2,-2} + Y_{2,2}) = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi$$

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



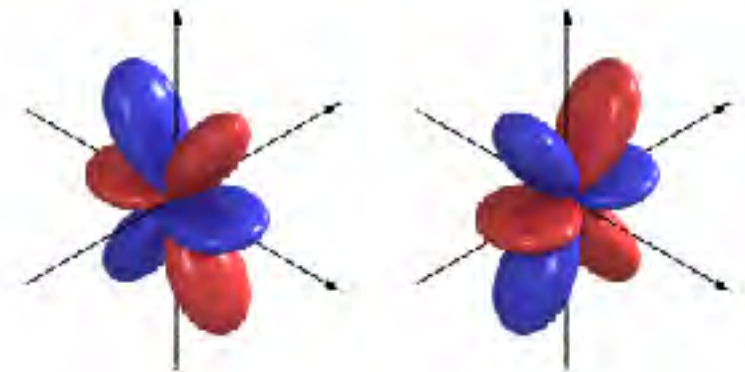
# real harmonics

$$f_{z(5z^2-3)} \quad Y_{3,0} = \sqrt{\frac{7}{16\pi}} (5 \cos^2 \theta - 3) \cos \theta$$



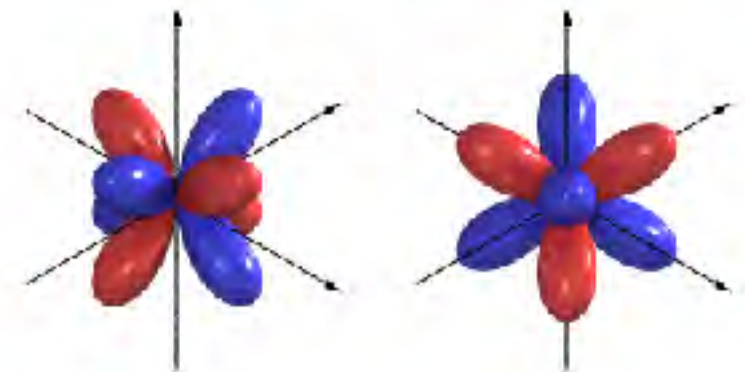
$$f_{x(5z^2-1)} \quad \sqrt{\frac{1}{2}} (Y_{3,-1} - Y_{3,1}) = \sqrt{\frac{21}{32\pi}} (5 \cos^2 \theta - 1) \sin \theta \cos \phi$$

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



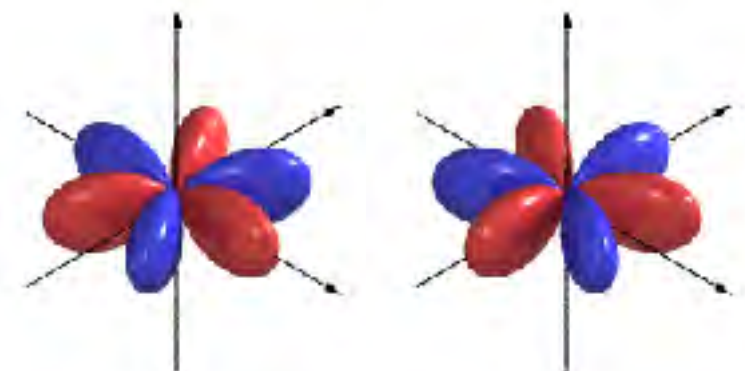
$$f_{z(x^2-y^2)} \quad \sqrt{\frac{1}{2}} (Y_{3,-2} + Y_{3,2}) = \sqrt{\frac{105}{16\pi}} \cos \theta \sin^2 \theta \cos 2\phi$$

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

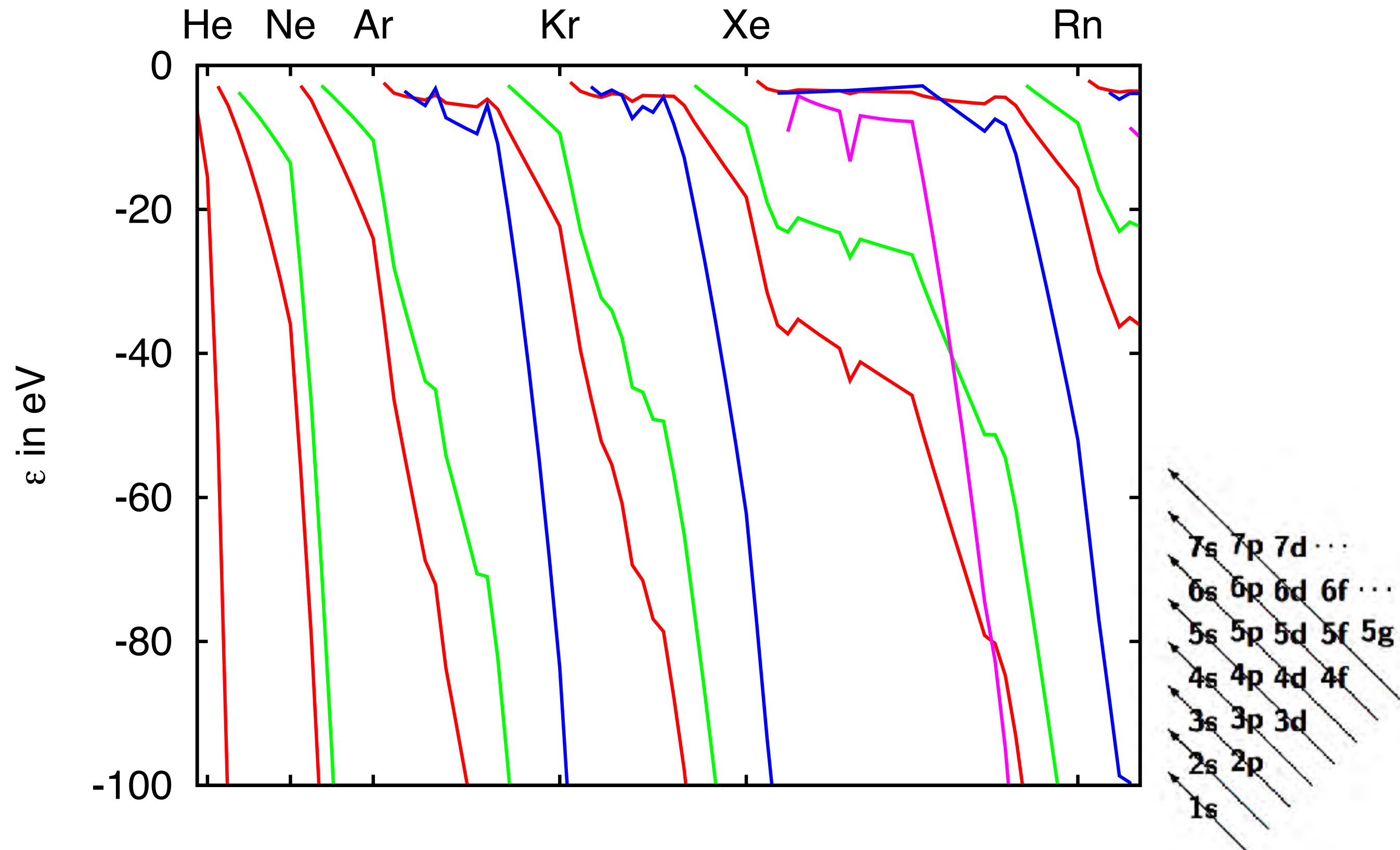


$$f_{x(x^2-3y^2)} \quad \sqrt{\frac{1}{2}} (Y_{3,-3} - Y_{3,3}) = \sqrt{\frac{35}{32\pi}} \sin^3 \theta \cos 3\phi$$

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



# atom in spherical mean-field approximation

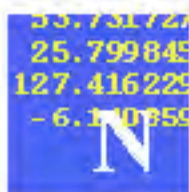




[Version History](#) - [Disclaimer](#)

## 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

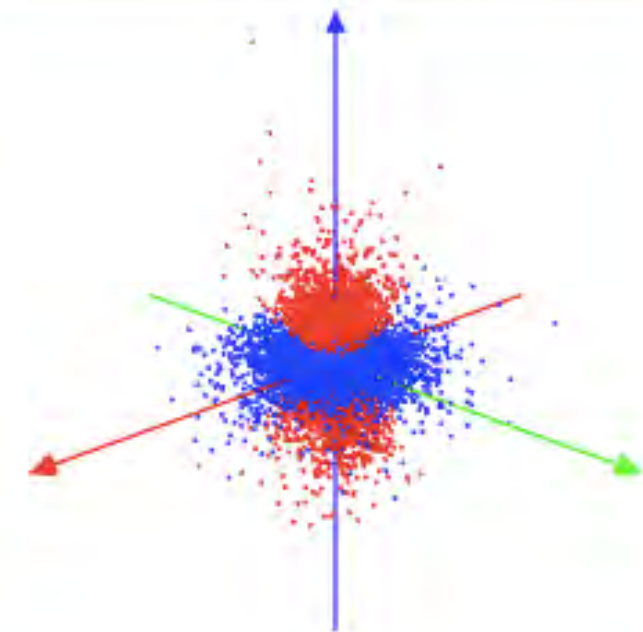
[GAMS](#) Guide to Available Mathematical Software

[PADE](#) NIST Parallel Applications Development Environment



1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
		57	58	59	60	61	62	63	64	65	66	67	68	69	70		
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		89	90	91	92	93	94	95	96	97	98	99	100	101	102		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

[Ar] 4s<sup>2</sup> 3d<sup>6</sup>

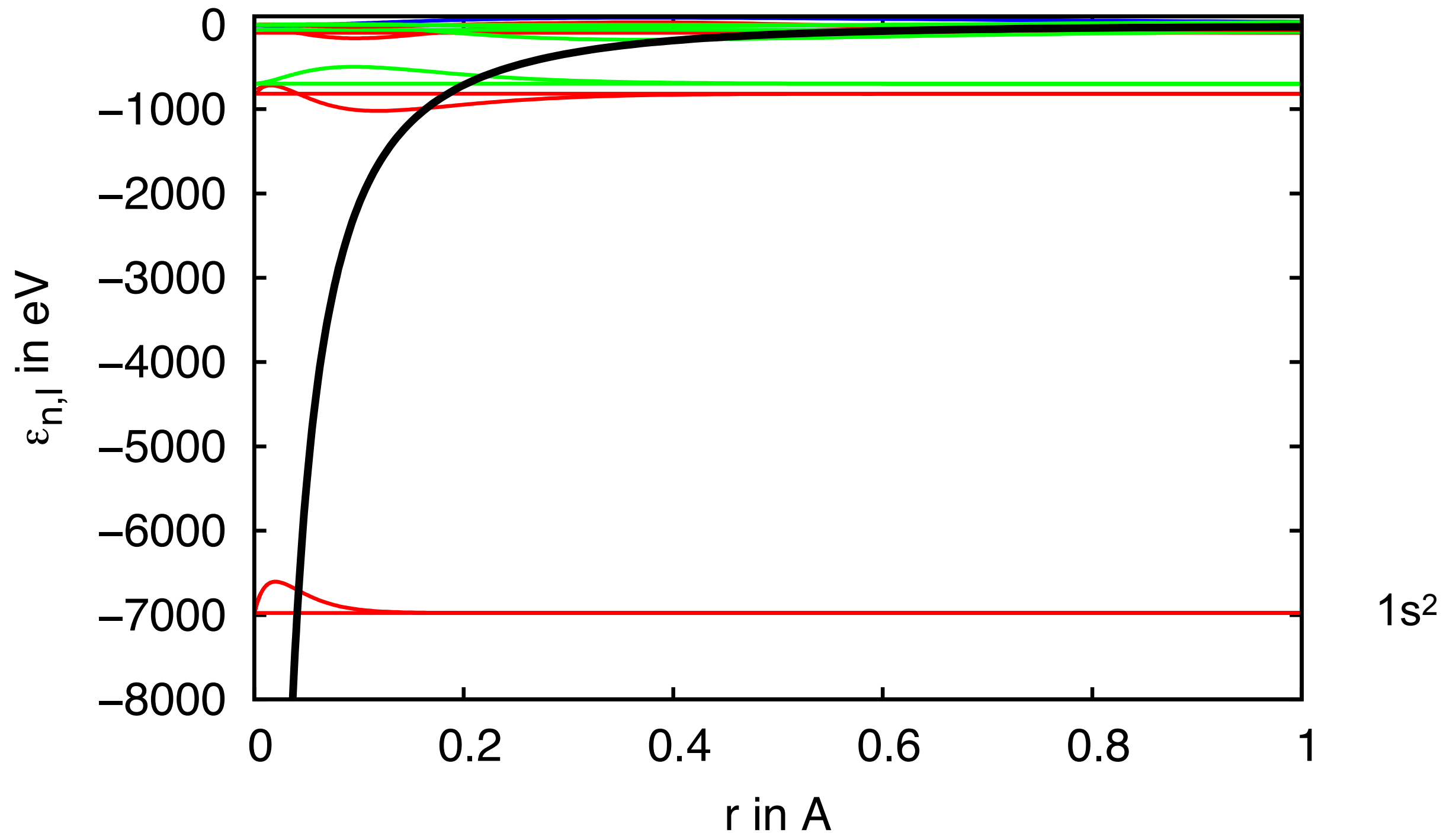
Realistic d\_3zz-1 

### Wave function plots



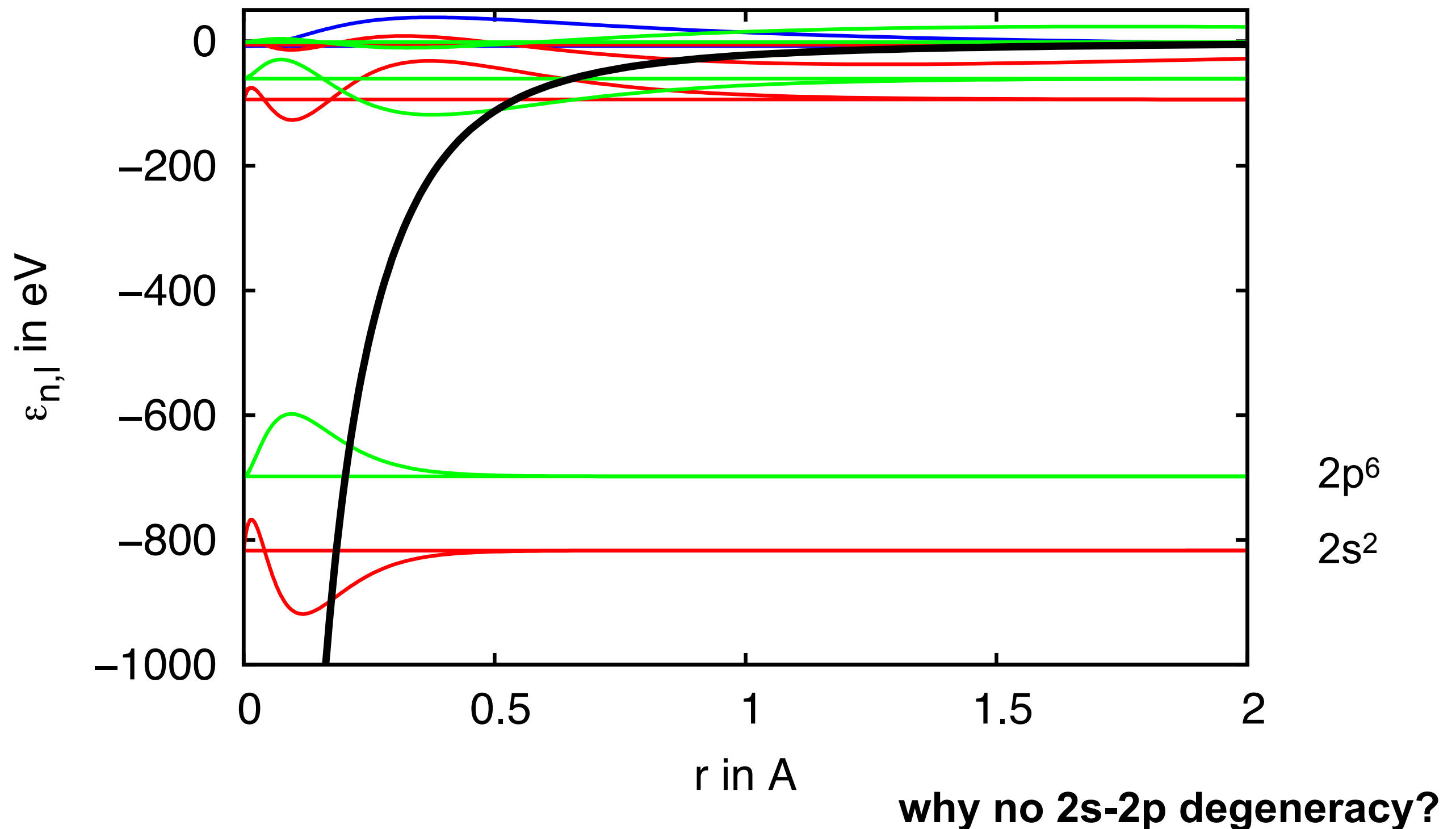
# atom in spherical mean-field approximation

Fe : [Ar] 3d<sup>6</sup> 4s<sup>2</sup> 4p<sup>0</sup>



# atom in spherical mean-field approximation

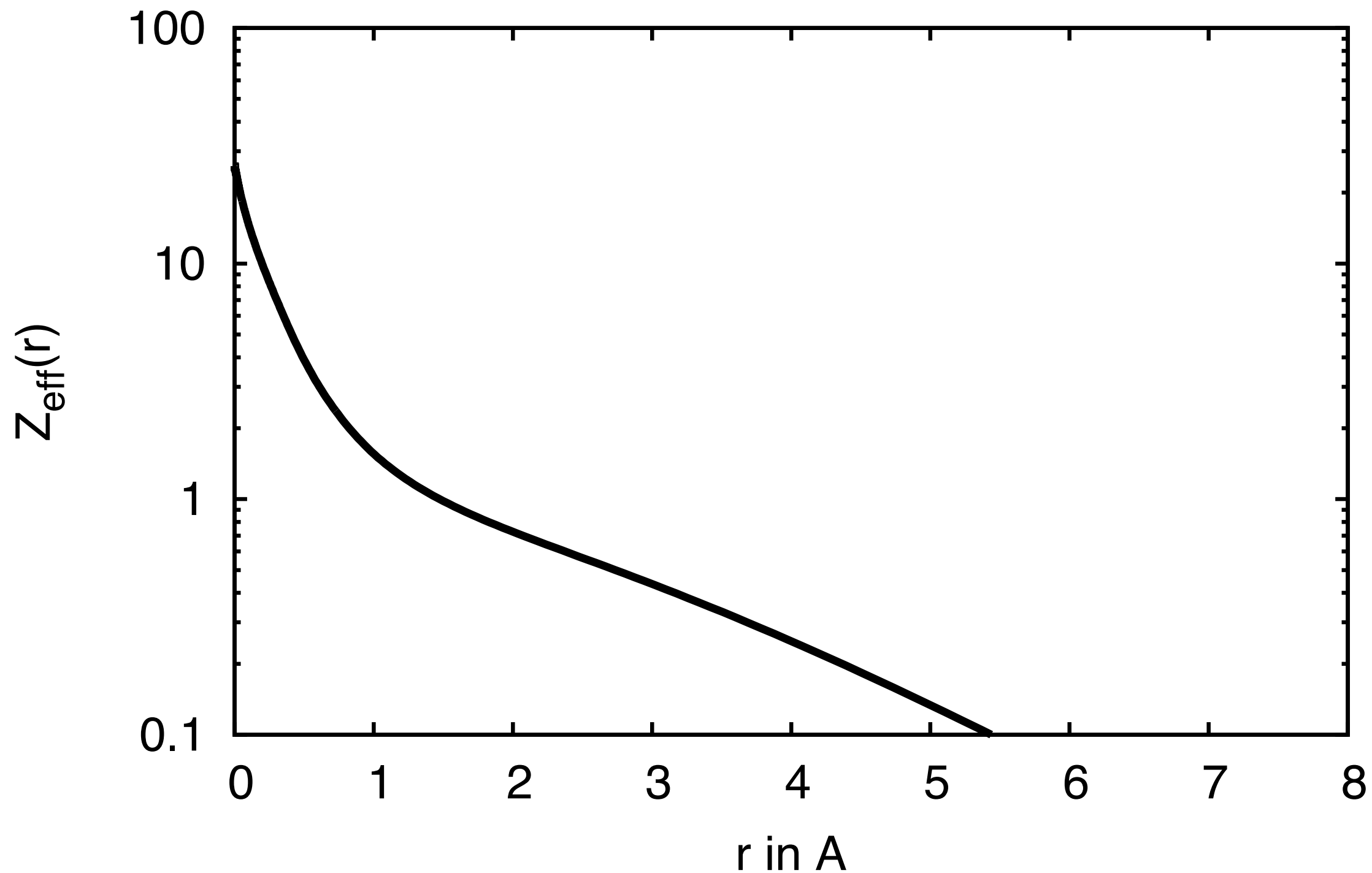
Fe : [Ar] 3d<sup>6</sup> 4s<sup>2</sup> 4p<sup>0</sup>



# atom in spherical mean-field approximation

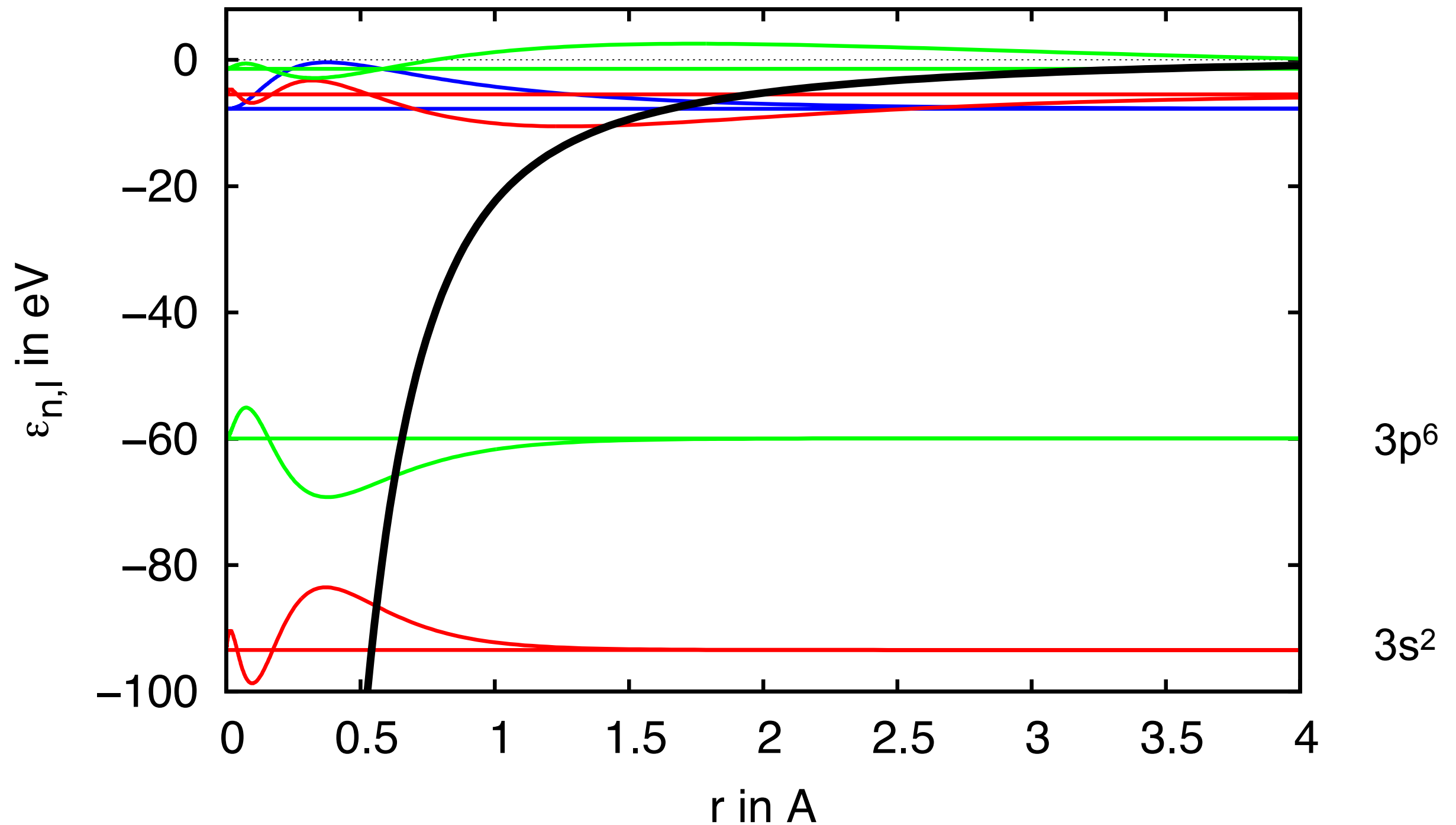
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Fe : [Ar] 3d<sup>6</sup> 4s<sup>2</sup> 4p<sup>0</sup>



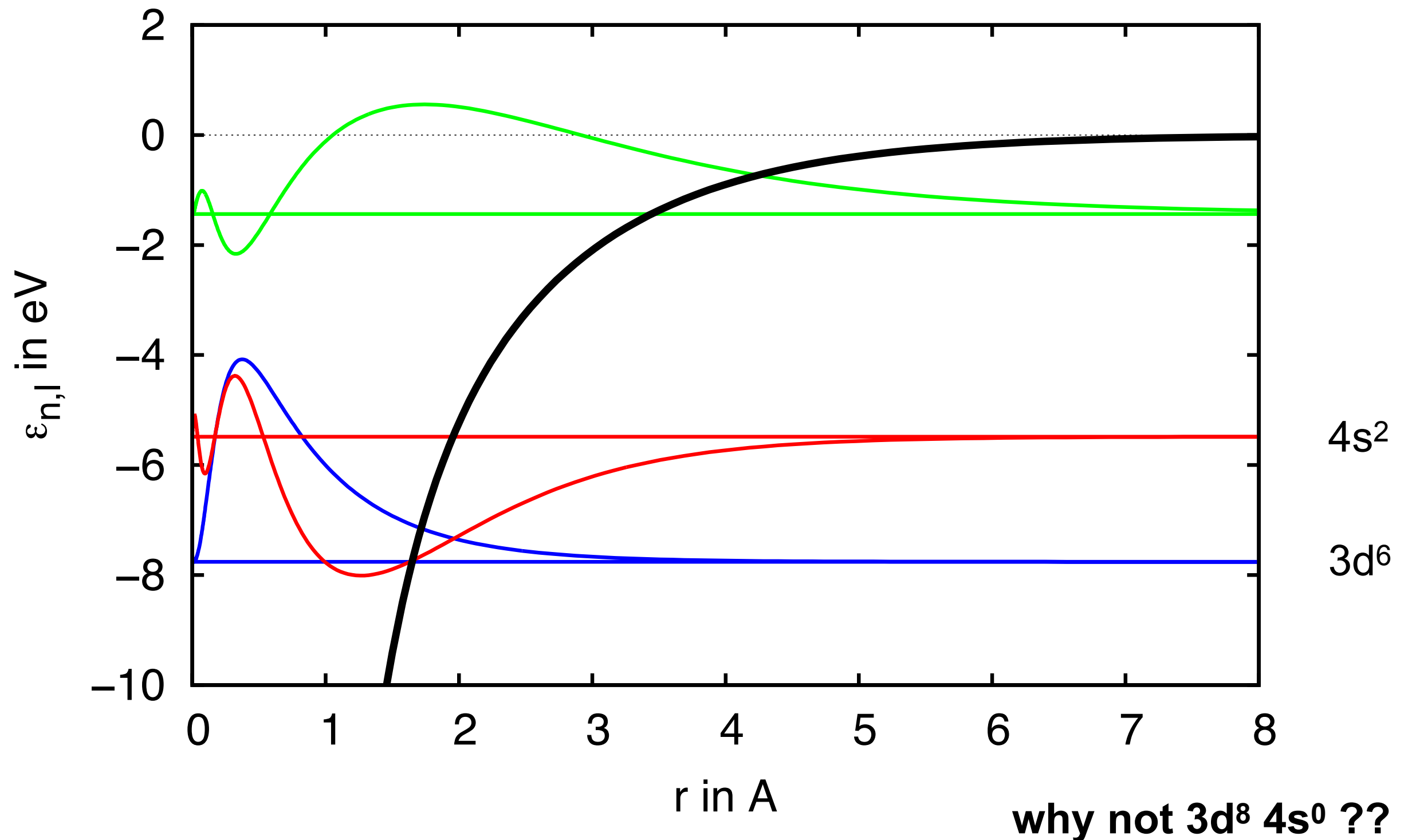
# atom in spherical mean-field approximation

Fe : [Ar] 3d<sup>6</sup> 4s<sup>2</sup> 4p<sup>0</sup>



# atom in spherical mean-field approximation

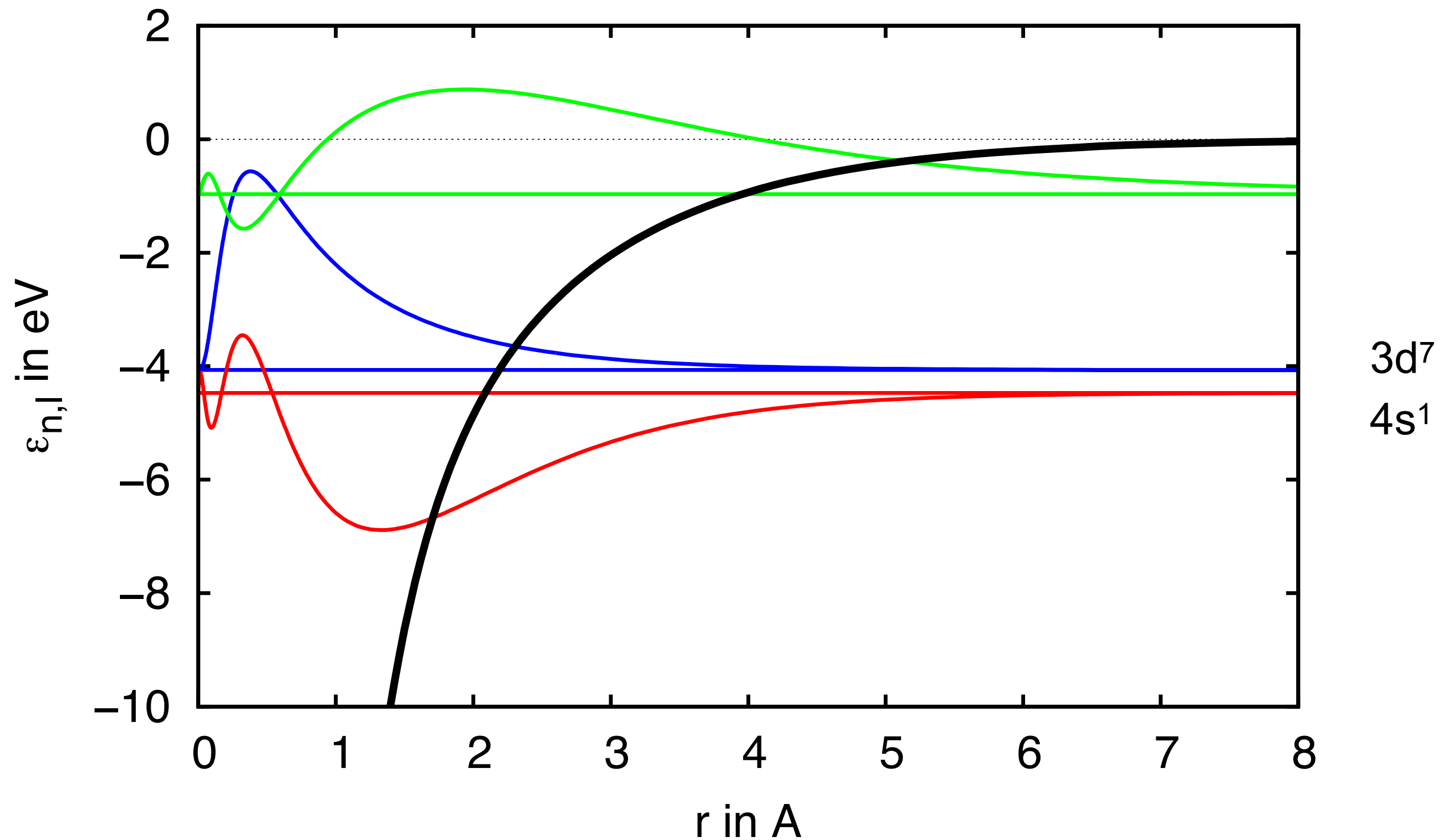
Fe : [Ar] 3d<sup>6</sup> 4s<sup>2</sup> 4p<sup>0</sup>



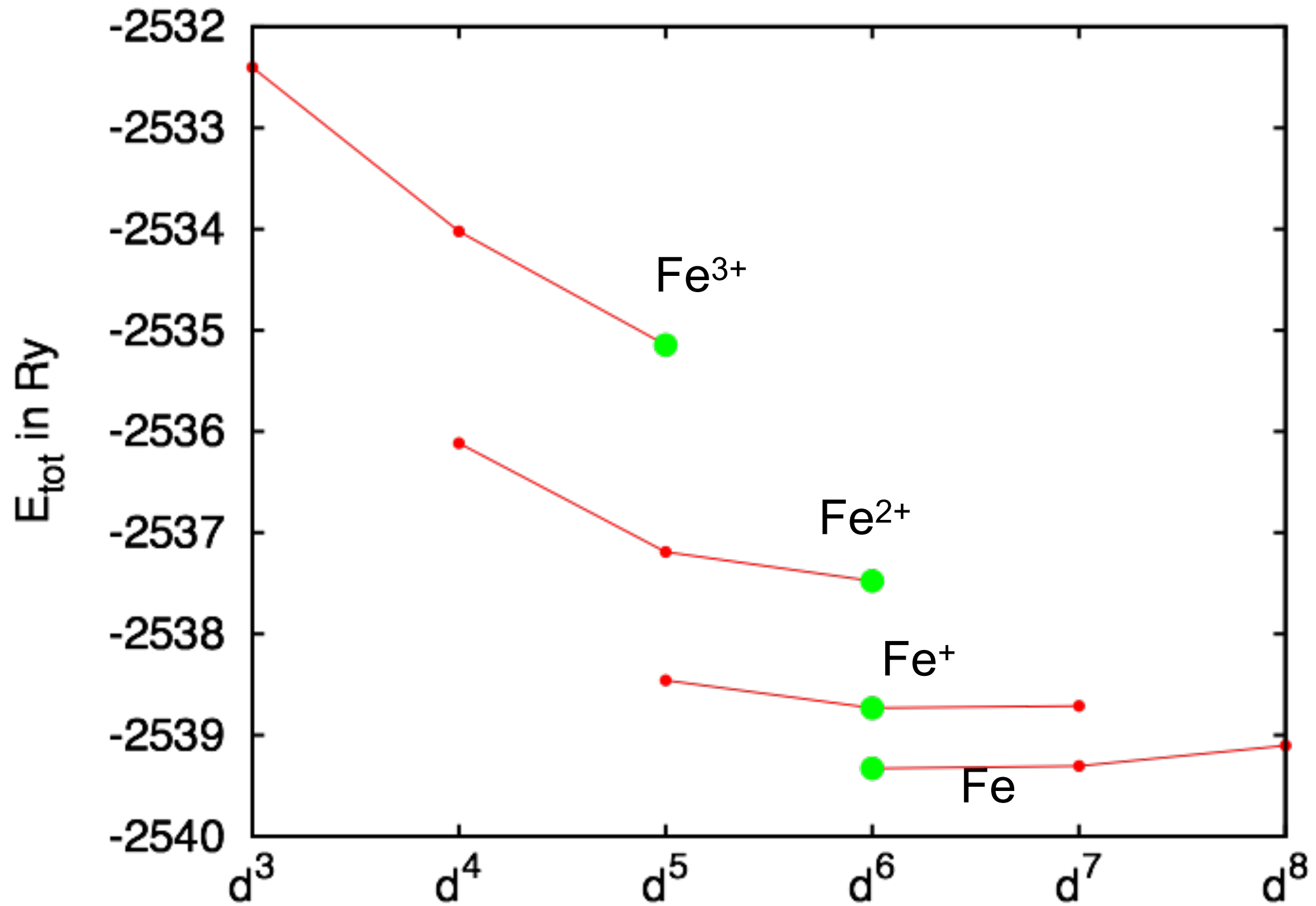


# atom in spherical mean-field approximation

Fe : [Ar] 3d<sup>7</sup> 4s<sup>1</sup> 4p<sup>0</sup>



# total energy



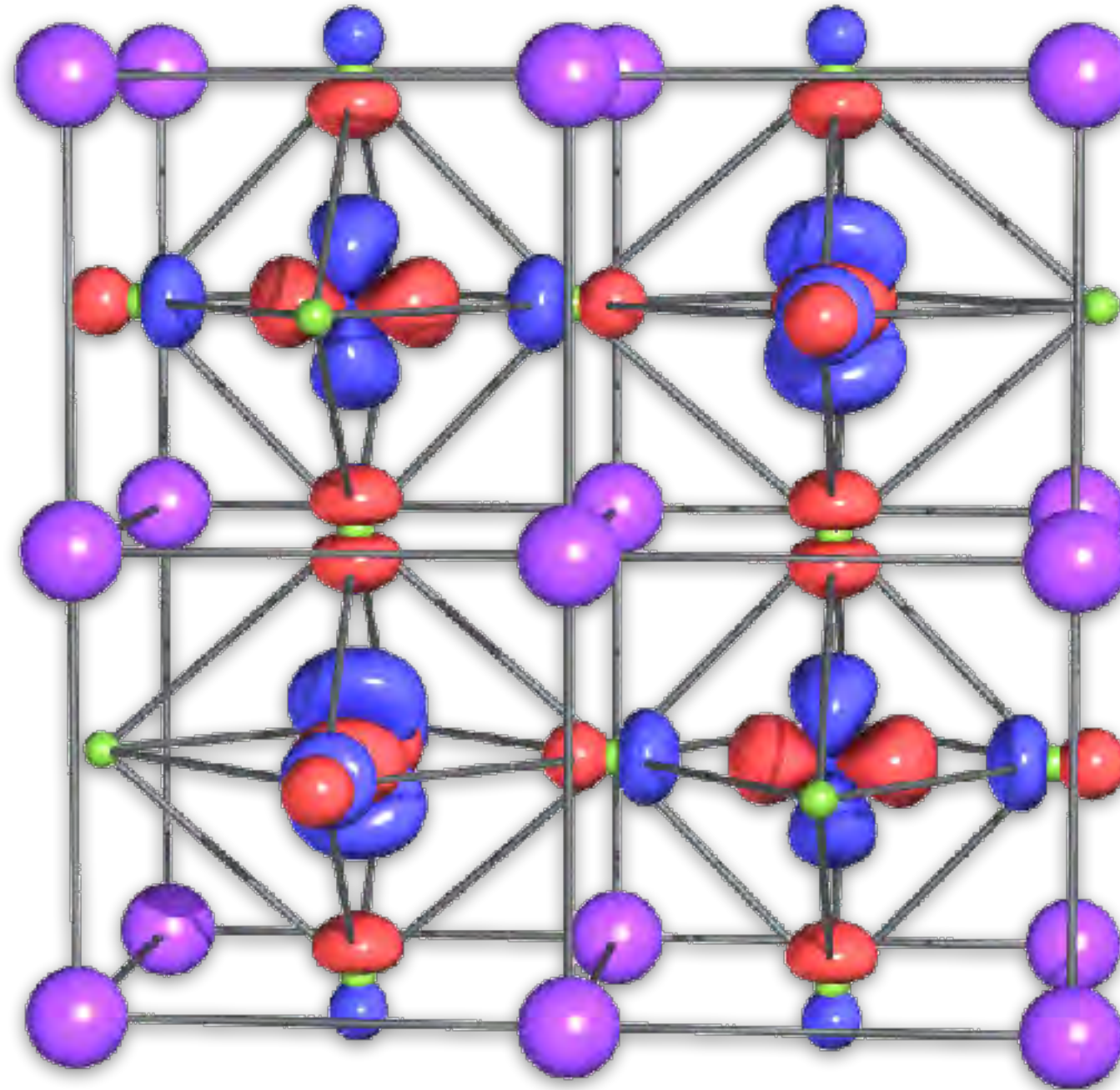
# tools: pse

```
#!/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        C    [He] 2s2 2p2
```

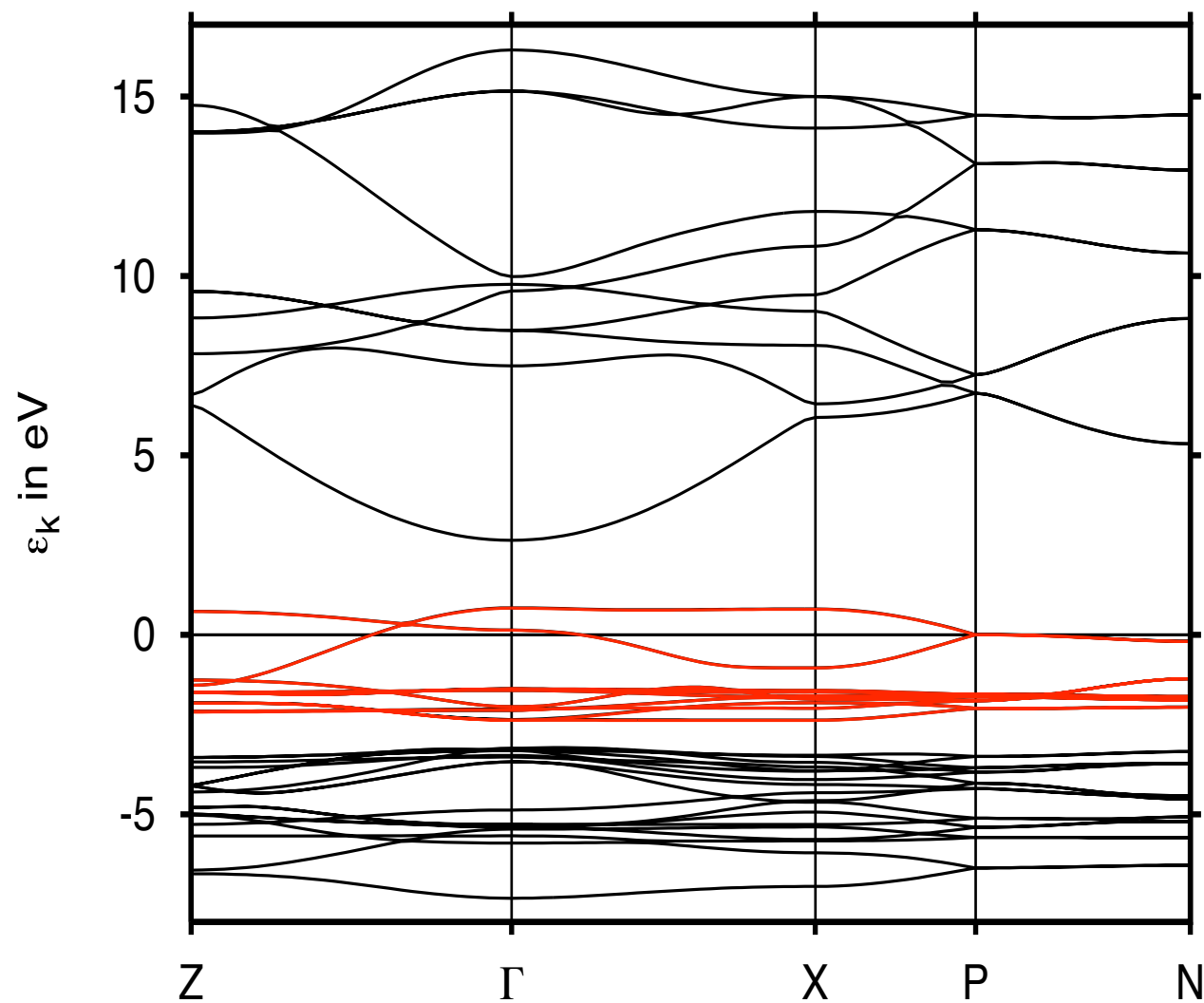
# crystals

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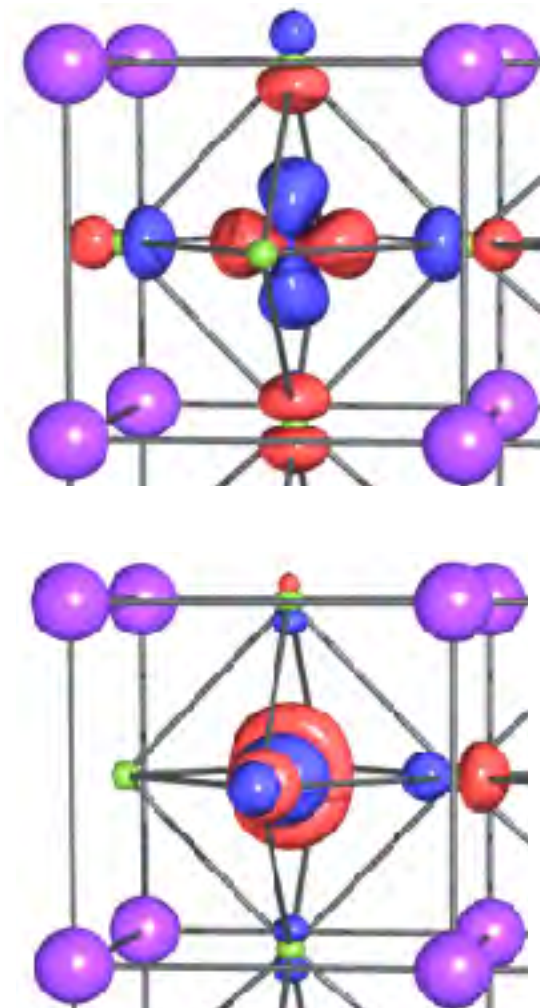
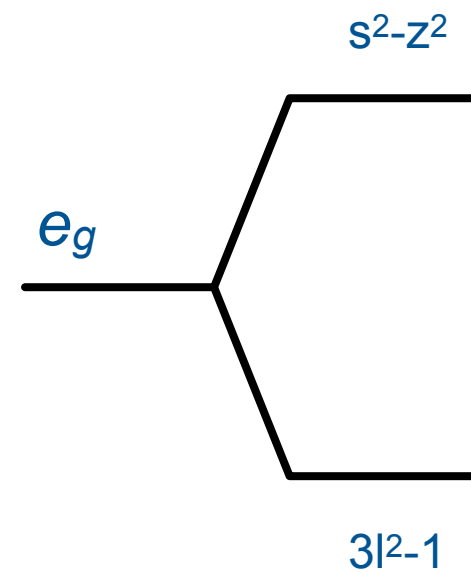
# KCuF<sub>3</sub>: orbital-ordering

*d*-bands; *e<sub>g</sub>* orbitals



orbital ordering

Cu *d*<sup>9</sup>





# *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

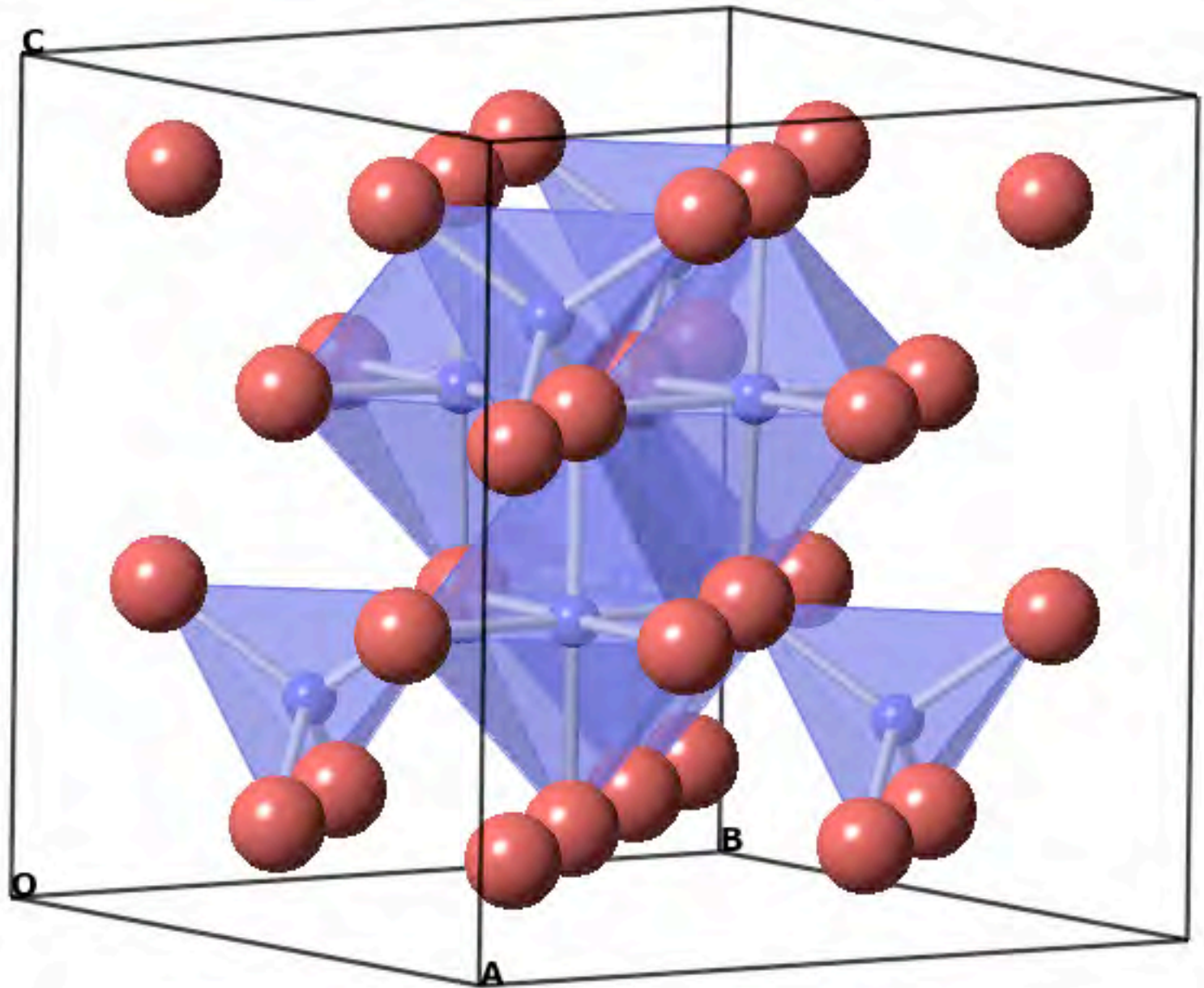
**intinerant vs. localized**

# magnetite $\text{Fe}_3\text{O}_4$



spinel structure  $\text{AB}_2\text{O}_4$ :  
O on fcc sites  
Fe in tetrahedral (1) and  
octahedral (2) sites

8 f.u. per unit cell  
space group  $\text{Fd-}3\text{m}$





# Inorganic Crystal Structure Database

<http://icsd.fiz-karlsruhe.de>

ICSD FIZ Karlsruhe

Home | Contact Welcome to ICSD Web. IP authenticated (134.94.123.1). Forschungszentrum Juelich GmbH | Close session

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Log in id:

Password:

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Lost password? Personalize account

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- Advanced search & retrieve
  - Bibliography
  - Cell
  - Chemistry
  - Symmetry
  - Cryst. Chemistry
  - Structure type
  - Experimental information
  - DB Info
- Query Management
  - Manage Queries
  - List Combined Queries
  - Create Combined Query
- Customer Survey
  - ICSD Customer Survey 2015

**Basic Search & Retrieve**

**Bibliography**

Authors:  Year of Publication:

Title of Journal:

Title of Article:

**Chemistry**

Composition:  Number of Elements:

**Cell**

Cell Parameters:

Cell Volume:  Tolerance: +/-  %

**Symmetry**

Space Group Symbol:  Space Group Number:

Crystal System:  Centering:

**Exp. Info. & Ref. Data**

New Data Only: ☐

PDF Number:  Temperature:  K

ICSD Collection Code:  Pressure:  MPa

**Search Action**

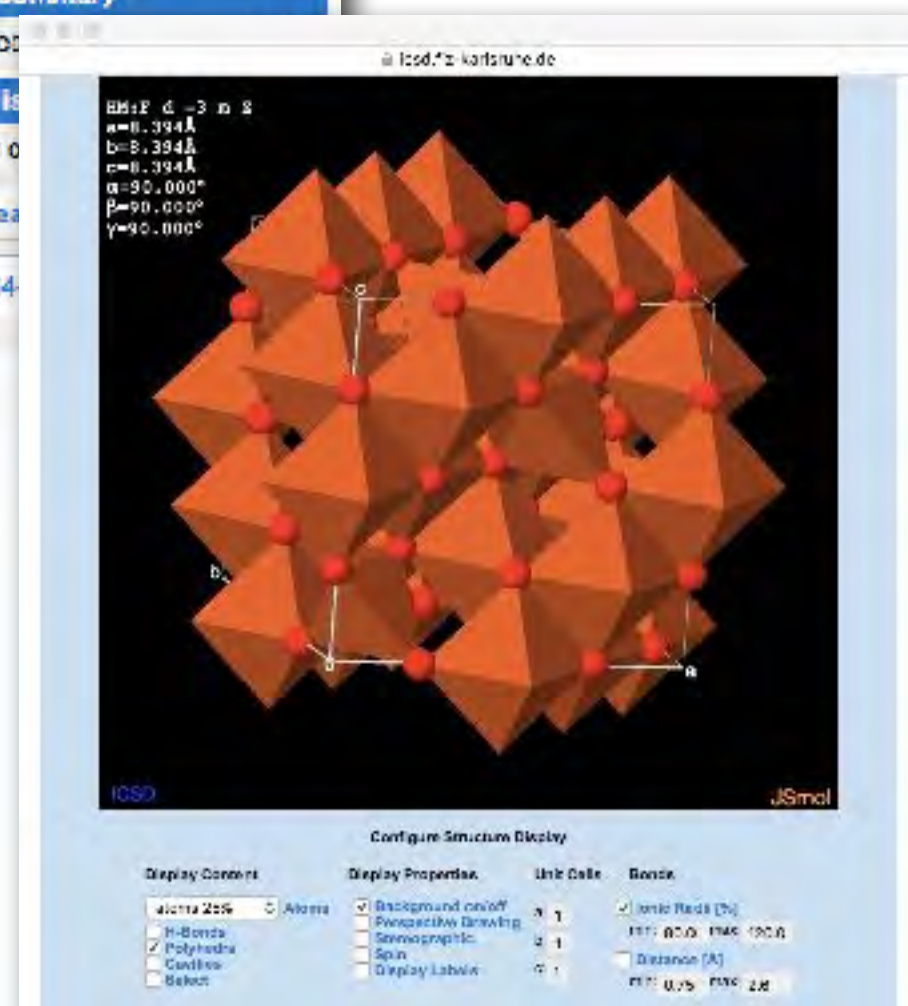
**Search Summary**

Basic Search

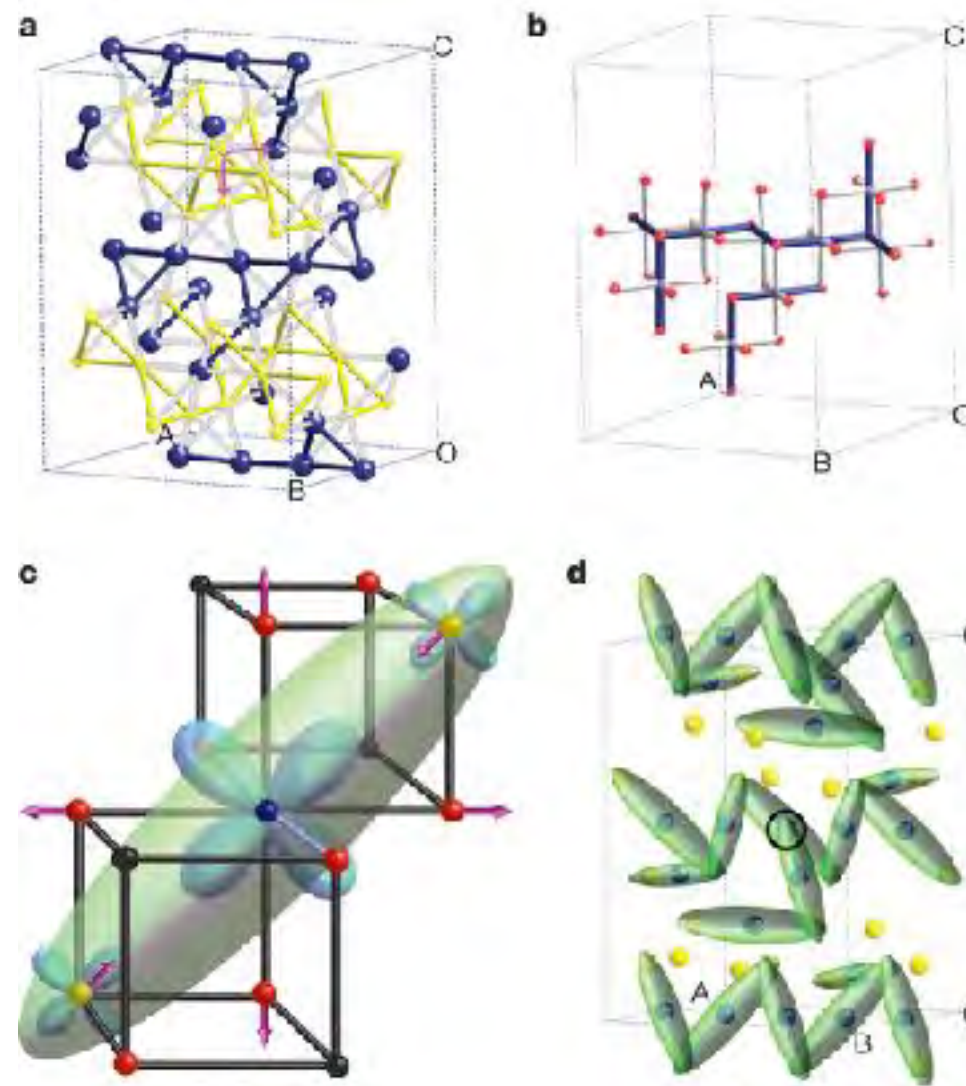
Query History

Number of

2016-04

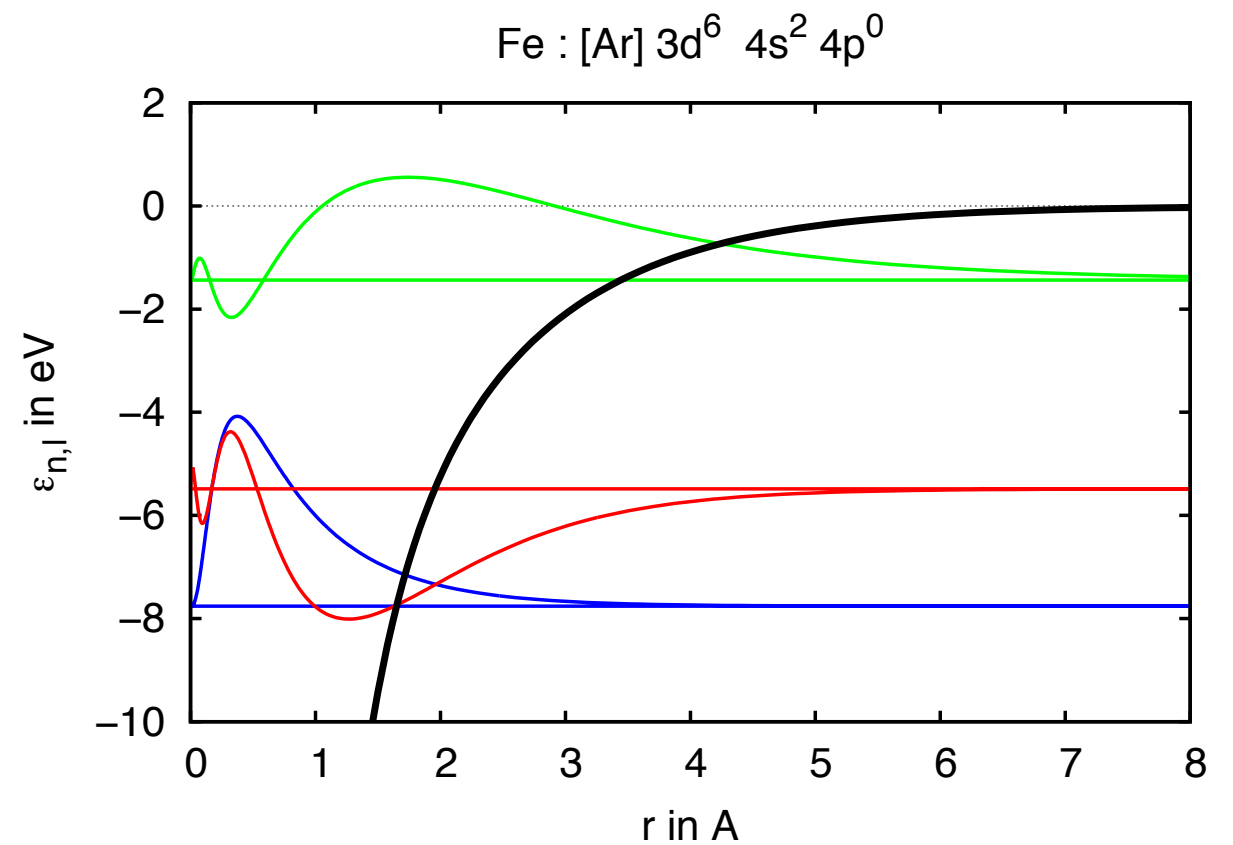
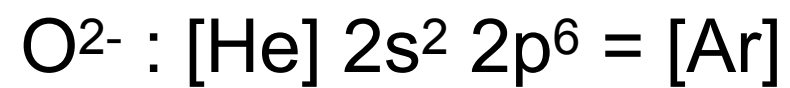
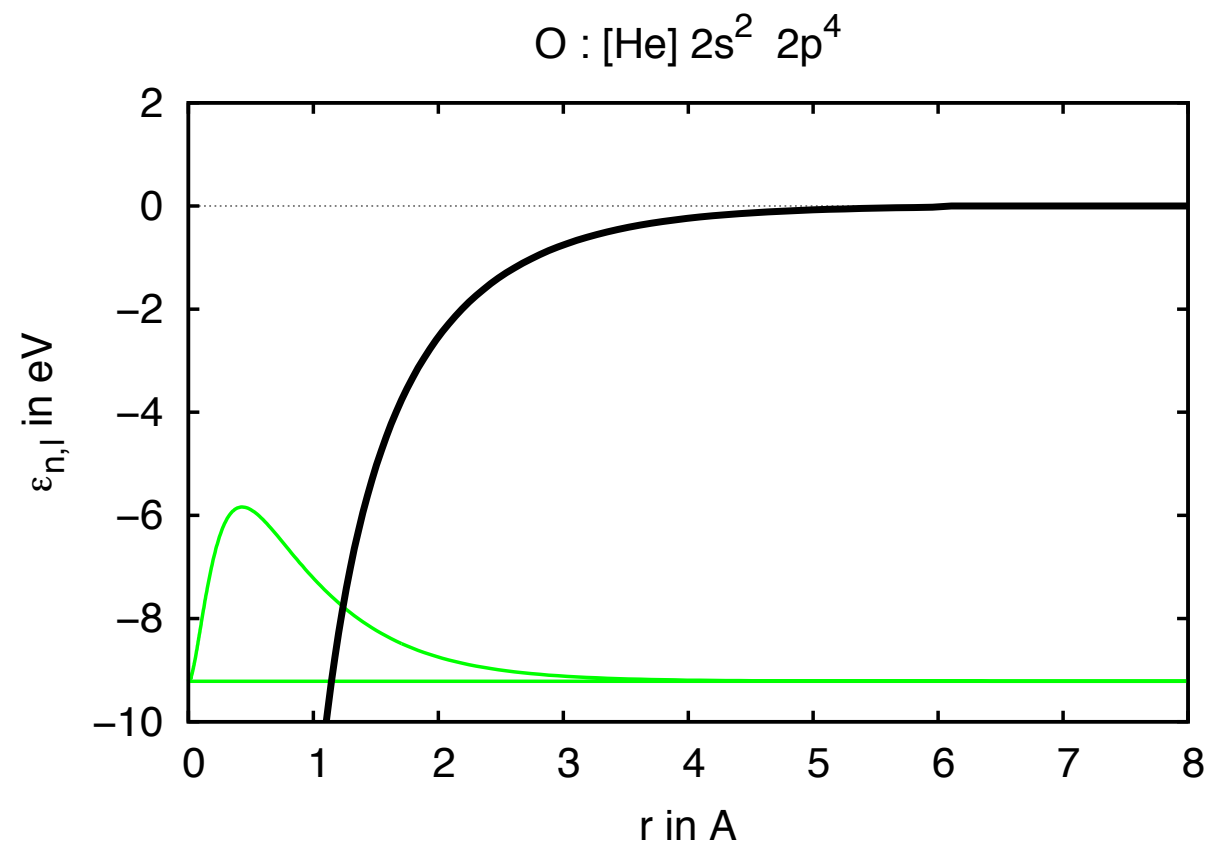


# Charge, orbital and trimeron order in the low-temperature magnetite structure.

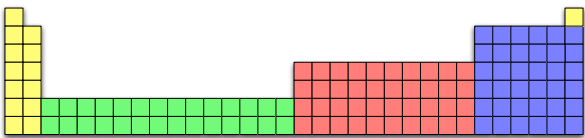


MS Senn *et al. Nature* **481**, 173 (2012) doi:10.1038/nature10704

# oxydation states



# typical charge states



+1 +2																		-2 -1							
H																			He						
Li	Be																	B	C	N	O	F	Ne		
Na	Mg	transition metals																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																	
alkali metals		alkaline-earths																pnictogens				chalcogens		halogens	noble gasses

