Multiplets and Spin-Orbit Coupling

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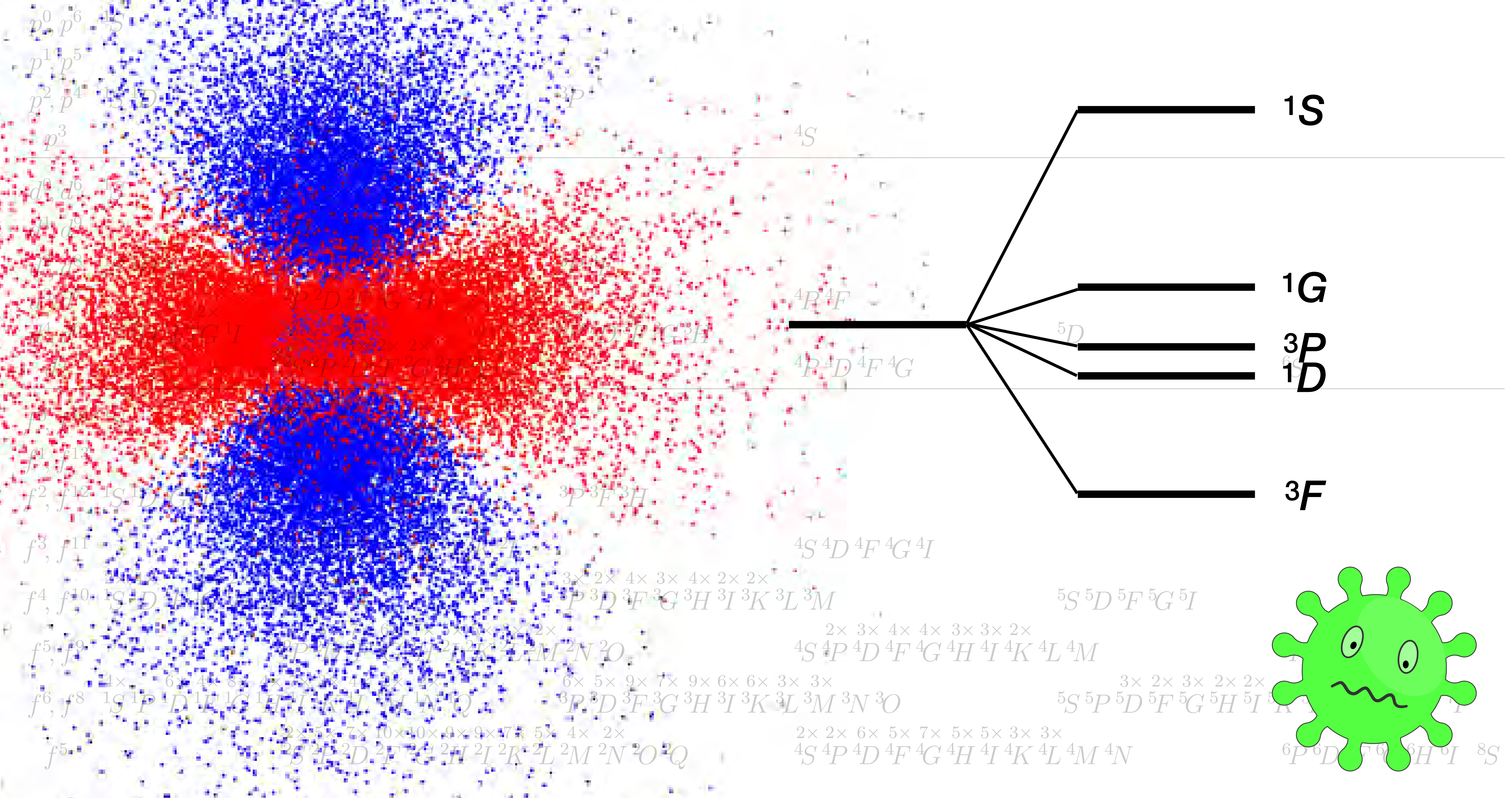


homework

Given:

atoms of nuclear charges Z_α at positions R_α.

Solve

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

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

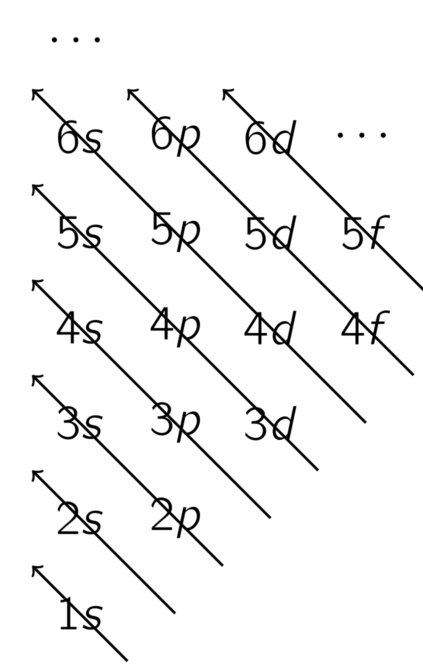
… the reductionist hypothesis does not by any means imply a ``constructionist'' one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe.
Sometimes, as in the case of superconductivity, the new symmetry — now called 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



Hamiltonian

$$H = \sum_i \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\left[\vec{L}_{tot},\, H\right] = 0$$

$$L_x \frac{1}{|\vec{r}-\vec{r}'|} = -i\left(r_y \frac{\partial}{\partial r_z} - r_z \frac{\partial}{\partial r_y}\right) \frac{1}{\sqrt{(r_x - r_x')^2 + (r_y - r_y')^2 + (r_z - r_z')^2}}$$

$$= \frac{+i}{2\sqrt{\cdots}^3}\Big(r_y\, 2(r_z - r_z')\,(+1) - r_z\, 2(r_y - r_y')\,(+1)\Big)$$

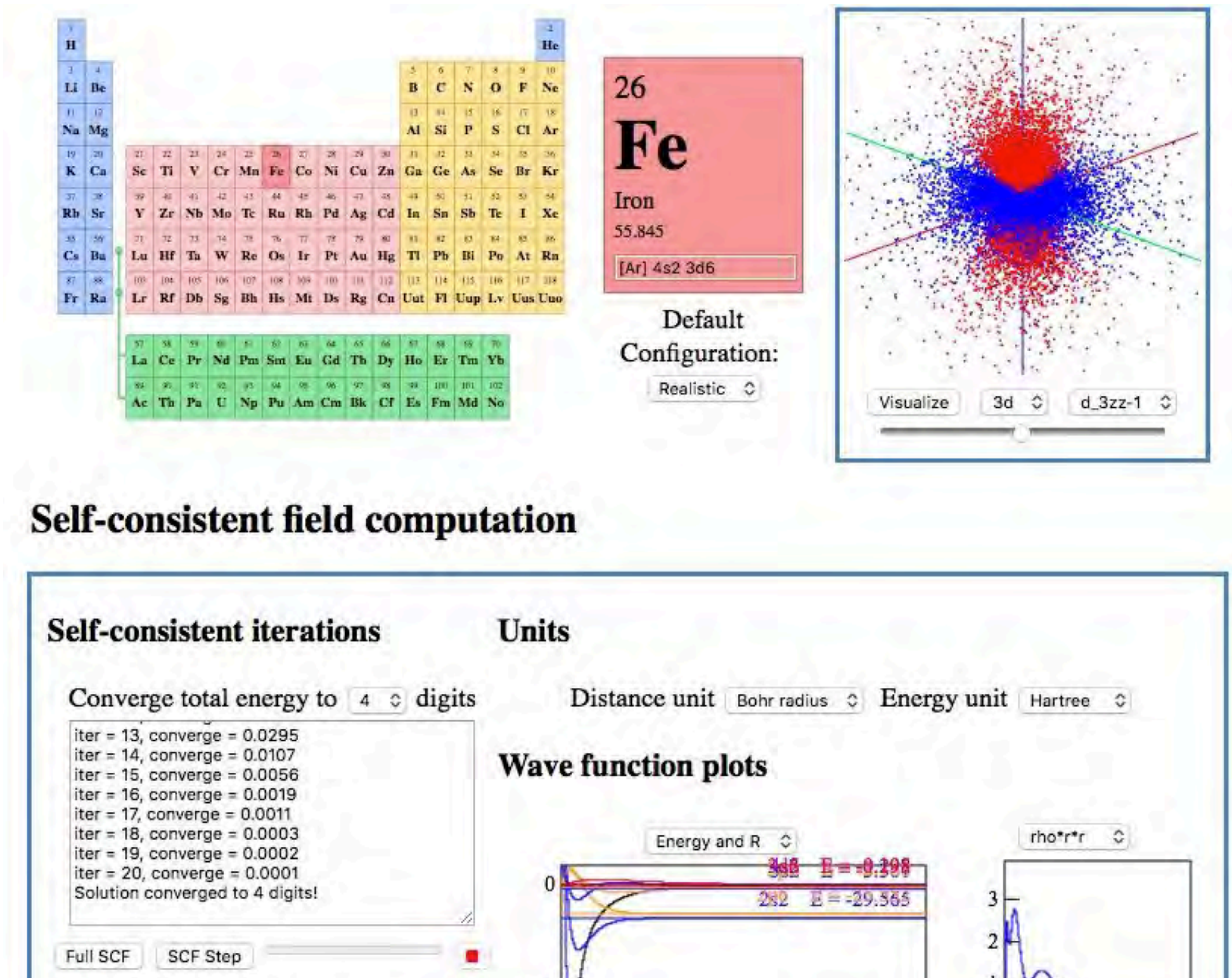
$$L_x' \frac{1}{|\vec{r}-\vec{r}'|} = \frac{+i}{2\sqrt{\cdots}^3}\Big(r_y'\, 2(r_z - r_z')\,(-1) - r_z'\, 2(r_y - r_y')\,(-1)\Big)$$

equations too complicated to be soluble

two-step approach:

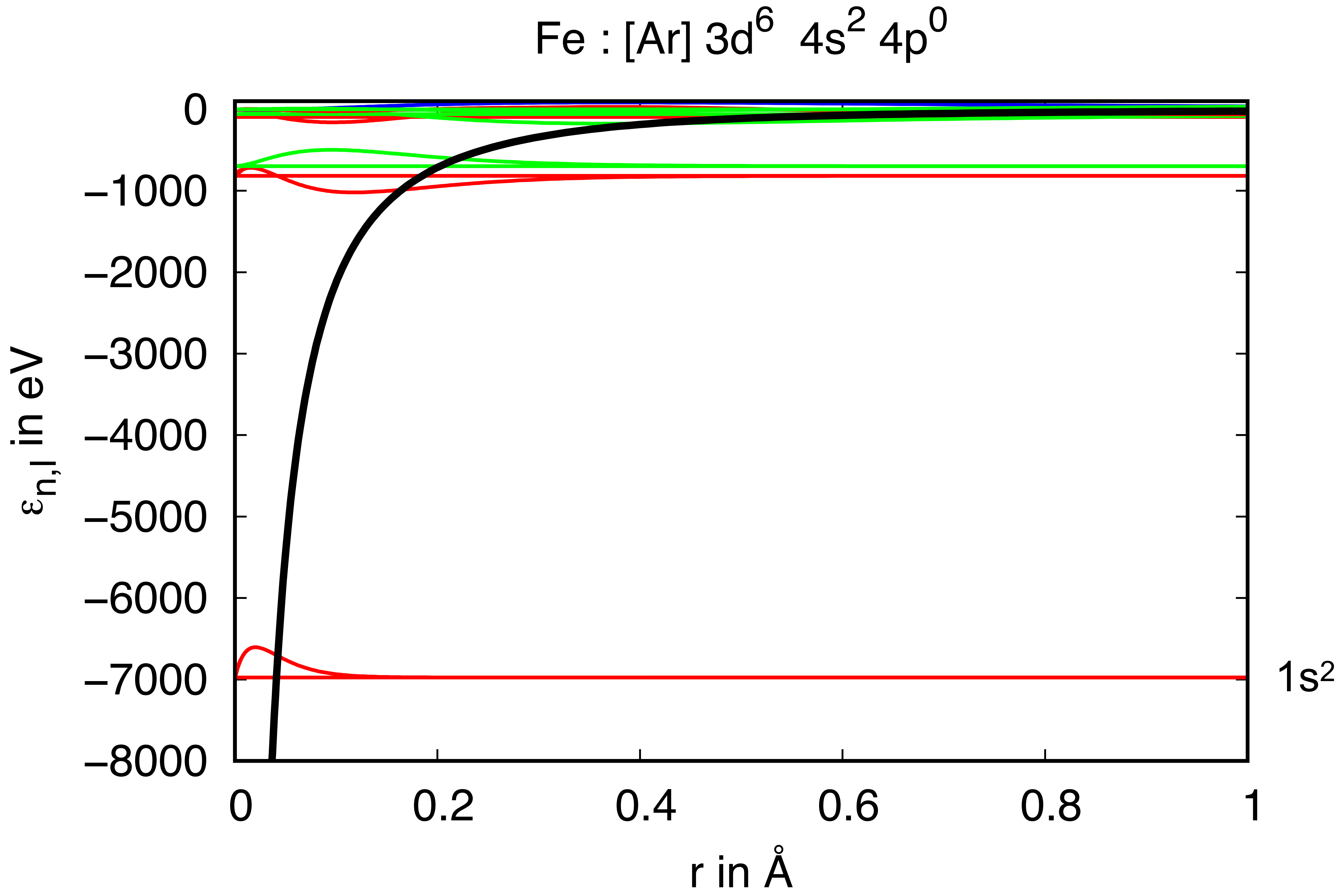
1. **(spherical) mean-field calculation**
2. **(degenerate) perturbation theory**

DFT

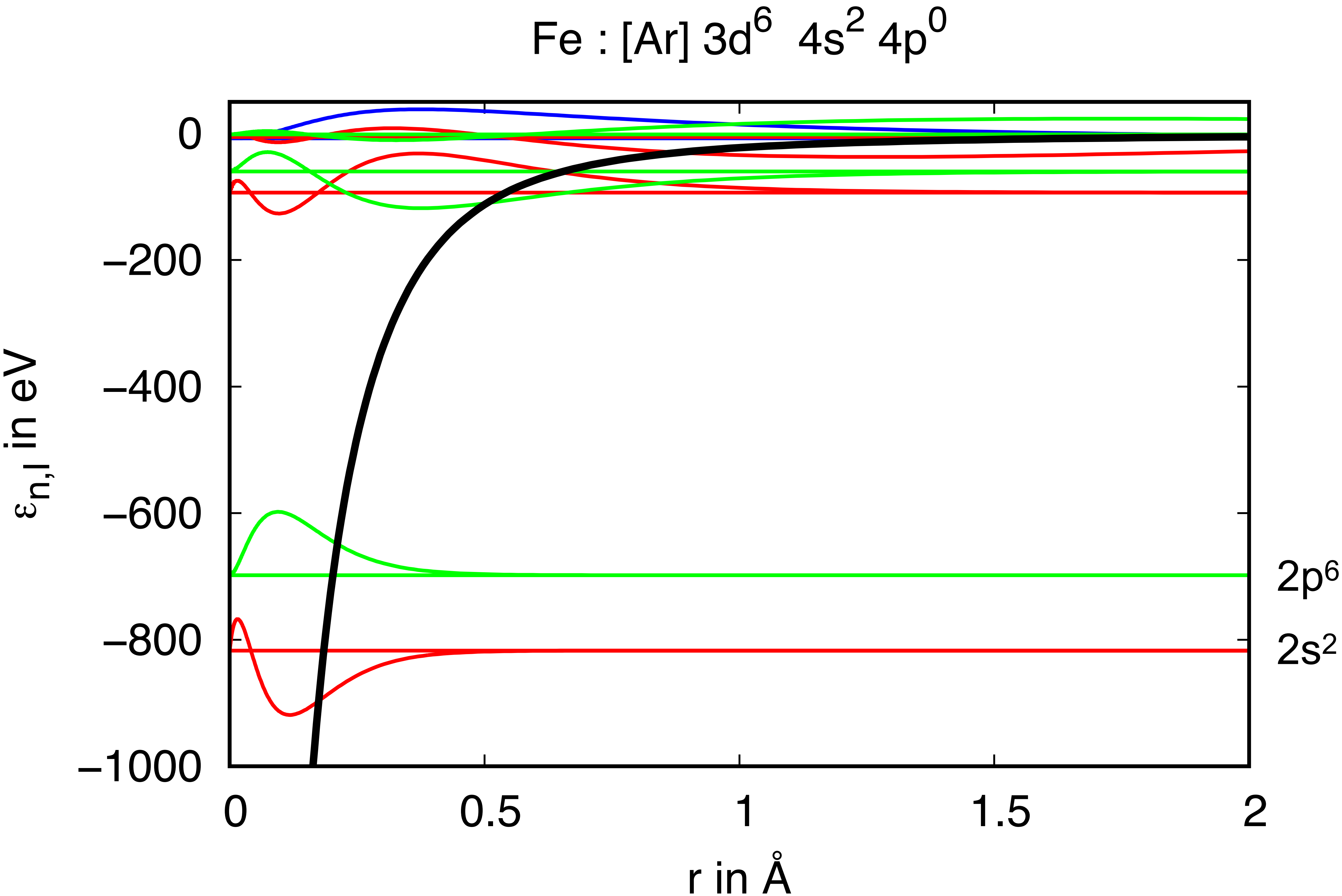


26
Fe
Iron
55.845
[Ar] 4s2 3d6
Default Configuration:
Realistic
Visualize
3d
d_3zz-1
Self-consistent field computation
Self-consistent iterations
Units
Converge total energy to 4 digits
iter = 13, converge = 0.0295
iter = 14, converge = 0.0107
iter = 15, converge = 0.0056
iter = 16, converge = 0.0019
iter = 17, converge = 0.0011
iter = 18, converge = 0.0003
iter = 19, converge = 0.0002
iter = 20, converge = 0.0001
Solution converged to 4 digits!
Full SCF
SCF Step
Distance unit
Bohr radius
Energy unit
Hartree
Wave function plots
Energy and R
rho*r*r
E = -29.565

spherical mean-field approximation

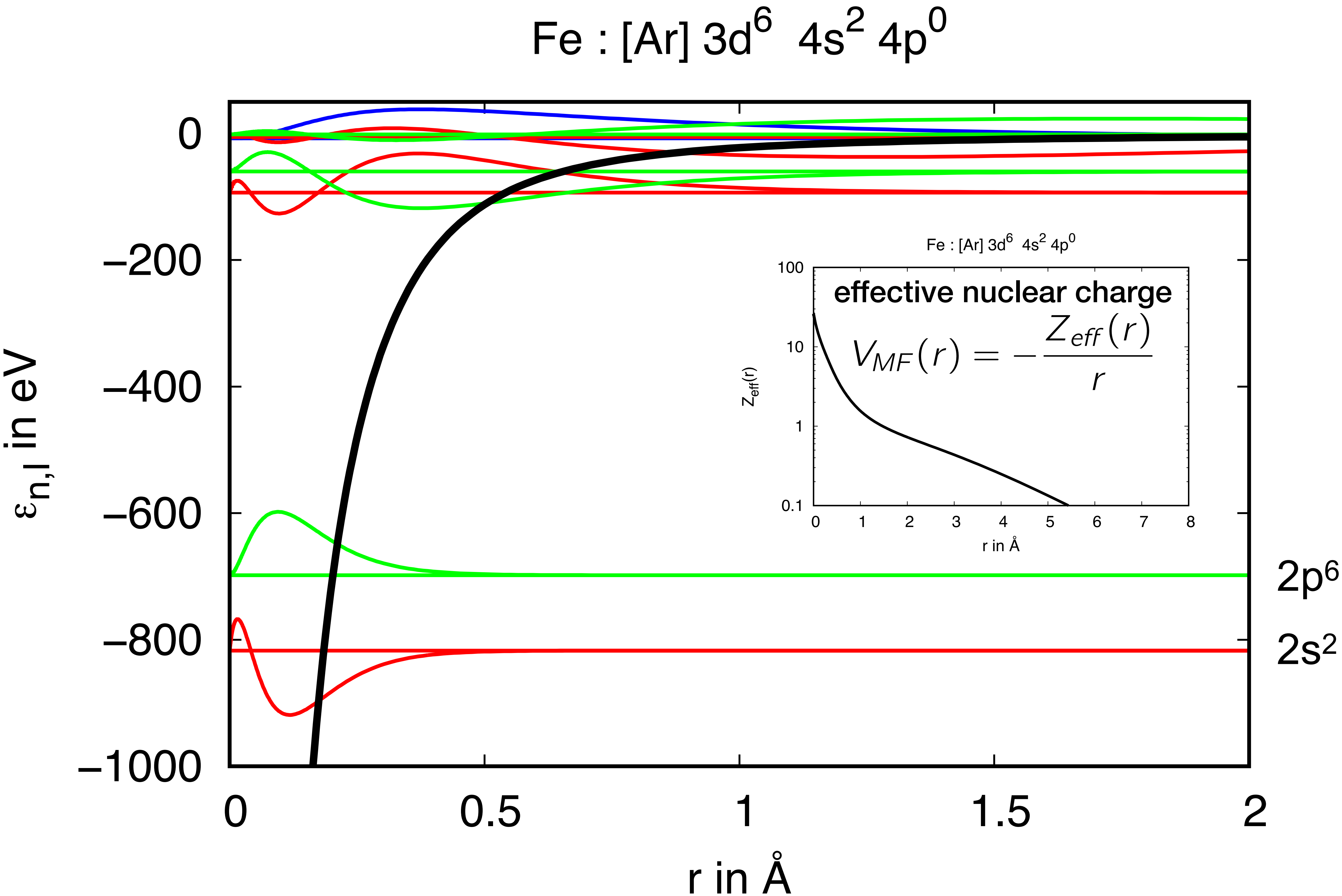


spherical mean-field approximation



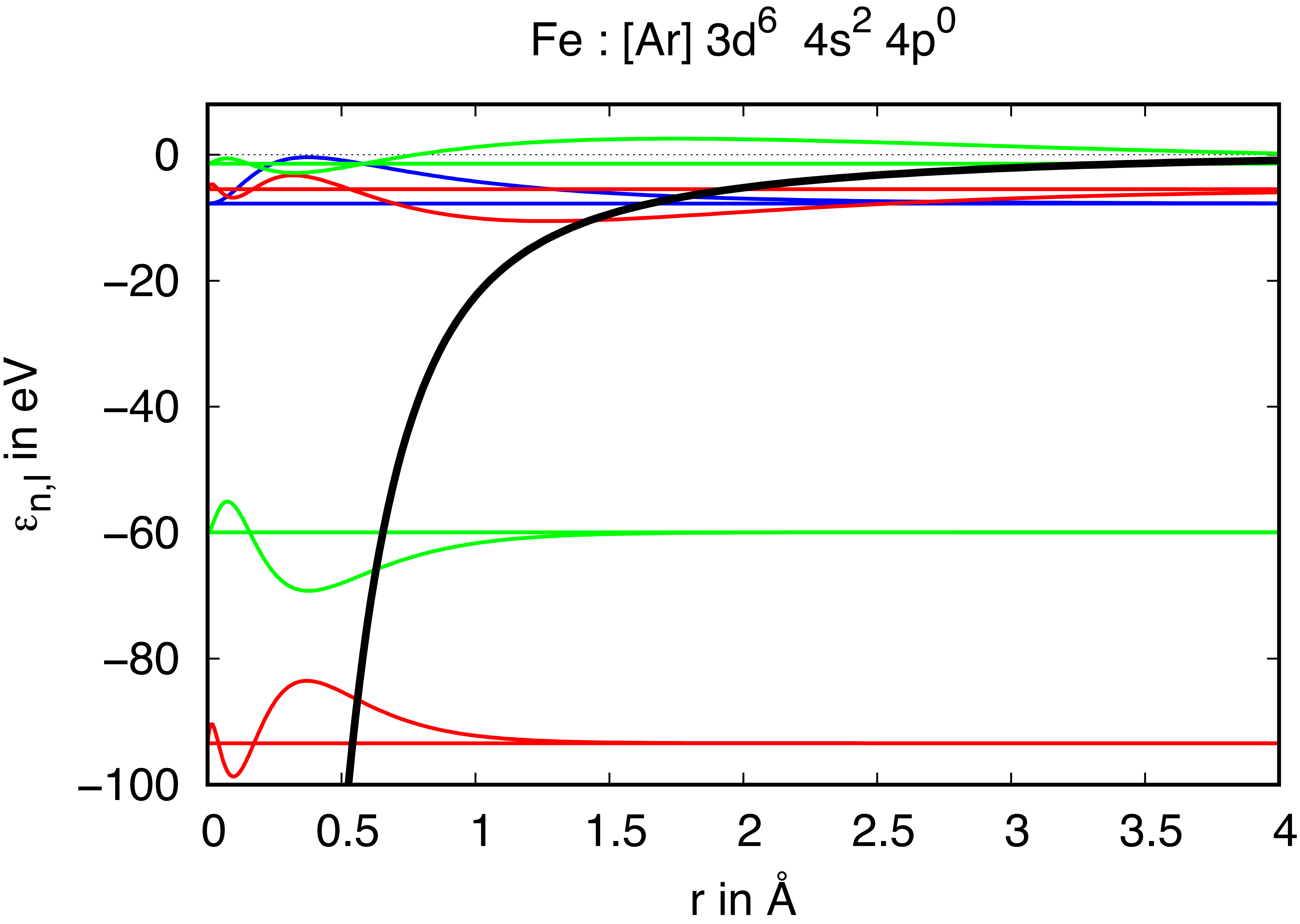
2s-2p degeneracy lifted

spherical mean-field approximation

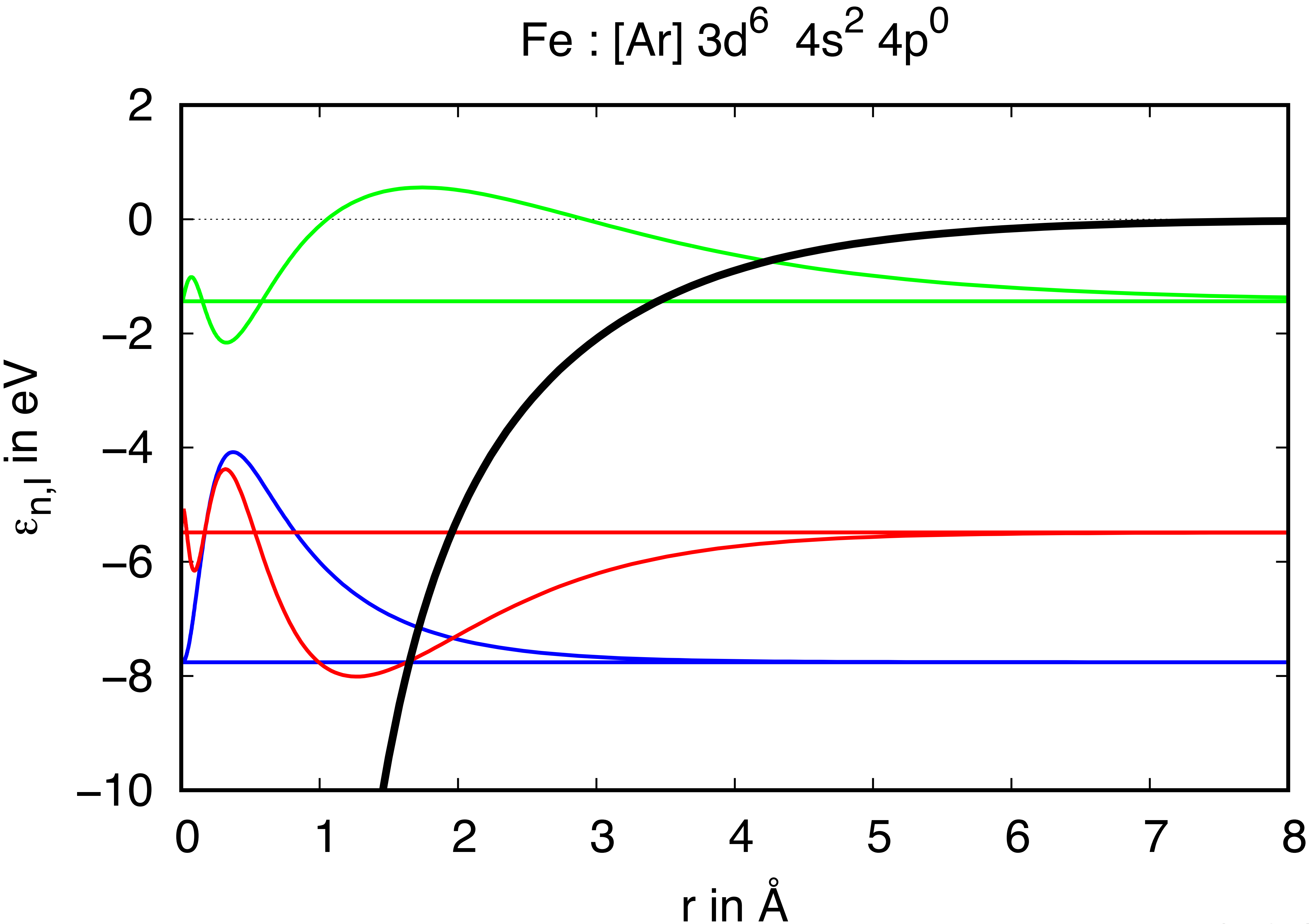


2s-2p degeneracy lifted

spherical mean-field approximation

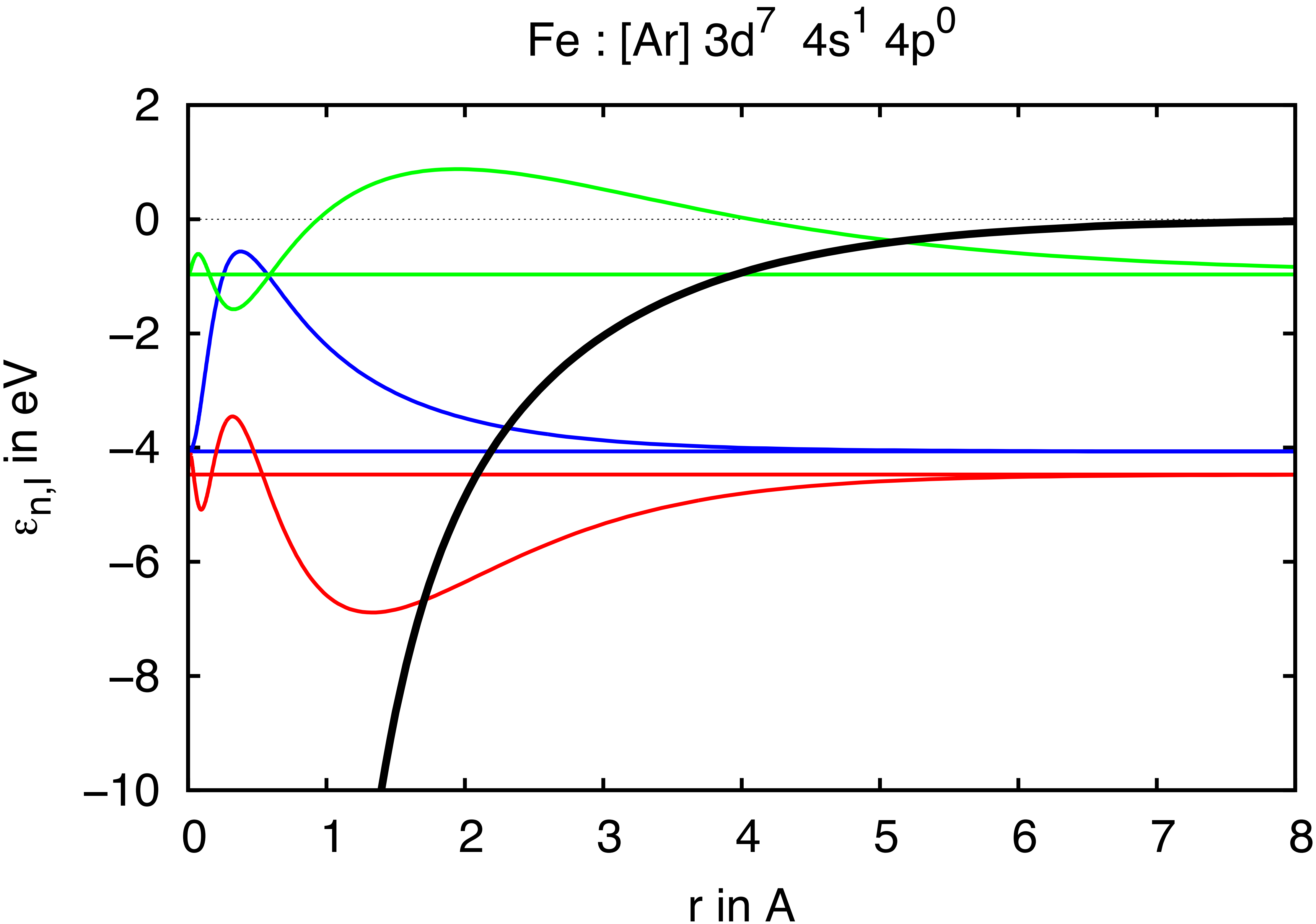


spherical mean-field approximation



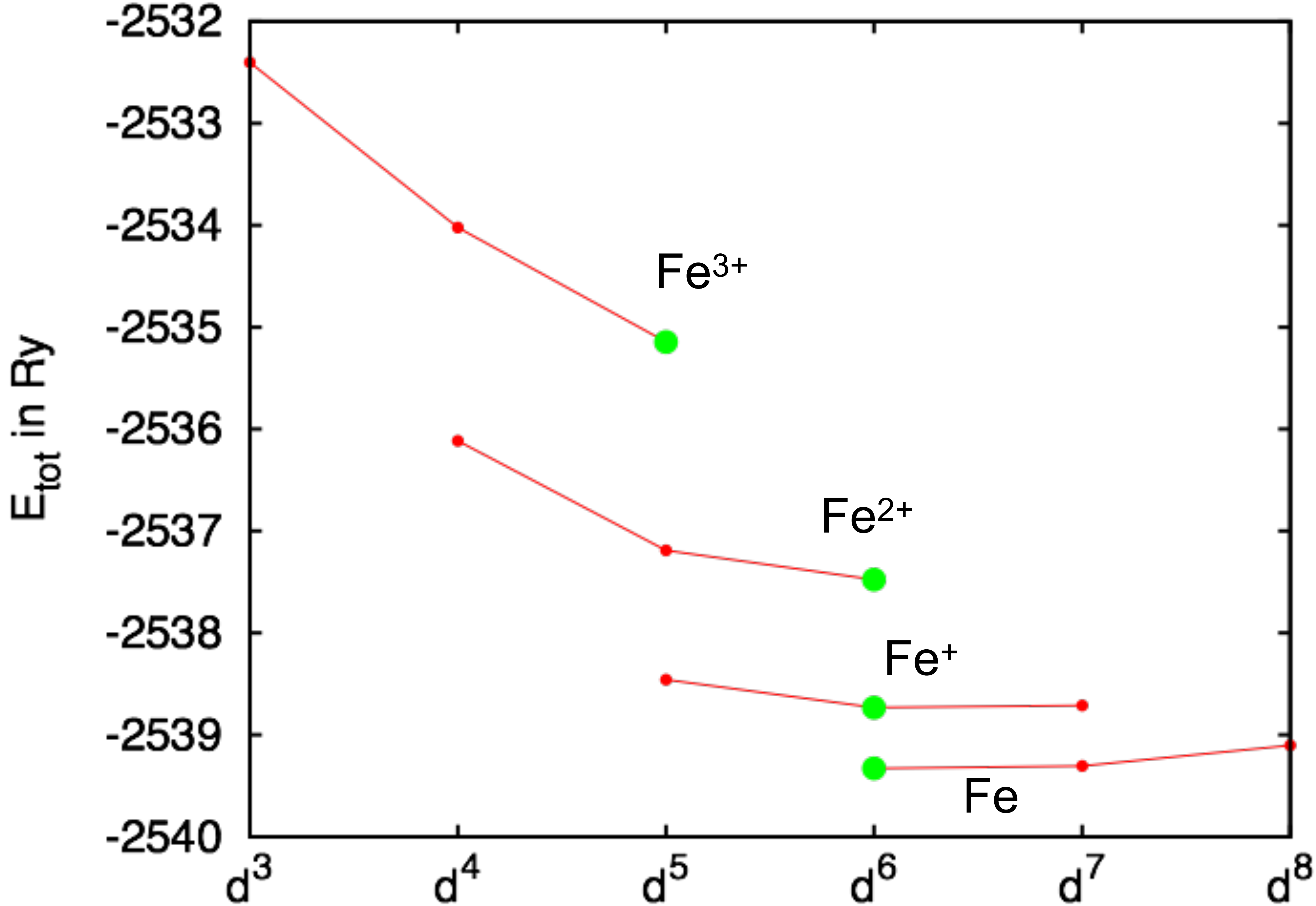
why not $3d^8$ $4s^0$??

spherical mean-field approximation



levels change with occupations

total energy



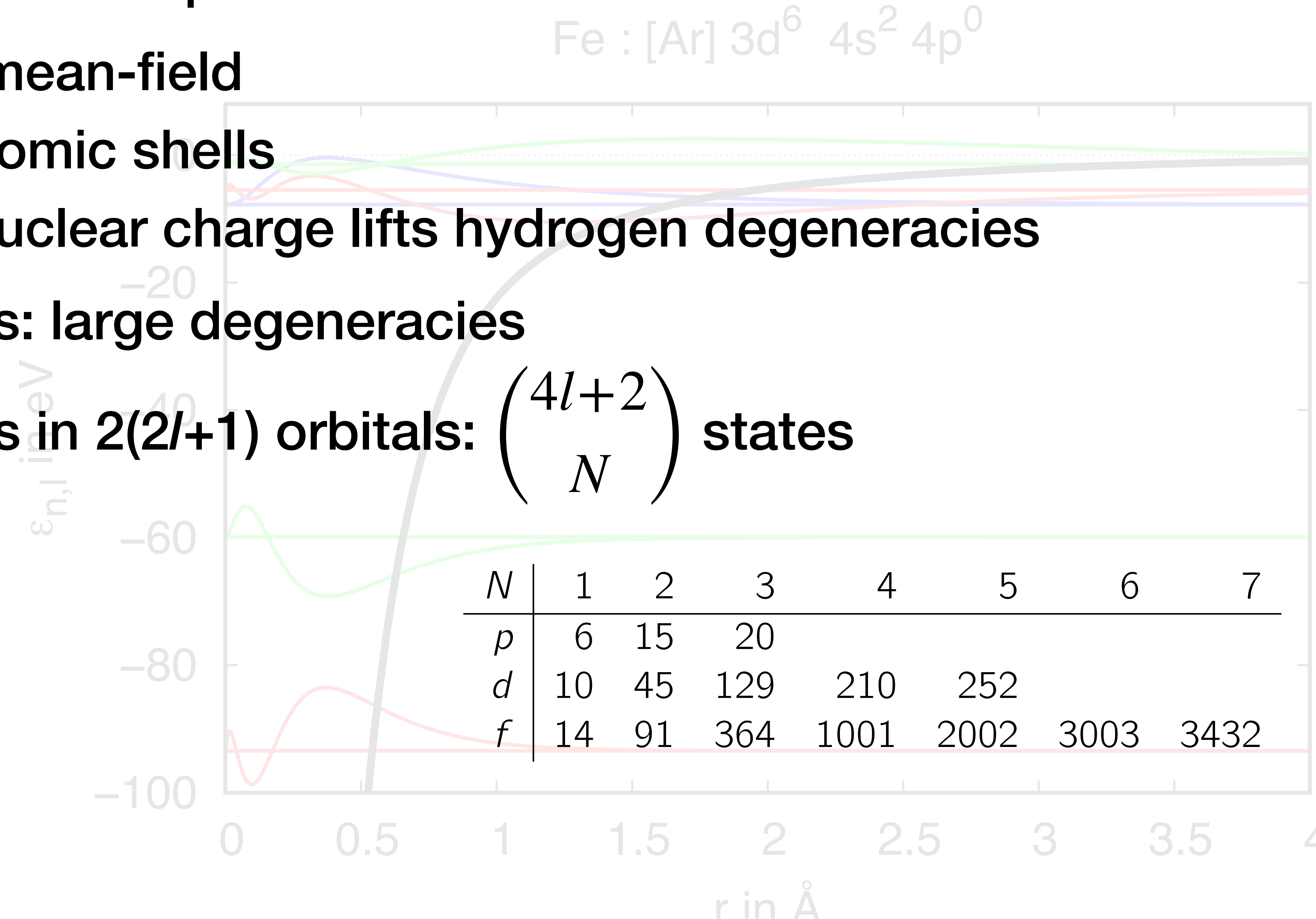
recap: spherical mean-field

- spherical symmetry: atoms are round
- atom still too complicated to be soluble
- spherical mean-field

  filling of atomic shells

  effective nuclear charge lifts hydrogen degeneracies
- open shells: large degeneracies

  N electrons in 2(2*l*+1) orbitals: $\binom{4l+2}{N}$ states



N	1	2	3	4	5	6	7
p	6	15	20				
d	10	45	129	210	252		
f	14	91	364	1001	2002	3003	3432

Atomic Spectra Database

Configuration	Term	J	Level (eV)	Uncertainty (eV)	Leading percentages	Reference
$3d^3$	a ^4F	$^3/_2$	0.00000		100	L7185
		$^5/_2$	0.01804		100	
		$^7/_2$	0.04234		100	
		$^9/_2$	0.07238		100	
$3d^3$	a ^4P	$^1/_2$	1.42753		100	
		$^3/_2$	1.43720		99	
		$^5/_2$	1.45926		100	
$3d^3$	a ^2G	$^7/_2$	1.48363		100	
		$^9/_2$	1.51100		100	
$3d^3$	a ^2P	$^3/_2$	1.92799		67 25 $3d^3$ $^2D2$	
		$^1/_2$	1.93165		100	
$3d^3$	a $^2D2$	$^3/_2$	2.02472		52 32 $3d^3$ ^2P	
		$^5/_2$	2.03020		77 22 $3d^3$ $^2D1$	
$3d^3$	a ^2H	$^9/_2$	2.08429		100	
		$^{11}/_2$	2.10495		100	
$3d^3$	a ^2F	$^7/_2$	3.43781		100	
		$^5/_2$	3.45256		100	
$3d^3$	b $^2D1$	$^5/_2$	5.24049		77 22 $3d^3$ $^2D2$	
		$^3/_2$	5.25336		77 23 $3d^3$ $^2D2$	
$3d^2(^3F)4s$	b ^4F	$^3/_2$	5.448174			
		$^5/_2$	5.468948			

V^{2+} : d^3

120 configurations split into 8 levels

$$\frac{10 \cdot 9 \cdot 8}{1 \cdot 2 \cdot 3}$$

physics.nist.gov/PhysRefData/ASD/

Multiplet Terms Hund-style

- $p^1: \ ^2P$

notation: ^{2S+1}L (*S P D F G H* ...)

- $pp' \to p(^2P)\, p': \ ^3D\ ^3P\ ^3S$

$^1D\ ^1P\ ^1S$

vector addition

$L = l + l',\ l + l' - 1, \ldots, |l - l'|$

same shell (*n*, *l*): orbitals $\varphi_{n,l,m,\sigma} \to m_\sigma$

^3D: $1_\uparrow\ 1_\uparrow$ occupied; $^3S: 0_\uparrow\ 0_\uparrow$ ✘ Pauli principle

$p^2: \ ^1D\ ^3P\ ^1S$ dimension: $\binom{6}{2} = 15 = 1 \cdot 5 + 3 \cdot 3 + 1 \cdot 1$

- $p^2 p' \to p^2(^3P)\, p': \ ^4D\ ^4P\ ^4S$

$^2D\ ^2P\ ^2S$

$p^2(^1D)\, p': \ ^2F\ ^2D\ ^2P$

$p^2(^1S)\, p': \ ^2P$

$^4D: 1_\uparrow 1_\uparrow 0_\uparrow;\quad ^4P: 1_\uparrow 0_\uparrow 0_\uparrow$ ✘

$^4S: 1_\uparrow\ 0_\uparrow\ -1_\uparrow$ ✔

$^2F: 1_\uparrow\ 1_\uparrow\ 1_\downarrow$ ✘

$p^3: \ ^4S\ ^2D\ ^2P$

$$\binom{6}{3} = 20 = 4 \cdot 1 + 2 \cdot 5 + 2 \cdot 3$$

$$p \otimes_{\mathscr{A}} p \otimes_{\mathscr{A}} p = \ ^4S \oplus \ ^2D \oplus \ ^2P$$

multiplet terms

s^0, s^2	^1S					
s^1		^2S				
p^0, p^6	^1S					
p^1, p^5		^2P				
p^2, p^4	$^1S\ ^1D$		^3P			
p^3		$^2P\ ^2D$		^4S		
d^0, d^6	^1S					
d^1, d^9		^2D				
d^2, d^8	$^1S\ ^1D\ ^1G$		$^3P\ ^3F$			
d^3, d^7		$^2P\ \overset{2\times}{^2D}\ ^2F\ ^2G\ ^2H$		$^4P\ ^4F$		
d^4, d^6	$\overset{2\times}{^1S}\ \overset{2\times}{^1D}\ ^1F\ \overset{2\times}{^1G}\ ^1I$		$\overset{2\times}{^3P}\ ^3D\ \overset{2\times}{^3F}\ ^3G\ ^3H$		^5D	
d^5		$^2S\ ^2P\ \overset{3\times}{^2D}\ \overset{2\times}{^2F}\ \overset{2\times}{^2G}\ ^2H\ ^2I$		$^4P\ ^4D\ ^4F\ ^4G$		^6S

Hund's rules from experimental spectra

s^0, s^2	^1S		
s^1		^2S	
p^0, p^6	^1S		
p^1, p^5		^2P	
p^2, p^4	^1S ^1D		^3P
p^3		^2P ^2D	
d^0, d^6	^1S		
d^1, d^9		^2D	
d^2, d^8	^1S ^1D ^1G		^3P
d^3, d^7		^2P $2\times\,^2D$ ^2F ^2G ^2H	
d^4, d^6	$2\times\,^1S$ $2\times\,^1D$ ^1F $2\times\,^1G$ ^1I		$2\times\,^3P$
d^5		^2S ^2P $3\times\,^2D$ $2\times\,^2F$ $2\times\,^2G$ ^2H ^2I	

Zeitschrift für Physik **33**, 345 (1925)

Zur Deutung verwickelter Spektren, insbesondere der Elemente Scandium bis Nickel.

Von **F. Hund** in Göttingen.

Mit drei Abbildungen. (Eingegangen am 22. Juni 1925.)

Auf Grund der Vorstellungen von Russell und Saunders, Pauli und Heisenberg über das Zusammenwirken mehrerer Elektronen bei der Aussendung von Spektrallinien werden die Spektralterme einiger Elemente auf ganz bestimmte, durch Quantenzahlen gekennzeichnete Anordnungen von Elektronen zurückgeführt. Insbesondere werden bei den Elementen Sc bis Ni für die Normalzustände der Elemente und (soweit bekannt) ihrer positiven Ionen, ferner für die übrigen tiefen Terme der Elemente die Quantenzahlen aller Elektronen angegeben. Damit ist der Zusammenhang hergestellt zwischen dem Bau dieser verwickelten Spektren und der Stellung der Elemente im periodischen System.

Man kann mehrere Stufen der Erklärung eines empirisch bekannten Spektrums unterscheiden. Beim Wasserstoff liefert die Bohrsche Quantentheorie mehrfach periodischer Systeme eine quantitativ genaue Festlegung der Spektralterme. Für die übrigen Elemente gibt es keine entsprechende strenge Theorie. Bei einer Anzahl von Elementen, im wesentlichen bei den in den ersten drei Spalten des periodischen Systems stehenden, lassen sich die Spektralterme bestimmten Quantenbahnen eines Elektrons (des Leuchtelektrons) zuordnen (Bohr, Sommerfeld) und die Energiewerte wenigstens angenähert abschätzen. Noch weniger war bisher bei den verwickelteren Spektren, z. B. bei Sc bis Ni möglich. Catalan und die ihm gefolgten Forscher[1]),

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[1]) Über Elemente der mit K beginnenden Periode: Ca: H. N. Russell und F. A. Saunders, Astrophys. Journ. **61**, 38, 1925. Sc: M. A. Catalan, An. Soc. Esp. d. Fis. y Quim. **20**, 606, 1922; **21**, 464, 1923. Ti: C. C. Kiess und H. K. Kiess, Journ. Washington Acad. Sc. **13**, 270, 1923; Journ. Opt. Soc. Amer. **8**, 607, 1924. V: W. F. Meggers, Journ. Washington Acad. Sc. **13**, 317, 1923; O. Laporte, Naturwissensch. **11**, 779, 1923; Phys. ZS. **24**, 510, 1923; M. A. Catalan, An. Soc. Esp. d. Fis. y Quim. **22**, 72, 1924; H. Gieseler und W. Grotrian, ZS. f. Phys. **25**, 342, 1924; K. Bechert und L. A. Sommer, ZS. f. Phys. **31**, 145, 1925. Cr: M. A. Catalan, Phil. Trans. Roy. Soc. London (A) **223**, 127, 1922; H. Gieseler, Ann. d. Phys. **69**, 147, 1922; C. C. und H. K. Kiess, Science **56**, 666, 1922, Nr. 1458; M. A. Catalan, An. Soc. Esp. d. Fis. y Quim. **21**, 84, 1923. Mn: M. A. Catalan, Phil. Trans. Roy. Soc. London (A) **223**, 127, 1922; A. Sommerfeld, Ann. d. Phys. **70**, 32, 1923; E. Back, ZS. f. Phys. **15**, 206, 1923. Fe: F. M. Walters jr., Journ. Washington Acad. Sc. **13**, 243, 1923; H. Gieseler und W. Grotrian, ZS. f. Phys. **22**, 245, 1924; **25**, 243, 1924; E. v. Angerer und G. Joos, Naturwissensch. **12**, 140, 1924; Ann. d. Phys. **74**, 743, 1924; O. Laporte, ZS. f. Phys. **23**, 135, 1924; **26**, 1, 1924. Co: F. M. Walters jr.,

Racah's fractional parentage

$$p^2 p' \rightarrow p^2(^3P)\, p' : \quad {}^4D\ {}^4P\ {}^4S$$

$$\qquad {}^2D\ {}^2P\ {}^2S$$

$$p^2(^1D)\, p' : \quad {}^2F\ {}^2D\ {}^2P$$

$$p^2(^1S)\, p' : \quad {}^2P$$

$p^3 :\ {}^4S\ {}^2D\ {}^2P$

${}^4S$ originates from $p^2(^3P)p$

${}^2D$ has parents in $p^2(^3P)p$ and $p^2(^1D)p$

${}^2P$ has parents in all three

multiplet states are those linear combinations of
the Clebsch-Gordan states that are antisymmetric
the corresponding expansion coefficients are the
coefficients of fractional parentage

$$|p^3(^2D)\rangle = c_{^3P}\,|p^2(^3P)p\rangle + c_{^1D}\,|p^2(^1D)p\rangle$$

fractional-parentage tables

FRACTIONAL PARENTAGE P2

3P	2P	1	
1S	2P	1	
1D	2P	1	

FRACTIONAL PARENTAGE P3

4S	3P	1	
2P	3P	-1	-1
	1S	1	1-2
	1D	-1	-1-2 1
2D	3P	1	-1
	1D	-1	-1

FRACTIONAL PARENTAGE D2

3P	2D	1	
3F	2D	1	
1S	2D	1	
1D	2D	1	
1G	2D	1	

FRACTIONAL PARENTAGE D3

4P	3P	-1	3-1-1
	3F	-1	0-1-1 1
4F	3P	-1	0 0-1
	3F	1	2 0-1
2P	3P	1	-1-1-1 1
	3F	-1	2-1-1
	1D	1	-1
2D1	3P	-1	-2 1-1
	3F	-1	-2 0-1 1
	1S	1	2-1-1
	1D	-1	-2-1
	1G	-1	-2 1-1
2D2	3P	-1	-2 0-1 1
	3F	1	-2 1-1
	1D	1	-2 2 0-1
	1G	-1	-2 0 1-1
2F	3P	1	1 0-1
	3F	1	-1 0-1
	1D	-1	0 0 0-1
	1G	-1	-1 0 1-1
2G	3F	1	-1
	1D	-1	0-1 1-1
	1G	1	-1-1 0-1 1
2H	3F	-1	-1
	1G	1	-1

FRACTIONAL PARENTAGE D4

5D	4P	1	-1 1-1
	4F	1	-1 0-1 1
3P1	4P	-1	3-2-1
	4F	-1	0-2-1 1
	2P	-1	-2-2-1 1
	2D1	1	-3 1
	2D2	-1	-3-2 0 1
	2F	-1	0-2-1 1
3P2	4P	-1	0-2-1 1
	4F	1	3-2-1
	2P	1	-1-2 1
	2D2	1	0-2
	2F	-1	-1-2 1
3D	4P	1	-1-1-1 1
	4F	-1	-1 0-1
	2P	-1	0-1-1
	2D2	1	1 0 0-1
	2F	-1	-1 0-1
	2G	1	-1 1 0-1
3F1	4P	-1	0-1-1
	4F	1	2-1-1
	2P	1	1-1-1-1
	2D1	1	-3 1
	2D2	1	-3 0 0-1
	2F	-1	-2-1-1
	2G	1	-2 1 0-1
	2H	1	-2-1 0-1 1
3F2	4P	-1	2-1-1
	4F	-1	0-1-1
	2P	-1	-1-1 1-1
	2D2	1	-1 0 0-1
	2F	-1	-4-1 1
	2G	-1	-4 3 0-1
	2H	1	-2-1 0-1 1
3G	4F	-1	0-1
	2D2	1	-1-1 1-1
	2F	1	-4 1
	2G	1	-4 2-1-1 1
	2H	1	-2-1-1 0 1
3H	4F	1	0-1
	2F	1	-2-1
	2G	-1	-2 1-1
	2H	1	-1-1-1 0 0 1

FRACTIONAL PARENTAGE D4

1S1	2D1	1	
1S2	2D2	1	
1D1	2P	-1	-2 1-1
	2D1	1	-3 1
	2D2	1	-3 2 0-1
	2F	1	-1 0-1
	2G	-1	-1 1 0-1
1D2	2P	1	-1 1-1
	2D2	1	0 0 0-1
	2F	1	-2 2-1
	2G	1	-2 1 0-1
1F	2P	1	-1 1 0-1
	2D2	1	-1 0 1-1
	2F	-1	-4 1
	2G	-1	-4 1-1-1
	2H	-1	-2 1-1-1 1
1G1	2D1	1	-3 1
	2D2	-1	-3-2 2-1
	2F	1	-2-2 1
	2G	1	-2-1 0-1 1
	2H	-1	-2-2 0 0 1
1G2	2D2	1	-1-2 0-1 1
	2F	1	-4-2 1 0 1
	2G	-1	-4-1 0-1 0 2
	2H	-1	-2-2
1I	2G	1	-1 1-1
	2H	1	-1 0-1 1

6S	5D	1	
4P	5D	-1	-2
	3P1	-1	4-
	3P2	1	-1-
	3D	1	-2-
	3F1	-1	1-
	3F2	1	1-
4D	5D	-1	-2
	3P2	1	-1
	3D	-1	-2
	3F2	-1	0
	3G	1	0
4F	5D	-1	-2
	3P1	-1	1
	3P2	-1	2
	3D	-1	-2
	3F1	1	3
	3F2	1	-1
	3G	-1	-1
	3H	-1	-1
4G	5D	-1	-2
	3D	1	-2-
	3F2	-1	-1-
	3G	-1	-1
	3H	1	-1-
2S	3D	1	0
	1D2	-1	1
2P	3P1	1	0-
	3P2	1	-1-
	3D	1	0-
	3F1	-1	3-
	3F2	-1	-1-
	1D1	1	0
	1D2	1	-1
	1F	-1	-1
2D1	3P1	-1	-1
	3F1	-1	-1
	1S1	1	0
	1D1	-1	-1
	1G1	-1	-1
2D2	3P1	-1	-1
	3P2	-1	0
	3D	1	1
	3F1	1	-1
	3F2	-1	-1
	3G	1	-1
	1S2	-1	0
	1D1	1	-1
	1D2	-1	0
	1F	1	-1
	1G1	-1	-1
	1G2	-1	-1
2D3	3P2	1	-1 2
	3D	1	0 1-1-1
	1G2	-1	-1 2-1 0 -1
	1I	-1	-1 0 0 1 -1

Spectroscopic Coefficients
for the p^n, d^n, and f^n Configurations

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2nd quantization

wave function $\varphi_\alpha(\vec{r}) \longrightarrow$ Dirac state $|\alpha\rangle$

get rid of coordinate: $\varphi_\alpha(\vec{r}) = \langle \vec{r}\,|\,\alpha\rangle = \langle 0\,|\,\hat{\Psi}(\vec{r})\; c_\alpha^\dagger\,|\,0\rangle$

analogous for Slater determinants

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \vdots & & \vdots \\ \varphi_{\alpha_1}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \left\langle 0 \middle| \hat{\Psi}(x_1)\cdots\hat{\Psi}(x_N)\; c_{\alpha_N}^\dagger \cdots c_{\alpha_1}^\dagger \middle| 0 \right\rangle$$

with vacuum state $|\,0\rangle$ and field operators $\hat{\Psi}(x)$ defined by

$\left\{\hat{\Psi}(x), \hat{\Psi}(x')\right\} = 0,\ \ \left\{\hat{\Psi}(x), \hat{\Psi}^\dagger(x')\right\} = \delta(x - x')$ and $\hat{\Psi}(x)\,|\,0\rangle = 0,\ \langle 0\,|\,0\rangle = 1$

$\{A, B\} := AB + BA$

2nd quantization: work with basis states

$c_{\alpha_N}^\dagger \cdots\, c_{\alpha_1}^\dagger\,|\,0\rangle$ where $c_\alpha^\dagger := \displaystyle\int dx\, \varphi_\alpha(x) \hat{\Psi}^\dagger(x)$

one-body operator

$$\vec{L}_{tot}(x_1, \ldots, x_N) = \sum_{n=1}^{N} \vec{L}(x_n)$$

include field operators in matrix elements

$$\int dx_1 \ldots dx_N \, \overline{\Phi_{\alpha_1 \ldots \alpha_N}(x_1, \ldots, x_N)} \, \vec{L}_{tot}(x_1, \ldots, x_N) \Phi_{\beta_1 \ldots \beta_N}(x_1, \ldots, x_N) =$$

$$\langle 0 | c_{\alpha_1} \cdots c_{\alpha_N} \underbrace{\frac{1}{N!} \int d\mathbf{x} \, \hat{\Psi}^\dagger(x_N) \cdots \hat{\Psi}^\dagger(x_1) \sum_n \vec{L}(x_n) \hat{\Psi}(x_1) \cdots \hat{\Psi}(x_N) \, c^\dagger_{\beta_N} \cdots c^\dagger_{\beta_1} | 0 \rangle}$$

$$= \langle 0 | c_{\alpha_1} \cdots c_{\alpha_N} \underbrace{\int dx \, \hat{\Psi}^\dagger(x) \vec{L}(x) \Psi(x)}_{=: \hat{L}} \, c^\dagger_{\beta_N} \cdots c^\dagger_{\beta_1} | 0 \rangle$$

operator $\hat{L}_{tot}$ independent of number of electrons

total angular momentum operator

expand field operators in orthonormal basis $\hat{\Psi}^\dagger(x) = \sum_{\alpha_n} \overline{\varphi_{\alpha_n}(x)}\, c^\dagger_{\alpha_n}$

$c^\dagger_\alpha := \int dx'\, \varphi_\alpha(x')\hat{\Psi}^\dagger(x')$

$$\hat{L} = \int dx\, \hat{\Psi}^\dagger(x)\vec{L}(x)\Psi(x) = \sum_{n,m} c^\dagger_{\alpha_n} \underbrace{\int dx\, \overline{\varphi_{\alpha_n}(x)} L(x) \varphi_{\alpha_m}(x)}_{\langle\alpha_n|L|\alpha_m\rangle} c_{\alpha_m}$$

basis of atomic orbitals $|n, l, m, \sigma\rangle$

$$\hat{L}_z = \sum_{n,l,m,\sigma} m\, c^\dagger_{n,l,m,\sigma} c_{n,l,m,\sigma}$$

$$\hat{L}_\pm = \sum_{n,l,m,\sigma} \sqrt{(l{\pm}m{+}1)(l{\mp}m)}\, c^\dagger_{n,l,m\pm1,\sigma} c_{n,l,m,\sigma}$$

similarly: total spin $\hat{S}_+ = \sum_{n,l,m} c^\dagger_{n,l,m,\uparrow} c_{n,m,m,\downarrow}$

p^2 shell

arrange basis determinants $|n_{1\uparrow}, n_{0\uparrow}, n_{-1\uparrow}, n_{1\downarrow}, n_{0\downarrow}, n_{-1\downarrow}\rangle := \prod \left(p^\dagger_{m,\sigma}\right)^{n_{m\sigma}} |0\rangle$

		Σ	
	1	0	−1
M = 2		$p^\dagger_{1\uparrow} p^\dagger_{1\downarrow}\|0\rangle$	
1	$p^\dagger_{1\uparrow} p^\dagger_{0\uparrow}\|0\rangle$	$p^\dagger_{1\uparrow} p^\dagger_{0\downarrow}\|0\rangle$ $p^\dagger_{0\uparrow} p^\dagger_{1\downarrow}\|0\rangle$	$p^\dagger_{1\downarrow} p^\dagger_{0\downarrow}\|0\rangle$
0	$p^\dagger_{1\uparrow} p^\dagger_{-1\uparrow}\|0\rangle$	$p^\dagger_{1\uparrow} p^\dagger_{-1\downarrow}\|0\rangle$ $p^\dagger_{0\uparrow} p^\dagger_{0\downarrow}\|0\rangle$ $p^\dagger_{-1\uparrow} p^\dagger_{1\downarrow}\|0\rangle$	$p^\dagger_{1\downarrow} p^\dagger_{-1\downarrow}\|0\rangle$
−1	$p^\dagger_{0\uparrow} p^\dagger_{-1\uparrow}\|0\rangle$	$p^\dagger_{0\uparrow} p^\dagger_{-1\downarrow}\|0\rangle$ $p^\dagger_{-1\uparrow} p^\dagger_{0\downarrow}\|0\rangle$	$p^\dagger_{0\downarrow} p^\dagger_{-1\downarrow}\|0\rangle$
−2		$p^\dagger_{-1\uparrow} p^\dagger_{-1\downarrow}\|0\rangle$	

construct multiplet states

construct eigenstates $|L, M;\ S, \Sigma\rangle$ of $\overrightarrow{L}_{tot}$ and $\overrightarrow{S}_{tot}$

basis states with maximum M and Σ are eigenstates:

$$\hat{L}_+ |\Phi_{M,\Sigma}\rangle = 0 = \hat{S}_+ |\Phi_{M,\Sigma}\rangle \ \rightsquigarrow \ |\Phi_{M,\Sigma}\rangle = |L, M; S, \Sigma\rangle$$

$$\overrightarrow{J}^2 = J_z(J_z+1) + J_-J_+$$

applying operators to basis states:

$$\hat{L}\, c_\alpha^\dagger c_\beta^\dagger |0\rangle = \left([\hat{L}, c_\alpha^\dagger] + c_\alpha^\dagger \hat{L}\right) c_\beta^\dagger |0\rangle$$

$$= [\hat{L}, c_\alpha^\dagger]\, c_\beta^\dagger |0\rangle + c_\alpha^\dagger [\hat{L}, c_\beta^\dagger] |0\rangle + c_\alpha^\dagger c_\beta^\dagger \hat{L} |0\rangle$$

$p^2\ (^3P)$

$$|1,1;\ 1,\ \ 1\rangle = p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}|0\rangle$$

$$\sqrt{2}\,|1,1;\ 1,\ \ 0\rangle = S_-\,|1,1;\ 1,1\rangle = \left(p^\dagger_{1\downarrow}p^\dagger_{0\uparrow} + p^\dagger_{1\uparrow}p^\dagger_{0\downarrow}\right)|0\rangle$$

$$2\,|1,1;\ 1,-1\rangle = S_-\,|1,1;\ 1,0\rangle = 2p^\dagger_{1\downarrow}p^\dagger_{0\downarrow}|0\rangle$$

	1	0	−1
2		$p^\dagger_{1\uparrow}p^\dagger_{1\downarrow}\vert 0\rangle$	
1	$p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}\vert 0\rangle$	$p^\dagger_{1\uparrow}p^\dagger_{0\downarrow}\vert 0\rangle$ $p^\dagger_{0\uparrow}p^\dagger_{1\downarrow}\vert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{0\downarrow}\vert 0\rangle$
0	$p^\dagger_{1\uparrow}p^\dagger_{-1\uparrow}\vert 0\rangle$	$p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow}\vert 0\rangle$ $p^\dagger_{0\uparrow}p^\dagger_{0\downarrow}\vert 0\rangle$ $p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\vert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{-1\downarrow}\vert 0\rangle$
−1	$p^\dagger_{0\uparrow}p^\dagger_{-1\uparrow}\vert 0\rangle$	$p^\dagger_{0\uparrow}p^\dagger_{-1\downarrow}\vert 0\rangle$ $p^\dagger_{-1\uparrow}p^\dagger_{0\downarrow}\vert 0\rangle$	$p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}\vert 0\rangle$
−2		$p^\dagger_{-1\uparrow}p^\dagger_{-1\downarrow}\vert 0\rangle$	

^3P

		Σ: 1	Σ: 0	Σ: −1
M	1	$p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}\vert 0\rangle$	$\frac{1}{\sqrt{2}}\left(p^\dagger_{1\uparrow}p^\dagger_{0\downarrow} - p^\dagger_{0\uparrow}p^\dagger_{1\downarrow}\right)\vert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{0\downarrow}\vert 0\rangle$
	0	$p^\dagger_{1\uparrow}p^\dagger_{-1\uparrow}\vert 0\rangle$	$\frac{1}{\sqrt{2}}\left(p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow} - p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\right)\vert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{-1\downarrow}\vert 0\rangle$
	−1	$p^\dagger_{0\uparrow}p^\dagger_{-1\uparrow}\vert 0\rangle$	$\frac{1}{\sqrt{2}}\left(p^\dagger_{0\uparrow}p^\dagger_{-1\downarrow} - p^\dagger_{-1\uparrow}p^\dagger_{0\downarrow}\right)\vert 0\rangle$	$p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}\vert 0\rangle$

p^2 (^1D)

$$\hat{L}_+ = \sqrt{2}\sum_\sigma \left(p^\dagger_{0\sigma} p_{1\sigma} + p^\dagger_{-1\sigma} p_{0\sigma}\right)$$

$$[\hat{L}_-,\ p^\dagger_{m\sigma}] = \sqrt{2}\left(p^\dagger_{0,\sigma}\,\delta_{m,1} + p^\dagger_{-1\sigma}\,\delta_{m,0}\right)$$

	1	0	−1
2		$p^\dagger_{1\uparrow} p^\dagger_{1\downarrow}\|0\rangle$	
1	$p^\dagger_{1\uparrow} p^\dagger_{0\uparrow}\|0\rangle$	$p^\dagger_{1\uparrow} p^\dagger_{0\downarrow}\|0\rangle$ $p^\dagger_{0\uparrow} p^\dagger_{1\downarrow}\|0\rangle$	$p^\dagger_{1\downarrow} p^\dagger_{0\downarrow}\|0\rangle$
0	$p^\dagger_{1\uparrow} p^\dagger_{-1\uparrow}\|0\rangle$	$p^\dagger_{1\uparrow} p^\dagger_{-1\downarrow}\|0\rangle$ $p^\dagger_{0\uparrow} p^\dagger_{0\downarrow}\|0\rangle$ $p^\dagger_{-1\uparrow} p^\dagger_{1\downarrow}\|0\rangle$	$p^\dagger_{1\downarrow} p^\dagger_{-1\downarrow}\|0\rangle$
−1	$p^\dagger_{0\uparrow} p^\dagger_{-1\uparrow}\|0\rangle$	$p^\dagger_{0\uparrow} p^\dagger_{-1\downarrow}\|0\rangle$ $p^\dagger_{-1\uparrow} p^\dagger_{0\downarrow}\|0\rangle$	$p^\dagger_{0\downarrow} p^\dagger_{-1\downarrow}\|0\rangle$
−2		$p^\dagger_{-1\uparrow} p^\dagger_{-1\downarrow}\|0\rangle$	

^1D		$\Sigma = 0$
	2	$p^\dagger_{1\uparrow} p^\dagger_{1\downarrow}\ \|0\rangle$
	1	$\frac{1}{\sqrt{2}}\left(p^\dagger_{1\uparrow} p^\dagger_{0\downarrow} + p^\dagger_{0\uparrow} p^\dagger_{1\downarrow}\right)\|0\rangle$
M	0	$\frac{1}{\sqrt{6}}\left(p^\dagger_{1\uparrow} p^\dagger_{-1\downarrow} + 2p^\dagger_{0\uparrow} p^\dagger_{0\downarrow} + p^\dagger_{-1\uparrow} p^\dagger_{1\downarrow}\right)\|0\rangle$
	−1	$\frac{1}{\sqrt{2}}\left(p^\dagger_{0\uparrow} p^\dagger_{-1\downarrow} + p^\dagger_{-1\uparrow} p^\dagger_{0\downarrow}\right)\|0\rangle$
	−2	$p^\dagger_{-1\uparrow} p^\dagger_{-1\downarrow}\ \|0\rangle$

p^2 (^1S)

$$|0,0;\ 0,0\rangle \in \mathrm{span}\left\{p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow}|0\rangle,\ p^\dagger_{0\uparrow}p^\dagger_{0\downarrow}|0\rangle,\ p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}|0\rangle\right\}$$

$$\perp\ |1,0;\ 1,0\rangle_{^3P}$$

$$\perp\ |2,0;\ 0,0\rangle_{^1D}$$

	1	0	−1
2		$p^\dagger_{1\uparrow}p^\dagger_{1\downarrow}\vert 0\rangle$	
1	$p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}\vert 0\rangle$	$p^\dagger_{1\uparrow}p^\dagger_{0\downarrow}\vert 0\rangle$ $p^\dagger_{0\uparrow}p^\dagger_{1\downarrow}\vert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{0\downarrow}\vert 0\rangle$
0	$p^\dagger_{1\uparrow}p^\dagger_{-1\uparrow}\vert 0\rangle$	$p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow}\vert 0\rangle$ $p^\dagger_{0\uparrow}p^\dagger_{0\downarrow}\vert 0\rangle$ $p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\vert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{-1\downarrow}\vert 0\rangle$
−1	$p^\dagger_{0\uparrow}p^\dagger_{-1\uparrow}\vert 0\rangle$	$p^\dagger_{0\uparrow}p^\dagger_{-1\downarrow}\vert 0\rangle$ $p^\dagger_{-1\uparrow}p^\dagger_{0\downarrow}\vert 0\rangle$	$p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}\vert 0\rangle$
−2		$p^\dagger_{-1\uparrow}p^\dagger_{-1\downarrow}\vert 0\rangle$	

^1S

$$|0,0;\ 0,0\rangle = \frac{1}{\sqrt{3}}\left(-p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow} + p^\dagger_{0\uparrow}p^\dagger_{0\downarrow} - p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\right)|0\rangle$$

constructed all eigenstates of H_{ee} for p^2 shell

d^3 shell

M		$\frac{3}{2}$			$\frac{1}{2}$	
	5			^2H	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{2\downarrow}\|0\rangle$	
	4			^2G	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{1\downarrow}\|0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{2\downarrow}\|0\rangle$
	3	^4F	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}\|0\rangle$	^2F	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{1\downarrow}\|0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{2\downarrow}\|0\rangle$
M	2		$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}\|0\rangle$	$2\times{}^2D$	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{0\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow}\|0\rangle$	$d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{1\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}\|0\rangle$
	1	^4P	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}\|0\rangle$	^2P	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-2\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{0\downarrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{0\downarrow}\|0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{1\downarrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}\|0\rangle$ $d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}\|0\rangle$
	0		$d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-2\uparrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}\|0\rangle$		$d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-2\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{-1\downarrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\downarrow}\|0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{0\downarrow}\|0\rangle$	$d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{0\downarrow}\|0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{1\downarrow}\|0\rangle$ $d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow}\|0\rangle$ $d^\dagger_{0\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}\|0\rangle$

d^3 ($2\times\,^2D$)

$$|2,2;\ \tfrac{1}{2},\tfrac{1}{2}\rangle \in \mathrm{span}\left\{\begin{array}{l} d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\downarrow}|0\rangle,\ d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{0\downarrow}|0\rangle,\ d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow}|0\rangle \\ d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{1\downarrow}|0\rangle,\ d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}|0\rangle,\ d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}|0\rangle \end{array}\right\}$$

$$\perp\ |3,2;\ \tfrac{3}{2},\tfrac{1}{2}\rangle_{^4F}$$

$$\perp\ |5,2;\ \tfrac{1}{2},\tfrac{1}{2}\rangle_{^2H}$$

$$\perp\ |4,2;\ \tfrac{1}{2},\tfrac{1}{2}\rangle_{^2G}$$

$$\perp\ |3,2;\ \tfrac{1}{2},\tfrac{1}{2}\rangle_{^2F}$$

need to diagonalize H_{ee} on
two-dimensional subspace

way to uniquely define function?
seniority

seniority

s^0, s^2	^1S					
s^1		^2S				
p^0, p^6	^1S					
p^1, p^5		^2P				
p^2, p^4	^1S ^1D		^3P			
p^3		^2P ^2D		^4S		
d^0, d^6	^1S					
d^1, d^9		^2D				
d^2, d^8	^1S ^1D ^1G		^3P ^3F			
d^3, d^7		^2P $2\times\,^2D$ ^2F ^2G ^2H		^4P ^4F		
d^4, d^6	$2\times\,^1S$ $2\times\,^1D$ ^1F $2\times\,^1G$ ^1I		$2\times\,^3P$ ^3D $2\times\,^3F$ ^3G ^3H		^5D	
d^5		^2S ^2P $3\times\,^2D$ $2\times\,^2F$ $2\times\,^2G$ ^2H ^2I		^4P ^4D ^4F ^4G		^6S

Kramers pair (L=0, S=0)

$$-p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow} + p^\dagger_{0\uparrow}p^\dagger_{0\downarrow} - p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}$$

$$d^\dagger_{2\uparrow}d^\dagger_{-2\downarrow} - d^\dagger_{1\uparrow}d^\dagger_{-1\downarrow} + d^\dagger_{0\uparrow}d^\dagger_{0\downarrow} - d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow} + d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}$$

multiplet terms

p^0, p^6	${}^1S$							
p^1, p^5		${}^2P$						
p^2, p^4	${}^1S\ {}^1D$		${}^3P$					
p^3		${}^2P\ {}^2D$		${}^4S$				
d^0, d^6	${}^1S$							
d^1, d^9		${}^2D$						
d^2, d^8	${}^1S\ {}^1D\ {}^1G$		${}^3P\ {}^3F$					
d^3, d^7		${}^2P\ \overset{2\times}{{}^2D}\ {}^2F\ {}^2G\ {}^2H$		${}^4P\ {}^4F$				
d^4, d^6	$\overset{2\times}{{}^1S}\ \overset{2\times}{{}^1D}\ {}^1F\ \overset{2\times}{{}^1G}\ {}^1I$		$\overset{2\times}{{}^3P}\ {}^3D\ \overset{2\times}{{}^3F}\ {}^3G\ {}^3H$		${}^5D$			
d^5		${}^2S\ {}^2P\ \overset{3\times}{{}^2D}\ \overset{2\times}{{}^2F}\ \overset{2\times}{{}^2G}\ {}^2H\ {}^2I$		${}^4P\ {}^4D\ {}^4F\ {}^4G$		${}^6S$		
f^0, f^{14}	${}^1S$							
f^1, f^{13}		${}^2F$						
f^2, f^{12}	${}^1S\ {}^1D\ {}^1G\ {}^1I$		${}^3P\ {}^3F\ {}^3H$					
f^3, f^{11}		${}^2P\ \overset{2\times}{{}^2D}\ \overset{2\times}{{}^2F}\ \overset{2\times}{{}^2G}\ \overset{2\times}{{}^2H}\ {}^2I\ {}^2K\ {}^2L$		${}^4S\ {}^4D\ {}^4F\ {}^4G\ {}^4I$				
f^4, f^{10}	$\overset{2\times}{{}^1S}\ \overset{4\times}{{}^1D}\ {}^1F\ \overset{4\times}{{}^1G}\ \overset{2\times}{{}^1H}\ \overset{3\times}{{}^1I}\ {}^1K\ \overset{2\times}{{}^1L}\ {}^1N$		$\overset{3\times}{{}^3P}\ \overset{2\times}{{}^3D}\ \overset{4\times}{{}^3F}\ \overset{3\times}{{}^3G}\ \overset{4\times}{{}^3H}\ \overset{2\times}{{}^3I}\ \overset{2\times}{{}^3K}\ {}^3L\ {}^3M$		${}^5S\ {}^5D\ {}^5F\ {}^5G\ {}^5I$			
f^5, f^9		$\overset{4\times}{{}^2P}\ \overset{5\times}{{}^2D}\ \overset{7\times}{{}^2F}\ \overset{6\times}{{}^2G}\ \overset{7\times}{{}^2H}\ \overset{5\times}{{}^2I}\ \overset{5\times}{{}^2K}\ \overset{3\times}{{}^2L}\ \overset{2\times}{{}^2M}\ {}^2N\ {}^2O$		${}^4S\ \overset{2\times}{{}^4P}\ \overset{3\times}{{}^4D}\ \overset{4\times}{{}^4F}\ \overset{4\times}{{}^4G}\ \overset{3\times}{{}^4H}\ \overset{3\times}{{}^4I}\ \overset{2\times}{{}^4K}\ {}^4L\ {}^4M$		${}^6P\ {}^6F\ {}^6H$		
f^6, f^8	$\overset{4\times}{{}^1S}\ {}^1P\ \overset{6\times}{{}^1D}\ \overset{4\times}{{}^1F}\ \overset{8\times}{{}^1G}\ \overset{4\times}{{}^1H}\ \overset{7\times}{{}^1I}\ \overset{3\times}{{}^1K}\ \overset{4\times}{{}^1L}\ \overset{2\times}{{}^1M}\ \overset{2\times}{{}^1N}\ {}^1Q$		$\overset{6\times}{{}^3P}\ \overset{5\times}{{}^3D}\ \overset{9\times}{{}^3F}\ \overset{7\times}{{}^3G}\ \overset{9\times}{{}^3H}\ \overset{6\times}{{}^3I}\ \overset{6\times}{{}^3K}\ \overset{3\times}{{}^3L}\ \overset{3\times}{{}^3M}\ {}^3N\ {}^3O$		${}^5S\ {}^5P\ \overset{3\times}{{}^5D}\ \overset{2\times}{{}^5F}\ \overset{3\times}{{}^5G}\ \overset{2\times}{{}^5H}\ \overset{2\times}{{}^5I}\ {}^5K\ {}^5L$		${}^7F$	
f^5		$\overset{2\times}{{}^2S}\ \overset{5\times}{{}^2P}\ \overset{7\times}{{}^2D}\ \overset{10\times}{{}^2F}\ \overset{10\times}{{}^2G}\ \overset{9\times}{{}^2H}\ \overset{9\times}{{}^2I}\ \overset{7\times}{{}^2K}\ \overset{5\times}{{}^2L}\ \overset{4\times}{{}^2M}\ \overset{2\times}{{}^2N}\ {}^2O\ {}^2Q$		$\overset{2\times}{{}^4S}\ \overset{2\times}{{}^4P}\ \overset{6\times}{{}^4D}\ \overset{5\times}{{}^4F}\ \overset{7\times}{{}^4G}\ \overset{5\times}{{}^4H}\ \overset{5\times}{{}^4I}\ \overset{3\times}{{}^4K}\ \overset{3\times}{{}^4L}\ {}^4M\ {}^4N$		${}^6P\ {}^6D\ {}^6F\ {}^6G\ {}^6H\ {}^6I$		${}^8S$

Kramers pair $\sum_m (-1)^m c^\dagger_{n,l,m,\uparrow} c^\dagger_{n,l,-m,\downarrow}$

electron-hole symmetry

$\boldsymbol{p^0}$: $|0\rangle$

$\boldsymbol{p^6}$: $p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}\,|0\rangle =: |p^6\rangle$

vacuum state:

$p_{m\sigma}|0\rangle = 0$ and $\langle 0|0\rangle$

$p^\dagger_{m\sigma}|p^6\rangle = 0$ and $\langle p^6|p^6\rangle = 1$

$\boldsymbol{p^1}$: $p^\dagger_{0\uparrow}|0\rangle$

$\boldsymbol{p^5}$: $p_{0\uparrow}|p^6\rangle = -\,p^\dagger_{1\uparrow}\;\;p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}|0\rangle$

hole operator $h^\dagger_{n,l,-m,-\sigma} := (-1)^{l-m+1/2-\sigma}c_{n,l,m,\sigma}$

$$\prod_{m,\sigma}\left(c^\dagger_{n,l,m,\sigma}\right)^{n_{m,\sigma}}|0\rangle = \prod_{m,\sigma}\left(h^\dagger_{n,l,-m,-\sigma}\right)^{1-n_{m\sigma}}|\,l^{4l+2}\rangle$$

angular momentum operators have same form, e.g.

$$L_z = \sum_{m,\sigma} m\, c^\dagger_{n,l,m,\sigma}c_{n,l,m,\sigma} = \sum_{m,\sigma} m\, h_{n,l,-m,-\sigma}h^\dagger_{n,l,-m,-\sigma}$$

same construction of states in hole representation

recap: multiplet terms

- multiplet terms: vector addition & exclusion principle
  Racah: coefficients of fractional parentage
- second quantization: Dirac representation for many-body states
  can only represent physical states and operators
- use ladder operators to construct multiplet states
  - diagonalizes Hamiltonian when eigenstates of
    total angular momenta are non-degenerate
  - residual eigenvalue problem for degenerate angular momenta,
    (partially) classify degenerate states using seniority (Kramers pairs)
- electron-hole transformation establishes relation between shells
  with N and $(4l+2-N)$ electrons

so far only used angular momenta, next consider Hamiltonian…

two-body operators

$$H_{ee}(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

second quantization

$$\hat{H}_{ee} = \frac{1}{2} \int dx \int dx' \, \hat{\Psi}^\dagger(x) \hat{\Psi}^\dagger(x') \frac{1}{|\vec{r} - \vec{r}'|} \hat{\Psi}(x') \hat{\Psi}(x)$$

expand in orthonormal basis

$$\hat{H}_{ee} = \frac{1}{2} \sum_{n,n',m,m'} \underbrace{\int dx \int dx' \, \frac{\overline{\varphi_n(x)}\, \overline{\varphi_{n'}(x')}\, \varphi_{m'}(x') \varphi_m(x)}{|\vec{r} - \vec{r}'|}}_{=: \langle n, n' | H_{ee} | m', m \rangle} \; c_n^\dagger c_{n'}^\dagger c_{m'} c_m$$

orbitals: $\varphi_{n,l,m}(x) = \dfrac{u_{n,l}(r)}{r} Y_{l.m}(\vartheta, \varphi) \chi_\sigma$

addition theorem for spherical harmonics

express $\dfrac{1}{|\vec{r}-\vec{r}\,'|}$ in spherical coordinates

$$f(\vec{r},\vec{r}\,') = \sum_{l,m} a_{l,m}(r,\ r',\vartheta',\varphi')\,Y_{l,m}(\vartheta,\varphi)$$

$$= \sum_{l,m}\Big(\sum_{l',m'} a_{\substack{l,m,\\ l',m'}}(r,r')\,Y_{l',m'}(\vartheta',\varphi')\Big)Y_{l,m}(\vartheta,\varphi)$$

special case: singlet $\left(\vec{L}+\vec{L}\,'\right)s(\vec{r},\vec{r}\,') = 0$

$$s(\vec{r},\vec{r}\,') = \sum_{l=0}^{\infty} a_l(r,r')\sum_{m=-l}^{l}(-1)^m Y_{l,-m}(\vartheta',\varphi')\,Y_{l,m}(\vartheta,\varphi)$$

cf. Kramers singlet

$$= \sum_{l=0}^{\infty} a_l(r,r')\sum_{m=-l}^{l}\overline{Y_{l,m}(\vartheta',\varphi')}\,Y_{l,m}(\vartheta,\varphi)$$

$$s(\vec{r},r'\hat{z}) = \sum a_l(r,r')\sqrt{\frac{2l+1}{4\pi}}Y_{l,0}(\vartheta,\varphi) \quad \rightsquigarrow \quad a_l(r,r')$$

Legendre polynomials

generating function $$\frac{1}{\sqrt{1-2xt+t^2}} = \sum_{n=0}^{\infty} P_n(x)\, t^n$$

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \frac{1}{\sqrt{r^2-2\vec{r}\cdot\vec{r}\,'+r'^2}} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}}\, P_l(\hat{r}\cdot\hat{r}')$$

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \overline{Y_{l,m}(\vartheta',\varphi')}\, Y_{l,m}(\vartheta,\varphi)$$

matrix elements

$$\left\langle \alpha,\beta \middle| \frac{1}{|\vec r-\vec r\,'|} \middle| \gamma,\delta \right\rangle = \int d^3r\, d^3r'\, \overline{\varphi_\alpha(\vec r)}\, \overline{\varphi_\beta(\vec r\,')}\, \frac{1}{|\vec r-\vec r\,'|}\, \varphi_\gamma(\vec r\,')\varphi_\delta(\vec r)\; \delta_{\sigma_\alpha,\sigma_\delta}\, \delta_{\sigma_\beta,\sigma_\gamma}$$

$$= \sum_k F^{(k)}_{\alpha,\beta,\gamma,\delta}\, \frac{4\pi}{2k+1} \sum_{\mu=-k}^{k} \langle Y_\alpha | Y_{k,\mu}\, Y_\delta\rangle\, \langle Y_\beta Y_{k,\mu} | Y_\gamma\rangle\; \delta_{\sigma_\alpha,\sigma_\delta}\, \delta_{\sigma_\beta,\sigma_\gamma}$$

Slater-Condon parameters

$$F^{(k)}_{\alpha,\beta,\gamma,\delta} := \int_0^\infty dr\, \overline{u_\alpha(r)}\, u_\delta(r) \int_0^\infty dr'\, \overline{u_\beta(r')}\, u_\gamma(r')\; \frac{r_<^k}{r_>^{k+1}}$$

Gaunt coefficients

$$c^{(k,l,l')}_{m,m'} := \sqrt{\frac{4\pi}{2k+1}}\, \left\langle Y_{l,m} \middle| Y_{k,m-m'} Y_{l',m'} \right\rangle = (-1)^{m'} \sqrt{\frac{4\pi}{2k+1}}\, \left\langle Y_{k,m'-m} \middle| Y_{l,-m} Y_{l',m'} \right\rangle$$

$$\hat H_{ee} = \frac{1}{2} \sum_{m\sigma,m'\sigma'} \sum_{k=0,2,\ldots,2l} F^{(k)}_{n,l} \sum_{\Delta m=-k}^{k} c^{(k,l,l)}_{m+\Delta m,m}\, c^{(k,l,l)}_{m',m'-\Delta m}\; l^\dagger_{m+\Delta m,\sigma}\, l^\dagger_{m'-\Delta m,\sigma'}\, l_{m',\sigma'}\, l_{m,\sigma}$$

Gaunt coefficients

$$Y_{l,m}(\vartheta,\varphi)\,Y_{l',m'}(\vartheta,\varphi) = \sum_{k=0}^{\infty}\sum_{\mu=-k}^{k} \left\langle Y_{k,\mu}\middle|Y_{l,m}Y_{l',m'}\right\rangle Y_{k,\mu}(\vartheta,\varphi)$$

products behave like independent angular momenta
(but are not normalized)
(Wigner-Eckart theorem)

$$L_+\,Y_{lm}Y_{l'm'} = \left(L_+Y_{lm}\right)Y_{l'm'} + Y_{lm}\left(L_+Y_{l'm'}\right)$$

product rule

$$c_{m,m'}^{(2,2,2)} = \sqrt{\frac{4\pi}{5}}\langle Y_{2,m}|Y_{2,m-m'}Y_{2,m'}\rangle = \frac{1}{7}\begin{pmatrix} -2 & \sqrt{6} & -2 & 0 & 0 \\ -\sqrt{6} & 1 & 1 & -\sqrt{6} & 0 \\ -2 & -1 & 2 & -1 & -2 \\ 0 & -\sqrt{6} & 1 & 1 & -\sqrt{6} \\ 0 & 0 & -2 & \sqrt{6} & -2 \end{pmatrix}$$

tensor vs two-body matrix

$$\hat{H} = \frac{1}{2} \sum_{n,n',m,m'} M_{n,n';m,m'} \; c_n^\dagger c_{n'}^\dagger c_{m'} c_m$$

$$= \sum_{n'>n,m'>m} \left(M_{n,n';m,m'} - M_{n',n;m,m'} \right) c_n^\dagger c_{n'}^\dagger c_{m'} c_m$$

direct and exchange terms
each set of operators appears only once

$$\hat{H} = \begin{pmatrix} c_{2\uparrow} c_{1\uparrow} \\ c_{1\uparrow} c_{1\downarrow} \\ c_{1\uparrow} c_{2\downarrow} \\ c_{2\uparrow} c_{1\downarrow} \\ c_{2\uparrow} c_{2\downarrow} \\ c_{2\downarrow} c_{1\downarrow} \end{pmatrix}^\dagger \left(\begin{array}{c|c|c} \mathbf{H}_{\uparrow\uparrow} & & \\ \hline & \mathbf{H}_{\uparrow\downarrow} & \\ \hline & & \mathbf{H}_{\downarrow\downarrow} \end{array} \right) \begin{pmatrix} c_{2\uparrow} c_{1\uparrow} \\ c_{1\uparrow} c_{1\downarrow} \\ c_{1\uparrow} c_{2\downarrow} \\ c_{2\uparrow} c_{1\downarrow} \\ c_{2\uparrow} c_{2\downarrow} \\ c_{2\downarrow} c_{1\downarrow} \end{pmatrix}$$

average traces

$$U_{avg} := \frac{\mathrm{Tr}\,\mathbf{H}_{\uparrow\downarrow}}{\dim(\mathbf{H}_{\uparrow\downarrow})} = \frac{1}{(2l+1)^2}\sum_{m,m'} U_{m,m'} = F^{(0)}_{n,l}$$

$$U_{avg} - J_{avg} := \frac{\mathrm{Tr}\,\mathbf{H}_{\uparrow\uparrow} + \mathrm{Tr}\,\mathbf{H}_{\downarrow\downarrow}}{\dim(\mathbf{H}_{\uparrow\uparrow} + \dim(\mathbf{H}_{\downarrow\downarrow})} = \frac{1}{2l(2l+1)}\sum_{m,m'} \left(U_{m,m'} - J_{m,m'}\right)$$

average energy for *N* electrons in *K* = 2(2*l*+1) orbitals:

average trace of full Hamiltonian

$$\left\langle E(l^N)\right\rangle = \frac{N(N-1)}{2}\left(U_{avg} - \frac{2l}{4l+1}J_{avg}\right)$$

electron-hole relation:

$$E(K-N) = E(N) + \left(\frac{K-1}{2}U_{avg} - \frac{K-2}{4}J_{avg}\right)\left((K-N) - N\right)$$

recap: Hamiltonian

- 2-electron matrix elements
  expand interaction in spherical functions
  - addition theorem for spherical harmonics
  - generating function of Legendre polynomials
- Slater-Condon parameters
  electrostatic multipoles
- Gaunt coefficients
  Clebsch-Gordan/Wigner-Eckart
- collect all operators of same type:
  two-body matrix instead of tensor

theory $\longrightarrow$ practice

practical calculations

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

Multiplet calculation

s p d f

$F^{(0)}$ = 0.707209

$F^{(2)}$ = 0.323427

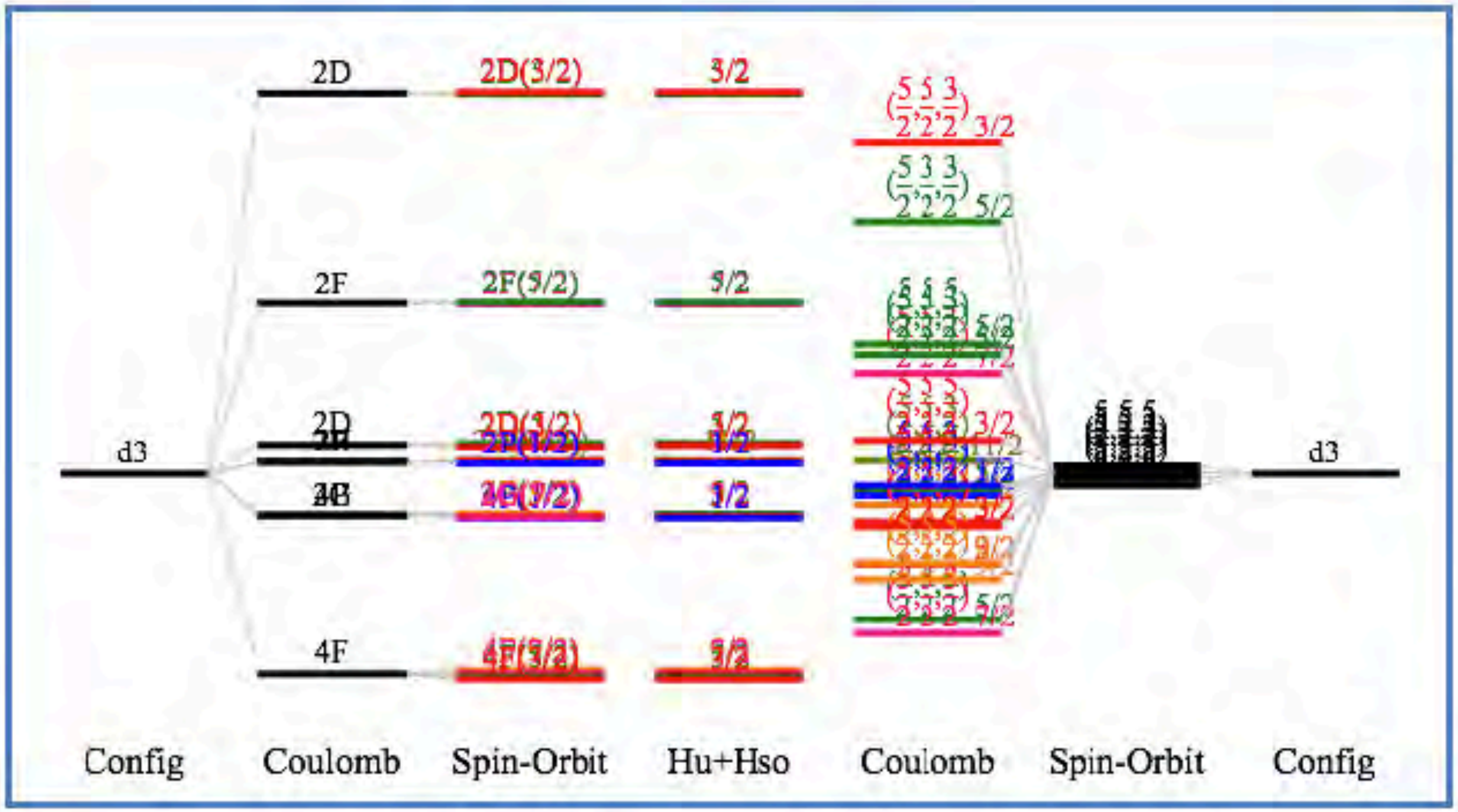
$F^{(4)}$ = 0.200450

$F^{(6)}$ =

SO = 0.001070

Number of e- = 3

Multiplet



^4F

$$E = F^{(0)}\left[3\right] + F^{(2)}\left[-\tfrac{15}{49}\right] + F^{(4)}\left[-\tfrac{8}{49}\right]$$

$$|3,\ 3, \frac{3}{2},\ \ \frac{3}{2}\rangle = c^\dagger_{0\uparrow} c^\dagger_{1\uparrow} c^\dagger_{2\uparrow} |0\rangle$$

$$|3,\ 3, \frac{3}{2},\ \ \frac{1}{2}\rangle = \frac{1}{\sqrt{3}}\left(c^\dagger_{2\downarrow} c^\dagger_{0\uparrow} c^\dagger_{1\uparrow} - c^\dagger_{1\downarrow} c^\dagger_{0\uparrow} c^\dagger_{2\uparrow} + c^\dagger_{0\downarrow} c^\dagger_{1\uparrow} c^\dagger_{2\uparrow}\right) |0\rangle$$