La structure électronique des matériaux

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Introduction

It is **not a classical problem** problem.

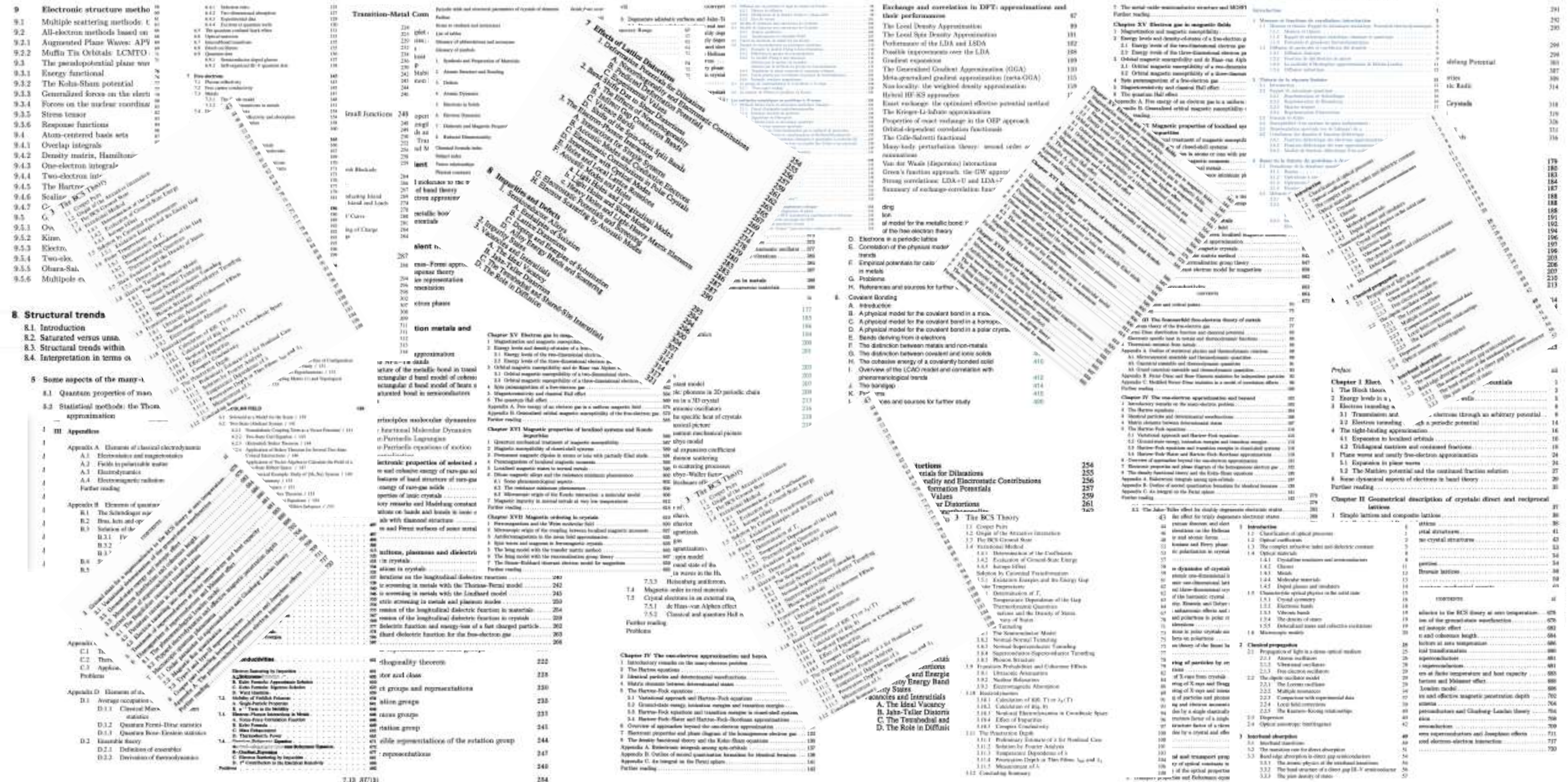
- Atoms cannot exist within classical electromagnetism
  - An electron revolving around a nuclei, must radiate, lose energy and decay.

- Materials (system of positive and negative charges) cannot exist with classical electromagnetism
  - Stable equilibrium cannot be reached in a system where the only interactions are electrostatic (Earnshaw's theorem)

Electronic properties

- We think in principle about : band structure, gap, density of states, simple excitations, ..
  - Electronic transport
  - Low temperature thermal transport in metals
  - Magnetism (the electron spin, origin of the effective electronic interactions, exchange, …)
  - Optics (adsorption, emission, luminescence, …)
  - Elastic properties (ductile, brittle, …)

Not included in this course



Summary

Slow discussion about concepts that one must understand and methods that one must manage
when one is interested on the electronic properties of
systems composed of atomic nuclei and electrons (molecules, solids, crystals, …)

- Entrée
  - The hydrogen atom to remember atomic orbitals
  - Multi-electron atoms to discuss the formation of shells and screening
  - A systems with two atoms and two electrons to discuss bonding

- Plat
  - Many atoms and many electrons
    - Methods and approximations neglecting the electron-electron interactions
      - Tight-binding method
      - Why some materials have an electronic gap
    - Methods and approximations taking into account the electron-electron interactions
      - Hartree
      - Hartree-Fock
      - Density Functional Theory

- Dessert
  - La *“surprise du chef “*

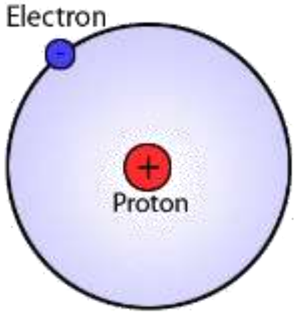
Entrée

Esqueixada
También con pimiento asado se elabora la esqueixada. Este plato frío, está hecho con bacalao desmigado y pimiento asado.
El contraste de sabores entre el bacalao salado, el dulzor del pimiento y el aceite de oliva hacen de este plato sencillo que los catalanes se sientan orgullosos.

The hydrogen atom

The hydrogen atom

$$H(\vec{r}) = -\frac{\hbar^2\nabla^2}{2m} - \frac{e^2}{r}$$



$$m = \frac{m_e m_p}{m_e + m_p}$$

The only physical quantity with units of length

$$a_0 = \frac{\hbar^2}{m_e\ e^2} = 0.5291\text{Å} = 1\ \text{bohr}$$

The only physical quantity with units of energy

$$E_0 = \frac{\hbar^2}{2\ m_e\ a_0^2} = 13.6\text{eV} = 1\ \text{Ry}$$

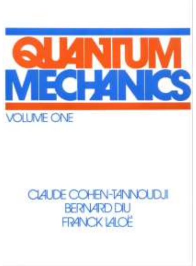
The Hamiltonian is rotational invariant we can use spherical coordinates

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi^2}$$

We search for

$$H(\vec{r})\ \varphi(\vec{r}) = E\ \varphi(\vec{r})$$

The hydrogen atom



The eigen-functions

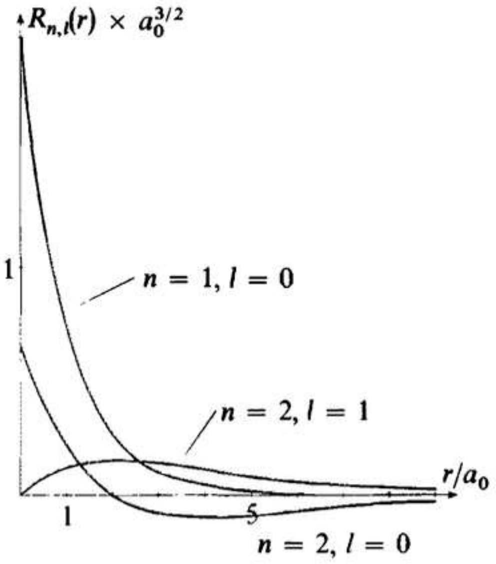
$$\varphi_{nlm}(r,\theta,\phi) = \underbrace{R_{nl}(r)}_{R_{nl}(r)\simeq r^l} \quad \underbrace{P_{lm}(\theta)\; e^{im\phi}}_{Y_{lm}(\theta,\phi)}$$

$r \rightarrow 0$

Spherical harmonics

n	Principal quantum number
l	Azimutal …
m	Magnetic …

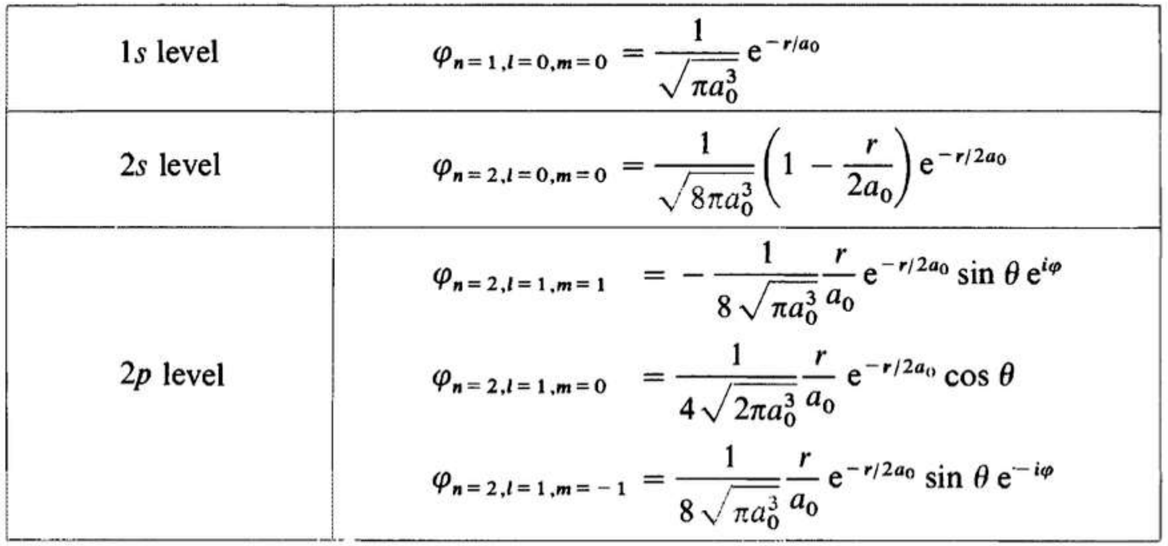
$$n = 1, 2, \ldots\infty$$
$$0 \leq l \leq n-1$$
$$-l \leq m \leq l$$



nodes in r	$n-l-1$
nodes in θ	$l-m$
nodes in ϕ	m
total	$n-1$

FIGURE 6

Radial dependence $R_{n,l}(r)$ of wave functions associated with the first few levels of the hydrogen atom. When $r \longrightarrow 0$, $R_{n,l}(r)$ behaves like r^l; only the s states (for which $l = 0$) have a non-zero position probability at the origin.



1s level	$\varphi_{n=1,l=0,m=0} = \dfrac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$
2s level	$\varphi_{n=2,l=0,m=0} = \dfrac{1}{\sqrt{8\pi a_0^3}}\left(1 - \dfrac{r}{2a_0}\right) e^{-r/2a_0}$
2p level	$\varphi_{n=2,l=1,m=1} = -\dfrac{1}{8\sqrt{\pi a_0^3}}\dfrac{r}{a_0}\, e^{-r/2a_0} \sin\theta\, e^{i\varphi}$ $\varphi_{n=2,l=1,m=0} = \dfrac{1}{4\sqrt{2\pi a_0^3}}\dfrac{r}{a_0}\, e^{-r/2a_0} \cos\theta$ $\varphi_{n=2,l=1,m=-1} = \dfrac{1}{8\sqrt{\pi a_0^3}}\dfrac{r}{a_0}\, e^{-r/2a_0} \sin\theta\, e^{-i\varphi}$

$$< r_{nlm} >= a_0 \frac{3n^2 - l(l+1)}{2}$$

The hydrogen atom

The eigen-energies

$$E_{nlm} = -\frac{E_0}{n^2}$$

n Principal quantum number

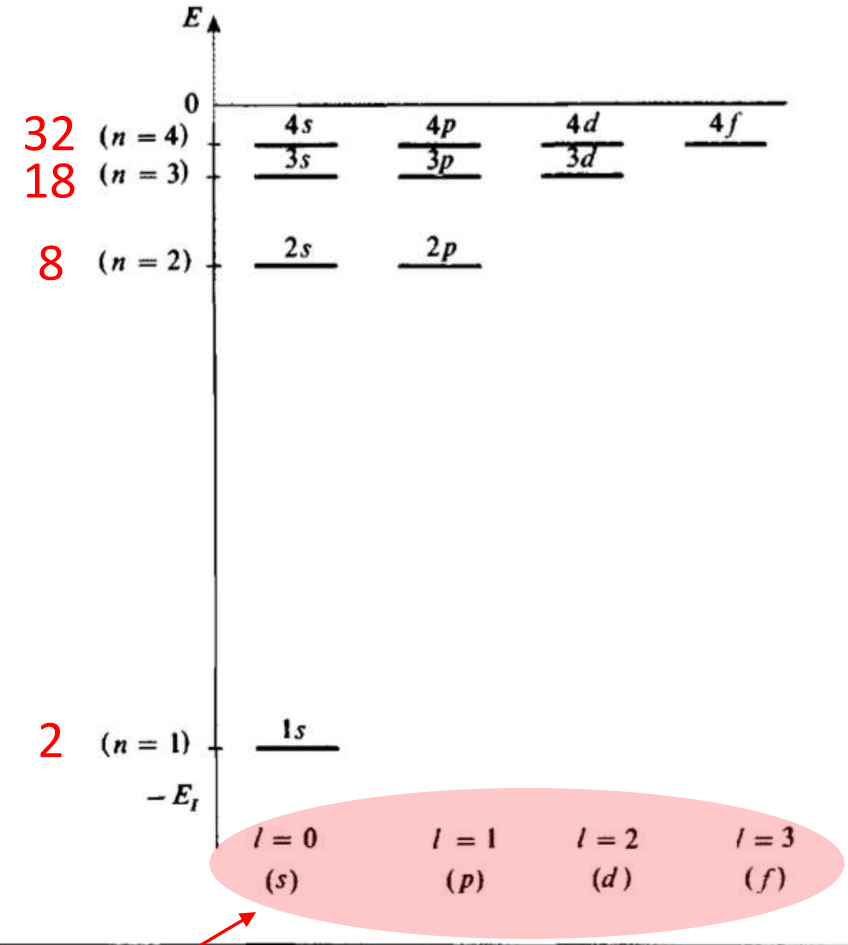
l Azimutal …

m Magnetic …

$$n = 1, 2, \ldots \infty$$

$$0 \leq l \leq n - 1$$

$$-l \leq m \leq l$$



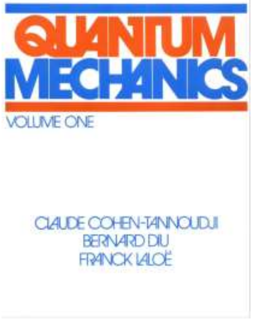


FIGURE 4

Energy levels of the hydrogen atom. The energy E_n of each level depends only on n. If n is fixed, several values of l are possible : $l = 0, 1, 2, \ldots, n - 1$. To each of these values of l correspond $(2l + 1)$ possible values for m :

$$m = -l, -l + 1, \ldots, l.$$

Consequently, the level E_n is n^2-fold degenerate.

Notation

Highly degenerate levels

$$g_n = \sum_{l=0}^{n-1} (2l + 1) = 2\frac{(n - 1)n}{2} + n = n^2$$

Spin → 2x

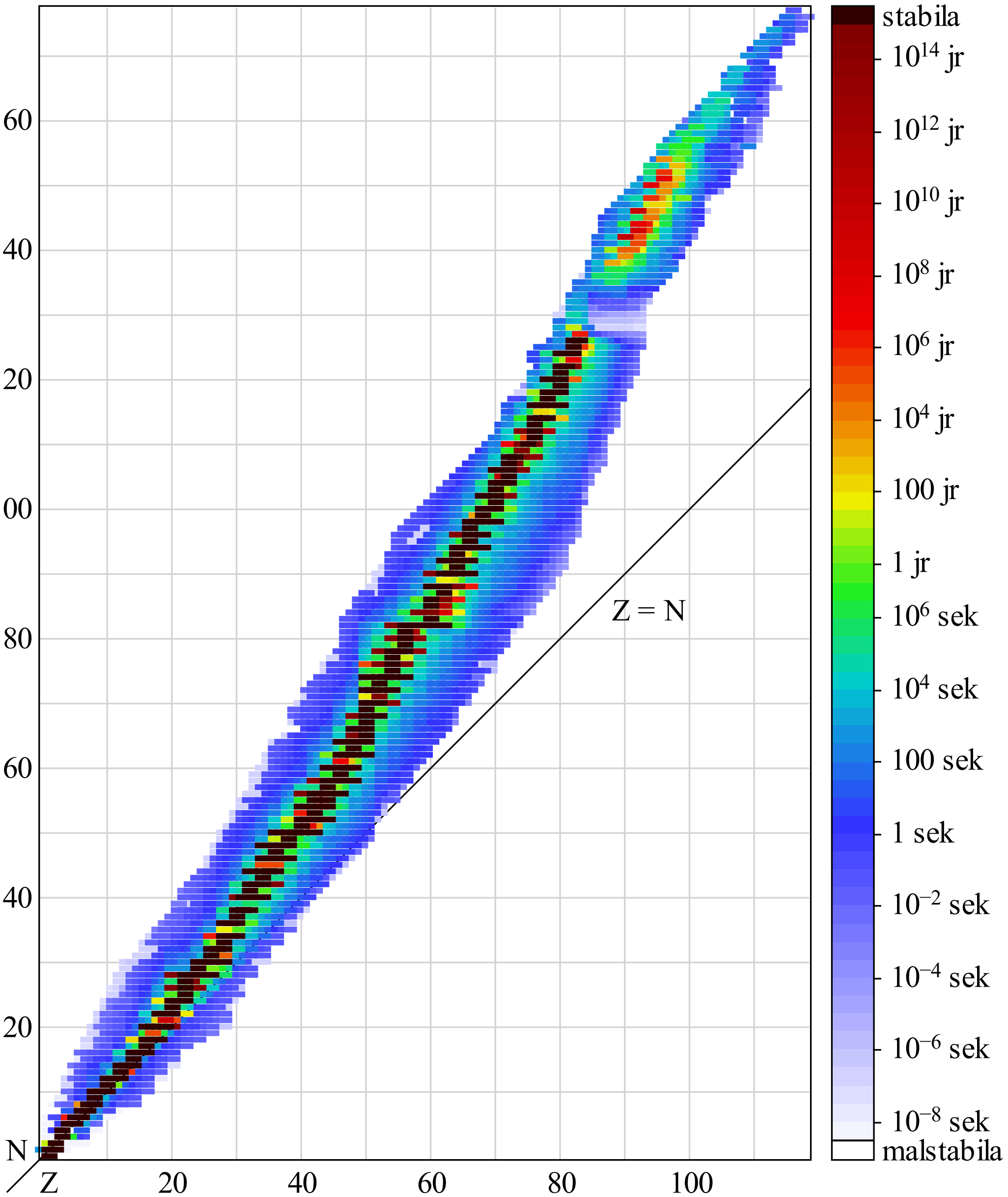
Multi-electron atoms

Multi-electron atom

Composed of

N	neutrons
Z	protons
Z	electrons

$$N \geq Z$$



Multi-electron atom without e-e interaction (*hydrogenic)*

$$H(\{\vec{r_\alpha}\}) = \underbrace{-\frac{\hbar^2}{2m}\sum_\alpha \nabla_\alpha^2}_{\text{Kinetic}} \underbrace{- Z\ e^2 \sum_\alpha \frac{1}{r_\alpha}}_{\text{Coulomb e-nucleus}} + e^2 \xcancel{\underbrace{\sum_{\alpha,\beta} \frac{1}{|\vec{r}_\alpha - \vec{r}_\beta|}}_{\text{Electron-electron}}}$$

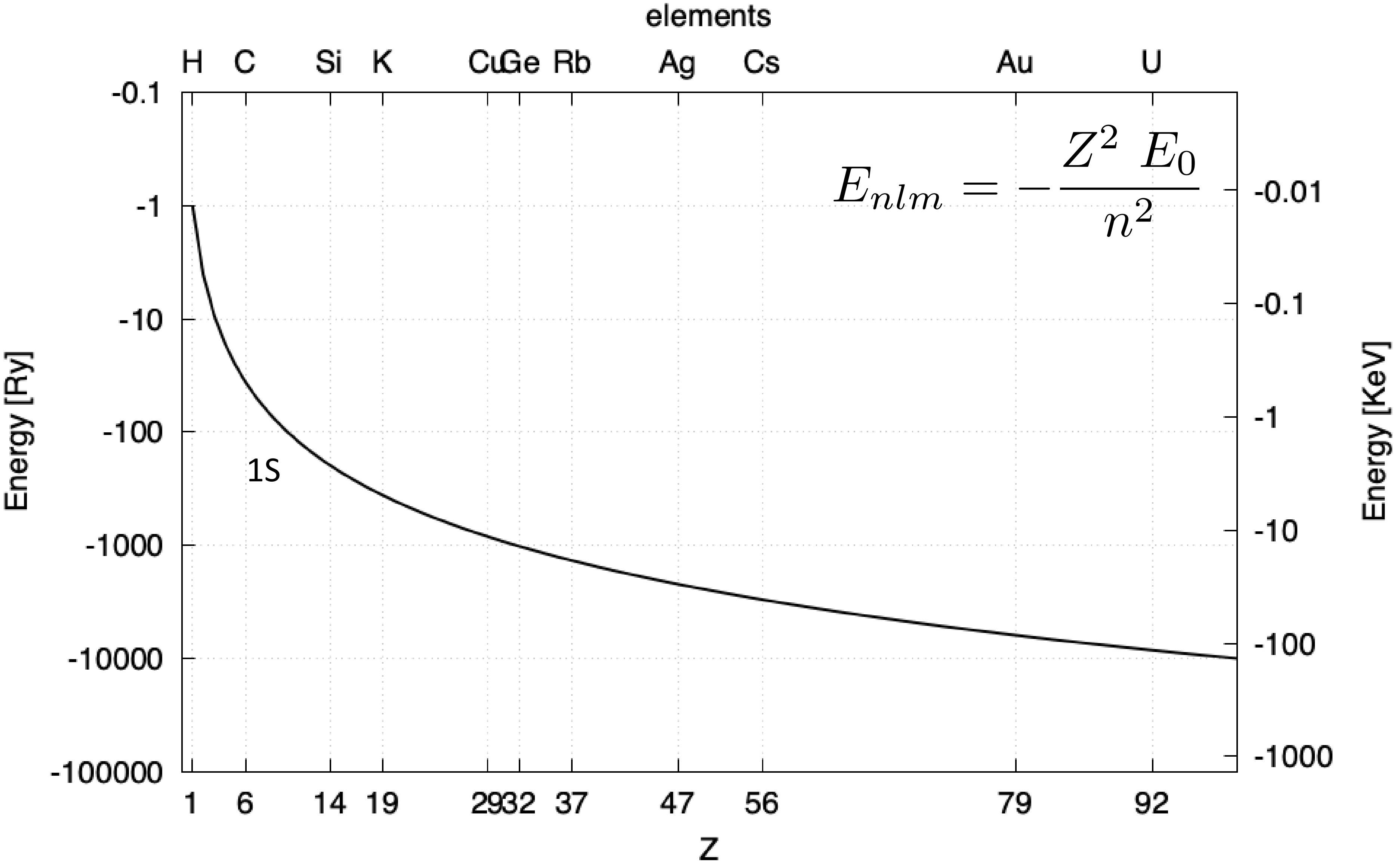
Same solution than the hydrogen atom but with

$$e^2 \rightarrow Ze^2$$

$$a_0 \rightarrow \frac{a_0}{Z}$$

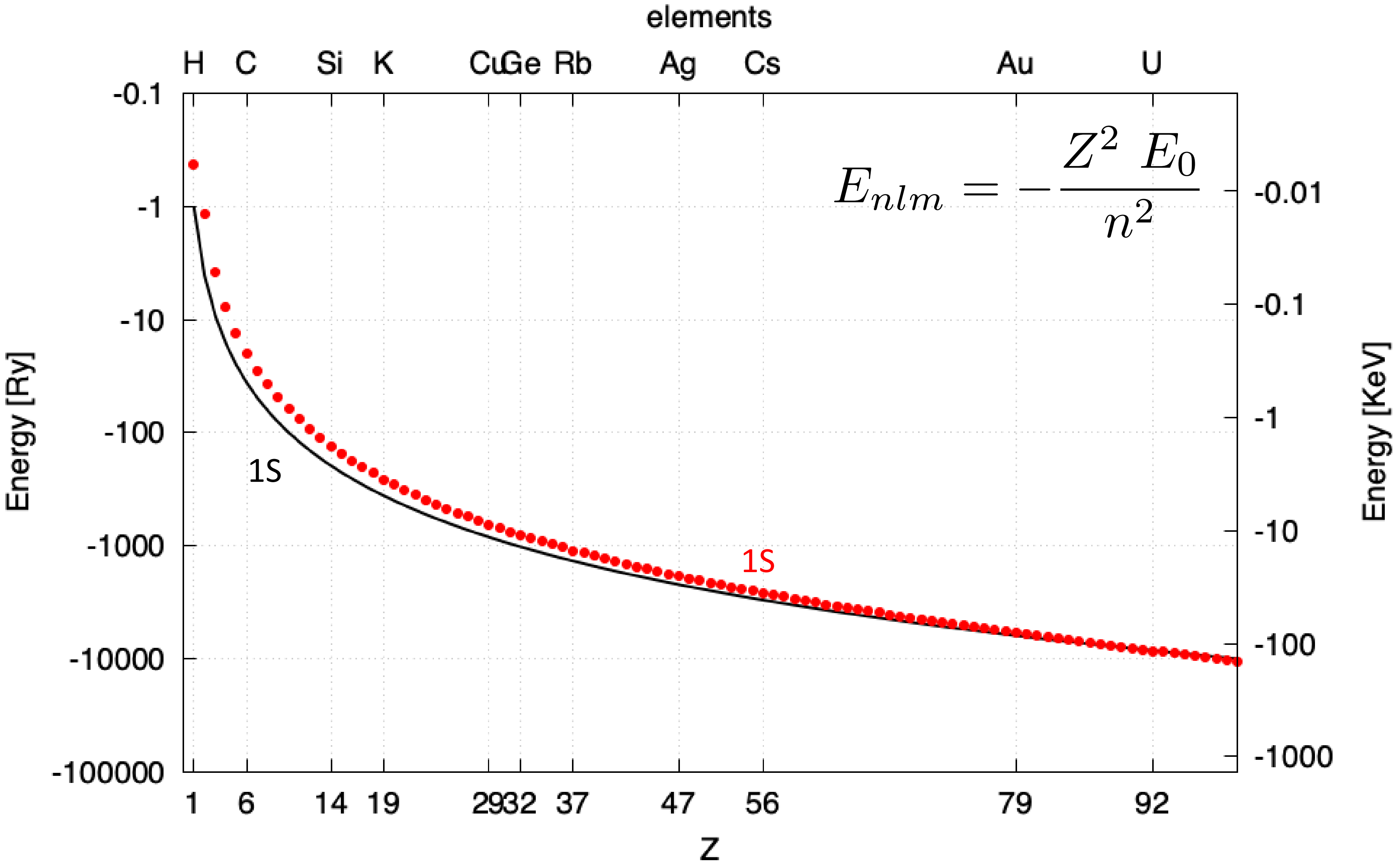
$$E_0 \rightarrow Z^2 E_0$$

Multi-electron atom *without* e-e interaction (*hydrogenic*)



The energy of 1s orbital for the *hydrogenic* atom decreases when the number of protons Z increases.

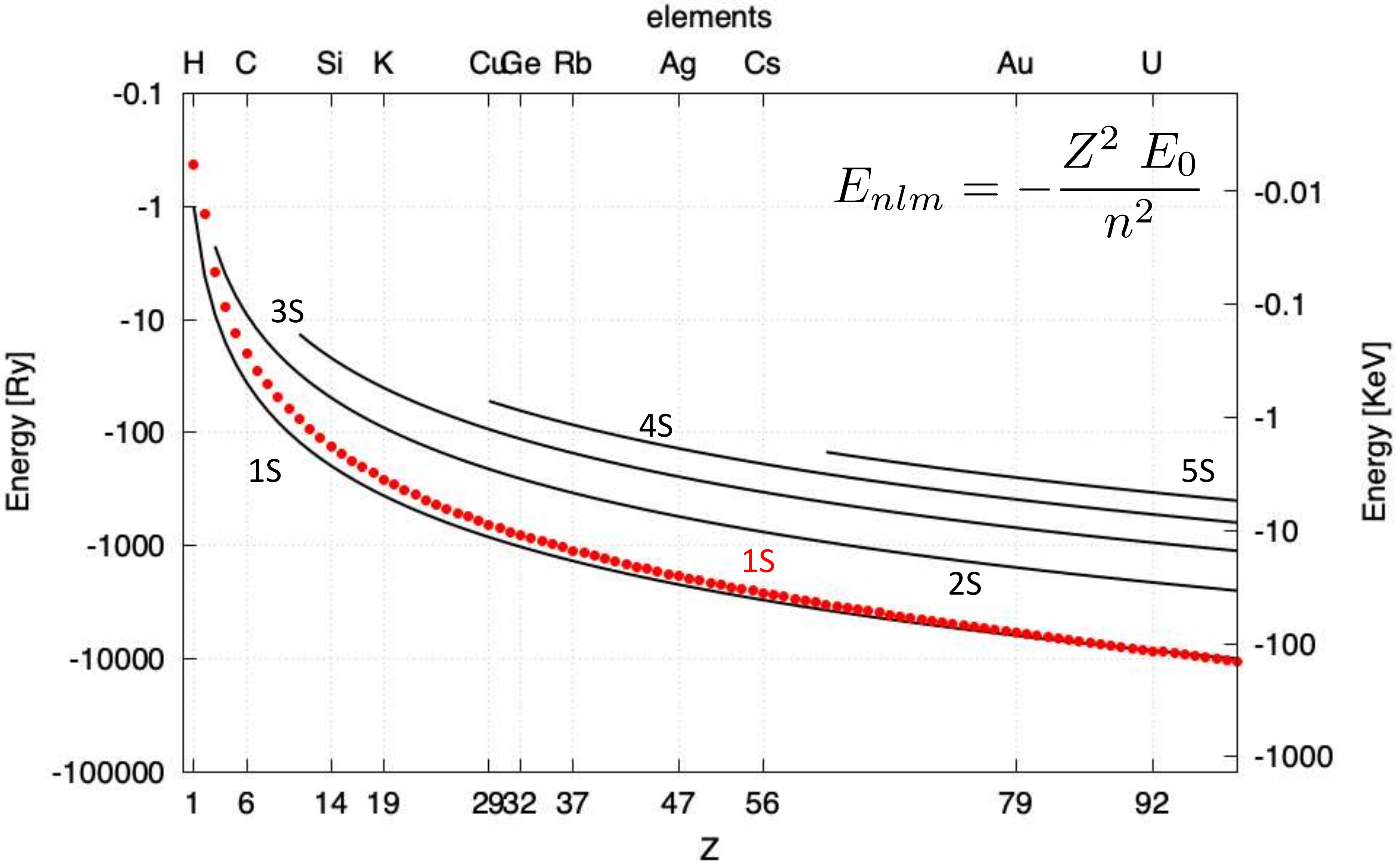
Multi-electron atom without e-e interaction (*hydrogenic*)



$$E_{nlm} = -\frac{Z^2\ E_0}{n^2}$$

It compares pretty well with the calculated energy of the 1s orbital when one includesthe e-e interaction

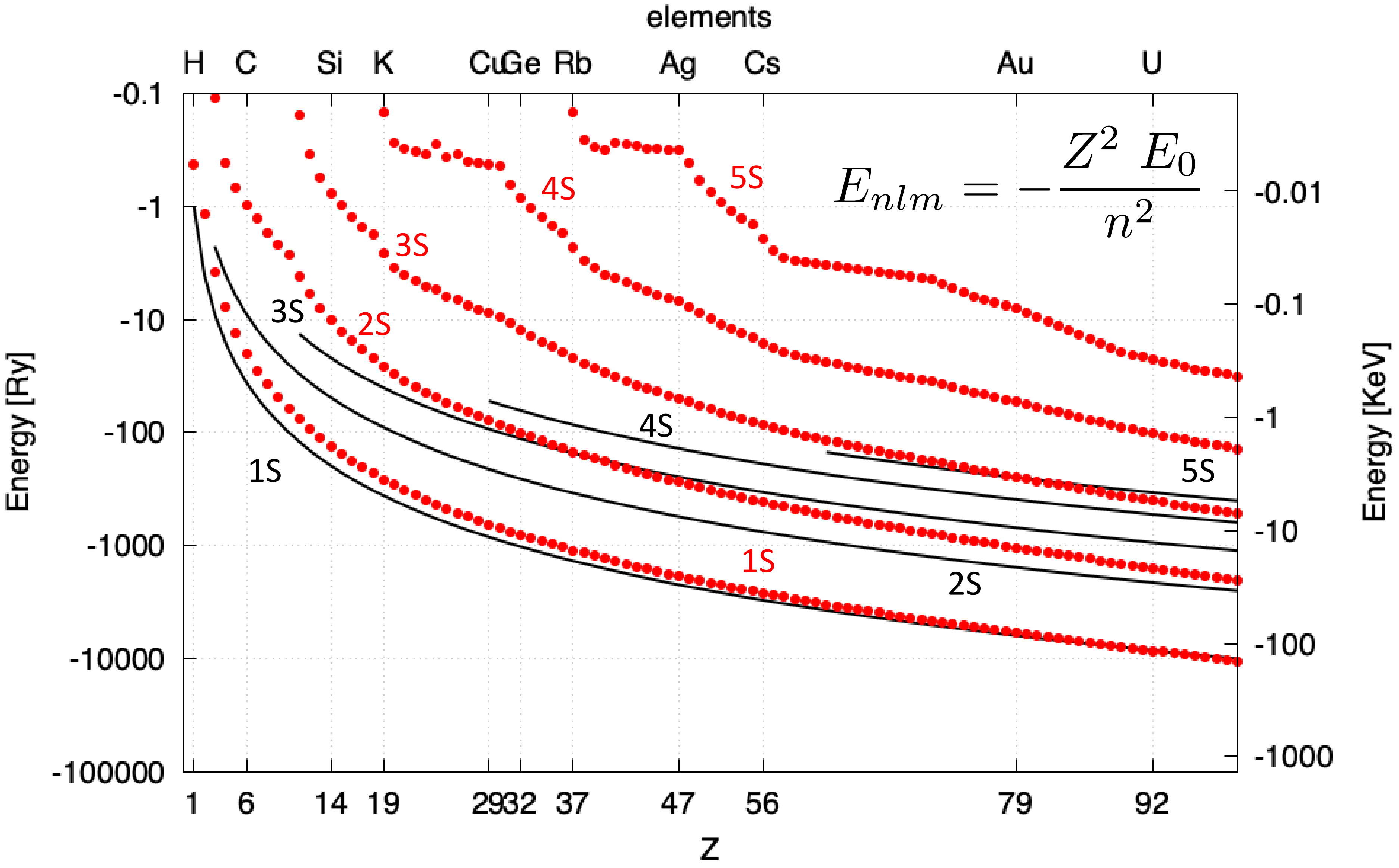
Multi-electron atom without e-e interaction (*hydrogenic)*



$$E_{nlm} = -\frac{Z^2\ E_0}{n^2}$$

The energy of ns orbitals for the *hydrogenic* slowly increases when n increases

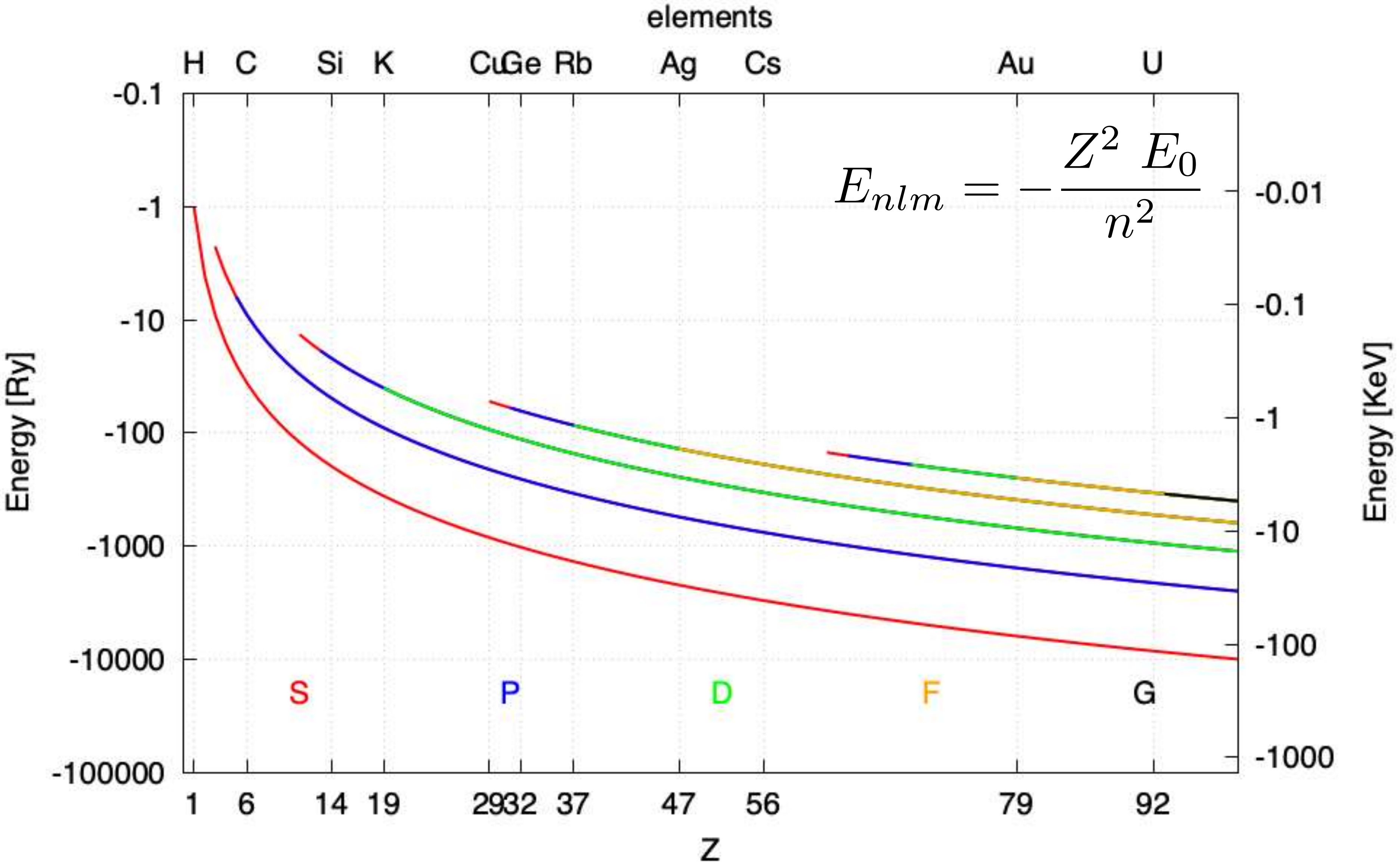
Multi-electron atom without e-e interaction (*hydrogenic)*



$$E_{nlm} = -\frac{Z^2\ E_0}{n^2}$$

The calculated energies increases much faster with n due to the screening of the core electrons

Multi-electron atom without e-e interaction (*hydrogenic)*

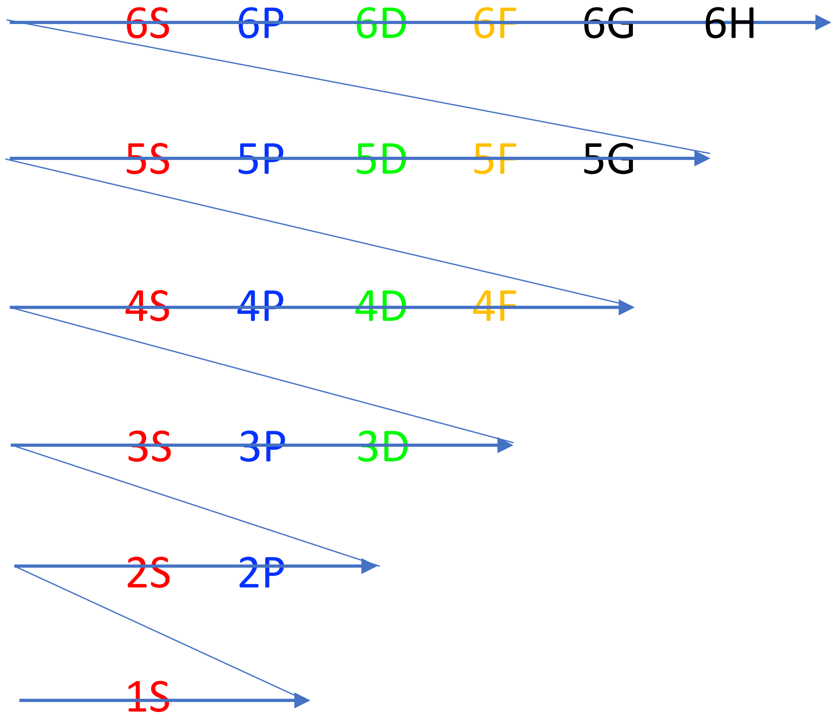


$$E_{nlm} = -\frac{Z^2\ E_0}{n^2}$$

The energies of the *hydrogenic* atom are highly degenerate

Filling is different

Without e-e interaction
Same degeneracy than the H atom



6S 6P 6D 6F 6G 6H

5S 5P 5D 5F 5G

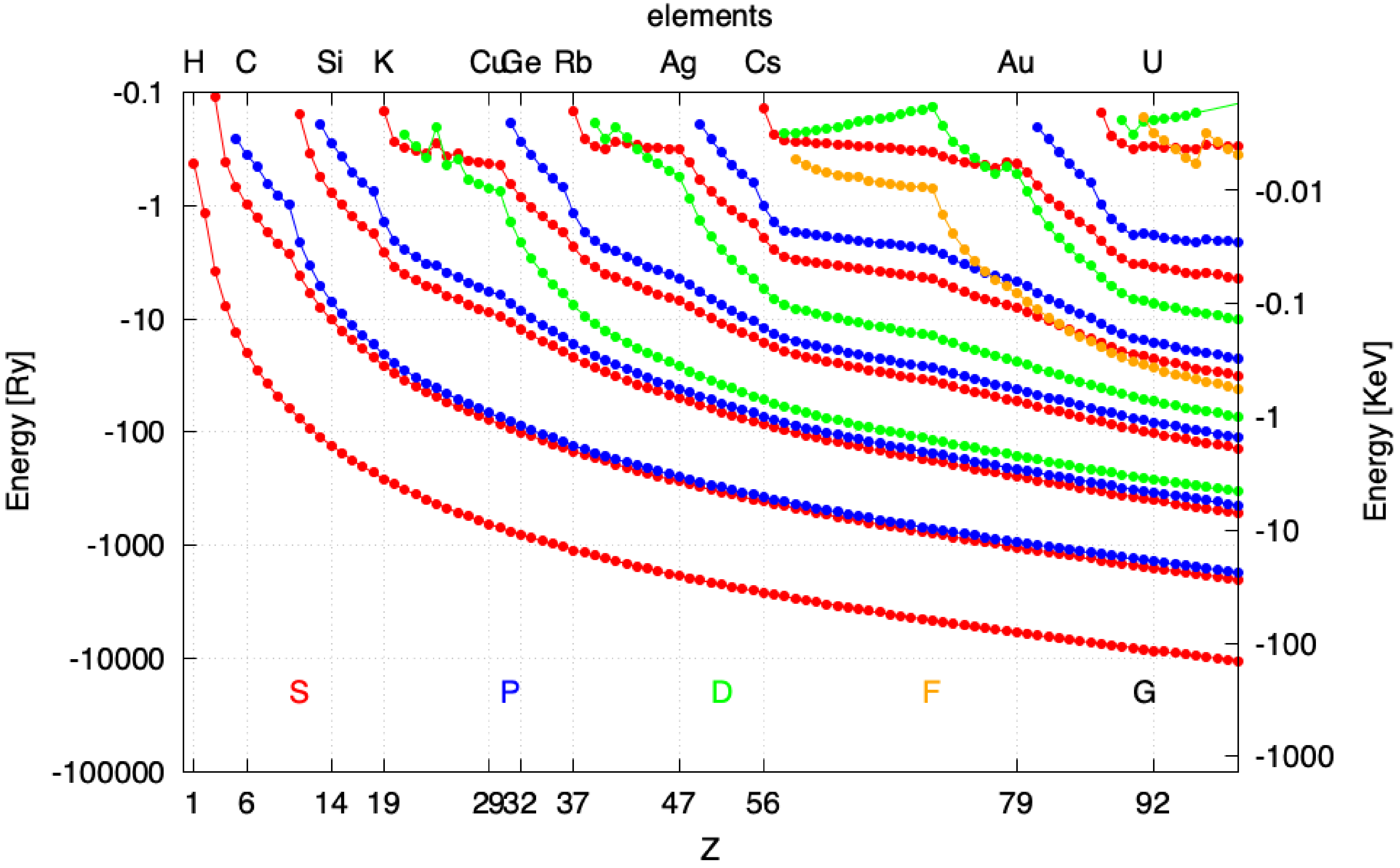
4S 4P 4D 4F

3S 3P 3D

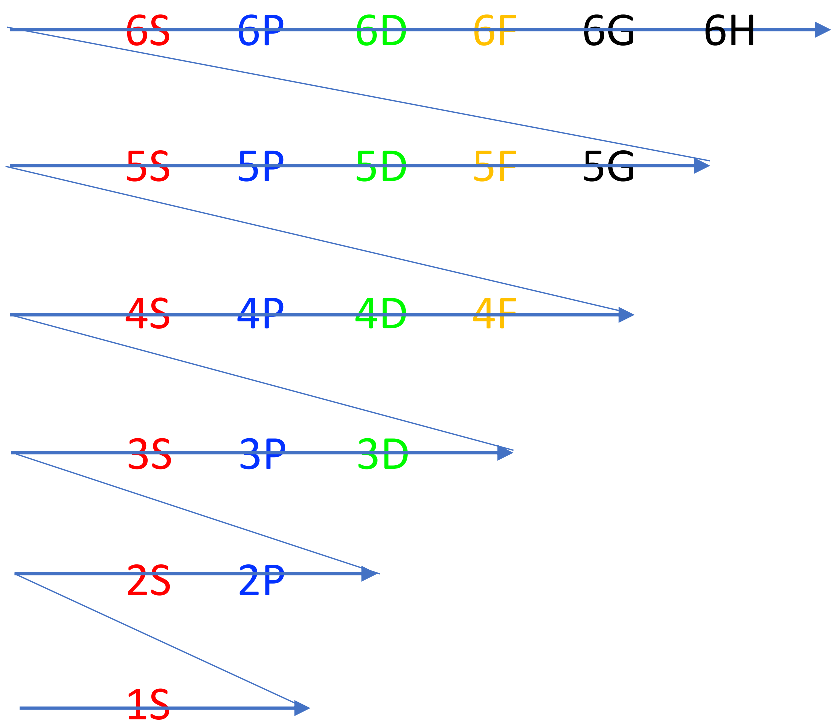
2S 2P

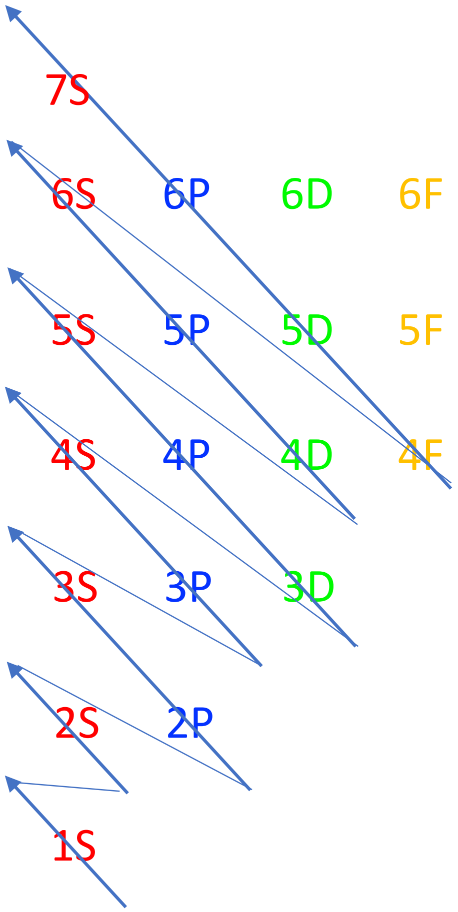
1S

Multi-electron atom with e-e interaction



Filling is different


Without e-e interaction
Same degeneracy than the H atom


With e-e interaction
Levels with different l and same n have different energy

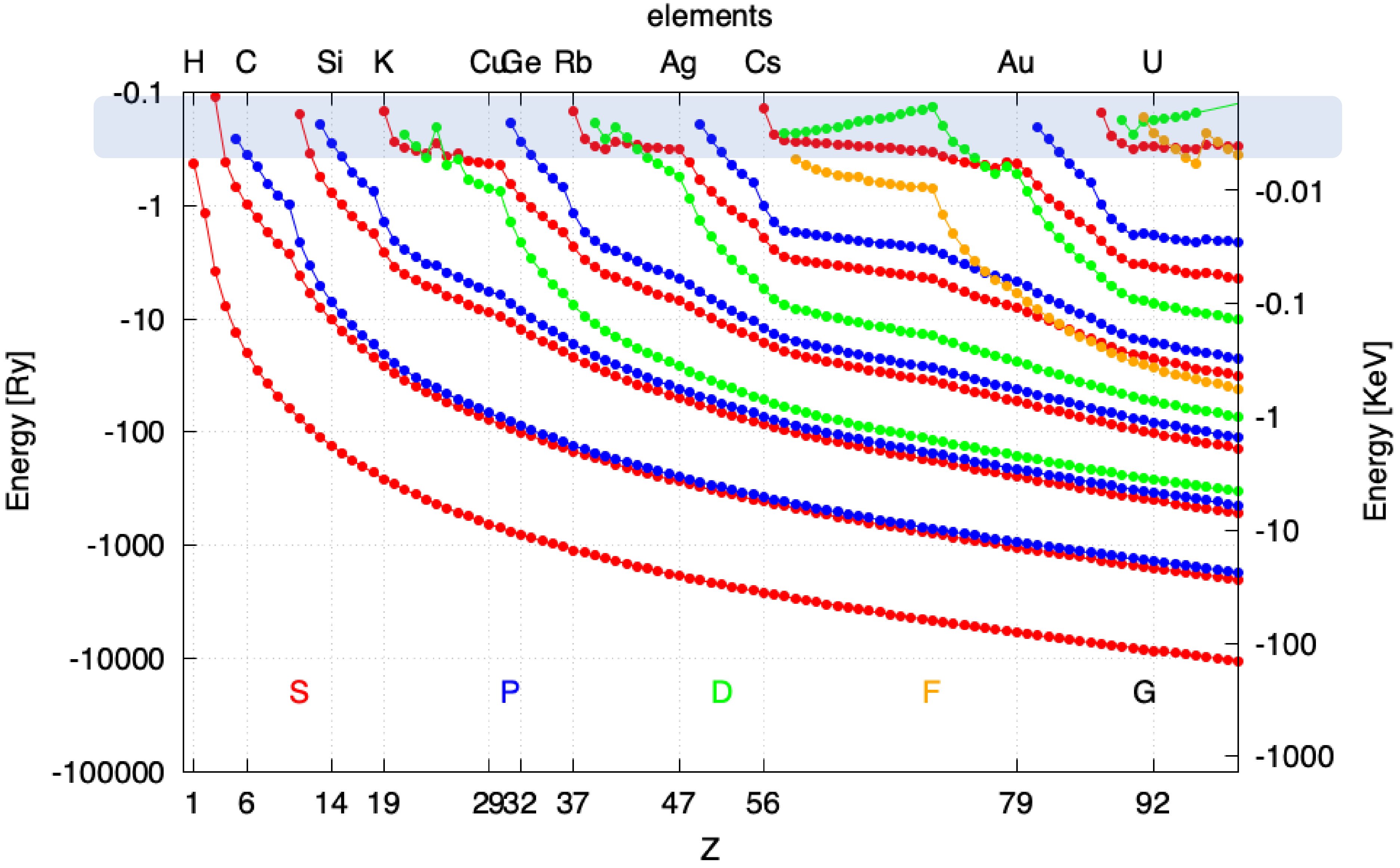
Periodic table of elements

Periodic Table of the Elements

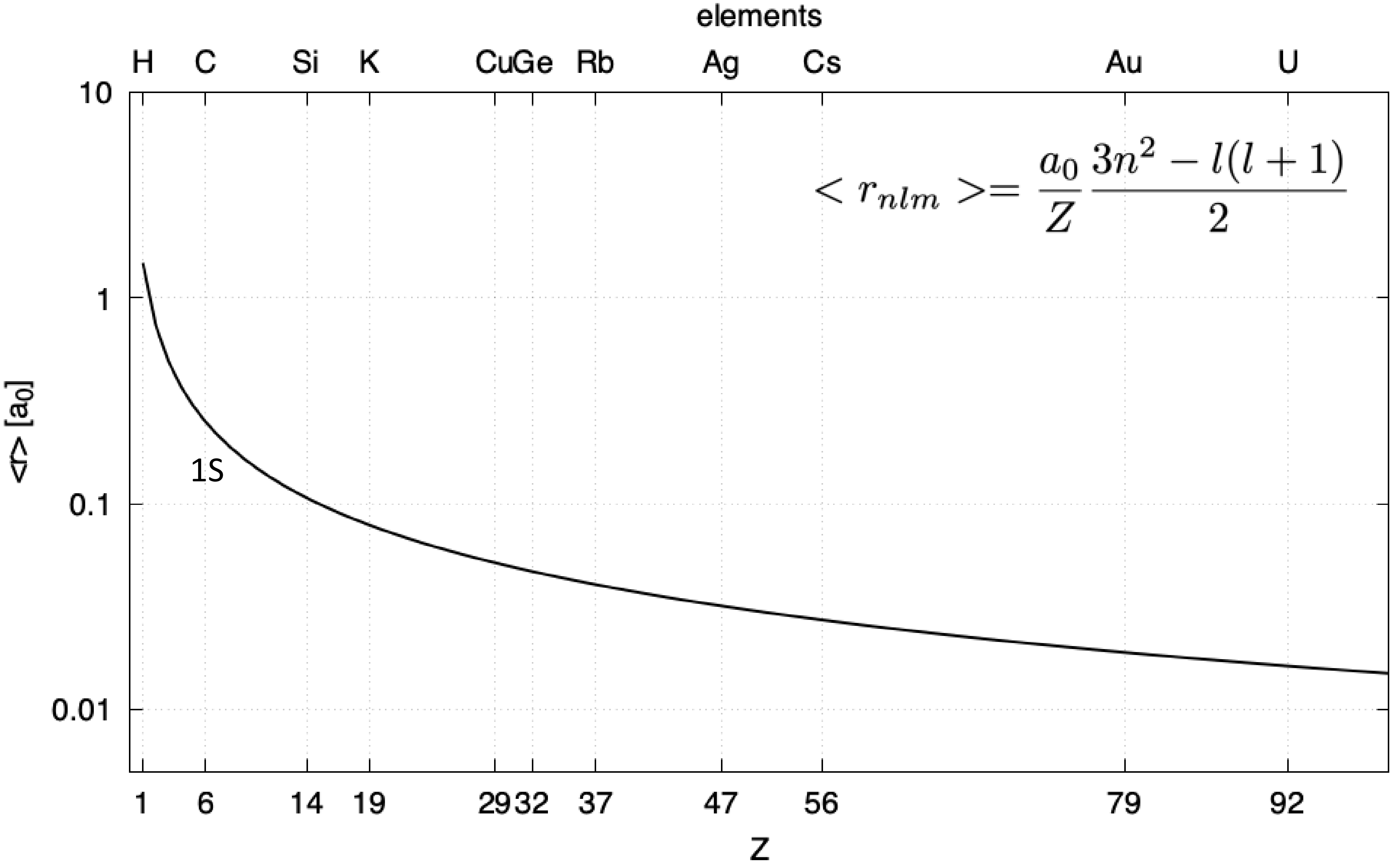
1**H** 1s																	2**He** 1s^{2}
3**Li** He2s	4**Be** He2s^{2}											5**B** He2s^{2}2p	6**C** He2s^{2}2p^{2}	7**N** He2s^{2}2p^{3}	8**O** He2s^{2}2p^{4}	9**F** He2s^{2}2p^{5}	10**Ne** He2s^{2}2p^{6}
11**Na** Ne3s	12**Mg** Ne3s^{2}											13**Al** Ne3s^{2}3p	14**Si** Ne3s^{2}3p^{2}	15**P** Ne3s^{2}3p^{3}	16**S** Ne3s^{2}3p^{4}	17**Cl** Ne3s^{2}3p^{5}	18**Ar** Ne3s^{2}3p^{6}
19**K** Ar4s	20**Ca** Ar4s^{2}	21**Sc** Ar3d^{1}4s^{2}	22**Ti** Ar3d^{2}4s^{2}	23**V** Ar3d^{3}4s^{2}	24**Cr** Ar3d^{5}4s^{1}	25**Mn** Ar3d^{5}4s^{2}	26**Fe** Ar3d^{6}4s^{2}	27**Co** Ar3d^{7}4s^{2}	28**Ni** Ar3d^{8}4s^{2}	29**Cu** Ar3d^{10}4s^{1}	30**Zn** Ar3d^{10}4s^{2}	31**Ga** Ar3d^{10}4s^{2}4p	32**Ge** Ar3d^{10}4s^{2}4p^{2}	33**As** Ar3d^{10}4s^{2}4p^{3}	34**Se** Ar3d^{10}4s^{2}4p^{4}	35**Br** Ar3d^{10}4s^{2}4p^{5}	36**Kr** Ar3d^{10}4s^{2}4p^{6}
37**Rb** Kr5s	38**Sr** Kr5s^{2}	39**Y** Kr4d^{1}5s^{2}	40**Zr** Kr4d^{2}5s^{2}	41**Nb** Kr4d^{3}5s^{2}	42**Mo** Kr4d^{5}5s^{1}	43**Tc** Kr4d^{5}5s^{2}	44**Ru** Kr4d^{6}5s^{2}	45**Rh** Kr4d^{7}5s^{2}	46**Pd** Kr4d^{8}5s^{2}	47**Ag** Kr4d^{10}5s^{1}	48**Cd** Kr4d^{10}5s^{2}	49**In** Kr4d^{10}5s^{2}5p	50**Sn** Kr4d^{10}5s^{2}5p^{2}	51**Sb** Kr4d^{10}5s^{2}5p^{3}	52**Te** Kr3d^{10}5s^{2}5p^{4}	53**I** Kr4d^{10}5s^{2}5p^{5}	54**Xe** Kr4d^{10}5s^{2}5p^{6}
55**Cs** Xe6s	56**Ba** Xe6s^{2}	57-71 **La-Lu**	72**Hf** Xe4f^{14}5d^{2}6s^{2}	73**Ta** Xe4f^{14}5d^{3}6s^{2}	74**W** Xe4f^{14}5d^{5}6s^{1}	75**Re** Xe4f^{14}5d^{5}6s^{2}	76**Os** Xe4f^{14}5d^{6}6s^{2}	77**Ir** Xe4f^{14}5d^{7}6s^{2}	78**Pt** Xe4f^{14}5d^{8}6s^{2}	79**Au** Xe4f^{14}5d^{10}6s^{1}	80**Hg** Xe4f^{14}5d^{10}6s^{2}	81**Tl** Xe4f^{14}5d^{10}6s^{2}6p	82**Pb** Xe4f^{14}5d^{10}6s^{2}6p^{2}	83**Bi** Xe4f^{14}5d^{10}6s^{2}6p^{3}	84**Po** Xe4f^{14}3d^{10}6s^{2}6p^{4}	85**At** Xe4f^{14}5d^{10}6s^{2}6p^{5}	86**Rn** Xe4f^{14}5d^{10}6s^{2}6p^{6}
87**Fr** Rn7s	88**Ra** Rn7s^{2}	89-103 **Ac-Lr**															

57**La** Xe5d6s^{2}	58**Ce** Xe4f^{2}6s^{2}	59**Pr** Xe4f^{3}6s^{2}	60**Nd** Xe4f^{4}6s^{2}	61**Pm** Xe4f^{5}6s^{2}	62**Sm** Xe4f^{6}6s^{2}	63**Eu** Xe4f^{7}6s^{2}	64**Gd** Xe4f^{7}5d6s^{2}	65**Tb** Xe4f^{9}6s^{2}	66**Dy** Xe4f^{10}6s^{2}	67**Ho** Xe4f^{11}6s^{2}	68**Er** Xe4f^{12}6s^{2}	69**Tm** Xe4f^{13}6s^{2}	70**Yb** Xe4f^{14}6s^{2}	71**Lu** Xe4f^{14}5d6s^{2}
89**Ac** Rn6d7s^{2}	90**Th** Rn6d^{2}7s^{2}	91**Pa** Rn5f^{2}6d^{1}7s^{2}	92**U** Rn5f^{3}6d^{1}7s^{2}	93**Np** Rn5f^{4}6d^{1}7s^{2}	94**Pu** Rn5f^{6}7s^{2}	95**Am** Rn5f^{7}7s^{2}	96**Cm** Rn5f^{7}6d7s^{2}	97**Bk** Rn5f^{9}7s^{2}	98**Cf** Rn5f^{10}7s^{2}	99**Es** Rn5f^{11}7s^{2}	100**Fm** Rn5f^{12}7s^{2}	101**Md** Rn5f^{13}7s^{2}	102**No** Rn5f^{14}7s^{2}	103**Lr** Rn5f^{14}6d7s^{2}

Multi-electron atom with e-e interaction



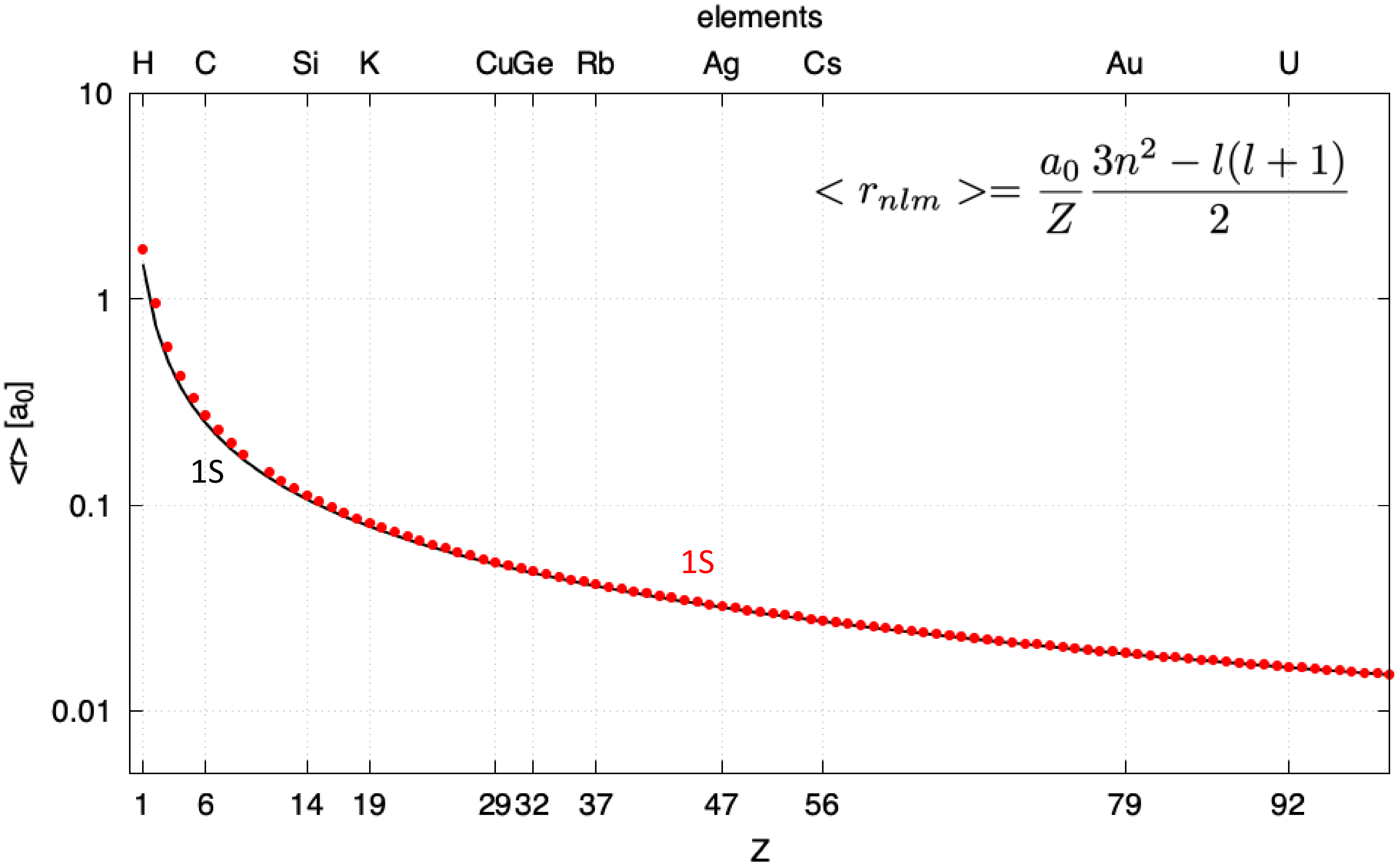
Multi-electron atom without e-e interaction (*hydrogenic*)



$$< r_{nlm} >= \frac{a_0}{Z}\frac{3n^2 - l(l+1)}{2}$$

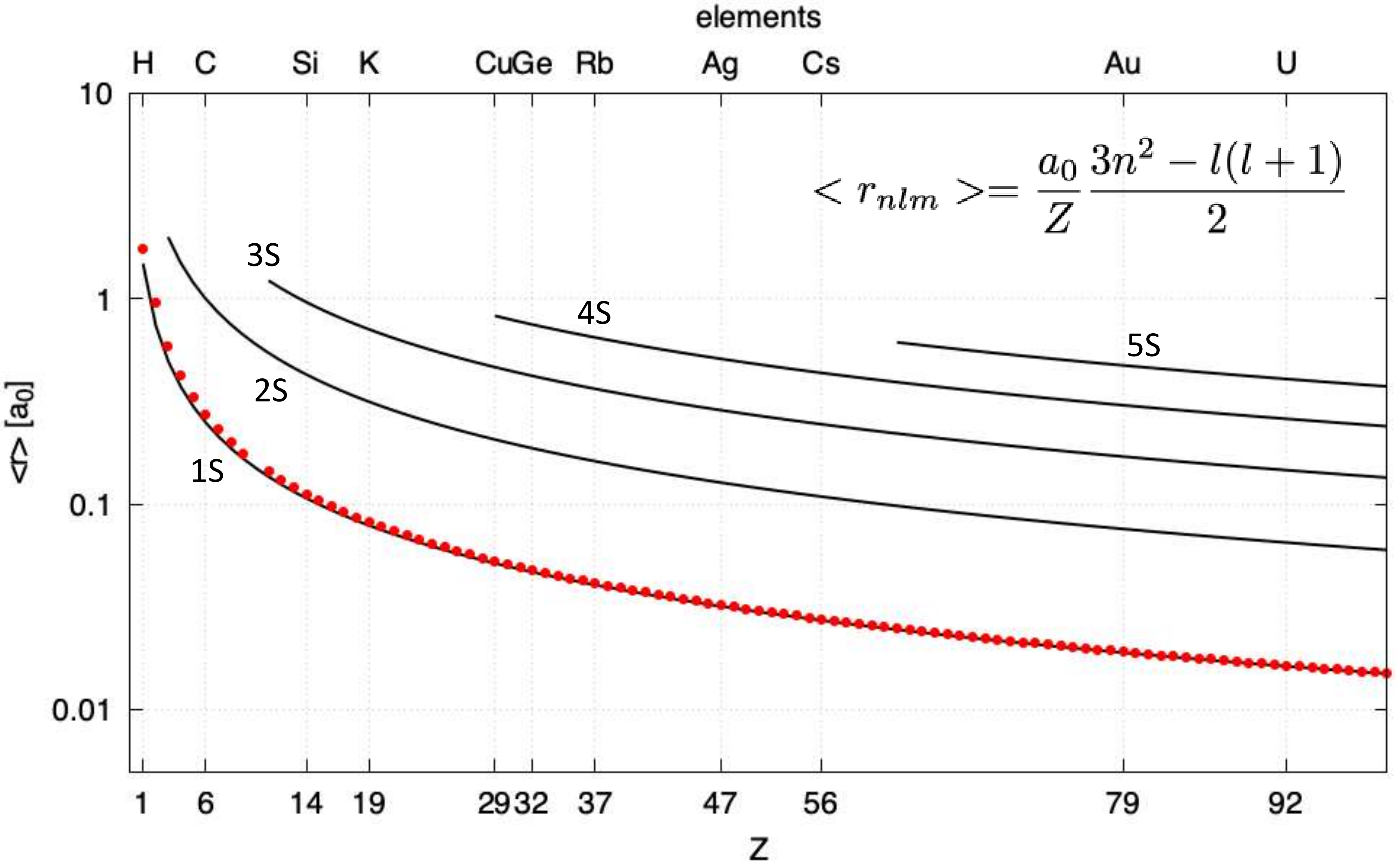
The mean radius (radial extent) of 1s orbital for the *hydrogenic* atom decreases when the number of protons Z increases.

Multi-electron atom without e-e interaction (*hydrogenic*)



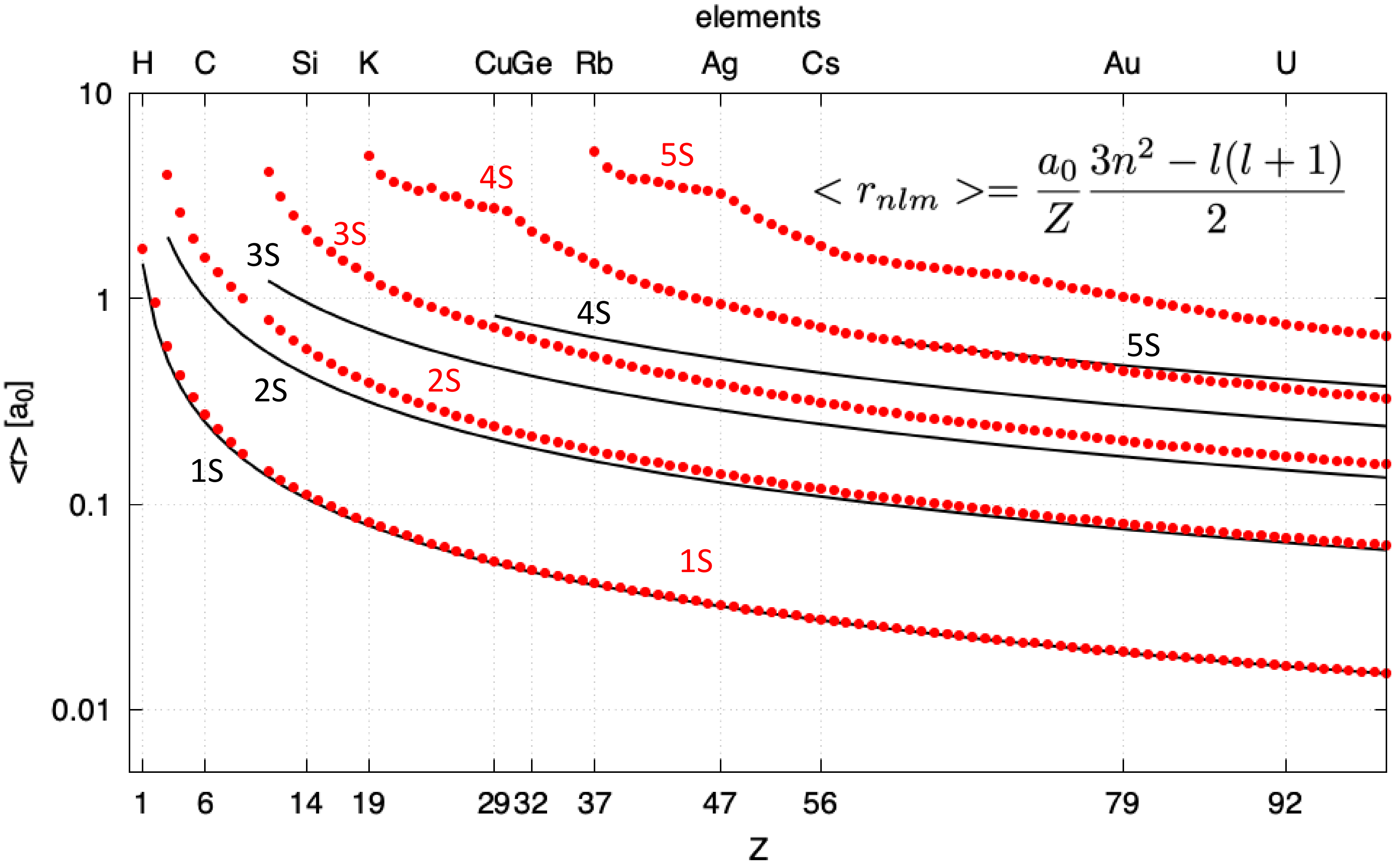
It compares pretty well with the calculated mean radius (radial extent) of the 1s orbital when one includesthe e-e interaction

Multi-electron atom without e-e interaction (*hydrogenic*)



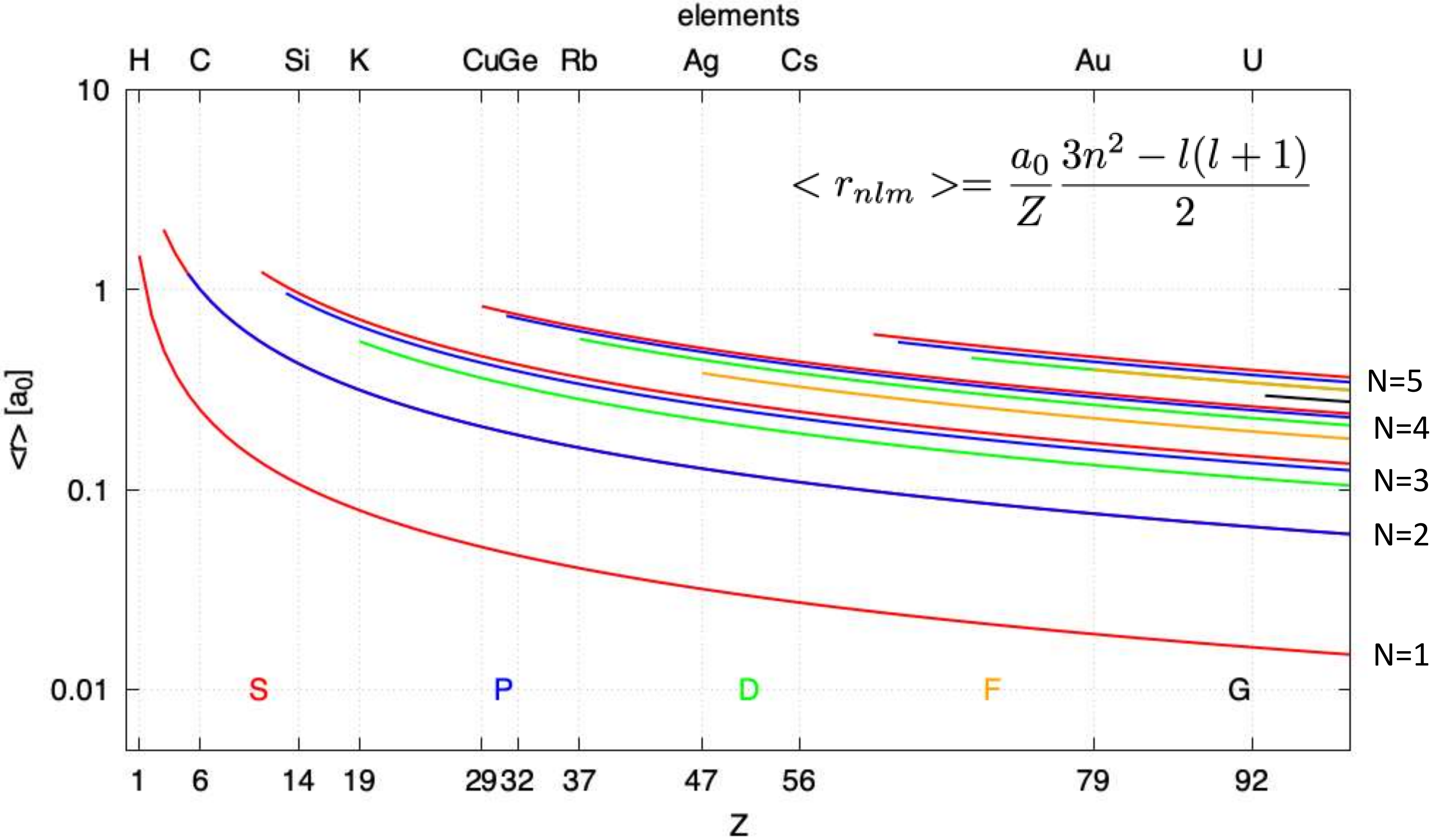
The mean radius (radial extent) of the ns orbitals for the *hydrogenic* slowly increases when n increases

Multi-electron atom without e-e interaction (*hydrogenic)*



The calculated mean radius increases much faster with n due to the screening of the core electrons

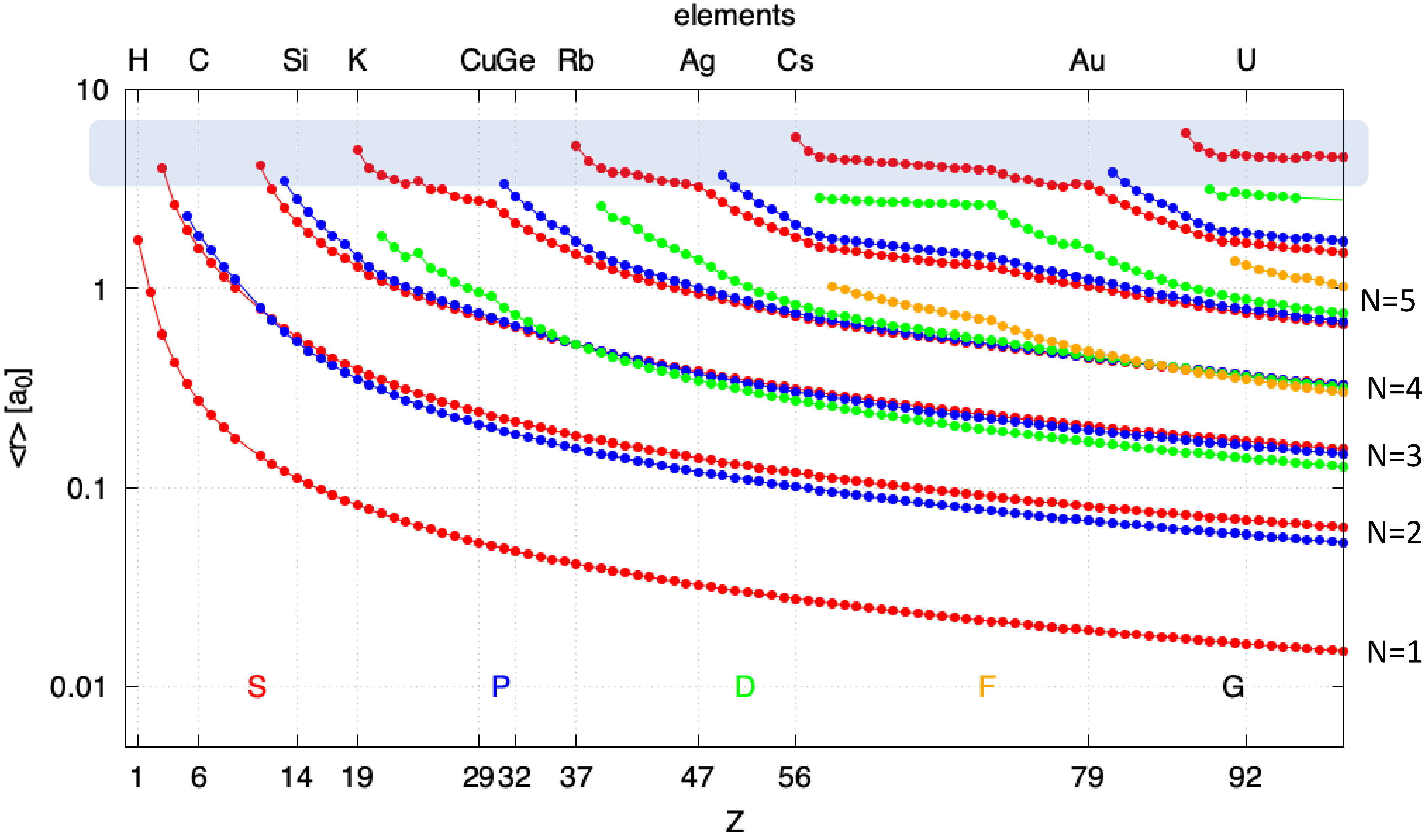
Multi-electron atom without e-e interaction (*hydrogenic*)



$$< r_{nlm} >= \frac{a_0}{Z}\frac{3n^2 - l(l+1)}{2}$$

The mean radius of the nls orbitals for the *hydrogenic* increases when n increases and decreases with l

Multi-electron atom with e-e interaction



Due to the screening there is less dispersion in the mean radius of the calculated atoms.

Orthogonality (for tomorrow …)

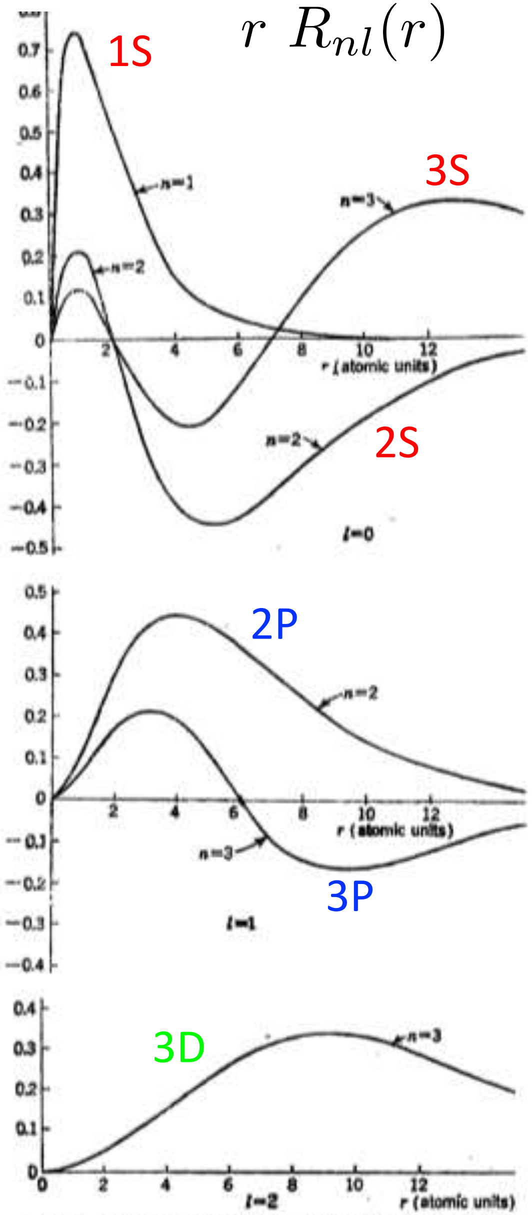


FIG. 7-2. Radial wave functions P(r) for hydrogen.

The figure shows the radial par of the wfc for the H atom but the remarks below are valid for any atom

- Two atomic wavefunctions are orthogonal

$$\int_0^{\infty}\int_{\Omega} \varphi_{nlm}(r,\Omega)\ \varphi_{n'l'm'}(r,\Omega)\ r^2\ dr\ d\Omega = \delta_{nn'}\ \delta_{ll'}\ \delta_{mm'}$$

- For different l the angular part does the job. The radial part are not orthogonal. See for example :

1S vs 3D
1S vs 2P

- Only the radial functions for the same l are orthogonal.

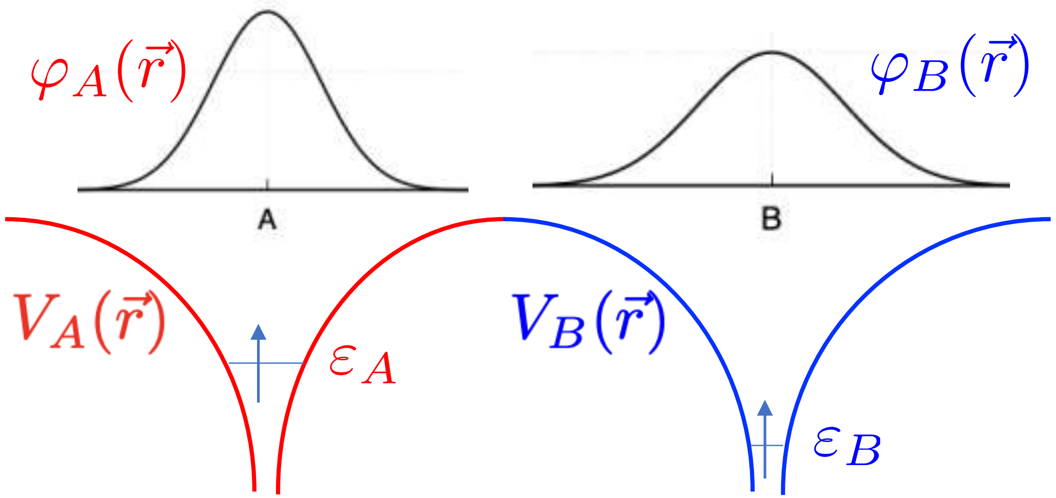
$$\int_0^{\infty} R_{nl}(r)\ R_{n'l}(r)\ r^2 dr = \delta_{nn'}$$

See for example :

1S vs 2S or 3S
2S vs 2P

Bonding

Bonding : toy model



For the isolated atoms (one orbital, one electron)

$$\left[\frac{p^2}{2m}+V_A(\vec{r})\right]\ \varphi_A(\vec{r})=\varepsilon_A\ \varphi_A(\vec{r})$$

$$\left[\frac{p^2}{2m}+V_B(\vec{r})\right]\ \varphi_B(\vec{r})=\varepsilon_B\ \varphi_B(\vec{r})$$

For the *molecule*

$$\left[\frac{p^2}{2m}+V_A(\vec{r})+V_B(\vec{r})\right]\ \psi(\vec{r})=\varepsilon\ \psi(\vec{r})$$

We search

$$\psi(\vec{r})=c_A\ \varphi_A(\vec{r})+c_B\ \varphi_B(\vec{r})$$

We replace the wavefunction in the Schrodinger equation, multiply by $\varphi_A^*(\vec{r})$ and integrate

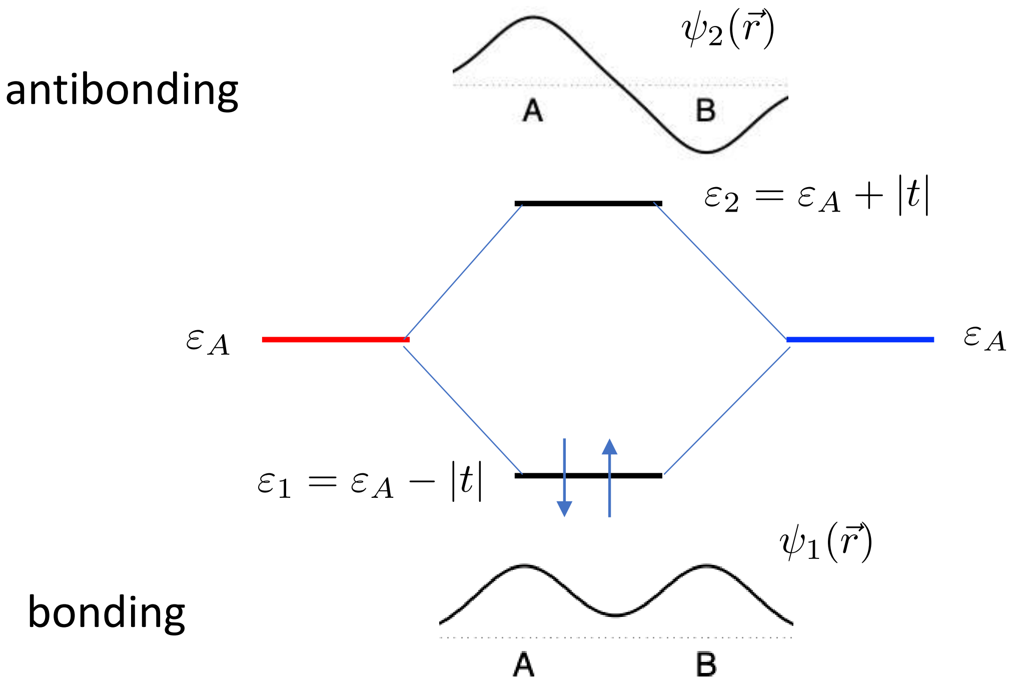
$$c_A\left[\underbrace{\int |\varphi_A(\vec{r})|^2\left\{\frac{p^2}{2m}+V_A(\vec{r})\right\} d^3r}_{\substack{\varepsilon_A \\ \text{atomic energy}}}+\cancel{\underbrace{\int |\varphi_A(\vec{r})|^2\ V_B(\vec{r})\ d^3r}_{\substack{\Delta\varepsilon_A \\ \text{crystal field}}}}\right]+c_B\underbrace{\int \varphi_A^*(\vec{r})\ H_{AB}\ \varphi_B(\vec{r})\ d^3r}_{\substack{t \\ \text{hopping}}}=\varepsilon\left\{c_A\underbrace{\int |\varphi_A(\vec{r})|^2 d^3r}_{\substack{1 \\ \text{normalization}}}+c_B\cancel{\underbrace{\int \varphi_A^*(\vec{r})\ \varphi_B(\vec{r})\ d^3r}_{\substack{S_{AB} \\ \text{overlap}}}}\right\}$$

Bonding : toy model

$$\begin{pmatrix} \varepsilon_A & t \\ t^* & \varepsilon_B \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \varepsilon \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

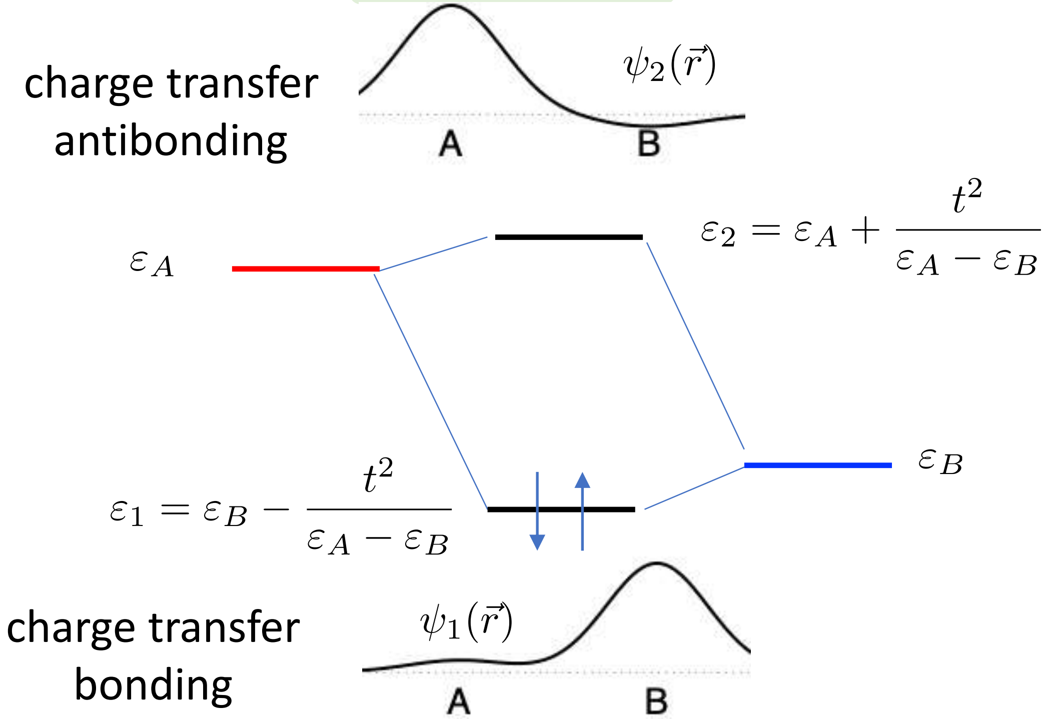
$$\varepsilon_{1,2} = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_A + \varepsilon_B)^2 + 4t^2}$$

$\varepsilon_A = \varepsilon_B$



Covalent bond
Formal charges
A^0 B^0

$\varepsilon_A >> \varepsilon_B$



Ionic bond
Formal charges
A^{+1} B^{-1}

Bonding : toy model

$$\varepsilon_A = \varepsilon_B$$

$$\varepsilon_A >> \varepsilon_B$$

bonding

$$\varepsilon_1 = \varepsilon_A - |t|$$

$$\Delta\varepsilon_{\mathrm{a}} = 2\ \varepsilon_1 - 2\ \varepsilon_A$$

$$= -2\ |t| < 0$$

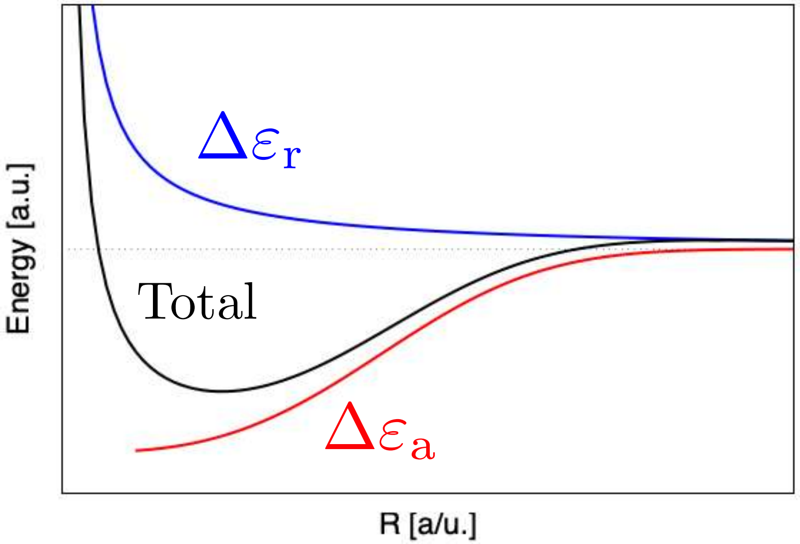
$$\varepsilon_1 = \varepsilon_B - \frac{t^2}{\varepsilon_A - \varepsilon_B}$$

charge transfer
bonding

$$\Delta\varepsilon_{\mathrm{a}} = 2\ \varepsilon_1 - \varepsilon_A - \varepsilon_B$$

$$= -(\varepsilon_A - \varepsilon_B)\left[1 + \frac{2\ t^2}{\varepsilon_A - \varepsilon_B}\right] < 0$$

This term represents only the attractive part of the interaction

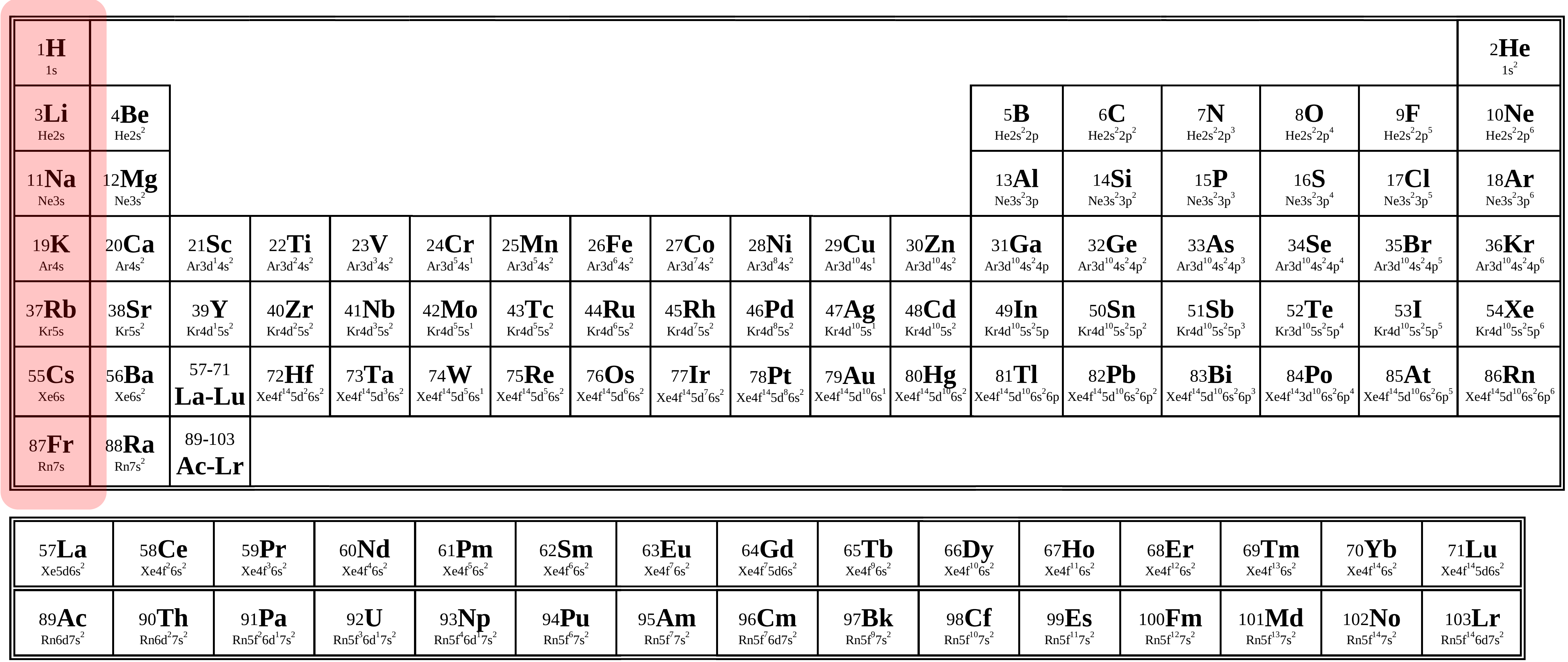


Covalent bond
Formal charges
$A^0\ B^0$

Ionic bond
Formal charges
$A^{+1}\ B^{-1}$

Alkali metals : ns^1

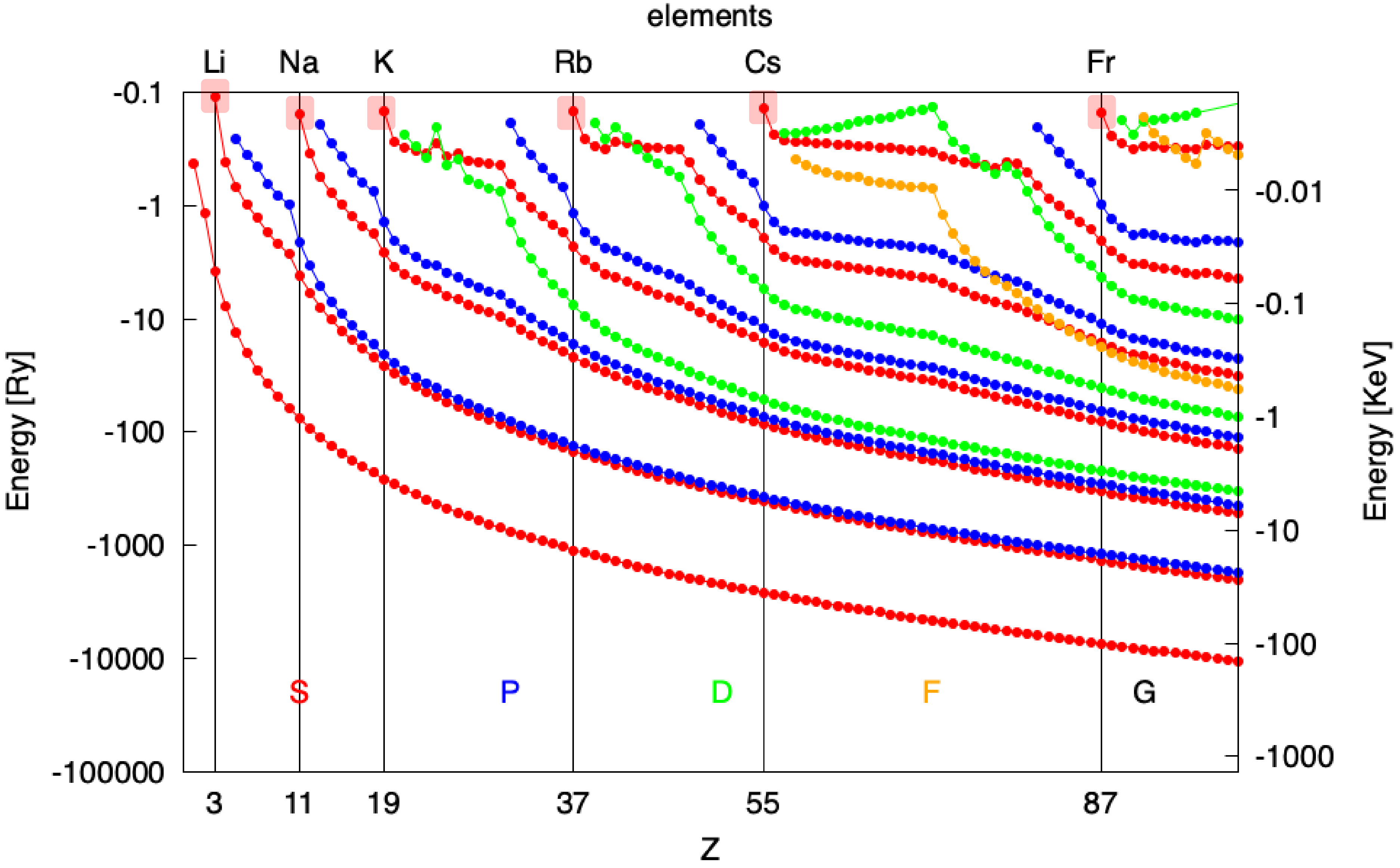
Periodic Table of the Elements



1**H** 1s																	2**He** 1s^2
3**Li** He2s	4**Be** He2s^2											5**B** He2s^{2}2p	6**C** He2s^{2}2p^2	7**N** He2s^{2}2p^3	8**O** He2s^{2}2p^4	9**F** He2s^{2}2p^5	10**Ne** He2s^{2}2p^6
11**Na** Ne3s	12**Mg** Ne3s^2											13**Al** Ne3s^{2}3p	14**Si** Ne3s^{2}3p^2	15**P** Ne3s^{2}3p^3	16**S** Ne3s^{2}3p^4	17**Cl** Ne3s^{2}3p^5	18**Ar** Ne3s^{2}3p^6
19**K** Ar4s	20**Ca** Ar4s^2	21**Sc** Ar3d^{1}4s^2	22**Ti** Ar3d^{2}4s^2	23**V** Ar3d^{3}4s^2	24**Cr** Ar3d^{5}4s^1	25**Mn** Ar3d^{5}4s^2	26**Fe** Ar3d^{6}4s^2	27**Co** Ar3d^{7}4s^2	28**Ni** Ar3d^{8}4s^2	29**Cu** Ar3d^{10}4s^1	30**Zn** Ar3d^{10}4s^2	31**Ga** Ar3d^{10}4s^{2}4p	32**Ge** Ar3d^{10}4s^{2}4p^2	33**As** Ar3d^{10}4s^{2}4p^3	34**Se** Ar3d^{10}4s^{2}4p^4	35**Br** Ar3d^{10}4s^{2}4p^5	36**Kr** Ar3d^{10}4s^{2}4p^6
37**Rb** Kr5s	38**Sr** Kr5s^2	39**Y** Kr4d^{1}5s^2	40**Zr** Kr4d^{2}5s^2	41**Nb** Kr4d^{3}5s^2	42**Mo** Kr4d^{5}5s^1	43**Tc** Kr4d^{5}5s^2	44**Ru** Kr4d^{6}5s^2	45**Rh** Kr4d^{7}5s^2	46**Pd** Kr4d^{8}5s^2	47**Ag** Kr4d^{10}5s^1	48**Cd** Kr4d^{10}5s^2	49**In** Kr4d^{10}5s^{2}5p	50**Sn** Kr4d^{10}5s^{2}5p^2	51**Sb** Kr4d^{10}5s^{2}5p^3	52**Te** Kr3d^{10}5s^{2}5p^4	53**I** Kr4d^{10}5s^{2}5p^5	54**Xe** Kr4d^{10}5s^{2}5p^6
55**Cs** Xe6s	56**Ba** Xe6s^2	57-71 **La-Lu**	72**Hf** Xe4f^{14}5d^{2}6s^2	73**Ta** Xe4f^{14}5d^{3}6s^2	74**W** Xe4f^{14}5d^{5}6s^1	75**Re** Xe4f^{14}5d^{5}6s^2	76**Os** Xe4f^{14}5d^{6}6s^2	77**Ir** Xe4f^{14}5d^{7}6s^2	78**Pt** Xe4f^{14}5d^{8}6s^2	79**Au** Xe4f^{14}5d^{10}6s^1	80**Hg** Xe4f^{14}5d^{10}6s^2	81**Tl** Xe4f^{14}5d^{10}6s^{2}6p	82**Pb** Xe4f^{14}5d^{10}6s^{2}6p^2	83**Bi** Xe4f^{14}5d^{10}6s^{2}6p^3	84**Po** Xe4f^{14}3d^{10}6s^{2}6p^4	85**At** Xe4f^{14}5d^{10}6s^{2}6p^5	86**Rn** Xe4f^{14}5d^{10}6s^{2}6p^6
87**Fr** Rn7s	88**Ra** Rn7s^2	89-103 **Ac-Lr**															

57**La** Xe5d6s^2	58**Ce** Xe4f^{2}6s^2	59**Pr** Xe4f^{3}6s^2	60**Nd** Xe4f^{4}6s^2	61**Pm** Xe4f^{5}6s^2	62**Sm** Xe4f^{6}6s^2	63**Eu** Xe4f^{7}6s^2	64**Gd** Xe4f^{7}5d6s^2	65**Tb** Xe4f^{9}6s^2	66**Dy** Xe4f^{10}6s^2	67**Ho** Xe4f^{11}6s^2	68**Er** Xe4f^{12}6s^2	69**Tm** Xe4f^{13}6s^2	70**Yb** Xe4f^{14}6s^2	71**Lu** Xe4f^{14}5d6s^2
89**Ac** Rn6d7s^2	90**Th** Rn6d^{2}7s^2	91**Pa** Rn5f^{2}6d^{1}7s^2	92**U** Rn5f^{3}6d^{1}7s^2	93**Np** Rn5f^{4}6d^{1}7s^2	94**Pu** Rn5f^{6}7s^2	95**Am** Rn5f^{7}7s^2	96**Cm** Rn5f^{7}6d7s^2	97**Bk** Rn5f^{9}7s^2	98**Cf** Rn5f^{10}7s^2	99**Es** Rn5f^{11}7s^2	100**Fm** Rn5f^{12}7s^2	101**Md** Rn5f^{13}7s^2	102**No** Rn5f^{14}7s^2	103**Lr** Rn5f^{14}6d7s^2

Energy of the last orbital of the alkali metals : *ns^1*



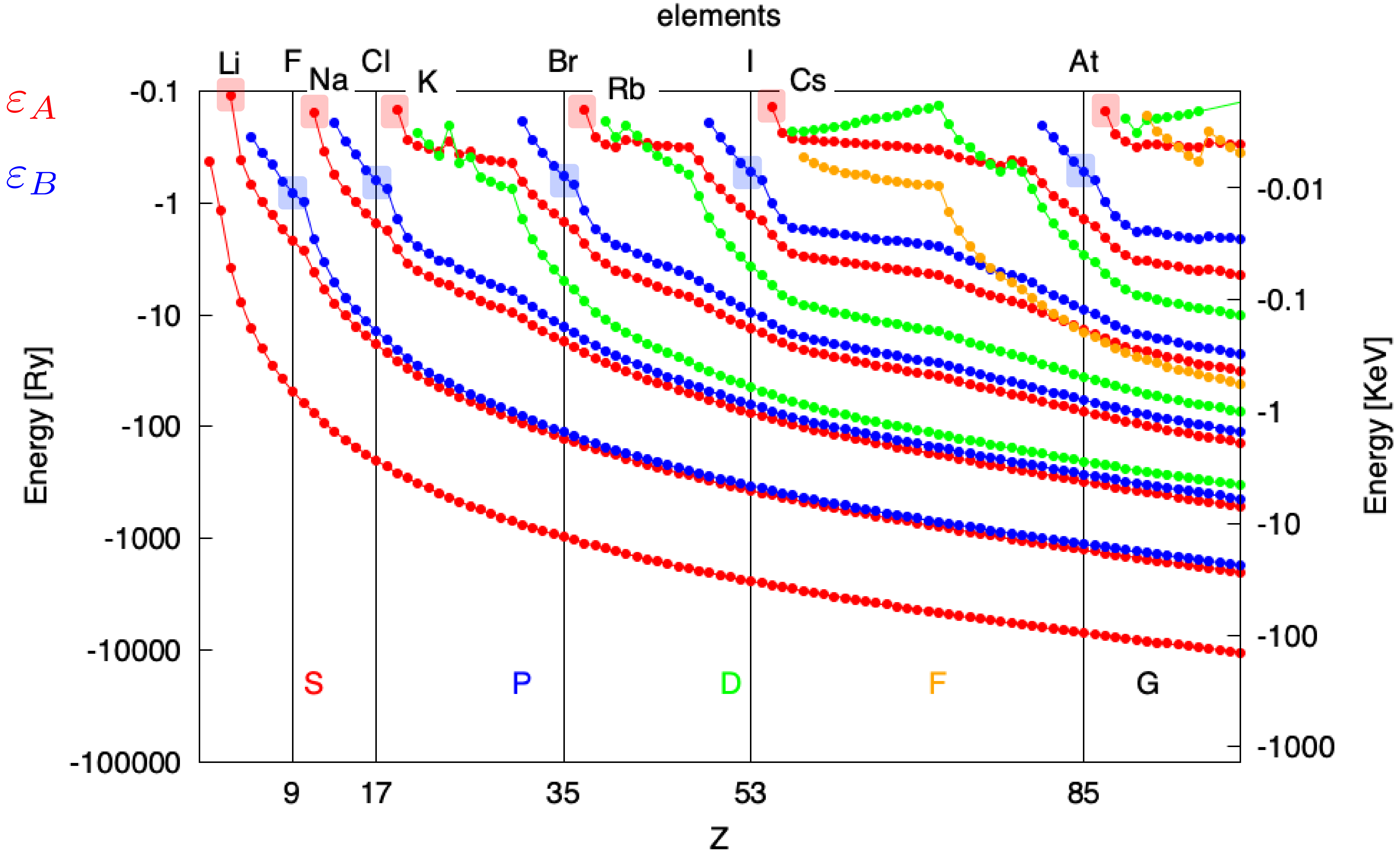
Halogens : $ns^2\ np^5$

Periodic Table of the Elements

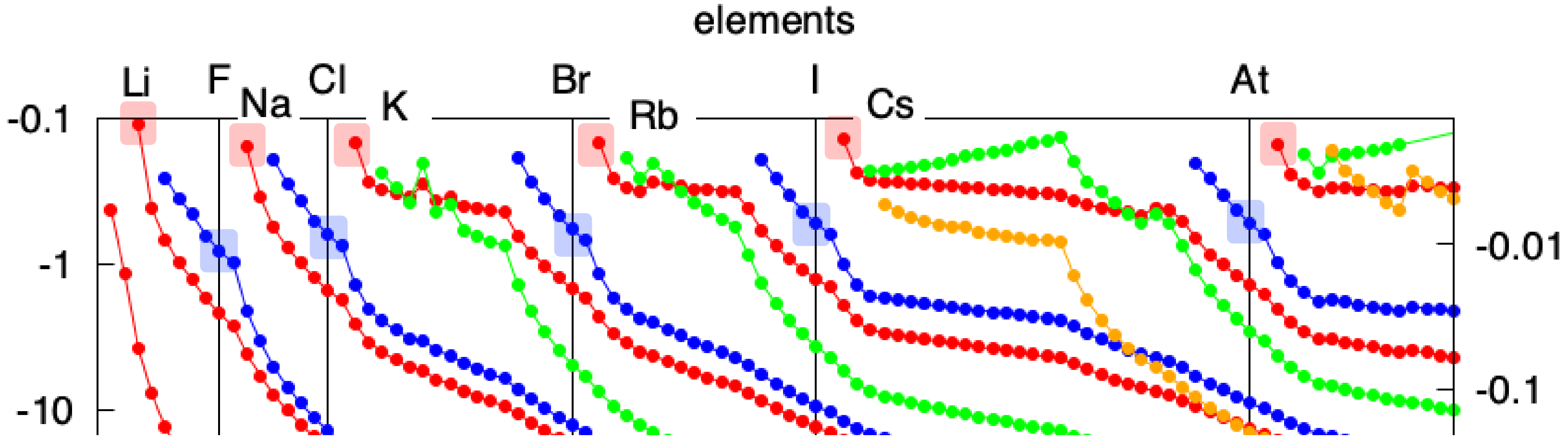
1**H** $1s$																	2**He** $1s^2$
3**Li** $He2s$	4**Be** $He2s^2$											5**B** $He2s^2 2p$	6**C** $He2s^2 2p^2$	7**N** $He2s^2 2p^3$	8**O** $He2s^2 2p^4$	9**F** $He2s^2 2p^5$	10**Ne** $He2s^2 2p^6$
11**Na** $Ne3s$	12**Mg** $Ne3s^2$											13**Al** $Ne3s^2 3p$	14**Si** $Ne3s^2 3p^2$	15**P** $Ne3s^2 3p^3$	16**S** $Ne3s^2 3p^4$	17**Cl** $Ne3s^2 3p^5$	18**Ar** $Ne3s^2 3p^6$
19**K** $Ar4s$	20**Ca** $Ar4s^2$	21**Sc** $Ar3d^1 4s^2$	22**Ti** $Ar3d^2 4s^2$	23**V** $Ar3d^3 4s^2$	24**Cr** $Ar3d^5 4s^1$	25**Mn** $Ar3d^5 4s^2$	26**Fe** $Ar3d^6 4s^2$	27**Co** $Ar3d^7 4s^2$	28**Ni** $Ar3d^8 4s^2$	29**Cu** $Ar3d^{10} 4s^1$	30**Zn** $Ar3d^{10} 4s^2$	31**Ga** $Ar3d^{10} 4s^2 4p$	32**Ge** $Ar3d^{10} 4s^2 4p^2$	33**As** $Ar3d^{10} 4s^2 4p^3$	34**Se** $Ar3d^{10} 4s^2 4p^4$	35**Br** $Ar3d^{10} 4s^2 4p^5$	36**Kr** $Ar3d^{10} 4s^2 4p^6$
37**Rb** $Kr5s$	38**Sr** $Kr5s^2$	39**Y** $Kr4d^1 5s^2$	40**Zr** $Kr4d^2 5s^2$	41**Nb** $Kr4d^3 5s^2$	42**Mo** $Kr4d^5 5s^1$	43**Tc** $Kr4d^5 5s^2$	44**Ru** $Kr4d^6 5s^2$	45**Rh** $Kr4d^7 5s^2$	46**Pd** $Kr4d^8 5s^2$	47**Ag** $Kr4d^{10} 5s^1$	48**Cd** $Kr4d^{10} 5s^2$	49**In** $Kr4d^{10} 5s^2 5p$	50**Sn** $Kr4d^{10} 5s^2 5p^2$	51**Sb** $Kr4d^{10} 5s^2 5p^3$	52**Te** $Kr3d^{10} 5s^2 5p^4$	53**I** $Kr4d^{10} 5s^2 5p^5$	54**Xe** $Kr4d^{10} 5s^2 5p^6$
55**Cs** $Xe6s$	56**Ba** $Xe6s^2$	57-71 **La-Lu**	72**Hf** $Xe4f^{14} 5d^2 6s^2$	73**Ta** $Xe4f^{14} 5d^3 6s^2$	74**W** $Xe4f^{14} 5d^5 6s^1$	75**Re** $Xe4f^{14} 5d^5 6s^2$	76**Os** $Xe4f^{14} 5d^6 6s^2$	77**Ir** $Xe4f^{14} 5d^7 6s^2$	78**Pt** $Xe4f^{14} 5d^8 6s^2$	79**Au** $Xe4f^{14} 5d^{10} 6s^1$	80**Hg** $Xe4f^{14} 5d^{10} 6s^2$	81**Tl** $Xe4f^{14} 5d^{10} 6s^2 6p$	82**Pb** $Xe4f^{14} 5d^{10} 6s^2 6p^2$	83**Bi** $Xe4f^{14} 5d^{10} 6s^2 6p^3$	84**Po** $Xe4f^{14} 3d^{10} 6s^2 6p^4$	85**At** $Xe4f^{14} 5d^{10} 6s^2 6p^5$	86**Rn** $Xe4f^{14} 5d^{10} 6s^2 6p^6$
87**Fr** $Rn7s$	88**Ra** $Rn7s^2$	89-103 **Ac-Lr**															

57**La** $Xe5d6s^2$	58**Ce** $Xe4f^2 6s^2$	59**Pr** $Xe4f^3 6s^2$	60**Nd** $Xe4f^4 6s^2$	61**Pm** $Xe4f^5 6s^2$	62**Sm** $Xe4f^6 6s^2$	63**Eu** $Xe4f^7 6s^2$	64**Gd** $Xe4f^7 5d6s^2$	65**Tb** $Xe4f^9 6s^2$	66**Dy** $Xe4f^{10} 6s^2$	67**Ho** $Xe4f^{11} 6s^2$	68**Er** $Xe4f^{12} 6s^2$	69**Tm** $Xe4f^{13} 6s^2$	70**Yb** $Xe4f^{14} 6s^2$	71**Lu** $Xe4f^{14} 5d6s^2$
89**Ac** $Rn6d7s^2$	90**Th** $Rn6d^2 7s^2$	91**Pa** $Rn5f^2 6d^1 7s^2$	92**U** $Rn5f^3 6d^1 7s^2$	93**Np** $Rn5f^4 6d^1 7s^2$	94**Pu** $Rn5f^6 7s^2$	95**Am** $Rn5f^7 7s^2$	96**Cm** $Rn5f^7 6d7s^2$	97**Bk** $Rn5f^9 7s^2$	98**Cf** $Rn5f^{10} 7s^2$	99**Es** $Rn5f^{11} 7s^2$	100**Fm** $Rn5f^{12} 7s^2$	101**Md** $Rn5f^{13} 7s^2$	102**No** $Rn5f^{14} 7s^2$	103**Lr** $Rn5f^{14} 6d7s^2$

Energy of the last orbital of the halogens : *ns*^{2} *np*^{5}



Energy of the last orbital of the halogens : $ns^2\ np^5$



ε_A

ε_B

$\varepsilon_A >> \varepsilon_B$

		Alkali metals				
		Lithium	Sodium	Potassium	Rubidium	Caesium
Halogens	Fluorine	LiF (3.0)	NaF (3.1)	KF (3.2)	RbF (3.2)	CsF (3.3)
	Chlorine	LiCl (2.0)	NaCl (2.1)	KCl (2.2)	RbCl (2.2)	CsCl (2.3)
	Bromine	LiBr (1.8)	NaBr (1.9)	KBr (2.0)	RbBr (2.0)	CsBr (2.1)
	Iodine	LiI (1.5)	NaI (1.6)	KI (1.7)	RbI (1.7)	CsI (1.8)

- Highly ionic compounds
- High melting temperature

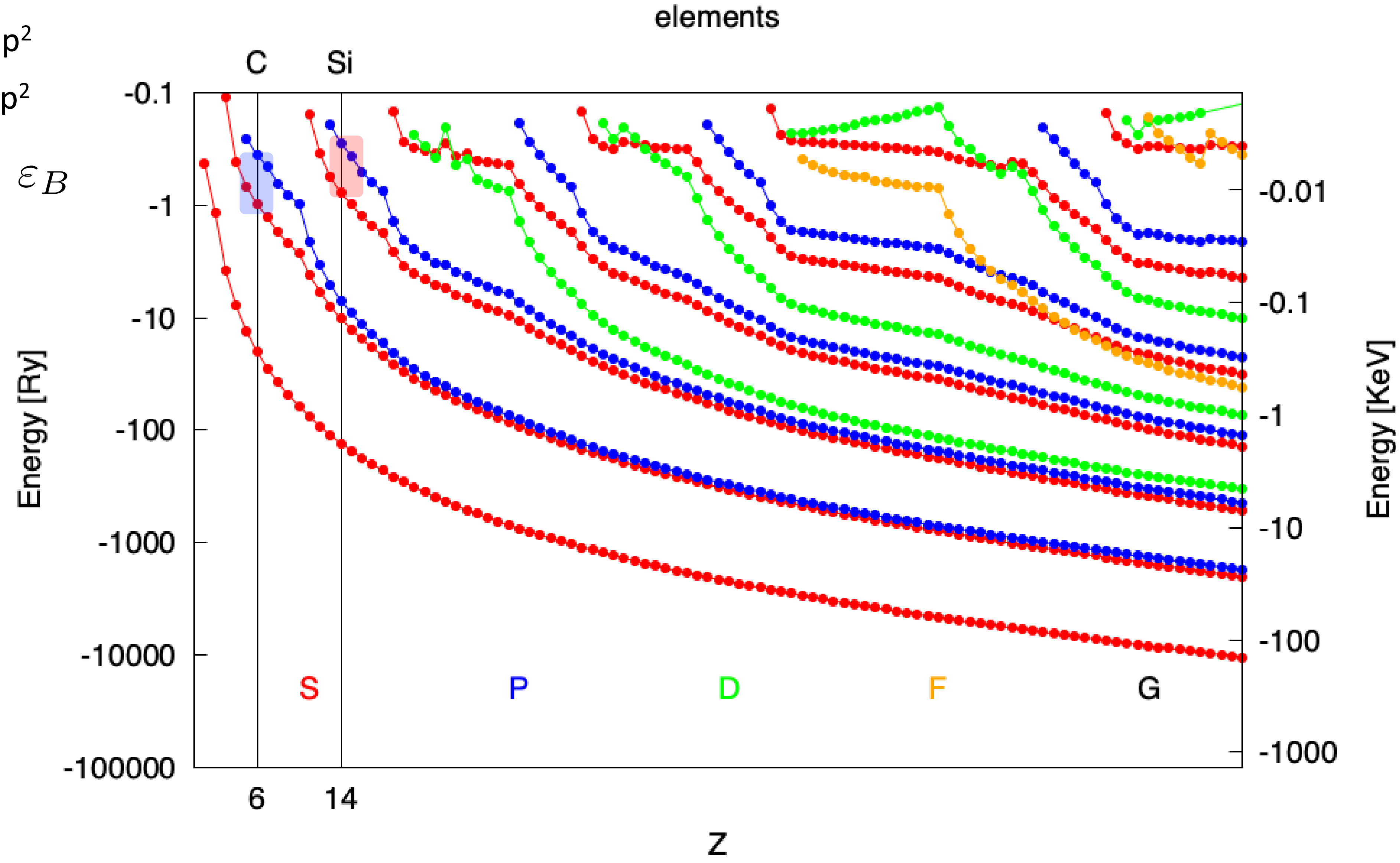
Lithium fluoride, .. chloride, .. bromide, .. iodide
Sodium fluoride, .. chloride, .. bromide, .. iodide
….

Charge transfer in silicon carbide SiC

C : [He] $2s^2\ 2p^2$

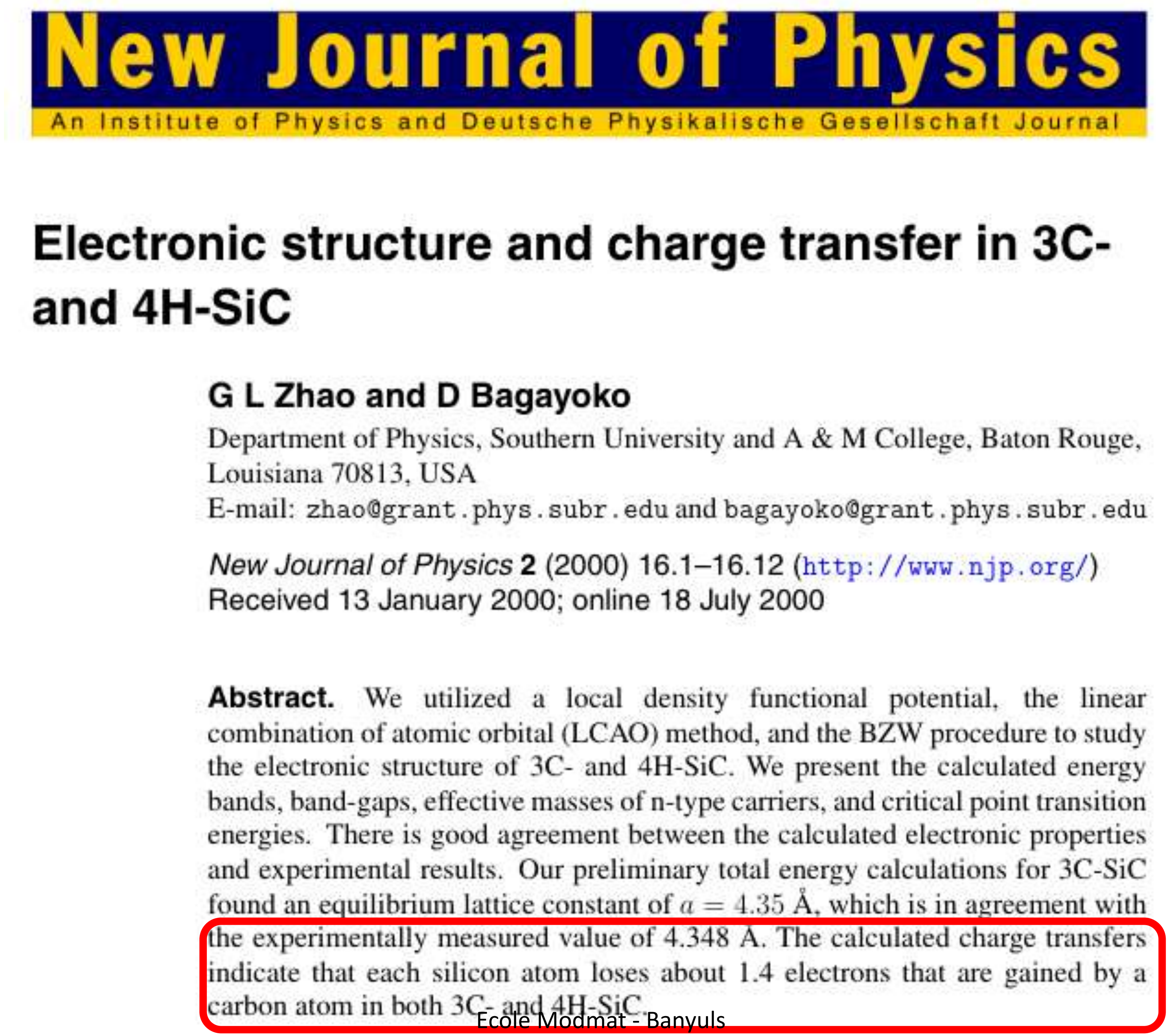
Si: [Ne] $3s^2\ 3p^2$

$$\varepsilon_A > \varepsilon_B$$



Iono-covalent bond with a small charge transfer from Si to C

Charge transfer in silicon carbide SiC



New Journal of Physics
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Electronic structure and charge transfer in 3C- and 4H-SiC

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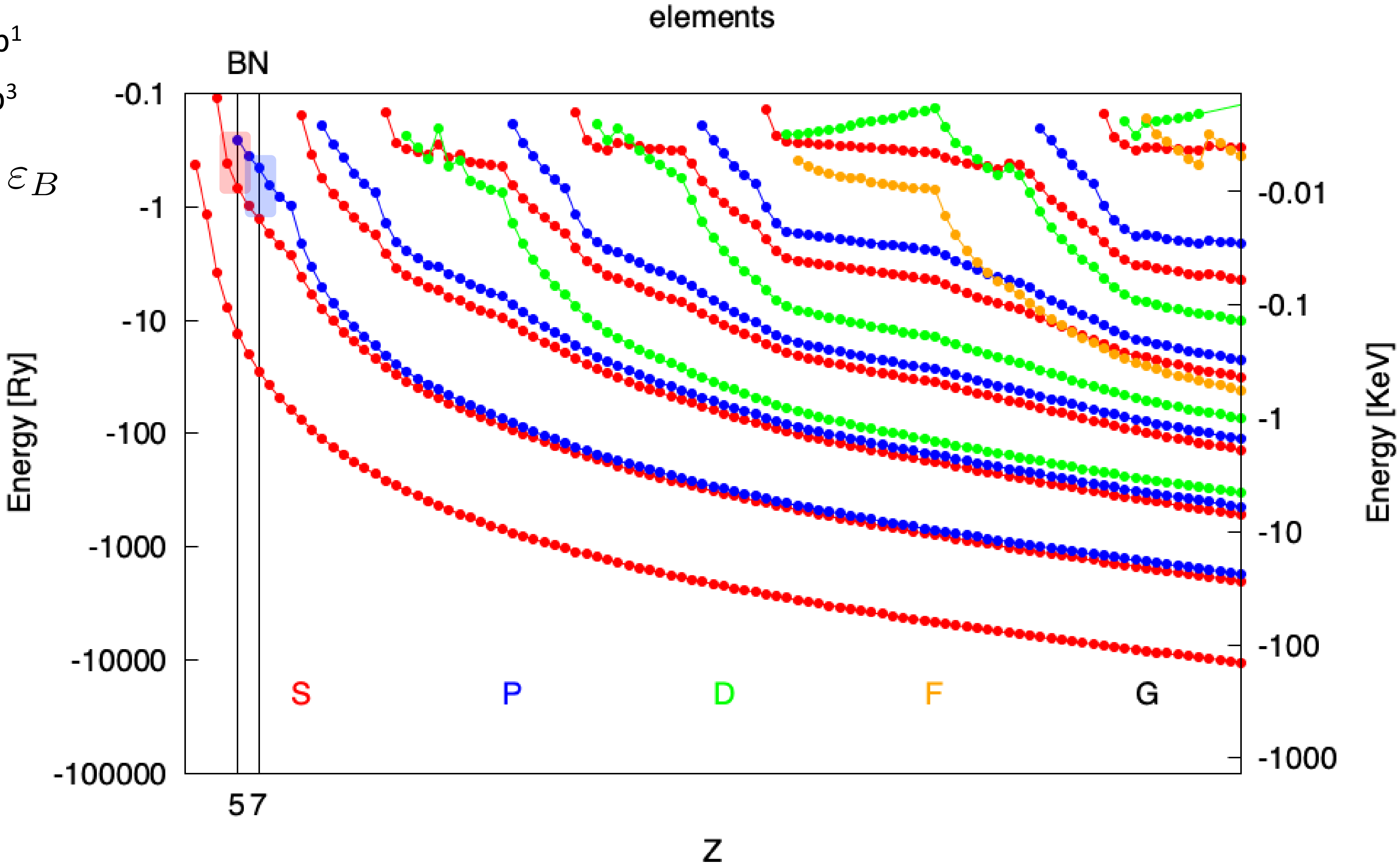
Abstract. We utilized a local density functional potential, the linear combination of atomic orbital (LCAO) method, and the BZW procedure to study the electronic structure of 3C- and 4H-SiC. We present the calculated energy bands, band-gaps, effective masses of n-type carriers, and critical point transition energies. There is good agreement between the calculated electronic properties and experimental results. Our preliminary total energy calculations for 3C-SiC found an equilibrium lattice constant of $a = 4.35$ Å, which is in agreement with the experimentally measured value of 4.348 Å. The calculated charge transfers indicate that each silicon atom loses about 1.4 electrons that are gained by a carbon atom in both 3C- and 4H-SiC.

Charge transfer in boron nitrode BN

B : [He] $2s^2$ $2p^1$

N: [He] $2s^2$ $3p^3$

$$\varepsilon_A > \varepsilon_B$$



Iono-covalent bond with a small charge transfer from B to N

Plat

Zarzuela
Se trata de un estofado a base de pescado y marisco con su picada. El pescado que se sirve es el de temporada.

Electronic structure of condensed atomic systems (molecules, solids, crystals, …)

Condensed atomic systems

Formed by

nuclei	$\vec{R}_I$	M_I	$\vec{P}_I$	$Z_i e$	$\cancel{I_i}$	$\cancel{Q_I}$	there are M
electrons	$\vec{r}_i$	m	$\vec{p}_i$	$-e$	σ_i		there are N
	positions	mass	moment	charge	spin	quadrupole	

The total Hamiltonian

$$H_{TOT} = \sum_i \frac{p_i^2}{2m} + \sum_I \frac{P_I^2}{2M_I} - \sum_i \sum_I \frac{Z_I \; e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I \; Z_J \; e^2}{|\vec{R}_I - \vec{R}_J|}$$

kinetic electrons — kinetic nuclei — Coulomb nuclei-electron — Coulomb electron-electron — Coulomb nuclei-nuclei

We need to solve the full non relativistic time independent Schrödinger equation

$$H_{TOT} \; \Phi(\vec{R}_1, \ldots, \vec{R}_M, \vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N) = E \; \Phi(\vec{R}_1, \ldots, \vec{R}_M, \vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N)$$

Approximations

Example I : one nuclei + one electron	H atom	analytical solution
Example II : one nuclei + two electrons	He atom	no solution
Example III : two nuclei + two electrons	H_2 molecule	no solution

First approximation : Born-Oppenheimer

Proton mass $938 \text{ MeV} = M_p c^2$

Electron mass $0.5 \text{ MeV} = mc^2$

$$\left.\begin{array}{l} 938 \text{ MeV} = M_p c^2 \\ 0.5 \text{ MeV} = mc^2 \end{array}\right\} \quad \frac{M_p}{m} \simeq 1758$$

We neglect $$\sum_I \frac{P_I^2}{2M_I}$$ the nuclei are fixed for the electrons

and $$\frac{1}{2}\sum_{I \neq J} \frac{Z_I \; Z_J \; e^2}{|\vec{R}_I - \vec{R}_J|}$$ is a constant

Approximations

The system is now formed only by the electrons, the nuclei are “external”, they produce an ”external potential”.

The electronic Hamiltonian is

$$H_{\text{elec}} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \sum_I \frac{Z_I\ e^2}{|\vec{r}_i - \vec{R}_I|}$$

$$= \overbrace{T}^{\substack{\text{kinetic}\\ \text{electrons}}} + \overbrace{V_{\text{ee}}}^{\substack{\text{Coulomb}\\ \text{electron-electron}}} + \overbrace{\sum_i V_{\text{ext}}(\vec{r}_i)}^{\substack{\text{Coulomb}\\ \text{nuclei-electron}}}$$

We can separate the nuclear and the electronic wavefunctions

$$\Phi(\vec{R}_1, \ldots, \vec{R}_M, \vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N) = \Theta(\vec{R}_1, \ldots, \vec{R}_M)\ \Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N)$$

The electronic wavefunction is antisymmetric

$$\Psi(\vec{r}_1\sigma_1, .., \vec{r}_i\sigma_i, .., \vec{r}_j\sigma_j, .., \vec{r}_N\sigma_N) = -\Psi(\vec{r}_1\sigma_1, .., \vec{r}_j\sigma_j, .., \vec{r}_i\sigma_i, .., \vec{r}_N\sigma_N)$$

Approximations

$$H_{\text{elec}} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \sum_I \frac{Z_I \ e^2}{|\vec{r}_i - \vec{R}_I|}$$

		T	V_{ee}	V_{ext}
Independent electrons. One electron problem One electron approximation	free electrons	yes	no	no
	nearly free electrons	yes	no	weak
	tight-binding	yes	no	strong
Correlated electrons Many-body problem	Wavefunction methods Hartree - Hartree-Fock – CI - etc	yes	yes	yes
	Density Functional Theory	yes	yes	yes
	Quantum Monte Carlo methods	yes	yes	yes

Libertad e independencia son dos cosas diferentes !!

Approximations

$$H_{\mathrm{elec}} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \sum_I \frac{Z_I\ e^2}{|\vec{r}_i - \vec{R}_I|}$$

		T	V_{ee}	V_{ext}
Independent electrons. One electron problem One electron approximation	free electrons	yes	no	no
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Correlated electrons Many-body problem	Wavefunction methods Hartree - Hartree-Fock – CI - etc	yes	yes	yes
	Density Functional Theory	yes	yes	yes
	Quantum Monte Carlo methods	yes	yes	yes

Independent and one electron problem

Why the case $V_{\mathrm{ee}} = 0$ is a “one electron problem” ?

Because the many-body anti-symmetric wavefunction can be written as a determinant of one electron wavefunctions

$$\Psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, .., \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(\vec{r}_1\sigma_1) & \psi_1(\vec{r}_2\sigma_2) & \dots & \psi_1(\vec{r}_N\sigma_N) \\ \psi_2(\vec{r}_1\sigma_1) & \psi_2(\vec{r}_2\sigma_2) & \dots & \psi_2(\vec{r}_N\sigma_N) \\ \psi_3(\vec{r}_1\sigma_1) & \psi_3(\vec{r}_2\sigma_2) & \dots & \psi_3(\vec{r}_N\sigma_N) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_N(\vec{r}_1\sigma_1) & \psi_N(\vec{r}_2\sigma_2) & \dots & \psi_N(\vec{r}_N\sigma_N) \end{pmatrix} = \frac{1}{\sqrt{N!}} \sum_{\alpha}^{N!} P_\alpha \{\psi_1(\vec{r}_1\sigma_1)\ \psi_2(\vec{r}_2\sigma_2)\ \dots\ \psi_N(\vec{r}_N\sigma_N)\}$$

permutations

Every $\varphi_i(\vec{r}\sigma)$ satisfies the same one electron Schrödinger equation

$$\left[\frac{p^2}{2m} + V_{\mathrm{ext}}(\vec{r})\right] \psi_i(\vec{r}, \sigma) = \varepsilon_i(\sigma)\ \psi_i(\vec{r}, \sigma)$$

“one electron problem”

$$E = \sum_{i=1}^{N} \varepsilon_i$$

Independent and one electron problem

If the “external” potential is periodic

$$V_{\text{ext}}(\vec{r}) = V_{\text{ext}}(\vec{r} + \vec{R}_{lmn}) \qquad \vec{R}_{lmn} = l\ \vec{a} + m\ \vec{b} + n\ \vec{c}$$

The one-electron wave-function can be written as

$$\left[\frac{p^2}{2m} + V_{\text{ext}}(\vec{r})\right]\psi_{n\vec{k}}(\vec{r}\sigma) = \varepsilon_{n\vec{k}}(\sigma)\ \psi_{n\vec{k}}(\vec{r}\sigma)$$

The wavefunction is “almost” periodic in real space, Bloch functions :

$$\psi_{n\vec{k}}(\vec{r} + \vec{R}_{lmn}\sigma) = \mathrm{e}^{i\vec{k}.\vec{R}_{lmn}}\ \psi_{n\vec{k}}(\vec{r}\sigma) \qquad \psi_{n\vec{k}}(\vec{r}\sigma) = \mathrm{e}^{i\vec{k}.\vec{r}}\ u_{n\vec{k}}(\vec{r}\sigma)$$

A phase

Periodic in real space

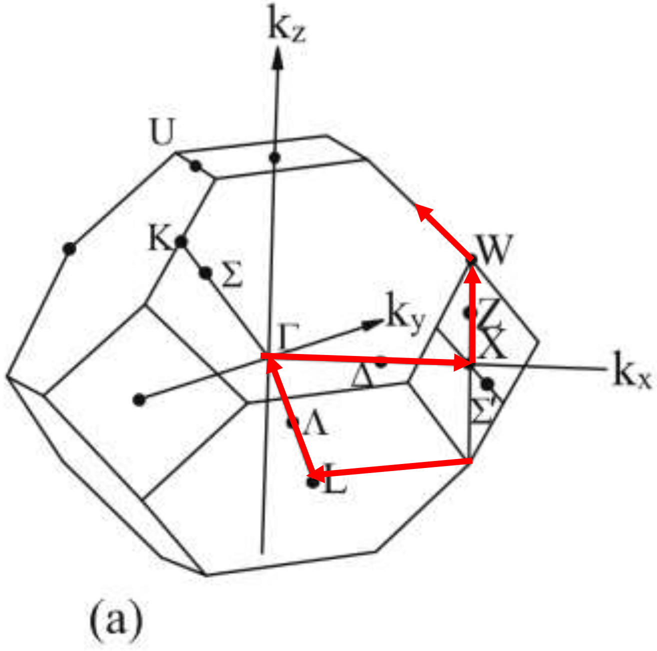
$$u_{n\vec{k}}(\vec{r} + \vec{R}_{lmn}\sigma) = u_{n\vec{k}}(\vec{r}\sigma)$$

Periodic in reciprocal space :

$$\varepsilon_{n\vec{k}}(\sigma) = \varepsilon_{n\vec{k}+\vec{G}}(\sigma)$$

$$\psi_{n\vec{k}+\vec{G}}(\vec{r}\sigma) = \psi_{n\vec{k}}(\vec{r}\sigma)$$

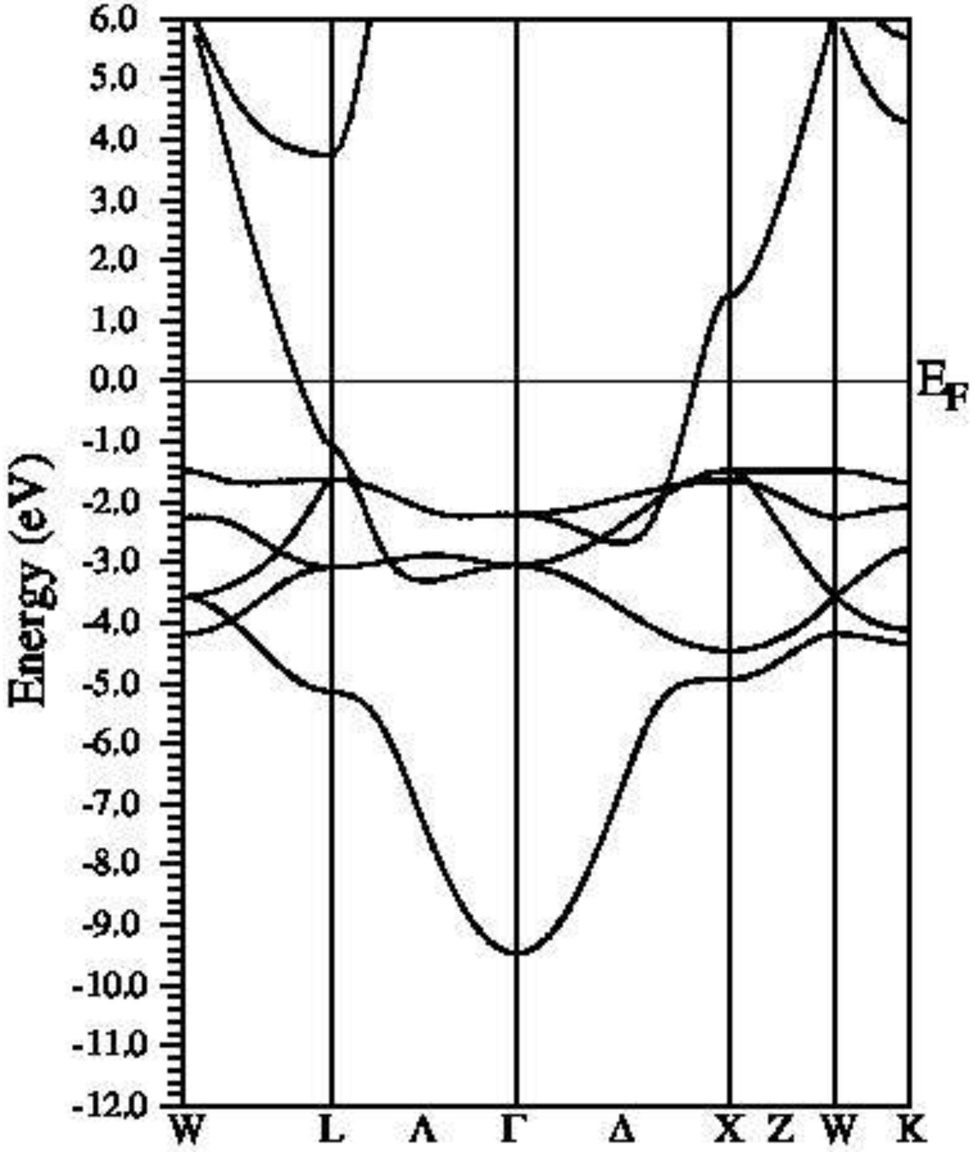
Band structure is a “one-electron” picture



Cu fcc

$3d^{10}4s^1$

11 electrons
5 full bands
1 half filled



The energies of a band structure are one electron energies.

There is always a determinant behind a band structure plot ….

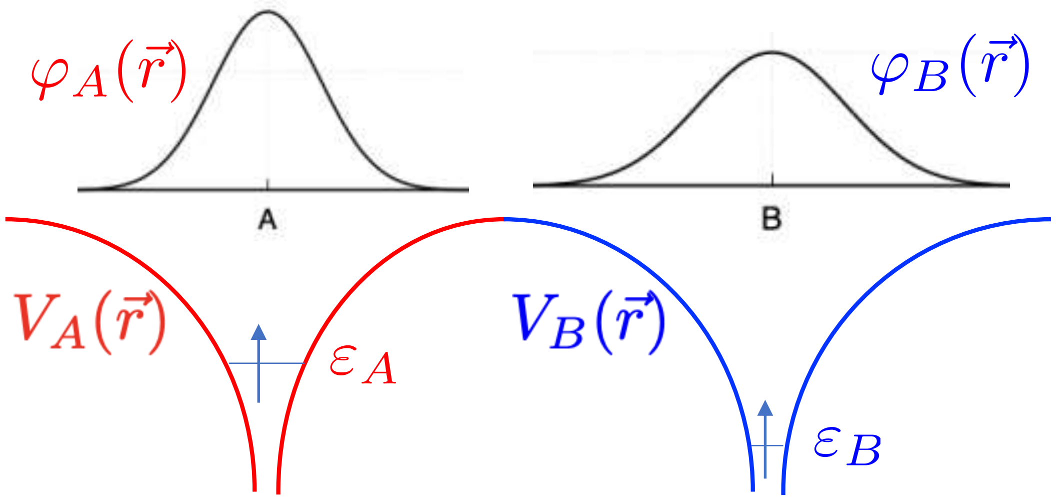
Band structure plots from DFT …? Will see!

Tight-binding

Tight-binding method

An electronic structure method that makes an hypothesis on the spatial dependence of the one electron wavefunction. Generalization of the “toy model”.

1) Two atoms, one orbital per site



For the isolated atoms (one orbital, one electron)

$$\left[\frac{p^2}{2m}+V_B(\vec{r})\right]\ \varphi_A(\vec{r})=\varepsilon_A\ \varphi_A(\vec{r})$$

$$\left[\frac{p^2}{2m}+V_B(\vec{r})\right]\ \varphi_B(\vec{r})=\varepsilon_B\ \varphi_B(\vec{r})$$

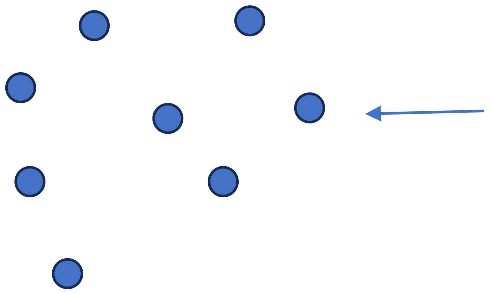
$$\psi(\vec{r})=c_A\ \varphi_A(\vec{r})+c_B\ \varphi_B(\vec{r})$$

$$\begin{pmatrix}\varepsilon_A & t\\ t^* & \varepsilon_B\end{pmatrix}\begin{pmatrix}c_A\\ c_B\end{pmatrix}=\varepsilon\begin{pmatrix}c_A\\ c_B\end{pmatrix}$$

Tight-binding method

An electronic structure method that makes an hypothesis on the spatial dependence of the one electron wavefunction. Generalization of the “toy model”.

1) Many atoms, one orbital per site



The “system”
a large molecule

Schrödinger equation for the isolated atoms (one orbital, neglect spin)

$$\left[\frac{p^2}{2m} + V_j(\vec{r})\right] \varphi_j(\vec{r}) = \varepsilon_j \, \varphi_j(\vec{r})$$

The Schrödinger equation for the “system”

$$\left[\frac{p^2}{2m} + \sum_j V_j(\vec{r})\right] \psi(\vec{r}) = \varepsilon \, \psi(\vec{r})$$

Where the wavefunction is a linear combination of the atomic wavefunctions

$$\psi(\vec{r}) = \sum_i c_i \, \varphi_i(\vec{r})$$

Replace the wavefunction in the Schrödinger equation

$$\left[\frac{p^2}{2m} + \sum_j V_j(\vec{r})\right] \sum_i c_i \, \varphi_i(\vec{r}) = \varepsilon \sum_i c_i \, \varphi_i(\vec{r})$$

Multiply by $\varphi_k^*(\vec{r})$ and integrate.

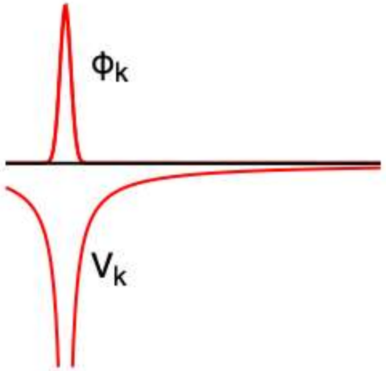
Tight-binding method

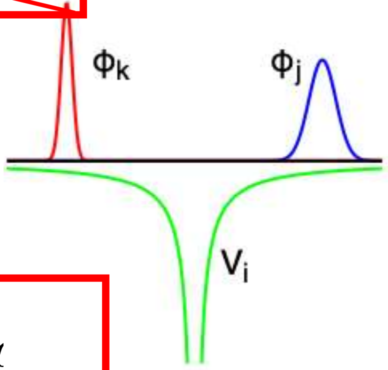
$$\boxed{c_k \int \varphi_k^*(\vec{r})\left[\frac{p^2}{2m}+V_k(\vec{r})\right]\varphi_k(\vec{r})\, d^3r} + \sum_{j\neq k} c_j \boxed{\xcancel{\int \varphi_k^*(\vec{r})\sum_{i\neq k} V_i(\vec{r})\,\varphi_j(\vec{r})\, d^3r}}$$

Atomic energy or on-site energy

ε_k

Three centers term





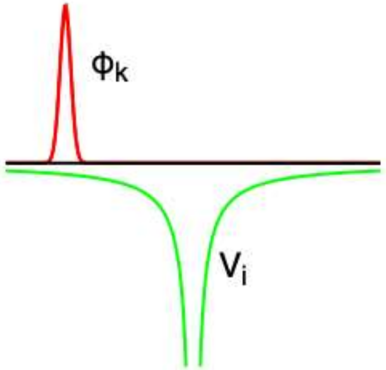
$$\boxed{c_k \int \varphi_k^*(\vec{r})\sum_{i\neq k} V_i(\vec{r})\,\varphi_k(\vec{r})\, d^3r} + \sum_{j\neq k} c_j \boxed{\int \varphi_k^*(\vec{r})\left[\frac{p^2}{2m}+V_k(\vec{r})\right]\varphi_j(\vec{r})}$$

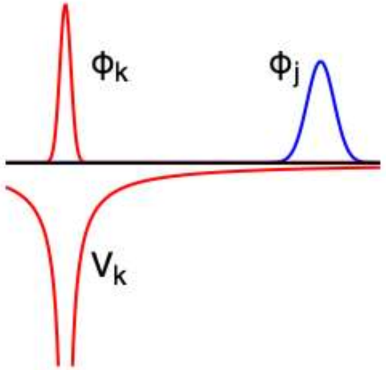
Crystal field : correction to the on-site

$\Delta\varepsilon_k$

Hooping terms

t_{kj}





$$= \varepsilon\left[c_k \boxed{\int \varphi_k^*(\vec{r})\,\varphi_k(\vec{r})\, d^3r} + \sum_{j\neq k} c_j \boxed{\int \varphi_k^*(\vec{r})\,\varphi_j(\vec{r})\, d^3r}\right]$$

Normalization

Uno

Overlap

S_{kj}

Tight-binding method

The one-electron energies and wavefunctions are obtained solving a generalized eigen-vector problem

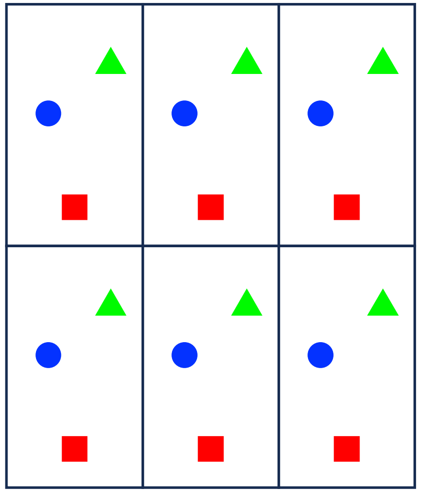
$$\begin{pmatrix} \varepsilon_1+\Delta\varepsilon_1 & t_{12} & t_{13} & \dots & t_{1N} \\ t_{21} & \varepsilon_2+\Delta\varepsilon_2 & t_{23} & \dots & t_{2N} \\ t_{31} & t_{32} & \varepsilon_3+\Delta\varepsilon_2 & \dots & t_{3N} \\ \vdots & \vdots & \vdots & & \\ t_{N1} & t_{N2} & t_{N3} & \dots & \varepsilon_N+\Delta\varepsilon_1 N \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} 1 & S_{12} & S_{13} & \dots & S_{1N} \\ S_{21} & 1 & S_{23} & \dots & S_{2N} \\ S_{31} & S_{32} & 1 & \dots & S_{3N} \\ \vdots & \vdots & \vdots & & \\ S_{N1} & S_{N2} & S_{N3} & \dots & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$

The parameters can be calculated from atomic data or
parametrized to fit experimental or calculated electronic structure data

A minimal tight-binding model usually neglects the crystal field correction and the overlap

$$\begin{pmatrix} \varepsilon_1 & t_{12} & t_{13} & \dots & t_{1N} \\ t_{21} & \varepsilon_2 & t_{23} & \dots & t_{2N} \\ t_{31} & t_{32} & \varepsilon_3 & \dots & t_{3N} \\ \vdots & \vdots & \vdots & & \\ t_{N1} & t_{N2} & t_{N3} & \dots & \varepsilon_N \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \varepsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix}$$

Tight-binding method for crystal systems



For a periodic system, the Hamiltonian has the potential of all the atoms in all the unit cells

$$\left[\frac{p^2}{2m} + \sum_{lmn}\sum_{i} V_i(\vec{r} - \vec{R}_{lmn})\right] \psi(\vec{r}) = \varepsilon\ \psi(\vec{r})$$

unit cells

the atoms in one unit cell

and we write the wavefunction as linear combination of all the orbitals of all the atoms in all the unit cells:

$$\psi(\vec{r}) = \sum_{lmn}\sum_{i}\sum_{\lambda_i}\ c_{i\lambda_i}(\vec{R}_{lmn})\ \varphi_{i\lambda_i}(\vec{r} - \vec{R}_{lmn})$$

unit cells

the atoms in one unit cell

the orbitals on atom i

To make the one-electron wavefunction compatible with Bloch,
the coefficients in one cell, have a phase, with respect to the coefficients in another.

$$c_{i\lambda_i}(\vec{R}_{lmn}) = \mathrm{e}^{i\vec{k}.\vec{R}_{lmn}}\ c_{i\lambda_i}$$

Tight-binding method for crystal systems

The wavefunction becomes

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{lmn} \mathrm{e}^{i\vec{k}.\vec{R}_{lmn}} \sum_{i} \sum_{\lambda_i} c^{n\vec{k}}_{i\lambda_i} \varphi_{i\lambda_i}(\vec{r}-\vec{R}_{lmn})$$

As before, we replace the system wavefunction in the Schrödinger equation, multiply by $\varphi^{*}_{k\lambda_k}(\vec{r})$ and integrate, to get :

$$\sum_{i} \sum_{\lambda_i} c^{n\vec{k}}_{i\lambda_i} \sum_{lmn} \mathrm{e}^{i\vec{k}.\vec{R}_{lmn}} \int \varphi^{*}_{k\lambda_k}(\vec{r})\; H(r)\; \varphi_{i\lambda_i}(\vec{r}-\vec{R}_{lmn}) = \varepsilon_{n\vec{k}}\; c^{n\vec{k}}_{k\lambda_k}$$

Let's simplify, one orbital per site, no crystal field :

$$c^{n\vec{k}}_{k}\left[\varepsilon_k + \sum_{lmn\neq 000} \mathrm{e}^{i\vec{k}.\vec{R}_{lmn}}\; t_{kk}(\vec{R}_{lmn})\right] + \sum_{i\neq k} c^{n\vec{k}}_{i} \sum_{lmn} \mathrm{e}^{i\vec{k}.\vec{R}_{lmn}}\; t_{ki}(\vec{R}_{lmn}) = \varepsilon_{n\vec{k}}\; c^{n\vec{k}}_{k}$$

Diagonal elements of the eigenvalue problem.
Atomic energy or *on-site energy* ε_k and the *hopping* with the same atom in the neighboring cells $\{lmn \neq 000\}$

Off-diagonal elements of the eigenvalue problem.
Hoppings with the other atoms in the same cell $\{lmn = 000\}$ and the neighboring cells $\{lmn \neq 000\}$

Tight-binding method for crystal systems

Eigenvalue problem of size N_{orb} *the total number of orbitals in the unit cell.*

$$N_{\mathrm{orb}} = \sum_{\alpha\,=\,\text{atoms in unit cell}} n_{\mathrm{orb}}(\alpha)$$

Every atom in the unit cell can contribute with a different number of orbitals

$$\underbrace{\underbrace{\underbrace{s,}_{1}\ \underbrace{p_x,\ p_y,\ p_z,}_{3}}_{4}\ \underbrace{d_{z^2},\ d_{xy},\ d_{xz},\ d_{yz},\ d_{x^2-y^2}}_{5}}_{9}$$

Tight-binding method for crystal systems

Fill the tight-binding matrix in three easy steps !!

1. Fill the diagonal elements with the on-site energies ε_k
2. Complete the diagonal elements with the hoppings t_{kk} between the same orbitals of the same atoms in different unit cells. Multiply each term by the phase $\mathrm{e}^{i\vec{k}.\vec{R}_{lmn}}$
3. Fill the off-diagonal elements with the hoppings t_{ki} between different orbitals of the same atom or different atoms. Multiply each term by the phase $\mathrm{e}^{i\vec{k}.\vec{R}_{lmn}}$

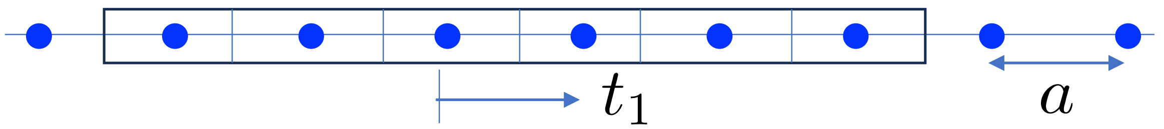
1D chain

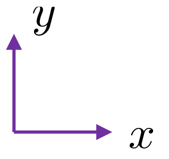
atoms per cell : one

orbital at 1 : s

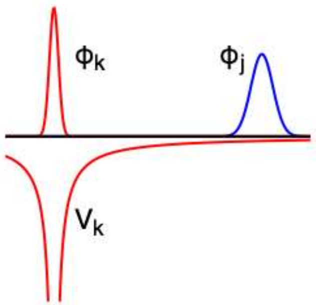
hoppings : first neighbors

$$N_{\mathrm{orb}} = 1$$

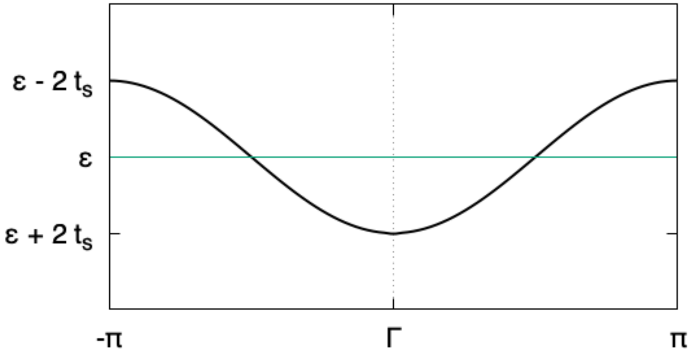




$$\varepsilon(\vec{k}) = \varepsilon_s + t_s\ \mathrm{e}^{ik_xa} + t_s\ \mathrm{e}^{-ik_xa} = \varepsilon_s + 2\ t_s \cos k_xa$$



$$t_s < 0$$

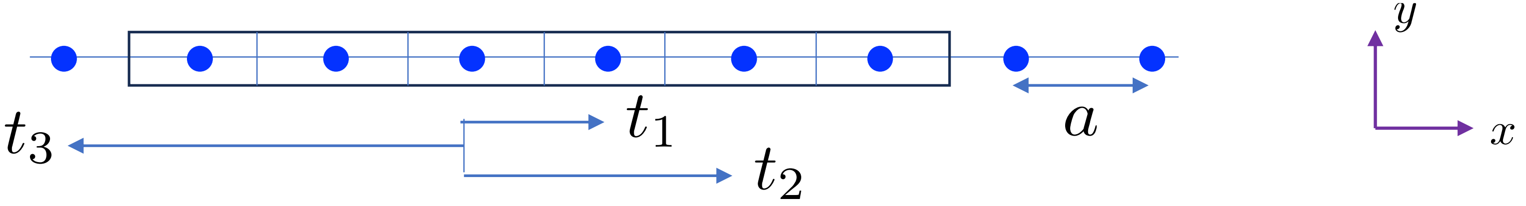


e_F

If 1 e$^-$ per site

Tight-binding method for crystal systems

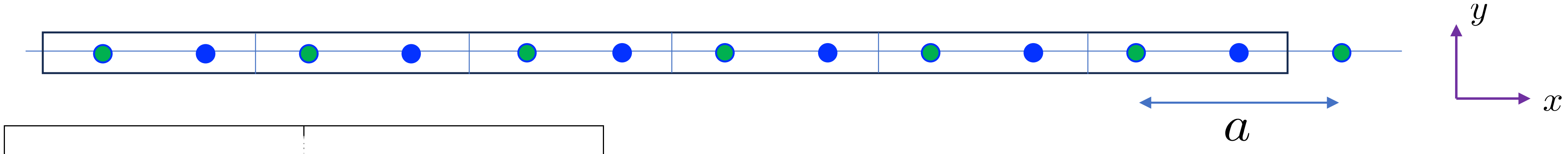
1D chain atoms per cell : one orbital at 1 : s hoppings : third neighbors $N_{\mathrm{orb}} = 1$

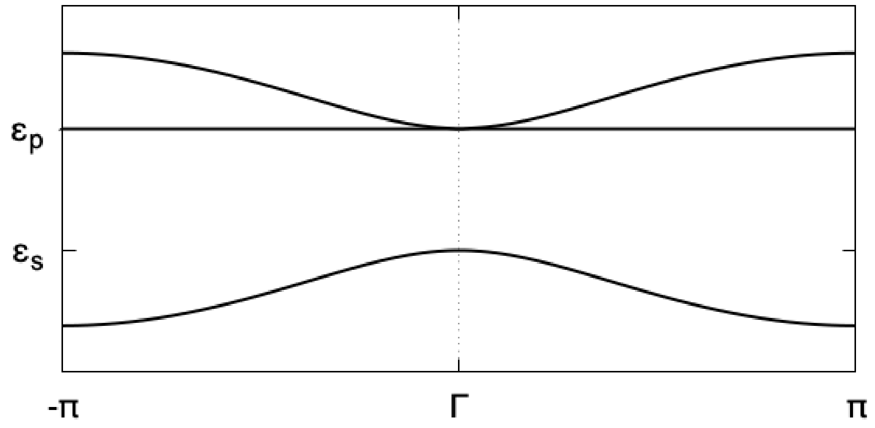


$$\varepsilon(\vec{k}) = \varepsilon_s + t_1\ \mathrm{e}^{ik_xa} + t_1\ \mathrm{e}^{-ik_xa} + t_2\ \mathrm{e}^{i2k_xa} + t_2\ \mathrm{e}^{-i2k_xa} + t_3\ \mathrm{e}^{i3k_xa} + t_3\ \mathrm{e}^{-i3k_xa}$$

$$\varepsilon(\vec{k}) = \varepsilon_s + 2t_1 \cos k_xa + 2t_2 \cos 2k_xa + 2t_3 \cos 3k_xa$$

1D chain atoms per cell : two orbital at 1 : s at 2 : $p_x\ p_y\ p_z$ hoppings : first neighbors $N_{\mathrm{orb}} = 4$

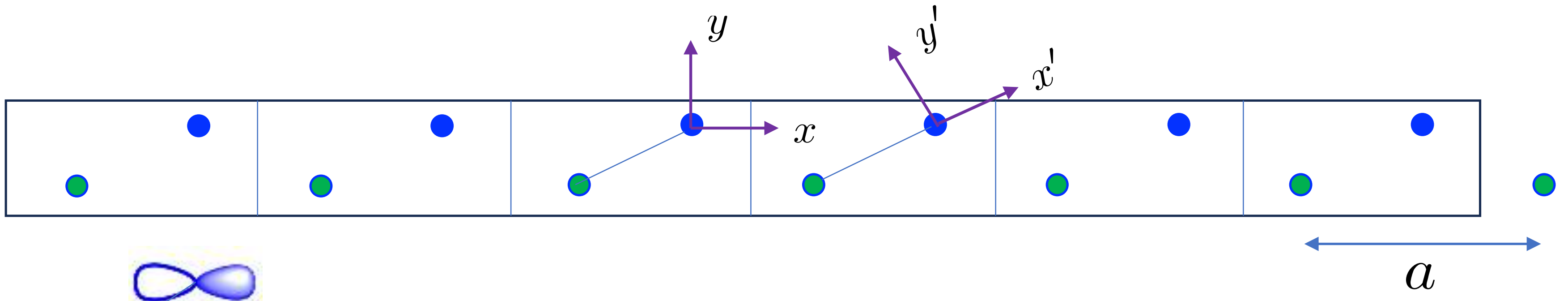




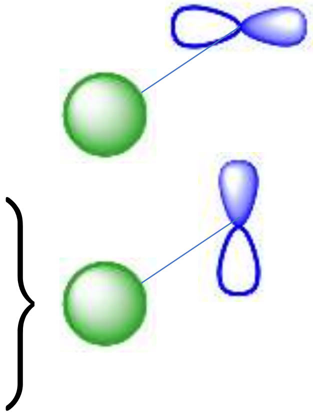
$$\begin{pmatrix} \varepsilon_s & t_{sp_x}(1 - \mathrm{e}^{-ik_xa}) & 0 & 0 \\ t_{sp_x}(1 - \mathrm{e}^{ik_xa}) & \varepsilon_p & 0 & 0 \\ 0 & 0 & \varepsilon_p & 0 \\ 0 & 0 & 0 & \varepsilon_p \end{pmatrix}$$

Tight-binding method for crystal systems

1D chain atoms per cell : two orbital at 1 : s at 2 : $p_x \; p_y \; p_z$ hoppings : first neighbors $N_{\mathrm{orb}} = 4$



$t_{sp_x} \neq 0$

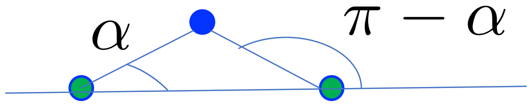


$t_{sp_y} \neq 0$

$t_{sp_z} \neq 0$

$$\begin{pmatrix} \varepsilon_s & t_{sp_x}(1-\mathrm{e}^{-ik_x a}) & t_{sp_y}(1-\mathrm{e}^{-ik_y a}) & t_{sp_z}(1-\mathrm{e}^{-ik_z a}) \\ t_{sp_x}(1-\mathrm{e}^{ik_x a}) & \varepsilon_p & 0 & 0 \\ t_{sp_y}(1-\mathrm{e}^{ik_z a}) & 0 & \varepsilon_p & \\ t_{sp_z}(1-\mathrm{e}^{ik_z a}) & 0 & 0 & \varepsilon_p \end{pmatrix}$$

If we rotate the p orbitals, only $t_{sp_{x'}} \neq 0$ and $t_{sp_{y'}} = 0 \;\; t_{sp_{z'}} = 0$



The only non zero hopping is called $t_{sp_{x'}} = t_{sp_\sigma}$ and all the hoppings can be calculated from it

$$t_{sp_x} = \cos\alpha \; t_{sp_\sigma} = l \; t_{sp_\sigma}$$

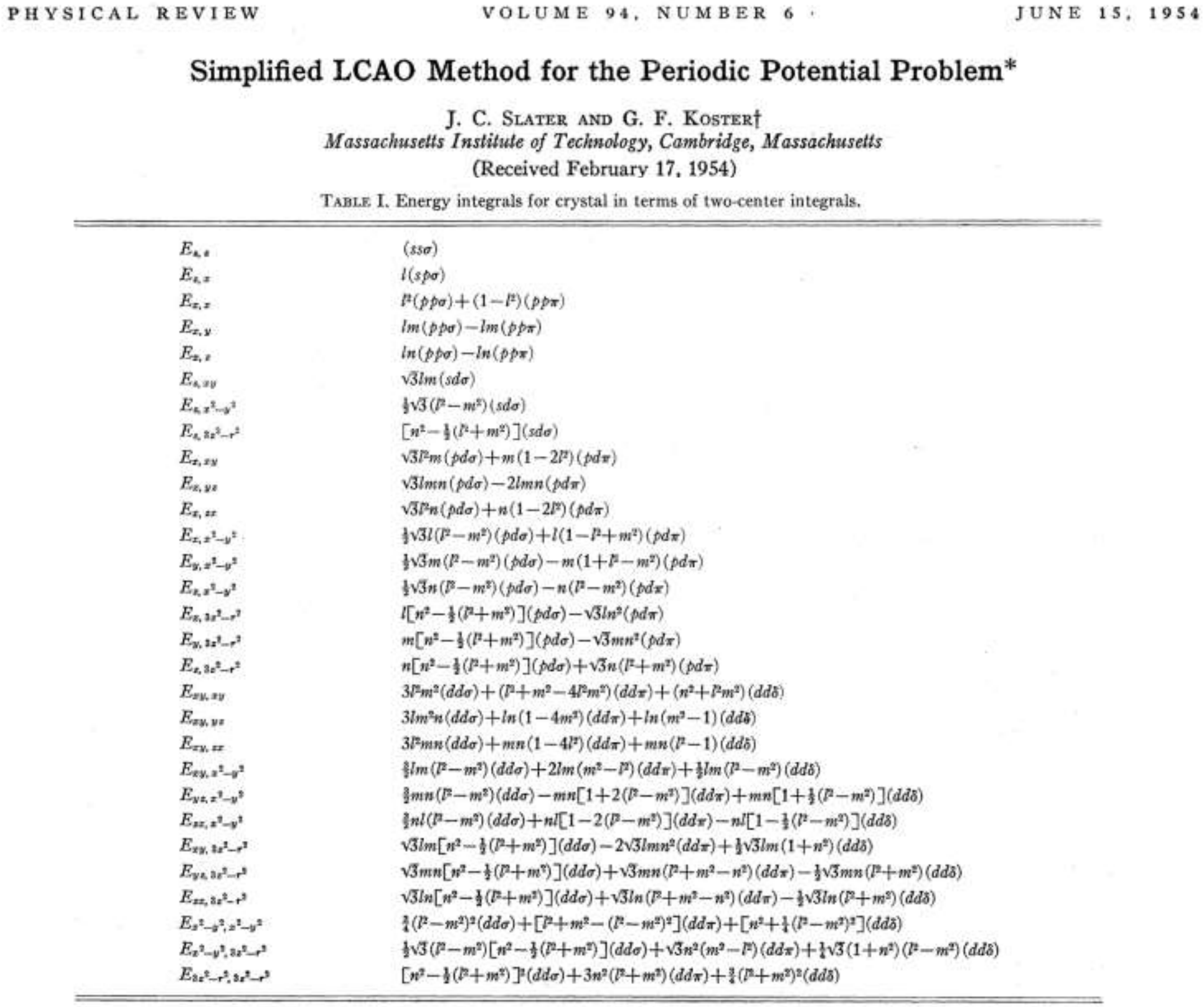
$$t_{sp_y} = \cos\beta \; t_{sp_\sigma} = m \; t_{sp_\sigma}$$

$$t_{sp_z} = \cos\gamma \; t_{sp_\sigma} = n \; t_{sp_\sigma}$$

$$\begin{pmatrix} \varepsilon_s & l\; t_{sp_\sigma}(1-\mathrm{e}^{-ik_x a}) & m\; t_{sp_\sigma}(1+\mathrm{e}^{-ik_y a}) & n\; t_{sp_\sigma}(1-\mathrm{e}^{-ik_x a}) \\ l\; t_{sp_\sigma}(1-\mathrm{e}^{ik_x a}) & \varepsilon_p & 0 & 0 \\ m\; t_{sp_\sigma}(1+\mathrm{e}^{ik_z a}) & 0 & \varepsilon_p & \\ n\; t_{sp_\sigma}(1-\mathrm{e}^{ik_x a}) & 0 & 0 & \varepsilon_p \end{pmatrix}$$

If the two atoms have different z coordinates

Slater and Koster



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Simplified LCAO Method for the Periodic Potential Problem*

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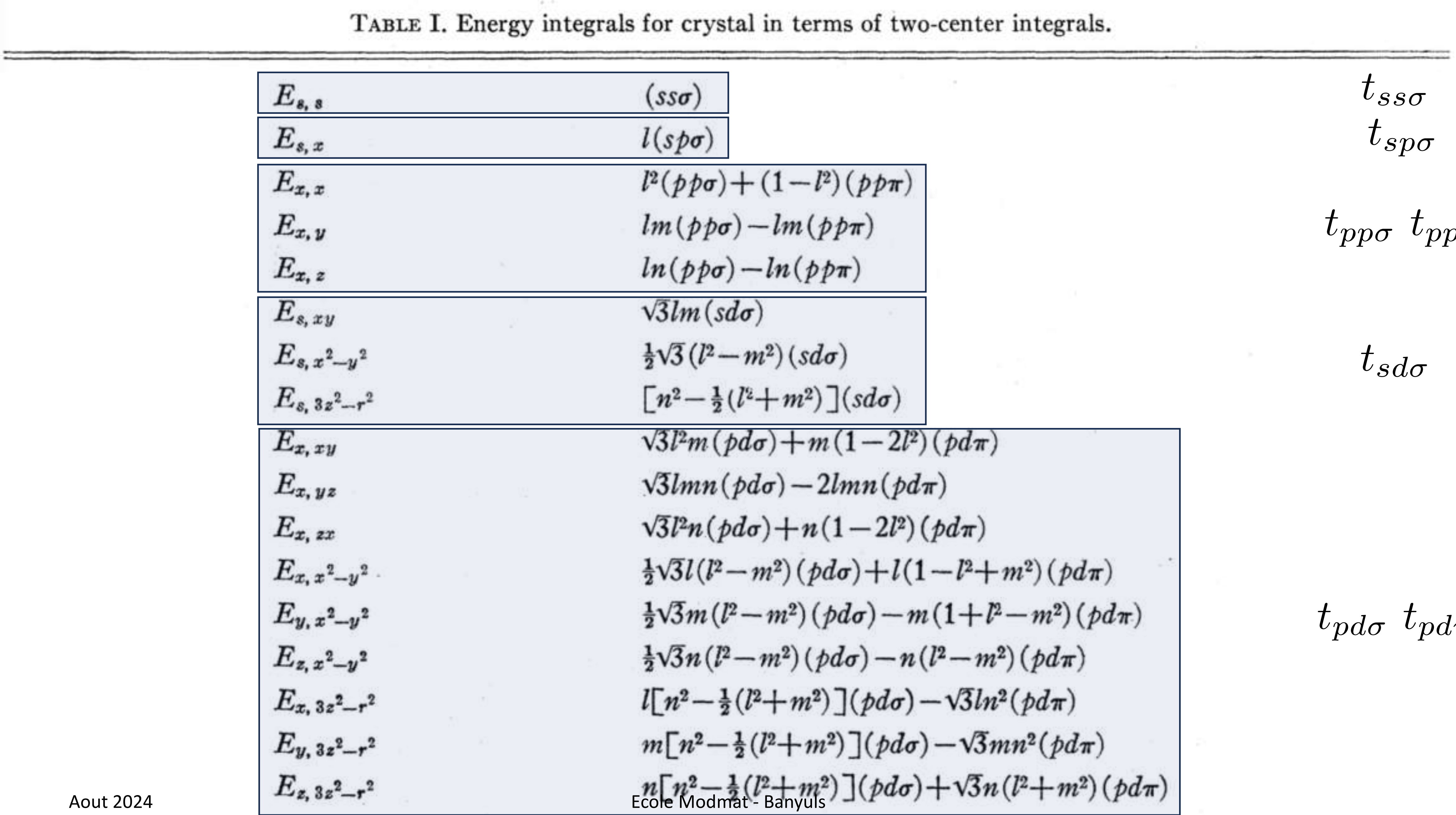
(Received February 17, 1954)

TABLE I. Energy integrals for crystal in terms of two-center integrals.

$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2-m^2)(sd\sigma)$
$E_{s,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)](sd\sigma)$
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$
$E_{x,yz}$	$\sqrt{3}lmn(pd\sigma)-2lmn(pd\pi)$
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma)+n(1-2l^2)(pd\pi)$
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2-m^2)(pd\sigma)+l(1-l^2+m^2)(pd\pi)$
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2-m^2)(pd\sigma)-m(1+l^2-m^2)(pd\pi)$
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma)-n(l^2-m^2)(pd\pi)$
$E_{x,3z^2-r^2}$	$l[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}ln^2(pd\pi)$
$E_{y,3z^2-r^2}$	$m[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}mn^2(pd\pi)$
$E_{z,3z^2-r^2}$	$n[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)+\sqrt{3}n(l^2+m^2)(pd\pi)$
$E_{xy,xy}$	$3l^2m^2(dd\sigma)+(l^2+m^2-4l^2m^2)(dd\pi)+(n^2+l^2m^2)(dd\delta)$
$E_{xy,yz}$	$3lm^2n(dd\sigma)+ln(1-4m^2)(dd\pi)+ln(m^2-1)(dd\delta)$
$E_{xy,zx}$	$3l^2mn(dd\sigma)+mn(1-4l^2)(dd\pi)+mn(l^2-1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2-m^2)(dd\sigma)+2lm(m^2-l^2)(dd\pi)+\frac{1}{2}lm(l^2-m^2)(dd\delta)$
E_{yz,x^2-y^2}	$\frac{3}{2}mn(l^2-m^2)(dd\sigma)-mn[1+2(l^2-m^2)](dd\pi)+mn[1+\frac{1}{2}(l^2-m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2-m^2)(dd\sigma)+nl[1-2(l^2-m^2)](dd\pi)-nl[1-\frac{1}{2}(l^2-m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)-2\sqrt{3}lmn^2(dd\pi)+\frac{1}{2}\sqrt{3}lm(1+n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}mn(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}mn(l^2+m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}ln(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}ln(l^2+m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2-m^2)^2(dd\sigma)+[l^2+m^2-(l^2-m^2)^2](dd\pi)+[n^2+\frac{1}{4}(l^2-m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2-m^2)[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}n^2(m^2-l^2)(dd\pi)+\frac{1}{4}\sqrt{3}(1+n^2)(l^2-m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)]^2(dd\sigma)+3n^2(l^2+m^2)(dd\pi)+\frac{3}{4}(l^2+m^2)^2(dd\delta)$

Slater and Koster



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$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$	$t_{pp\sigma}$ $t_{pp\pi}$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$	
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$	
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$	$t_{sd\sigma}$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2-m^2)(sd\sigma)$	
$E_{s,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)](sd\sigma)$	
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$	$t_{pd\sigma}$ $t_{pd\pi}$
$E_{x,yz}$	$\sqrt{3}lmn(pd\sigma)-2lmn(pd\pi)$	
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma)+n(1-2l^2)(pd\pi)$	
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2-m^2)(pd\sigma)+l(1-l^2+m^2)(pd\pi)$	
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2-m^2)(pd\sigma)-m(1+l^2-m^2)(pd\pi)$	
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma)-n(l^2-m^2)(pd\pi)$	
$E_{x,3z^2-r^2}$	$l[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}ln^2(pd\pi)$	
$E_{y,3z^2-r^2}$	$m[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}mn^2(pd\pi)$	
$E_{z,3z^2-r^2}$	$n[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)+\sqrt{3}n(l^2+m^2)(pd\pi)$	

Slater and Koster

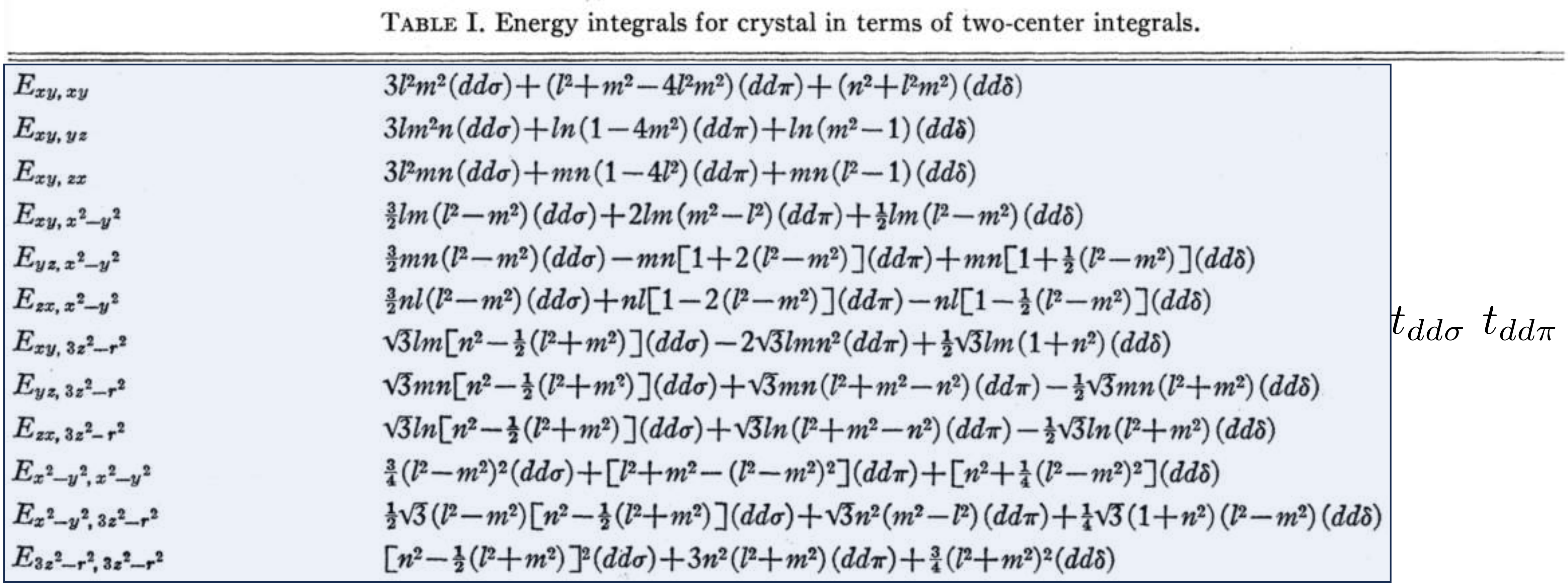
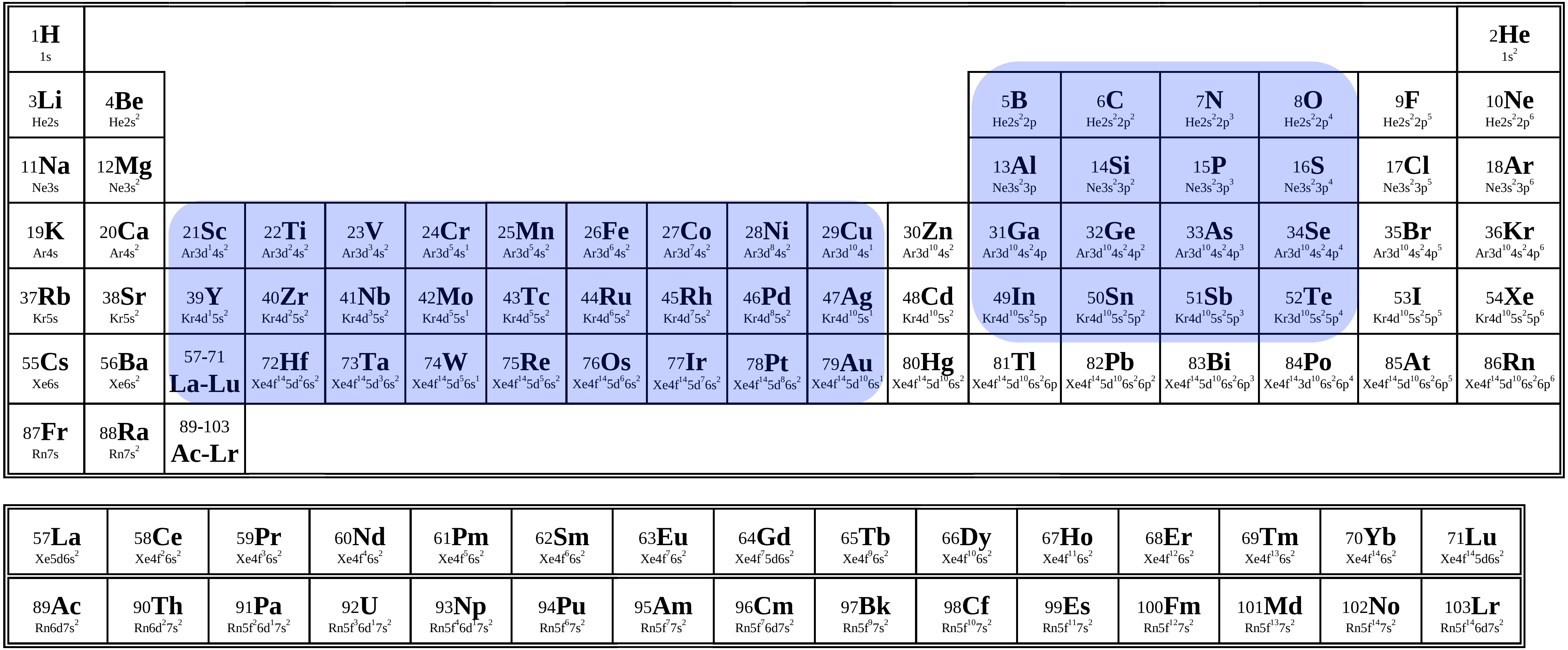


TABLE I. Energy integrals for crystal in terms of two-center integrals.

$E_{xy,xy}$	$3l^2m^2(dd\sigma)+(l^2+m^2-4l^2m^2)(dd\pi)+(n^2+l^2m^2)(dd\delta)$
$E_{xy,yz}$	$3lm^2n(dd\sigma)+ln(1-4m^2)(dd\pi)+ln(m^2-1)(dd\delta)$
$E_{xy,zx}$	$3l^2mn(dd\sigma)+mn(1-4l^2)(dd\pi)+mn(l^2-1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2-m^2)(dd\sigma)+2lm(m^2-l^2)(dd\pi)+\frac{1}{2}lm(l^2-m^2)(dd\delta)$
E_{yz,x^2-y^2}	$\frac{3}{2}mn(l^2-m^2)(dd\sigma)-mn[1+2(l^2-m^2)](dd\pi)+mn[1+\frac{1}{2}(l^2-m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2-m^2)(dd\sigma)+nl[1-2(l^2-m^2)](dd\pi)-nl[1-\frac{1}{2}(l^2-m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)-2\sqrt{3}lmn^2(dd\pi)+\frac{1}{2}\sqrt{3}lm(1+n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}mn(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}mn(l^2+m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}ln(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}ln(l^2+m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2-m^2)^2(dd\sigma)+[l^2+m^2-(l^2-m^2)^2](dd\pi)+[n^2+\frac{1}{4}(l^2-m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2-m^2)[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}n^2(m^2-l^2)(dd\pi)+\frac{1}{4}\sqrt{3}(1+n^2)(l^2-m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)]^2(dd\sigma)+3n^2(l^2+m^2)(dd\pi)+\frac{3}{4}(l^2+m^2)^2(dd\delta)$

$t_{dd\sigma}$ $t_{dd\pi}$ $t_{dd\delta}$

Tight-binding : good for localized and directional orbitals



Periodic Table of the Elements

1**H** 1s																	2**He** 1s^{2}
3**Li** He2s	4**Be** He2s^{2}											5**B** He2s^{2}2p	6**C** He2s^{2}2p^{2}	7**N** He2s^{2}2p^{3}	8**O** He2s^{2}2p^{4}	9**F** He2s^{2}2p^{5}	10**Ne** He2s^{2}2p^{6}
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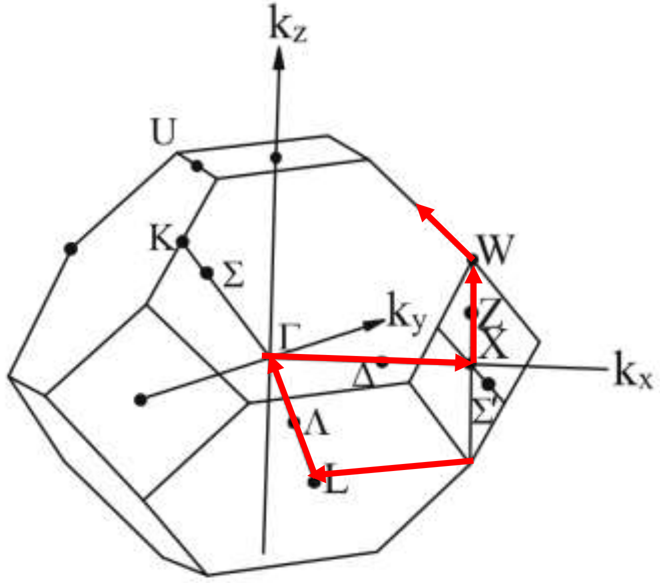
55**Cs** Xe6s	56**Ba** Xe6s^{2}	57-71 **La-Lu**	72**Hf** Xe4f^{14}5d^{2}6s^{2}	73**Ta** Xe4f^{14}5d^{3}6s^{2}	74**W** Xe4f^{14}5d^{5}6s^{1}	75**Re** Xe4f^{14}5d^{5}6s^{2}	76**Os** Xe4f^{14}5d^{6}6s^{2}	77**Ir** Xe4f^{14}5d^{7}6s^{2}	78**Pt** Xe4f^{14}5d^{8}6s^{2}	79**Au** Xe4f^{14}5d^{10}6s^{1}	80**Hg** Xe4f^{14}5d^{10}6s^{2}	81**Tl** Xe4f^{14}5d^{10}6s^{2}6p	82**Pb** Xe4f^{14}5d^{10}6s^{2}6p^{2}	83**Bi** Xe4f^{14}5d^{10}6s^{2}6p^{3}	84**Po** Xe4f^{14}3d^{10}6s^{2}6p^{4}	85**At** Xe4f^{14}5d^{10}6s^{2}6p^{5}	86**Rn** Xe4f^{14}5d^{10}6s^{2}6p^{6}
87**Fr** Rn7s	88**Ra** Rn7s^{2}	89-103 **Ac-Lr**															

57**La** Xe5d6s^{2}	58**Ce** Xe4f^{2}6s^{2}	59**Pr** Xe4f^{3}6s^{2}	60**Nd** Xe4f^{4}6s^{2}	61**Pm** Xe4f^{5}6s^{2}	62**Sm** Xe4f^{6}6s^{2}	63**Eu** Xe4f^{7}6s^{2}	64**Gd** Xe4f^{7}5d6s^{2}	65**Tb** Xe4f^{9}6s^{2}	66**Dy** Xe4f^{10}6s^{2}	67**Ho** Xe4f^{11}6s^{2}	68**Er** Xe4f^{12}6s^{2}	69**Tm** Xe4f^{13}6s^{2}	70**Yb** Xe4f^{14}6s^{2}	71**Lu** Xe4f^{14}5d6s^{2}
89**Ac** Rn6d7s^{2}	90**Th** Rn6d^{2}7s^{2}	91**Pa** Rn5f^{2}6d^{1}7s^{2}	92**U** Rn5f^{3}6d^{1}7s^{2}	93**Np** Rn5f^{4}6d^{1}7s^{2}	94**Pu** Rn5f^{6}7s^{2}	95**Am** Rn5f^{7}7s^{2}	96**Cm** Rn5f^{7}6d7s^{2}	97**Bk** Rn5f^{9}7s^{2}	98**Cf** Rn5f^{10}7s^{2}	99**Es** Rn5f^{11}7s^{2}	100**Fm** Rn5f^{12}7s^{2}	101**Md** Rn5f^{13}7s^{2}	102**No** Rn5f^{14}7s^{2}	103**Lr** Rn5f^{14}6d7s^{2}

Why some materials have an electronic gap

Why some materials are semiconductors ?



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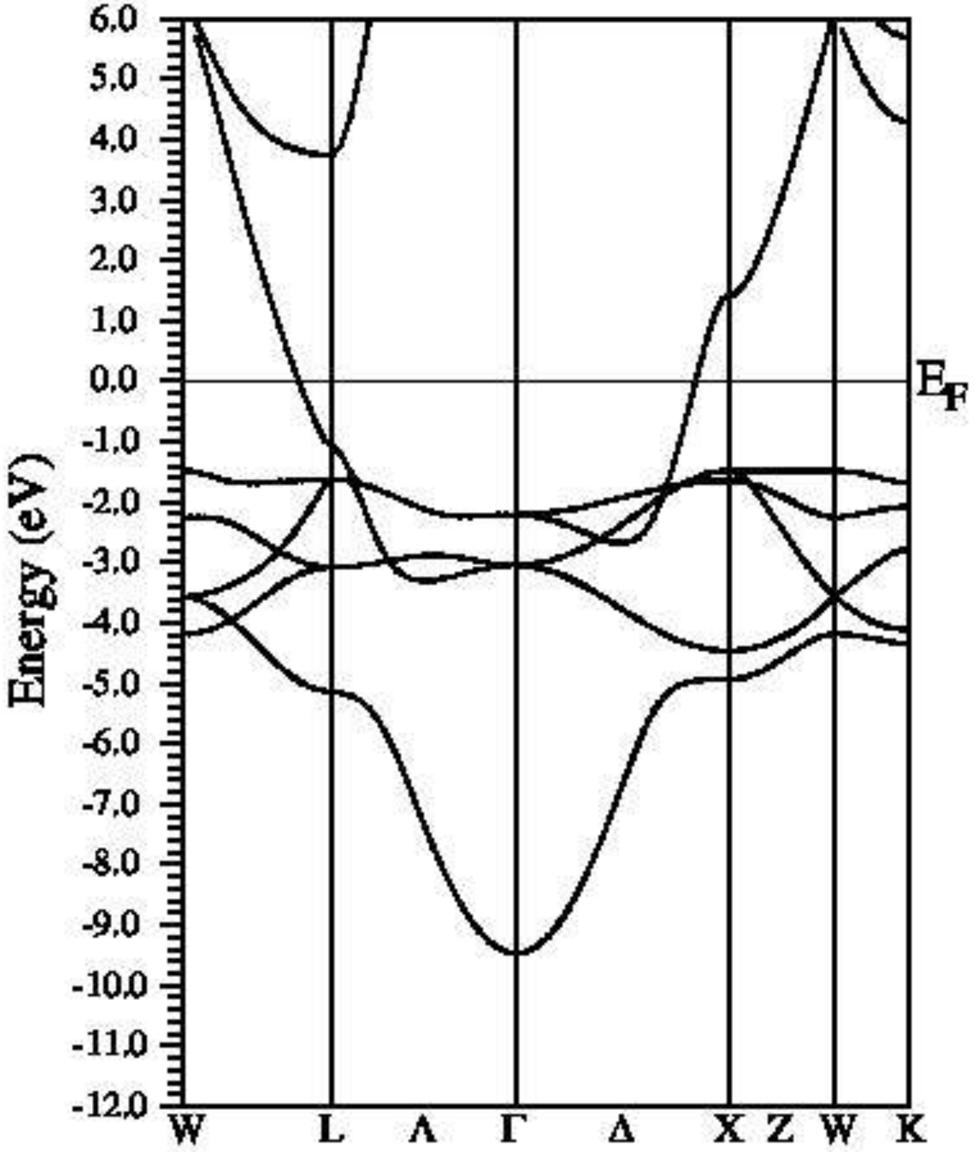

Cu fcc

$3d^{10}4s^1$

11 electrons
5 full bands
1 half filled

Why some materials are semiconductors ?

Periodic Table of the Elements

1**H** 1s												III	IV	V			2**He** 1s^{2}
3**Li** He2s	4**Be** He2s^{2}											5**B** He2s^{2}2p	6**C** He2s^{2}2p^{2}	7**N** He2s^{2}2p^{3}	8**O** He2s^{2}2p^{4}	9**F** He2s^{2}2p^{5}	10**Ne** He2s^{2}2p^{6}
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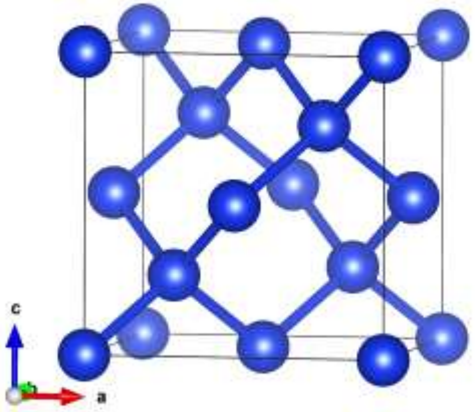
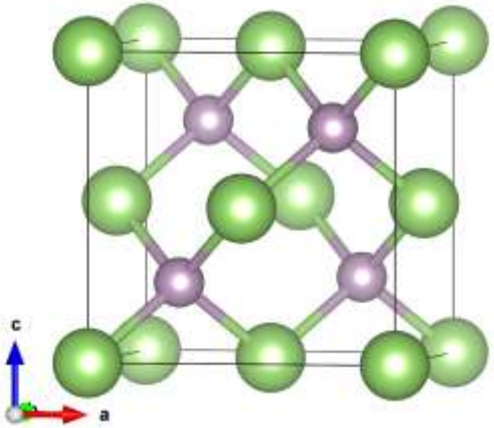
Semiconductors with tetrahedrally coordinated structures



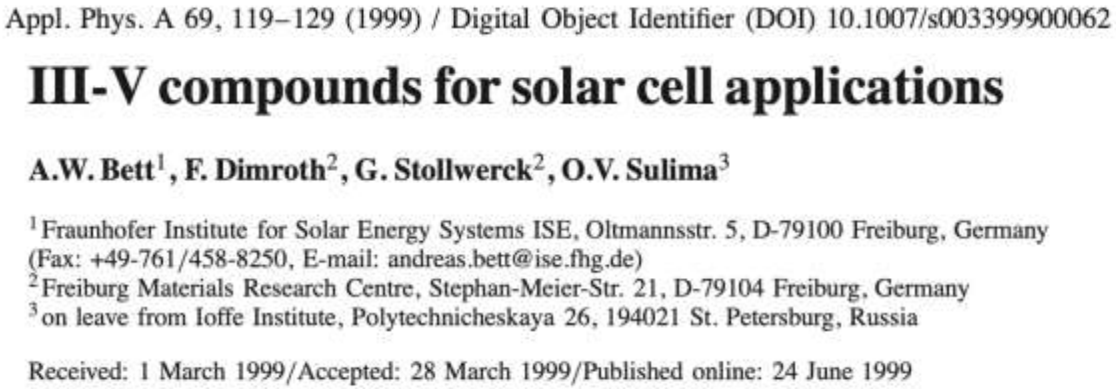
Group IV
C, Si, Ge
Two atoms per unit cell
$2 \times ns^2np^2$



Group III-V
GaP, GaAs, GaSb
Two atoms per unit cell
$n_1s^2n_1p^1 \; n_2s^2n_2p^3$

A minimum tight-binding needs 8 orbitals

Let’s explain the idea first with a 1D model



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III-V compounds for solar cell applications

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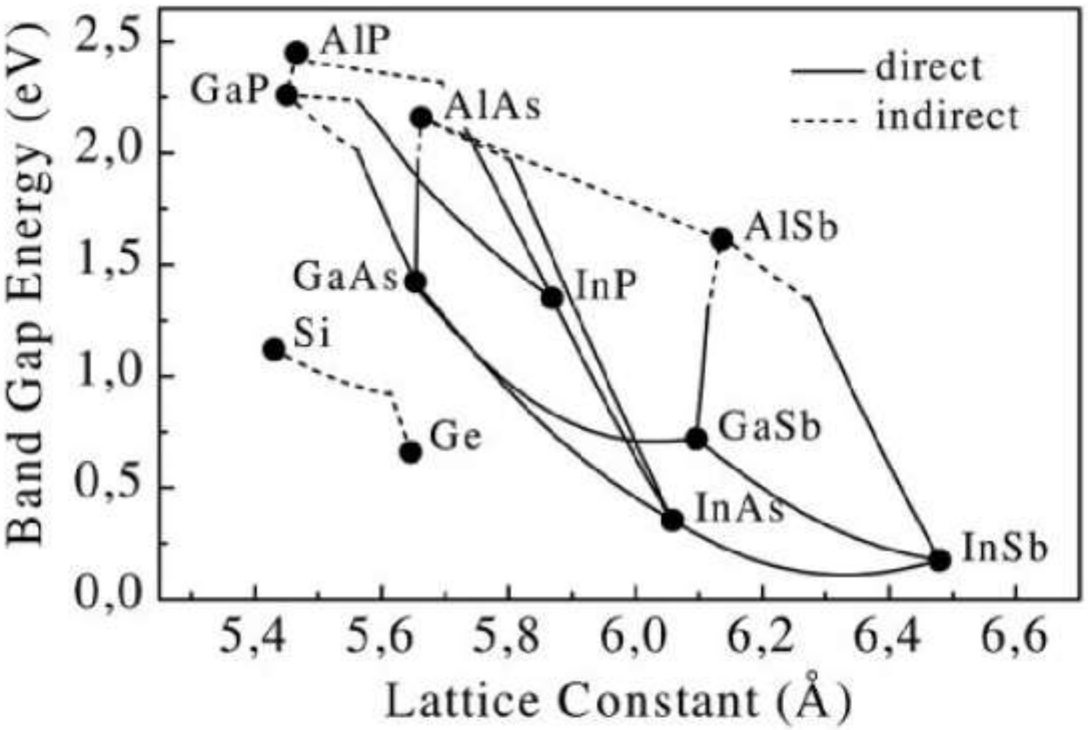
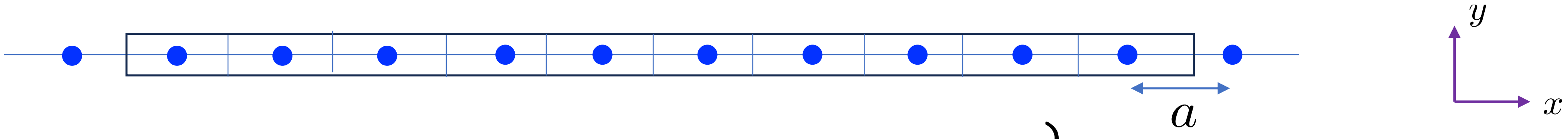


Fig. 1. Band gap versus lattice constant for different III-V materials

Why some materials are semiconductors ? Toy model.

1D chain atoms per cell : one orbitals : $s \; p_x \; p_y \; p_z$ hoppings : first neighbors $N_{\mathrm{orb}} = 4$

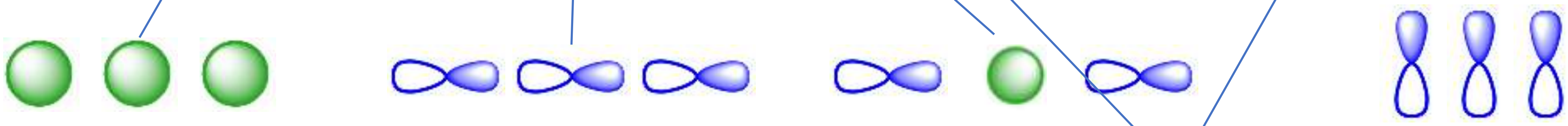


For a simple model of a tetrahedrally coordinated semiconductor, we imagine a 1D chain with one atom per unit cell, and s and p orbitals.

4 orbitals and 2 electrons per site, n atoms
4 n orbitals, 2 n electrons in total

The Hamiltonian matrix is :

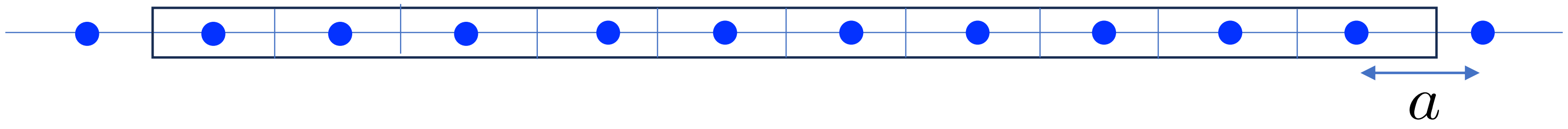
$$\begin{pmatrix} \varepsilon_s + 2\, t_{ss} \cos ka & 2\, i\, t_{sp_\sigma} \sin ka & 0 & 0 \\ -2\, i\, t_{sp_\sigma} \sin ka & \varepsilon_p + 2\, t_{pp\sigma} \cos ka & 0 & 0 \\ 0 & 0 & \varepsilon_p + \Delta\varepsilon_p + t_{pp\pi} \cos ka & 0 \\ 0 & 0 & 0 & \varepsilon_p + \Delta\varepsilon_p + 2\, t_{pp\pi} \cos ka \end{pmatrix}$$

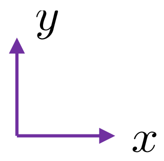


To consider only the s and p_x orbitals we can imagine that there is a large crystal field that pushes the p_y and p_z orbitals to higher energies.

Why some materials are semiconductors ? Toy model.

1D chain   atoms per cell : one   orbitals : $s \; p_x \; p_y \; p_z$ hoppings : first neighbors $N_{\text{orb}} = 4$





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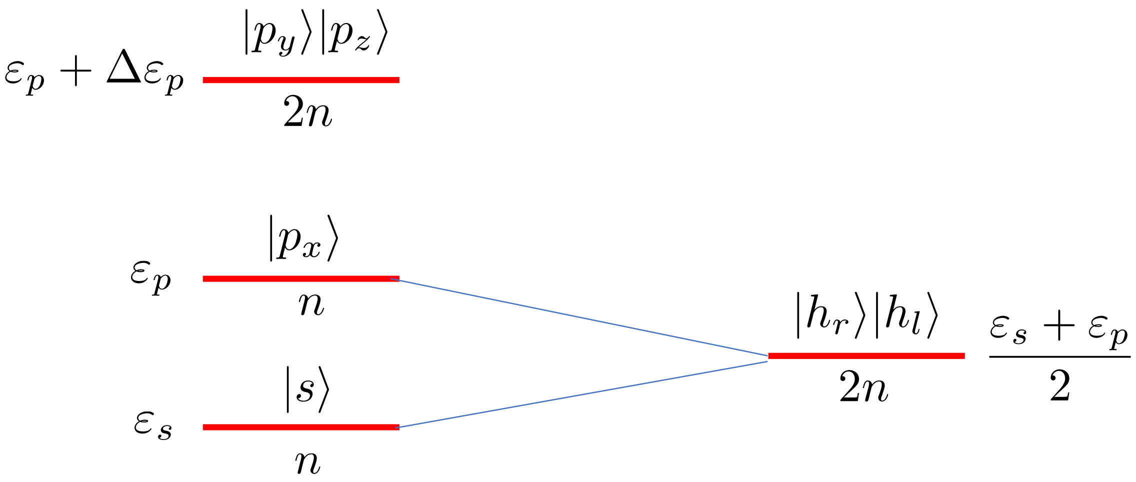


$\varepsilon_p + \Delta\varepsilon_p$ $|p_y\rangle|p_z\rangle$ $2n$

ε_p $|p_x\rangle$ n

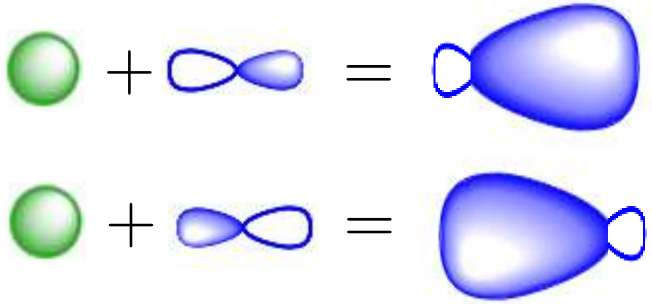
ε_s $|s\rangle$ n

$|h_r\rangle|h_l\rangle$ $2n$ $\dfrac{\varepsilon_s + \varepsilon_p}{2}$

With the s and p_x orbitals we can construct *hybrid* orbitals

$$|h_r\rangle = \frac{1}{\sqrt{2}}(|s\rangle + |p_x\rangle) = \quad + \quad =$$

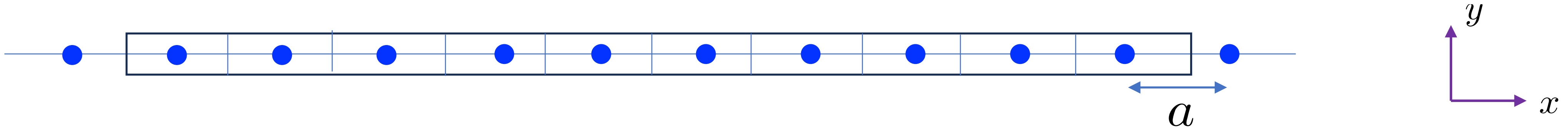
$$|h_l\rangle = \frac{1}{\sqrt{2}}(|s\rangle - |p_x\rangle) = \quad + \quad =$$



$$\left.\right\} \quad \varepsilon_{h_r} = \varepsilon_{h_l} = \frac{\varepsilon_s + \varepsilon_p}{2}$$

Why some materials are semiconductors ? Toy model.

1D chain atoms per cell : one orbitals : s p_x p_y p_z hoppings : first neighbors $N_{\text{orb}} = 4$



4 orbitals and 2 electrons per site, n atoms
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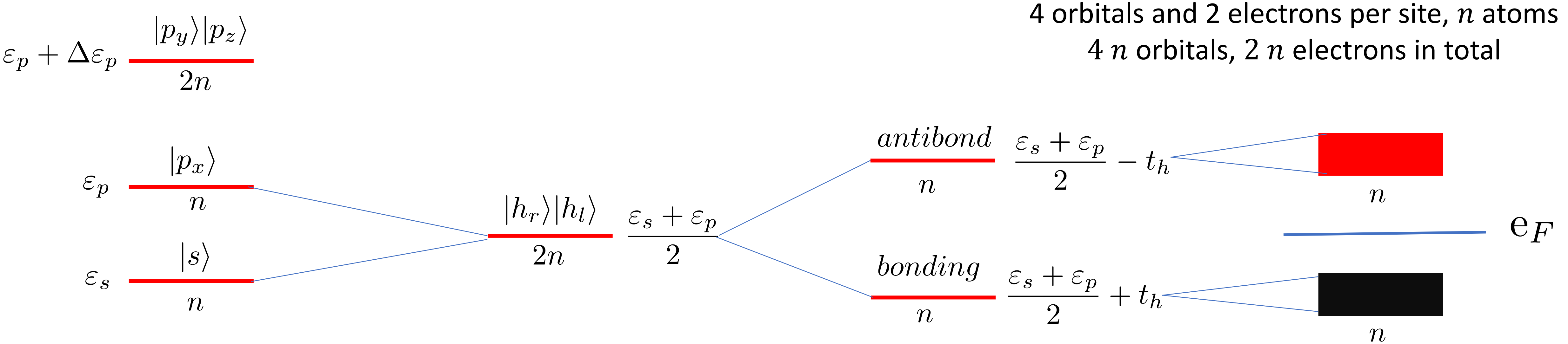
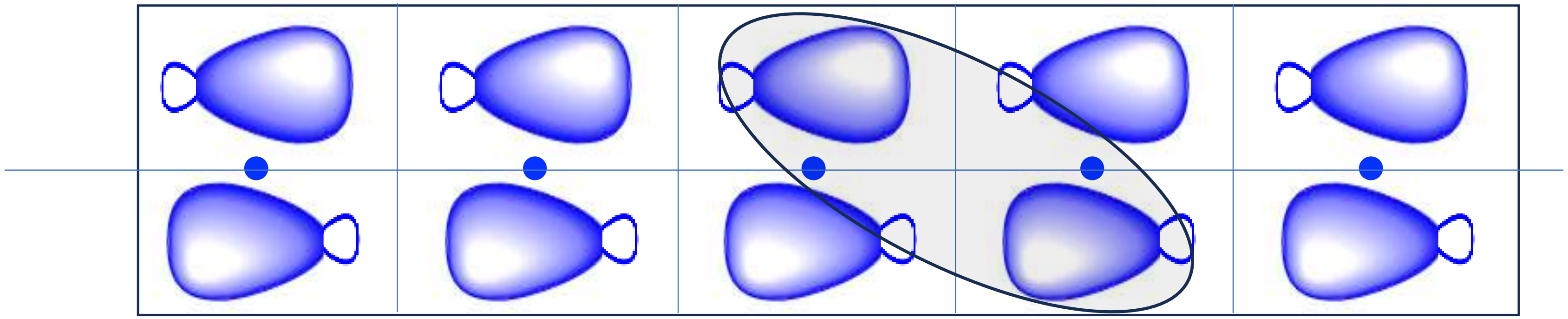


There are two hybrid orbitals on each site : the largest hopping t_h is between the $|h_l>$ in one site with the $|h_r>$ on the right

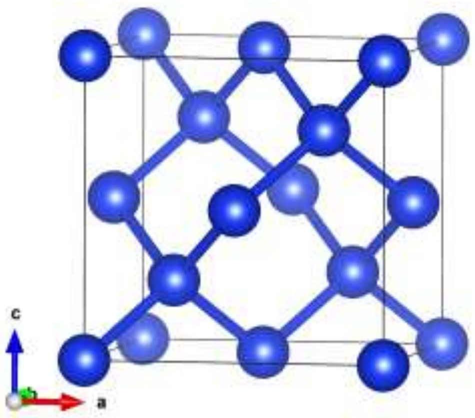


We can form bonding and antibonding molecular orbitals

The small remaining interactions form bands

Semiconductors with tetrahedrally coordinated structures

3D system atoms per cell : two orbitals : $s\ p_x\ p_y\ p_z$ hoppings : first neighbors $N_{\mathrm{orb}} = 8$



Group IV
C, Si, Ge

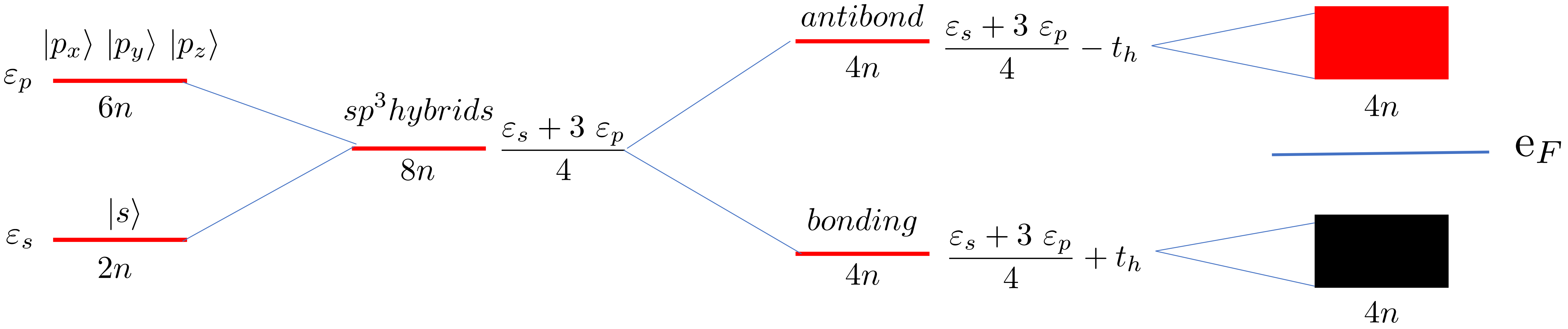
Two atoms per unit cell, n unit cells, 2 n atoms
Orbitals : 4 per atom, 8 n in total

$2 \times s^2 p^2$
Electrons : 4 per atom, 8 n in total

With the s and the three p orbitals we can construct four *hybrid* orbitals per atom

$$|h_{111}\rangle = \frac{1}{2}\,[\ |s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle\ ] \qquad |h_{\bar{1}1\bar{1}}\rangle = \frac{1}{2}\,[\ |s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle\ ]$$

$$|h_{1\bar{1}\bar{1}}\rangle = \frac{1}{2}\,[\ |s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle\ ] \qquad |h_{\bar{1}\bar{1}1}\rangle = \frac{1}{2}\,[\ |s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle\ ]$$



$|p_x\rangle\ |p_y\rangle\ |p_z\rangle$

ε_p

$6n$

$|s\rangle$

ε_s

$2n$

$sp^3 hybrids$ $\frac{\varepsilon_s + 3\,\varepsilon_p}{4}$

$8n$

$antibond$ $\frac{\varepsilon_s + 3\,\varepsilon_p}{4} - t_h$

$4n$

$4n$

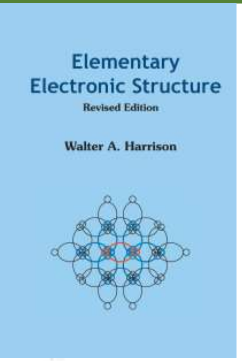
e_F

$bonding$ $\frac{\varepsilon_s + 3\,\varepsilon_p}{4} + t_h$

$4n$

$4n$

Semiconductors with tetrahedrally coordinated structures



Elementary
Electronic Structure
Revised Edition

Walter A. Harrison

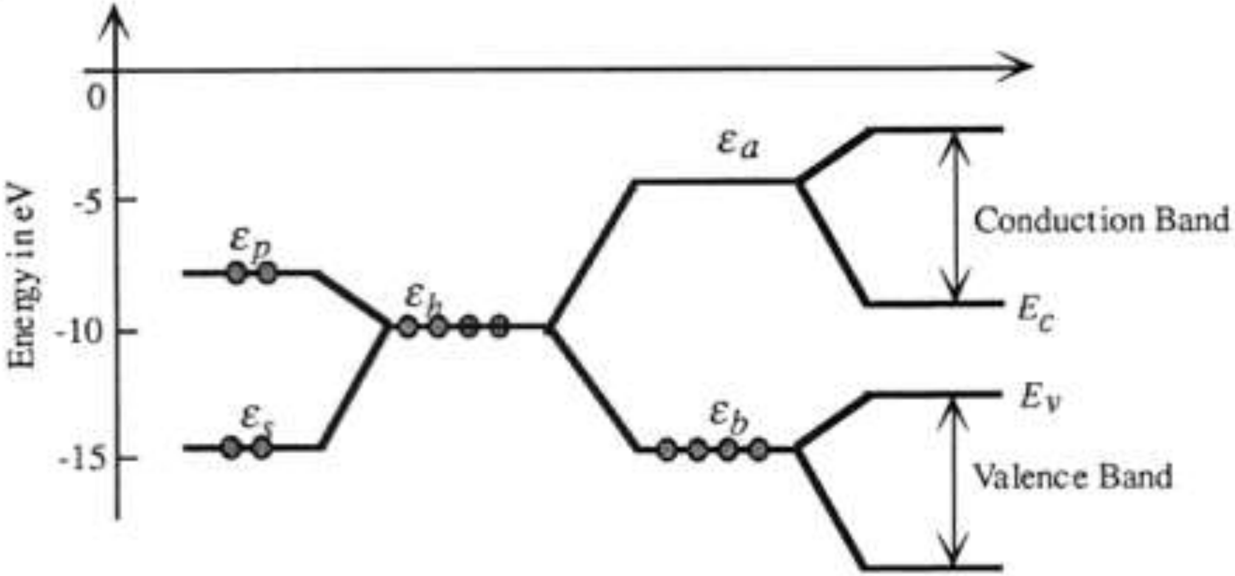


Fig. 2-4. Development of the electronic structure of silicon. The single s-states and p-states on each atom are transformed to four hybrid states, which are combined with neighboring hybrids to form bonds. The Bond-Orbital Approximation stops at that point and neglects additional couplings which finally broaden the bonding and antibonding levels into energy bands in the crystal.

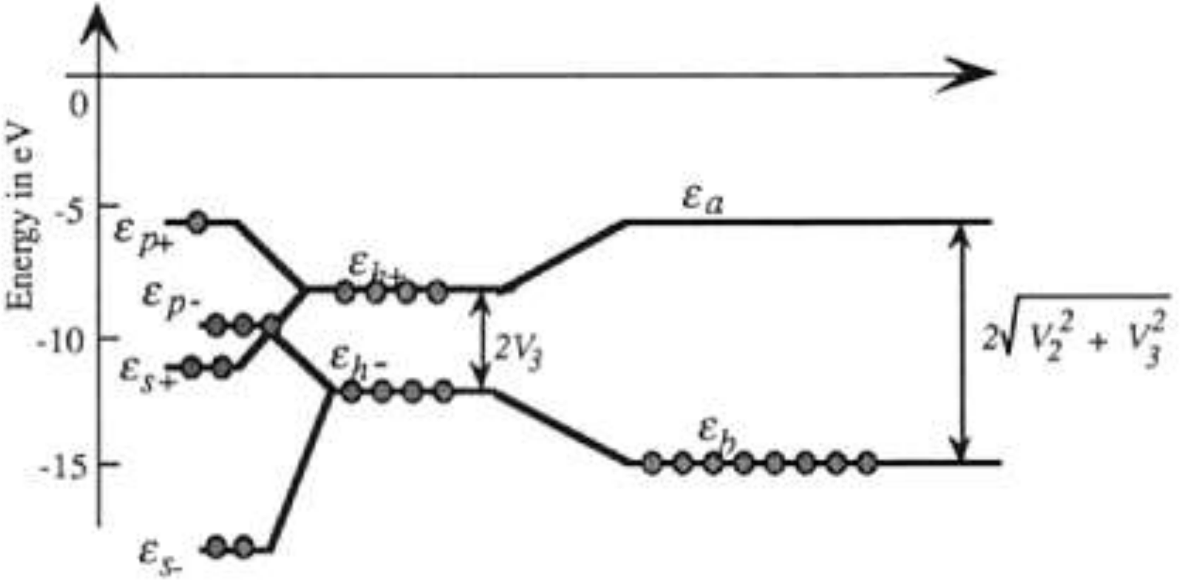
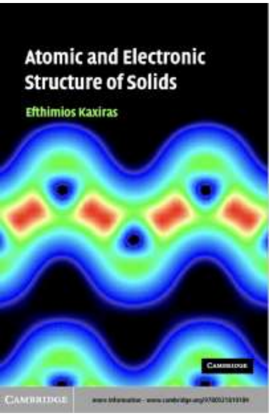
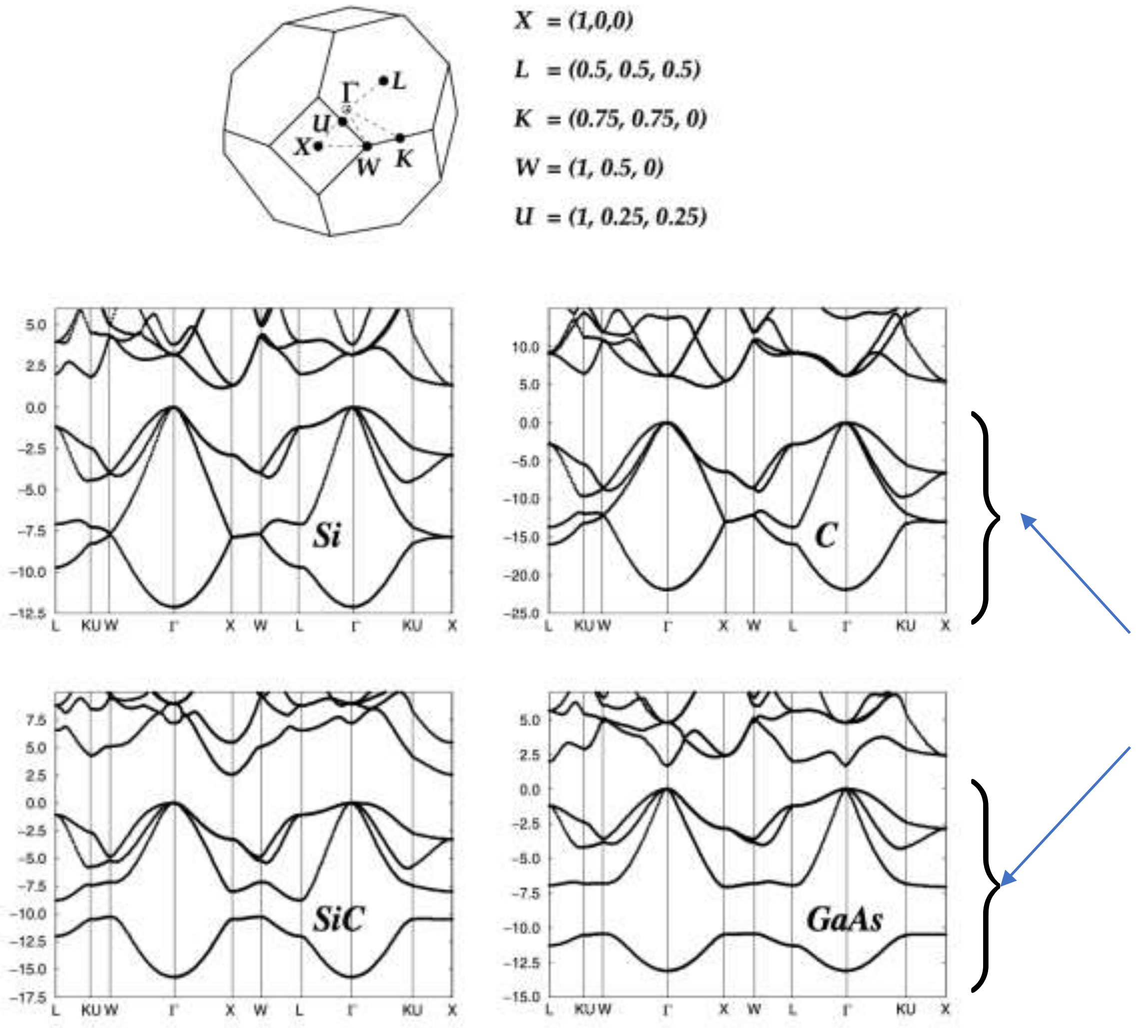


Fig. 2-5. Development of the electronic structure of gallium arsenide. The s-state and p-state energies given in Table 1-1 are transformed to individual hybrids, each with energy $(\varepsilon_s + 3\varepsilon_p)/4$ for the atom in question, which then form bonding and antibonding states with the other hybrid in the bond. We have shown all eight electrons for an atom pair for gallium arsenide. In the promotion of electrons to hybrids we left half the electrons in gallium hybrids and half in arsenic hybrids costing $4E_{pro}$ for each pair of atoms, with E_{pro} the energy per bond given in the text.

Semiconductors with tetrahedrally coordinated structures





$X = (1,0,0)$

$L = (0.5, 0.5, 0.5)$

$K = (0.75, 0.75, 0)$

$W = (1, 0.5, 0)$

$U = (1, 0.25, 0.25)$

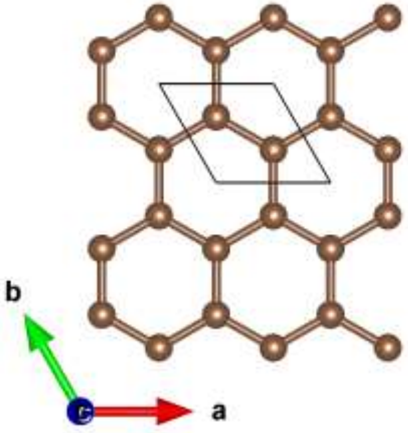
Figure 4.8. Band structure of four representative covalent solids: Si, C, SiC, GaAs. The first and the last are semiconductors, the other two are insulators. The small diagram above the band structure indicates the Brillouin Zone for the FCC lattice, with the special **k**-points X, L, K, W, U identified and expressed in units of $2\pi/a$, where a is the lattice constant; Γ is the center of the BZ. The energy scale is in electronvolts and the zero is set at the Valence Band Maximum. (Based on calculations by I.N. Remediakis.)

Four bands formed by the bonding sp^3 hybrids.

Filled with 8 electrons

Graphene

2D system atoms per cell : two orbitals : $s \ p_x \ p_y \ p_z$ hoppings : first neighbors $N_{\mathrm{orb}} = 8$



Graphene

Two atoms per unit cell, n unit cells, 2 n atoms
Orbitals : 4 per atom, 8 n in total

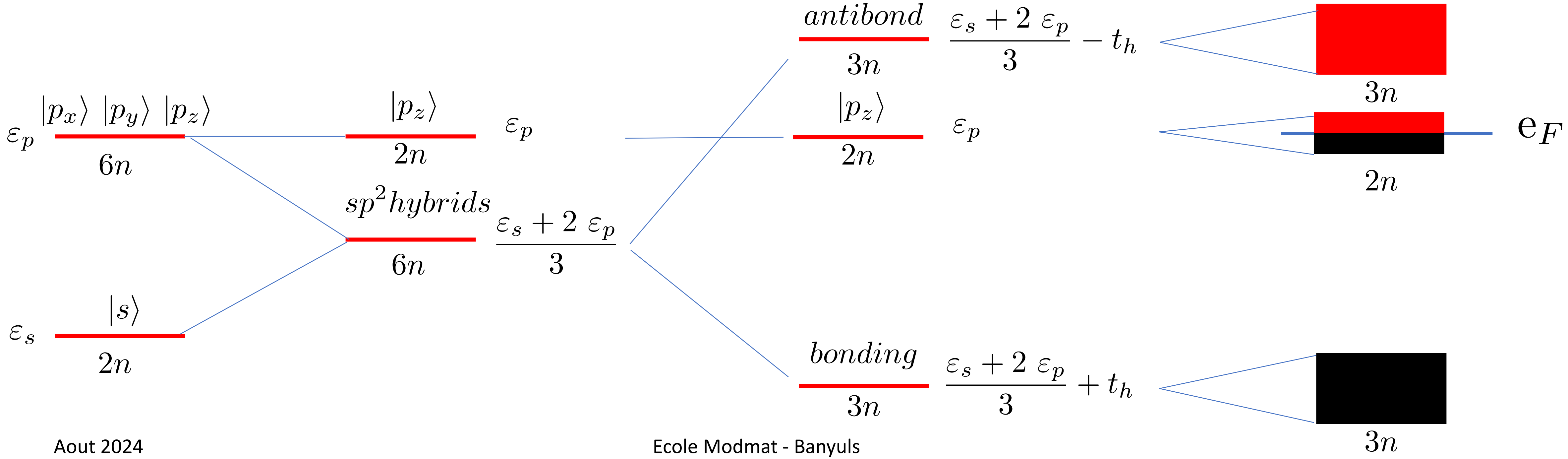
$2 \times 2s^2 2p^2$
Electrons : 4 per atom, 8 n in total

With the s and the two p orbitals we can construct three *hybrid* orbitals per atom

$$|h_1\rangle = \frac{1}{\sqrt{6}} \left[\sqrt{2}\ |s\rangle + 2\ |p_x\rangle \right]$$

$$|h_2\rangle = \frac{1}{\sqrt{6}} \left[\sqrt{2}\ |s\rangle - |p_x\rangle - \sqrt{3}\ |p_y\rangle \right]$$

$$|h_3\rangle = \frac{1}{\sqrt{6}} \left[\sqrt{2}\ |s\rangle - |p_x\rangle + \sqrt{3}\ |p_y\rangle \right]$$



ε_p $|p_x\rangle \ |p_y\rangle \ |p_z\rangle$ $6n$

ε_s $|s\rangle$ $2n$

$|p_z\rangle$ $2n$ ε_p

$sp^2 hybrids$ $6n$ $\dfrac{\varepsilon_s + 2\ \varepsilon_p}{3}$

$antibond$ $3n$ $\dfrac{\varepsilon_s + 2\ \varepsilon_p}{3} - t_h$

$|p_z\rangle$ $2n$ ε_p

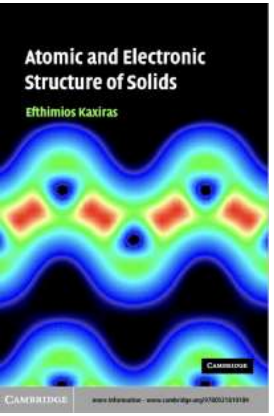
$bonding$ $3n$ $\dfrac{\varepsilon_s + 2\ \varepsilon_p}{3} + t_h$

$3n$

$2n$ e_F

$3n$

Graphene



Atomic and Electronic Structure of Solids

Efthimios Kaxiras

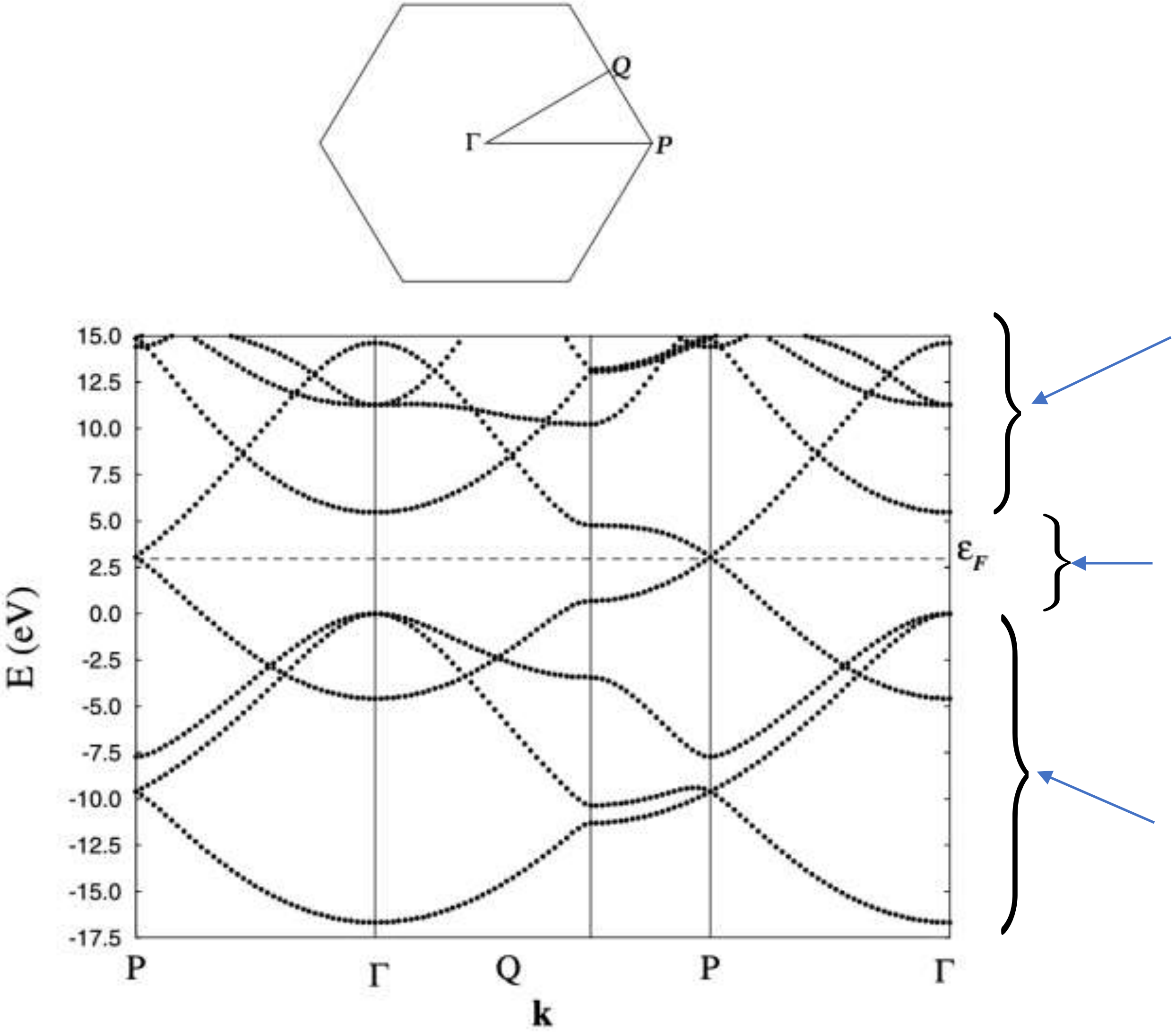


Figure 4.6. Band structure of a graphite sheet, calculated with the PPW method. The zero of the energy scale is set arbitrarily to the value of the highest σ-bonding state at Γ. The dashed line indicates the position of the Fermi level. The small diagram above the band structure indicates the corresponding Brillouin Zone with the special **k** points Γ, *P*, *Q* identified. (Based on calculations by I.N. Remediakis.)

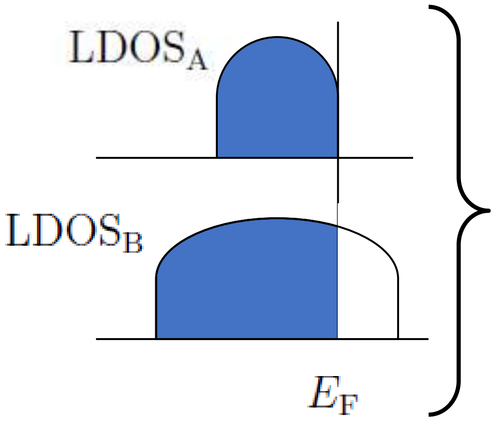
Three empty bands formed by the antibonding sp^2 hybrids.

Two bands formed by the p_π orbitals.
Filled with 1 electron

Three bands formed by the bonding sp^2 hybrids.
Filled with 6 electrons

Extensions

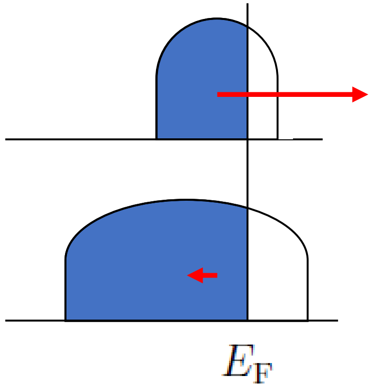
Charge self-consistency



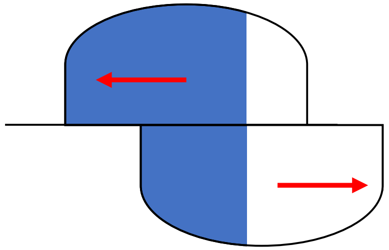
$$n_\mathrm{A} > n_\mathrm{B}$$

$$\varepsilon_\mathrm{A} = \varepsilon_\mathrm{A}^0 + U_\mathrm{A}\,(n_\mathrm{A} - n_\mathrm{A}^0)$$

$$\varepsilon_\mathrm{B} = \varepsilon_\mathrm{B}^0 + U_\mathrm{B}\,(n_\mathrm{B} - n_\mathrm{B}^0)$$



Spin polarization



$$\epsilon^\uparrow = \epsilon^0 - I\,(n^\uparrow - n^\downarrow)$$

$$\epsilon^\downarrow = \epsilon^0 + I\,(n^\uparrow - n^\downarrow)$$

$$H = \left[\begin{array}{c|c} \uparrow\uparrow & 0 \\ \hline 0 & \downarrow\downarrow \end{array}\right]$$

Spin-orbit-interaction

$$\boxed{H_{so} = \xi\,\frac{\hbar}{2}\begin{bmatrix} L'_z\cos\theta + \frac{1}{2}\left[L'_+e^{-i\phi} + L'_-e^{i\phi}\right]\sin\theta & -L'_z\sin\theta - L'_+e^{-i\phi}\sin^2\frac{\theta}{2} + L'_-e^{i\phi}\cos^2\frac{\theta}{2} \\ -L'_z\sin\theta + L'_+e^{-i\phi}\cos^2\frac{\theta}{2} - L'_-e^{i\phi}\sin^2\frac{\theta}{2} & -L'_z\cos\theta - \frac{1}{2}\left[L'_+e^{-i\phi} + L'_-e^{i\phi}\right]\sin\theta \end{bmatrix}}$$

$$H = \left[\begin{array}{c|c} \uparrow\uparrow & \uparrow\downarrow \\ \hline \downarrow\uparrow & \downarrow\downarrow \end{array}\right]$$

With the representation of the angular momentum operators in the atomic orbitals basis.

Tight-binding conclusion

Generalities

- A must-have electronic structure method indispensable in the solid-state physicist's toolbox.
- Natural link between numerical simulations and model Hamiltonians
  - Strongly correlated electrons, Hubbard, Anderson, super-exchange, etc.
- Facilitates links with quantum chemistry.
- Simplicity for analytical calculations.

Also (not mentioned today)

- Molecular dynamics for intermediate atom numbers 1000 < N < 100,000
- Monte Carlo, keeping the electronic structure

Limitations

- Parameterize a multicomponent system (artist's work...)

Taking into account the electron-electron interactions

Variational principle

QUANTUM MECHANICS
VOLUME TWO

CLAUDE COHEN-TANNOUDJI
BERNARD DIU
FRANCK LALOË

Let's $\phi(\vec{r}\sigma)$ be a normalized wavefunction

$$\langle\phi|\phi\rangle = \sum_{\sigma}\int \phi^*(\vec{r}\sigma)\ \phi(\vec{r}\sigma)\ d^3r = 1$$

of a quantum system whose Hamiltonian is :

$$H = \frac{p^2}{2m} + V(\vec{r}) = -\frac{\hbar^2\ \nabla^2}{2m} + V(\vec{r})$$

The mean energy associated to this wavefunction is

$$E = \langle\phi|H|\phi\rangle = \sum_{\sigma}\int \phi^*(\vec{r}\sigma)\Big[\frac{p^2}{2m} + V(\vec{r})\Big]\phi(\vec{r}\sigma)\ d^3r$$

using a Lagrange multiplier λ, we search a wavefunction that minimizes the energy under the constraint of normalization, :

$$F\Big[\phi,\lambda\Big] = \langle\phi|H|\phi\rangle - \lambda\langle\phi|\phi\rangle$$

The result is, that the wavefunction that minimizes the energy must satisfy the following equation (Schrödinger !) :

$$\Big[\frac{p^2}{2m} + V(\vec{r})\Big]\ \phi(\vec{r}\sigma) = \lambda\ \phi(\vec{r}\sigma)$$

Approximations

After using Born-Oppenheimer : the system is formed only by the electrons, the nuclei produce an ”external potential”.

$$H_{\text{elec}} = \underbrace{\sum_i \frac{p_i^2}{2m}}_{\text{kinetic}} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{electron-electron}} - \underbrace{\sum_i\sum_I \frac{Z_I\ e^2}{|\vec{r}_i - \vec{R}_I|}}_{\text{nuclei-electron}}$$

$$= \quad T \quad + \quad V_{\text{ee}} \quad + \quad \sum_i V_{\text{ext}}(\vec{r}_i)$$

		T	V_{ee}	V_{ext}
Independent electrons. One electron problem One electron approximation	free electrons	yes	no	no
	nearly free electrons	yes	no	weak
	tight-binding	yes	no	strong
Correlated electrons Many-body problem	Wavefunction methods Hartree - Hartree-Fock – CI - etc	yes	yes	yes
	Density Functional Theory	yes	yes	yes
	Quantum Monte Carlo methods	yes	yes	yes

Hartree

Hartree

After using Born-Oppenheimer : the system is formed only by the electrons, the nuclei produce an ”external potential”.

$$H_{\text{elec}} = \underbrace{\sum_i \frac{p_i^2}{2m}}_{\text{kinetic}} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{electron-electron}} - \underbrace{\sum_i \sum_I \frac{Z_I\ e^2}{|\vec{r}_i - \vec{R}_I|}}_{\text{nuclei-electron}}$$

$$= \quad T \quad + \quad V_{\text{ee}} \quad + \quad \sum_i V_{\text{ext}}(\vec{r}_i)$$

The electronic wavefunction **MUST BE** antisymmetric

$$\Psi(\vec{r}_1\sigma_1, .., \vec{r}_i\sigma_i, .., \vec{r}_j\sigma_j, .., \vec{r}_N\sigma_N) = -\Psi(\vec{r}_1\sigma_1, .., \vec{r}_j\sigma_j, .., \vec{r}_i\sigma_i, .., \vec{r}_N\sigma_N)$$

Hartree

In the Hartree theory the many electron wave-function is a product of one electron orbitals:

$$|\Psi^{\mathrm{H}}\rangle = |\psi_1(\vec{r}_1\sigma_1)\ \psi_2(\vec{r}_2\sigma_2)\ \dots\ \psi_N(\vec{r}_N\sigma_N)\rangle = \prod_{k=1}^{N} |\psi_k(\vec{r}_k\sigma_k)\rangle$$

Which is not antisymmetric.

The Pauli principle is satisfied by using a different one electron wavefunction (quantum state) for every electron

$$E^{\mathrm{H}} = \langle\Psi^{\mathrm{H}}|H|\Psi^{\mathrm{H}}\rangle = \langle\Psi^{\mathrm{H}}|\Big[\underbrace{\sum_{i}^{N}\frac{p_i^2}{2m} + V_{\mathrm{ext}}(\vec{r}_i)}_{i} + \underbrace{\frac{1}{2}\sum_{i\neq j}^{N}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}}_{i,j}\Big]|\Psi^{\mathrm{H}}\rangle$$

$$\prod_{l} \qquad\qquad \prod_{k}$$

Where the mean value means to evaluate a sum over the spin variables and an integral.

$$\langle\psi_k(\vec{r}\sigma)|A(\vec{r})|\psi_k(\vec{r}\sigma)\rangle = \sum_{\sigma}\int \psi^*(\vec{r}\sigma)\ A(\vec{r})\ \underset{\text{psi}}{\psi}(\vec{r}\sigma)\ d^3r = \int \underset{\text{phi}}{\phi^*}(\vec{r})\ A(\vec{r})\ \phi(\vec{r})\ d^3r$$

Hartree

After washing, rinsing and spinning (après lavage, rinçage et essorage …)

$$E^{\mathrm{H}} = \sum_{i}^{N} \int \phi_i^*(\vec{r}_i)\left[-\frac{p_i^2}{2m}+V_{\mathrm{ext}}(\vec{r}_i)\right]\phi_i(\vec{r}_i)\, d^3r_i + \frac{e^2}{2}\sum_{i\neq j}^{N} \int\int \underbrace{|\phi_i(\vec{r}_i)|^2}_{\rho_i(\vec{r}_i)} \frac{1}{|\vec{r}_i-\vec{r}_j|} \underbrace{|\phi_j(\vec{r}_j)|^2}_{\rho_j(\vec{r}_j)} d^3r_i d^3r_j$$

Sum of one electron contributions

Electronic density associated with orbital i

Electronic density associated with orbital j

Every electron contributes with a “one-electron” energy : kinetic plus the interaction with the external field (nuclei)

The electronic interactions appear as a classical Coulomb interaction between the electronic densities associated to every pair of electrons

$$= \sum_{i}^{N} h_{ii} + \frac{1}{2}\sum_{i\neq j}^{N} K_{ij}$$

Hartree

To obtain the one-electron wavefunctions, we use the variational principle. If we minimize with respect to $\phi_i(\vec{r}_i)$:

$$\left[-\frac{\hbar\ \nabla_i^2}{2m} + V_{\text{ext}}(\vec{r}_i) + e^2 \int \sum_{j\neq i}^{N} \frac{|\phi_j(\vec{r})|^2}{|\vec{r}_i - \vec{r}|}\, d^3r\right] \phi_i(\vec{r}_i) = \varepsilon_i\ \phi_i(\vec{r}_i)$$

Every equation is different, because

We obtain the Schrödinger equation for $\phi_i(\vec{r}_i)$.
There are N equations that has to be solved in a "self-consistent" way.

Total electronic density →

$$\rho_T(\vec{r}) = \sum_{j}^{N} |\phi_j(\vec{r})|^2 = \sum_{j\neq i}^{N} |\phi_j(\vec{r})|^2 + |\phi_i(\vec{r})|^2$$

$$\left[-\frac{\hbar\ \nabla_i^2}{2m} + V_{\text{ext}}(\vec{r}_i) + e^2 \int \frac{\rho_T(\vec{r})}{|\vec{r}_i - \vec{r}|}\, d^3r - e^2 \int \frac{|\phi_i(\vec{r})|^2}{|\vec{r}_i - \vec{r}|}\, d^3r\right] \phi_i(\vec{r}_i) = \varepsilon_i\ \phi_i(\vec{r}_i)$$

$V_{\text{Hartree}}(\vec{r}_i)$

It contains the self-interaction

Subtract the self-interaction

Hartree

If we multiply the Schrödinger equation by $\phi_i(\vec{r}_i)$ and integrate, we obtain :

$$\varepsilon_i = h_{ii} + \sum_{j \neq i}^{N} K_{ij}$$

The one-electron energy for atom i, has the kinetic energy and the interaction with the nuclei in h_{ii} plus the interaction with the other electrons K_{ij} .

The total energy is :

$$E^{\mathrm{H}} = \sum_{i}^{N} \varepsilon_i - \frac{1}{2} \sum_{i \neq j}^{N} K_{ij}$$

The total energy is the sum of the one electron energies where we count twice the the interaction with the other electrons. We need to subtract every interaction once.

Hartree conclusion

- (1922) Bohr tries to explain the periodic table
- (1925) Discovery of the electron spin
- (1925) Pauli exclusion principle
- (1928) Hartree method
- (1930) Hartree-Fock

- It was proposed for solving atomic spectra
- It is a mean-field theory (… DFT)
- Introduces the idea of self-consistent solution (… DFT)
- Introduces the Hartree potential and the self-interaction (… DFT, and to understand functionals)
- The physics related with the electron spin is absent

Hartree-Fock

Hartree-Fock

In the Hartree-Fock theory the many electron wave-function is a determinant of one electron orbitals:

$$\Psi^{\mathrm{HF}}(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, .., \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(\vec{r}_1\sigma_1) & \psi_1(\vec{r}_2\sigma_2) & \dots & \psi_1(\vec{r}_N\sigma_N) \\ \psi_2(\vec{r}_1\sigma_1) & \psi_2(\vec{r}_2\sigma_2) & \dots & \psi_2(\vec{r}_N\sigma_N) \\ \psi_3(\vec{r}_1\sigma_1) & \psi_3(\vec{r}_2\sigma_2) & \dots & \psi_3(\vec{r}_N\sigma_N) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_N(\vec{r}_1\sigma_1) & \psi_N(\vec{r}_2\sigma_2) & \dots & \psi_N(\vec{r}_N\sigma_N) \end{pmatrix}$$

It is the simplest antisymmetric wavefunction that one can build.

$$E^{\mathrm{HF}} = \langle \Psi^{\mathrm{HF}} | H | \Psi^{\mathrm{HF}} \rangle = \langle \Psi^{\mathrm{HF}} | \Big[\underbrace{\sum_i \frac{p_i^2}{2m} + V_{\mathrm{ext}}(\vec{r}_i)}_{i} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{i,j} \Big] | \Psi^{\mathrm{HF}} \rangle$$

$$\sum_{\mathrm{Perm}} \prod_{l}$$

$$\sum_{\mathrm{Perm}} \prod_{k}$$

Hartree-Fock

After washing, rinsing and spinning (après lavage, rinçage et essorage …)

$$E^{\mathrm{HF}} = \sum_i^N \int \phi_i^*(\vec{r}_i)\left[-\frac{p_i^2}{2m}+V_{\mathrm{ext}}(\vec{r}_i)\right]\phi_i(\vec{r}_i)\, d^3r_i + \frac{e^2}{2}\sum_{i\neq j}^N \int\int |\phi_i(\vec{r}_i)|^2 \frac{1}{|\vec{r}_i - \vec{r}_j|}|\phi_j(\vec{r}_j)|^2 d^3r_i d^3r_j$$

Sum of one electron contributions

Coulomb interaction between the charge densities

$$-\frac{e^2}{2}\sum_{i\neq j}^N\sum_{\sigma_i\sigma_j}\int\int \psi_i^*(\vec{r}_j\sigma_j)\,\psi_j^*(\vec{r}_i\sigma_i)\,\frac{1}{|\vec{r}_i-\vec{r}_j|}\,\psi_i(\vec{r}_i\sigma_i)\,\psi_j(\vec{r}_j\sigma_j)\; d^3r_i d^3r_j$$

Exchange interaction

It only exists if the two orbitals have the same spin (more, later …)

$$= \sum_i^N h_{ii} + \frac{1}{2}\sum_{i\neq j}^N K_{ij} - \frac{1}{2}\sum_{\substack{i\neq j\\ \text{same spin}}}^N J_{ij}$$

Hartree-Fock

Once again, using the variational principle, we obtain the Schrödinger equation:

$$\underbrace{\Big[-\frac{\hbar\,\nabla_i^2}{2m} + V_{\text{ext}}(\vec{r}_i)}_{\text{One electron}} + \underbrace{e^2\int\sum_{j\neq i}^{N}\frac{|\phi_j(\vec{r})|^2}{|\vec{r}_i-\vec{r}|}\,d^3r}_{\text{Coulomb without the self interaction}}\Big]\,\phi_i(\vec{r}_i) - \underbrace{\Big[e^2\int\sum_{j\neq i}^{N}\frac{\phi_j^*(\vec{r})\phi_i(\vec{r})}{|\vec{r}_i-\vec{r}|}\,d^3r\Big]}_{\text{Exchange. Non-local interaction}}\,\phi_j(\vec{r}_i) = \varepsilon_i\,\phi_i(\vec{r}_i)$$

One can add the $i = j$ term in both the Coulomb interaction and the exchange :

In HF the exchange interaction cancel exactly the self-interaction !!

$$V_{\text{Hartree}}(\vec{r}_i)\;\phi_i(\vec{r}_i) = \Big[e^2\int\frac{\rho_{\text{T}}(\vec{r})}{|\vec{r}_i-\vec{r}|}\,d^3r\Big]\;\phi_i(\vec{r}_i)$$

Local
Hartree

$$V_{\text{Exchange}}(\vec{r}_i)\;\phi_i(\vec{r}_i) = \Big[e^2\sum_{j}^{N}\int\frac{\phi_j^*(\vec{r}_j)\;\phi_i(\vec{r})}{|\vec{r}_i-\vec{r}|}\,d^3r\Big]\;\phi_j(\vec{r}_i)$$

Non-local
Exchange

Correlation in Hartree-Fock

$$E^{\mathrm{HF}} = \sum_{i}^{N} h_{ii} + \frac{1}{2}\sum_{i \neq j}^{N} K_{ij} - \frac{1}{2}\sum_{\substack{i \neq j \\ \text{same spin}}}^{N} J_{ij}$$

$$J_{ij} > 0 \text{ and } E^{\mathrm{HF}} < E^{\mathrm{H}}$$

- The exchange term forbids the electrons to be at the same position diminishing the repulsive Coulomb energy
- In reality, “they forbid the electrons to bring close if they have the same spin”

$$E^{\mathrm{HF}}(\uparrow\uparrow) < E^{\mathrm{HF}}(\uparrow\downarrow)$$

Ferro Anti-ferro

- The direct exchange interaction stabilizes a ferromagnetic order.
- The effective magnetic interaction between electrons is a consequence of the Pauli principle and the repulsive Coulomb interaction.

Correlation in Hartree-Fock

In statistics

independence means

$$P(A \wedge B) = P(A)\ P(B)$$

correlation means

$$P(A \wedge B) \neq P(A)\ P(B)$$

In the electronic structure language

$$P(\vec{r}_1, \vec{r}_2) \overset{?}{=} P(\vec{r}_1)\ P(\vec{r}_2)$$

Probability to find one electron in $\vec{r}_1$ when there is another electron in $\vec{r}_2$

The spin is important, let's see …

$$\underset{\text{psi}}{\psi}(\vec{r}\sigma) = \underset{\text{phi}}{\phi}(\vec{r})\ \underset{\text{chi}}{\chi}(\sigma)$$

$$\sigma = \{\downarrow, \uparrow\}$$

$\phi(\vec{r})$ Is a generic function of the spatial coordinates $\vec{r}$. If we want the electron to be in a specific orbital $\phi_{1s}(\vec{r})$

$\chi(\sigma)$ Is a generic function of the spin variable σ . If we want the electron to be ↑ we use $\alpha(\sigma)$ for ↓ we use $\beta(\sigma)$

$$\left.\begin{array}{l}\alpha(\sigma)\\ \\ \beta(\sigma)\end{array}\right\} \quad \begin{array}{ll}\alpha(\uparrow) = 1 & \alpha(\downarrow) = 0\\ \beta(\uparrow) = 0 & \beta(\downarrow) = 1\end{array}$$

Correlation in Hartree-Fock

The electrons with a Hartree wavefunction are uncorrelated

$$\Psi^{\mathrm{H}}_{\uparrow\uparrow}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2) = \phi_1(\vec{r}_1)\ \alpha(\sigma_1)\ \phi_2(\vec{r}_2)\ \alpha(\sigma_2)$$

$$P(\vec{r}_1,\vec{r}_2) = \sum_{\sigma_1,\sigma_2} |\Psi^{\mathrm{H}}_{\uparrow\uparrow}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2)|^2 = |\phi_1(\vec{r}_1)\ |^2\ |\phi_2(\vec{r}_2)|^2 = P(\vec{r}_1)\ P(\vec{r}_2)$$

The result is the same for $\Psi^{\mathrm{H}}_{\uparrow\downarrow},\ \Psi^{\mathrm{H}}_{\downarrow\uparrow},\ \Psi^{\mathrm{H}}_{\downarrow\downarrow}$

What happens with the Hartree-Fock wavefunctions ?

$$\Psi^{\mathrm{HF}}_{\uparrow\uparrow}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2) = \frac{1}{\sqrt{2}}\left\{\phi_1(\vec{r}_1)\ \alpha(\sigma_1)\ \phi_2(\vec{r}_2)\ \alpha(\sigma_2) - \phi_1(\vec{r}_2)\ \alpha(\sigma_2)\ \phi_2(\vec{r}_1)\ \alpha(\sigma_1)\right\}$$

$$\Psi^{\mathrm{HF}}_{\uparrow\downarrow}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2) = \frac{1}{\sqrt{2}}\left\{\phi_1(\vec{r}_1)\ \alpha(\sigma_1)\ \phi_2(\vec{r}_2)\ \beta(\sigma_2) - \phi_1(\vec{r}_2)\ \alpha(\sigma_2)\ \phi_2(\vec{r}_1)\ \beta(\sigma_1)\right\}$$

Correlation in Hartree-Fock

$$P_{\uparrow\downarrow}(\vec{r}_1,\vec{r}_2) = \sum_{\sigma_1,\sigma_2} |\Psi^{\mathrm{HF}}_{\uparrow\downarrow}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2)|^2 \;= \frac{1}{2}\left\{ |\phi_1(\vec{r}_1)|^2\ |\phi_2(\vec{r}_2)|^2 \;+\; |\phi_1(\vec{r}_2)|^2\ |\phi_2(\vec{r}_1)|^2 \right\}$$

The electrons with different spin are uncorrelated.
It is the product of the probability of having electron 1 in ϕ_1 and electron 2 in ϕ_2 ,
and the inverse because they are indistinguishable.

$$\lim_{\vec{r}_1\to\vec{r}_2} P_{\uparrow\downarrow}(\vec{r}_1,\vec{r}_2) = |\phi_1(\vec{r}_1)|^2\ |\phi_2(\vec{r}_1)|^2$$

$$P_{\uparrow\uparrow}(\vec{r}_1,\vec{r}_2) = \sum_{\sigma_1,\sigma_2} |\Psi^{\mathrm{HF}}_{\uparrow\uparrow}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2)|^2$$

$$= \frac{1}{2}\left\{ |\phi_1(\vec{r}_1)|^2\ |\phi_2(\vec{r}_2)|^2 + |\phi_1(\vec{r}_2)|^2\ |\phi_2(\vec{r}_1)|^2 - 2\,\Re\left[\phi_1^*(\vec{r}_1)\ \phi_2^*(\vec{r}_2)\ \phi_1(\vec{r}_2)\ \phi_2(\vec{r}_1)\right] \right\}$$

The electrons with the same spin are correlated

$$\lim_{\vec{r}_1\to\vec{r}_2} P_{\uparrow\uparrow}(\vec{r}_1,\vec{r}_2) = 0$$

The probability to have two electrons with the same spin at the same place is zero.
Around every electron, there is “a lack of other electrons”, a hole (the Fermi hole)

Hartree-Fock conclusion

- An important improvement to the Hartee method.
- Introduces the idea of exchange interaction. Shows that the exchange cancels exactly the self interaction of the Hartree potential
- Starting point of many Quantum Chemistry calculations because any antisymmetric wavefunction can be written as a linear combination of Slater determinants (they form a basis).

$$\Psi_{\mathrm{antisym}}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2,..,\vec{r}_N\sigma_N) = \sum_K B_K \Psi_{\mathrm{Slater}}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2,..,\vec{r}_N\sigma_N)$$

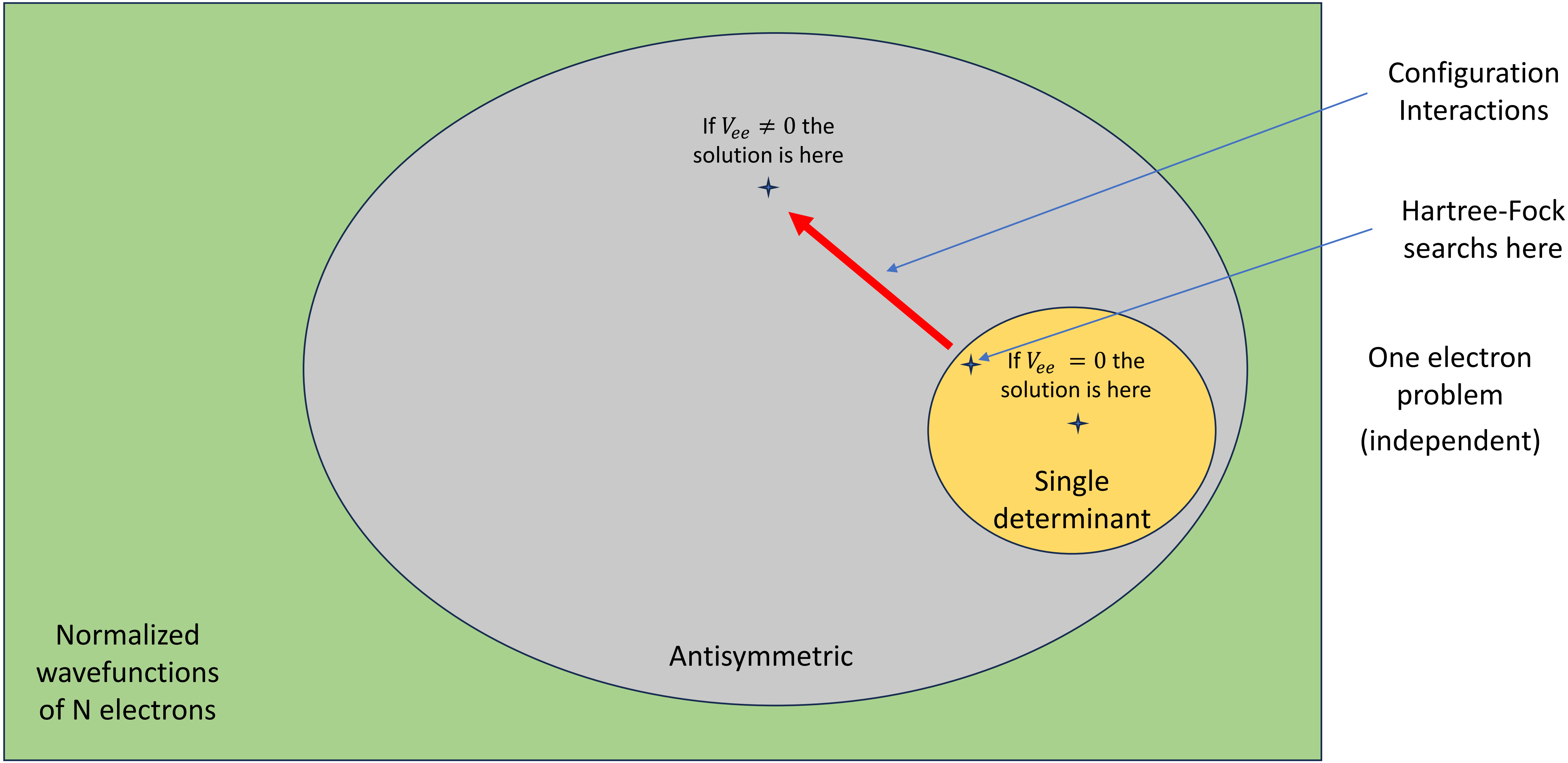
Configuration interaction (CI) : post Hartree-Fock methods

- The one-electron orbitals are written in a basis (Gaussian, atomic orbitals, etc …) of functions

$$\Psi^{\mathrm{HF}}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2,..,\vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(\vec{r}_1\sigma_1) & \psi_1(\vec{r}_2\sigma_2) & \dots & \psi_1(\vec{r}_N\sigma_N) \\ \psi_2(\vec{r}_1\sigma_1) & \psi_2(\vec{r}_2\sigma_2) & \dots & \psi_2(\vec{r}_N\sigma_N) \\ \psi_3(\vec{r}_1\sigma_1) & \psi_3(\vec{r}_2\sigma_2) & \dots & \psi_3(\vec{r}_N\sigma_N) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_N(\vec{r}_1\sigma_1) & \psi_N(\vec{r}_2\sigma_2) & \dots & \psi_N(\vec{r}_N\sigma_N) \end{pmatrix}$$

$$\psi(\vec{r}_i\sigma_i) = \sum_\alpha A_{i\alpha}\, \xi_\alpha(\vec{r}_i)\, \chi(\sigma_i)$$

Hartree-Fock conclusion



Configuration Interactions

Hartree-Fock searches here

One electron problem

(independent)

If $V_{ee} \neq 0$ the solution is here

If $V_{ee} = 0$ the solution is here

Single determinant

Antisymmetric

Normalized wavefunctions of N electrons

Density Functional Theory

Density Functional Theory

Until now we discussed how to obtain the wavefunction that solves the full electronic Hamiltonian.
It a complex antisymmetric function that depends on $3N$ coordinates ($4N$ with the spin).
Very complicated in a molecule where there are hundred or thousand of electrons or a solid where there are 10^{23} electrons !!

The electronic density is a real function that only depends on 3 spatial coordinates

$$\rho(\vec{r}) = \int\int\cdots\int |\Psi(\vec{r}_1, \vec{r}_2, .., \vec{r})|^2 \underbrace{d^3r_1\ d^3r_2\ \ldots d^3r_{N-1}}_{N-1}$$

Can we have an equation to obtain the electronic density and calculate the properties of the system ?

The idea was explored by Thomas and Fermi (1927) and extended by Dirac (1930).

The “modern formulation” is based in two papers : Hohenberg and Kohn (1964) and Kohn and Sham (1965).

Density Functional Theory

Hohenberg and Kohn (1964)

Theorem I

- The external potential is uniquely determined by the ground state electronic density.
- In other words, if we know the ground state electronic density we can determine exactly which nuclei are in the system and where they are located !!

$$V_{\text{ext}}(\vec{r}) = f[\rho(\vec{r})]$$

Corollary

- As the ground state electronic density determines the external potential and the Schrodinger equation allows to calculate the electronic wavefunction, then the electronic density determines the many-body wavefunction !!

$$\begin{tikzcd}
V_{\text{ext}}(\vec{r}) \arrow[r, "\text{Schrödinger}"'] & \Psi(\vec{r}_1, \vec{r}_2, .., \vec{r}) \arrow[r, "{\rho(\vec{r}) = \int |\Psi(\vec{r}_1, .., \vec{r})|^2 \; d^3r_1 \; \ldots d^3r_{N-1}}"'] & \rho(\vec{r}) \arrow[ll, bend right, "\text{Theorem 1}"'] \arrow[l, bend left, "\text{Corollary}"]
\end{tikzcd}$$

Density Functional Theory

Hohenberg and Kohn (1964)

Theorem II

- Let $V_{\text{ext}}(\vec{r})$ be the external potential of our system.
- Let $\tilde{\rho}(\vec{r})$ be an electronic density, and $\tilde{V}_{\text{ext}}(\vec{r})$ **(Theorem I)** the external potential that has $\tilde{\rho}(\vec{r})$ as the GS density.
- Let $\Psi[\tilde{\rho}]$ **(Corollary)** be the wavefunction determined by $\tilde{\rho}(\vec{r})$.
- We can define a functional, that allows to calculate the energy "a real number" from a function, the density $\tilde{\rho}(\vec{r})$

$$E_{V_{\text{ext}}}[\tilde{\rho}(\vec{r})] = \langle\ \Psi[\tilde{\rho}]\ |\ T + V_{\text{ee}}\ |\ \Psi[\tilde{\rho}]\ \rangle + \int \tilde{\rho}(\vec{r})\ V_{\text{ext}}(\vec{r})\ d^3r$$

- The $\rho(\vec{r})$ that has $V_{\text{ext}}(\vec{r})$ as external potential, minimizes the functional !!

$$E_{V_{\text{ext}}}[\rho(\vec{r})] \leq E_{V_{\text{ext}}}[\tilde{\rho}(\vec{r})]$$

$$\begin{tikzcd}
V_{\text{ext}}(\vec{r}) \arrow[r, "\text{Schrödinger}"'] & \Psi(\vec{r}_1, \vec{r}_2, .., \vec{r}) \arrow[r, "\rho(\vec{r}) = \int |\Psi(\vec{r}_1, .., \vec{r})|^2\ d^3r_1\ \ldots d^3r_{N-1}"'] & \rho(\vec{r}) \arrow[ll, bend right, "\text{Theorem 1}"'] \arrow[l, bend left, "\text{Corollary}"]
\end{tikzcd}$$

Density Functional Theory – Kohn-Sham

Kohn and Sham (1965)

We search

$$E_0 = \min_{\rho(\vec{r})} \; E[\rho] = \min_{\rho(\vec{r})} \left[T[\rho] + E_{\mathrm{ee}}[\rho] \; + \int \rho \; V_{\mathrm{ext}} \; d^3r \right]$$

Problem ! We do not know, neither $T[\rho]$ nor $E_{\mathrm{ee}}[\rho]$

- Let’s suppose that there exists a fictional system of non-interacting electrons $V_{\mathrm{ee}} = 0$ with same density $\rho(\vec{r})$
- There exists **(Theorem I)** an external potential $V_{\mathrm{S}}(\vec{r})$ such that

$$\underbrace{E_{\mathrm{S}}[\rho]}_{\neq E[\rho]} = \underbrace{T_{\mathrm{S}}[\rho]}_{\neq T[\rho]} + \int \overbrace{V_{\mathrm{S}}}^{\neq V_{\mathrm{ext}}} \; \underbrace{\rho}_{\text{same density}} \; d^3r$$

- For this fictional system one can get **(Corollary)** a many body wavefunction, which is a determinant, because $V_{\mathrm{ee}} = 0$

$$\Psi_S(\vec{r}_1, \vec{r}_2, .., \vec{r}_N) = \frac{1}{N!} \det\left[\phi_1(\vec{r}_1), \phi_2(\vec{r}_2), \ldots, \phi_N(\vec{r}_N)\right]$$

Density Functional Theory – Kohn-Sham

Kohn and Sham (1965)

- For a wavefunction that is a determinant, the kinetic energy functional is simply :

$$T_{\mathrm{S}}[\rho] = -\frac{\hbar^2}{2m}\sum_i^N \int \phi_i^*(\vec{r})\ \nabla^2\phi_i(\vec{r})\ d^3r$$

- Coming back to our problem of unknown functionals

$$E[\rho] = T[\rho] + E_{\mathrm{ee}}[\rho]\ + \int \rho\ V_{\mathrm{ext}}\ d^3r$$

$$= \overbrace{T[\rho] + T_{\mathrm{S}}[\rho] - T_{\mathrm{S}}[\rho]} \overbrace{+ E_{\mathrm{ee}}[\rho]\ + E_{\mathrm{Hartree}}[\rho]\ - E_{\mathrm{Hartree}}[\rho]} \overbrace{+ \int \rho\ V_{\mathrm{ext}}\ d^3r}$$

Density Functional Theory – Kohn-Sham

Kohn and Sham (1965)

- Reordering the terms

$$E[\rho] = \underbrace{T_{\mathrm{S}}[\rho] + E_{\mathrm{Hartree}}[\rho] + \int \rho\, V_{\mathrm{ext}}\, d^3r}_{\text{I know how to calculate these three terms}} + \underbrace{T[\rho] - T_{\mathrm{S}}[\rho] + E_{\mathrm{ee}}[\rho] - E_{\mathrm{Hartree}}[\rho]}_{E_{\mathrm{XC}}[\rho]}$$

The exchange and correlation energy

$$T_{\mathrm{S}}[\rho] = -\frac{\hbar^2}{2m} \sum_i^N \int \phi_i^*(\vec{r})\, \nabla^2 \phi_i(\vec{r})\, d^3r$$

$$E_{\mathrm{Hartree}} = e^2 \int \frac{\rho(\vec{r})\, \rho(\vec{r'})}{|\vec{r} - \vec{r'}|}\, d^3r\, d^3r'$$

- The “trash”, it has
  - The correlation that is lacking in $E_{\mathrm{Hartree}}[\rho]$
  - The exchange
  - The correlation that is lacking in $T[\rho]$
- It has to compensate the self-energy in $E_{\mathrm{Hartree}}[\rho]$

- In practice, we solve a system of coupled differential equations

$$\left[-\frac{\hbar\, \nabla_i^2}{2m} + V_{\mathrm{ext}}(\vec{r}) + V_{\mathrm{H}}(\vec{r}) + V_{\mathrm{XC}}(\vec{r})\right] \phi_i(\vec{r_i}) = \varepsilon_i\, \phi_i(\vec{r_i})$$

$$V_{\mathrm{H}}(\vec{r}) = \frac{\partial E_{\mathrm{H}}}{\partial \rho} \qquad V_{\mathrm{XC}}(\vec{r}) = \frac{\partial E_{\mathrm{XC}}}{\partial \rho}$$

Density Functional Theory – Functionals

We do not know $V_{\mathrm{XC}}(\vec{r})$

The easiest (and it was also the first) choice, calculate $E_{\mathrm{XC}}[\rho]$ for an homogeneous system

$$E_{\mathrm{XC}}^{\mathrm{LDA}}[\rho] = \int \rho(\vec{r})\ \epsilon_{\mathrm{XC}}^{\mathrm{LDA}}[\rho(\vec{r})]\ d^3r$$

Local Density Approximation (LDA)

$$E_{\mathrm{XC}}^{\mathrm{LSDA}}[\rho_\uparrow, \rho_\downarrow] = \int \rho(\vec{r})\ \epsilon_{\mathrm{XC}}^{\mathrm{LSDA}}[\rho_\uparrow(\vec{r}), \rho_\downarrow(\vec{r})]\ d^3r$$

Local Spin Density Approximation (LSDA)

$$E_{\mathrm{XC}}^{\mathrm{GGA}}[\rho_\uparrow, \rho_\downarrow] = \int \rho(\vec{r})\ \epsilon_{\mathrm{XC}}^{\mathrm{GGA}}(\rho_\uparrow, \rho_\downarrow, \nabla\rho_\uparrow, \nabla\rho_\downarrow)\ d^3r$$

Generalized Gradient Approximation (GGA)

Many others

- Hybrids : adds a part of exact exchange (the one in Hartree-Fock!) to cancel the self-interaction
- metaGGA : add terms that depend on the kinetic energy
- PBE : the workhorse in solid state physics (is a GGA functional)
- B3LYP : the workhorse in solid state physics (is an hybryd)
- ….

Density Functional Theory - Wavefunctions

$$\left[-\frac{\hbar\,\nabla_i^2}{2m} + V_{\text{ext}}(\vec{r}) + V_{\text{H}}(\vec{r}) + V_{\text{XC}}(\vec{r})\right]\phi_i(\vec{r}_i) = \varepsilon_i\;\phi_i(\vec{r}_i)$$

The one-electron wavefunctions $\phi_i(\vec{r}_i)$ and energies ε_i are the ones of the non-interacting system.

In a periodic crystal, the one-electron wave-functions are Bloch functions

$$\psi_{n\vec{k}}(\vec{r}\sigma) = \mathrm{e}^{i\vec{k}.\vec{r}}\,u_{n\vec{k}}(\vec{r}\sigma) \longleftarrow u_{n\vec{k}}(\vec{r}\sigma) = \sum_{hkl} C_{hkl}\;\mathrm{e}^{i\vec{K}_{hkl}.\vec{r}}$$

0

$$K_{min} = \frac{2\,\pi}{a}$$

$$K_{\max} \simeq \frac{2\,\pi}{\lambda_{min}}$$

The minimum K is given by he size of the unit cell, the maximum one should be 2 π over the minimum feature that one want to describe, let's say the extent of the 1*s* orbital

$$\#\text{K's} \simeq \left[\frac{K_{\max}}{K_{\min}}\right]^3 \simeq \left[\frac{a}{\lambda_{min}}\right]^3 \simeq \left[\frac{a}{<r_{1s}>/10}\right]^3 \simeq \left[\frac{10\times 3.6\ \text{Å}}{0.05\ a_0}\right]^3 \simeq 1360^3$$

If we want to describe the periodic part of he Bloch function using PWs,
for a simple system (Cu, one atom per cell), we need a few thousand PWs in each direction, billions (≈ 10^9) in total !!

Density Functional Theory - Wavefunctions

If the system has N atoms with different chemical species in the unit cell, the total number of PWs will scale as

$$\frac{N}{< r_{1\mathrm{s}}(\mathrm{min}) >^3}$$

To decrease the number of plane waves, we can either increase K_{min} or decrease K_{max}

$$\#\mathrm{K's} \simeq \left[\frac{K_{\mathrm{max}}}{K_{\mathrm{min}}}\right]^3$$

But we cannot modify K_{min} because it is defined by the periodicity of the lattice $\simeq \dfrac{2\ \pi}{a}$

We can decrease K_{max} if we do not describe the core electrons with PWs !!!

Density Functional Theory - Programs

Two solutions

Partition the space in non overlapping spheres (regions I) around each atom plus an interstitial region (region II)

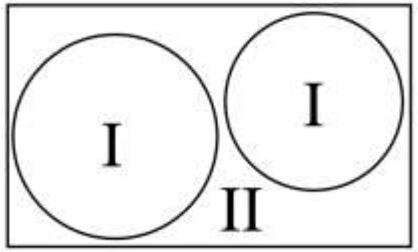


Figure 2.1: Partitioning of the unit cell into atomic spheres (I) and an interstitial region (II)

$$u_{n\vec{k}}(\vec{r}\sigma) = \sum_{hkl} C_{hkl} \begin{cases} e^{i\vec{K}_{hkl}.\vec{r}} & \text{if } \vec{r} \,\epsilon\, \text{II} \\ \sum \text{atomic like orbitals} & \text{if } \vec{r} \,\epsilon\, \text{I} \end{cases}$$

Paying the price of using a complicated basis set (Plane Waves + Atomic Orbitals), we can perform all electron (valence and core) calculations.

Method : Full Potential Linearized Augmented Plane Waves
Programs (FP-LAPW) : WIEN2K, Fleur, Exciting, ELK

Based in a frozen core approximation, assume that the core electrons in the system are not very different that the same core electrons in the free atom.

Include their interaction with the valence electrons to the nuclei attraction in a pseudopotential.

Calculate pseudo-wavefunctions which are smooth close to the atoms and evolve continuously to the real wavefunctions far from the atoms.

Paying the price of using fake potentials (pseudopotential) one can perform calculations for the valence electrons using a simple basis set (Plane waves).

Method : Plane wave Pseudopotential
Programs : Quantum Espresso, Abinit, VASP, …

Density Functional Theory - Programs

Two solutions

Cu with WIEN2K

Lattice parameter	3.60 Å
Radius of sphere	1.26 Å

$$K_{\text{max}} \simeq 3.2 \ a_0^{-1}$$

$$E_{\text{cut}} = 9.8 \ \text{Ry}$$

$$\#\text{K's} = 63$$

Cu with if PWs and all electrons

$$K_{\text{max}} \simeq \frac{2 \ \pi}{< r_{1\text{s}} > /10} \simeq 1260 \ a_0^{-1}$$

$$E_{\text{cut}} = \frac{\hbar^2 \ K_{\text{max}}^2}{2 \ m_e} = 1.6 \ 10^6 \ \text{Ry}$$

$$\#\text{K's} \simeq \left[\frac{K_{\text{max}}}{K_{\text{min}}}\right]^3 \simeq 1360^3$$

Cu with Quantum Espresso

Lattice parameter	3.60 Å
Pseudopotential	ONCV

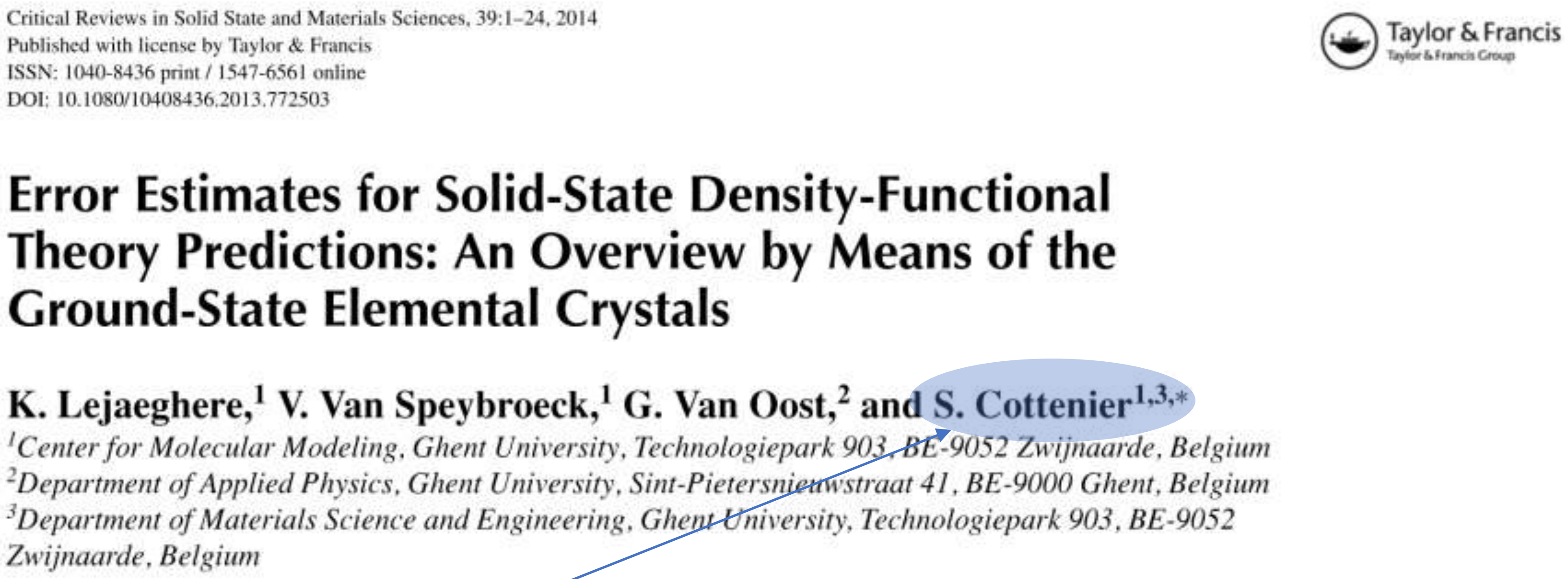
$$K_{\text{max}} \simeq 9.5 \ a_0^{-1}$$

$$E_{\text{cut}} = 90 \ \text{Ry}$$

$$\#\text{K's} = 1140$$

Density Functional Theory - Programs

2014



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Error Estimates for Solid-State Density-Functional Theory Predictions: An Overview by Means of the Ground-State Elemental Crystals

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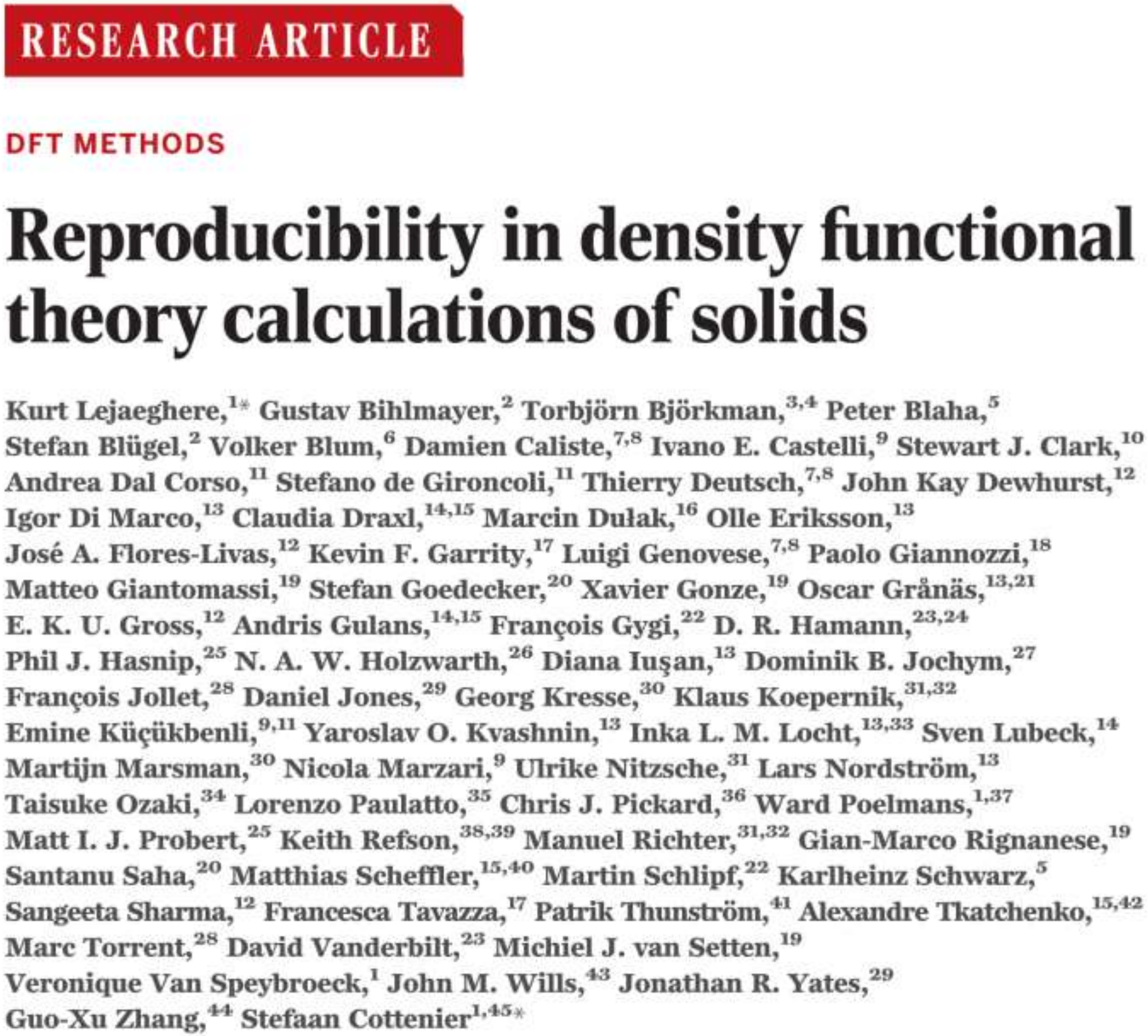
Density Functional Theory - Programs

2016



RESEARCH ARTICLE

DFT METHODS

Reproducibility in density functional theory calculations of solids

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Density Functional Theory - Programs

2023

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How to verify the precision of density-functional-theory implementations via reproducible and universal workflows

Emanuele Bosoni, Louis Beal, Marnik Bercx, Peter Blaha, Stefan Blügel, Jens Bröder, Martin Callsen, Stefaan Cottenier, Augustin Degomme, Vladimir Dikan, Kristjan Eimre, Espen Flage-Larsen, Marco Fornari, Alberto Garcia, Luigi Genovese, Matteo Giantomassi, Sebastiaan P. Huber, Henning Janssen, Georg Kastlunger, Matthias Krack, Georg Kresse, Thomas D. Kühne, Kurt Lejaeghere, Georg K. H. Madsen, Martijn Marsman, Nicola Marzari, Gregor Michalicek, Hossein Mirhosseini, Tiziano M. A. Müller, Guido Petretto, Chris J. Pickard, Samuel Poncé, Gian-Marco Rignanese, Oleg Rubel, Thomas Ruh, Michael Sluydts, Danny E. P. Vanpoucke, Sudarshan Vijay, Michael Wolloch, Daniel Wortmann, Aliaksandr V. Yakutovich, Jusong Yu, Austin Zadoks, Bonan Zhu & Giovanni Pizzi ✉

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Density Functional Theory - Programs

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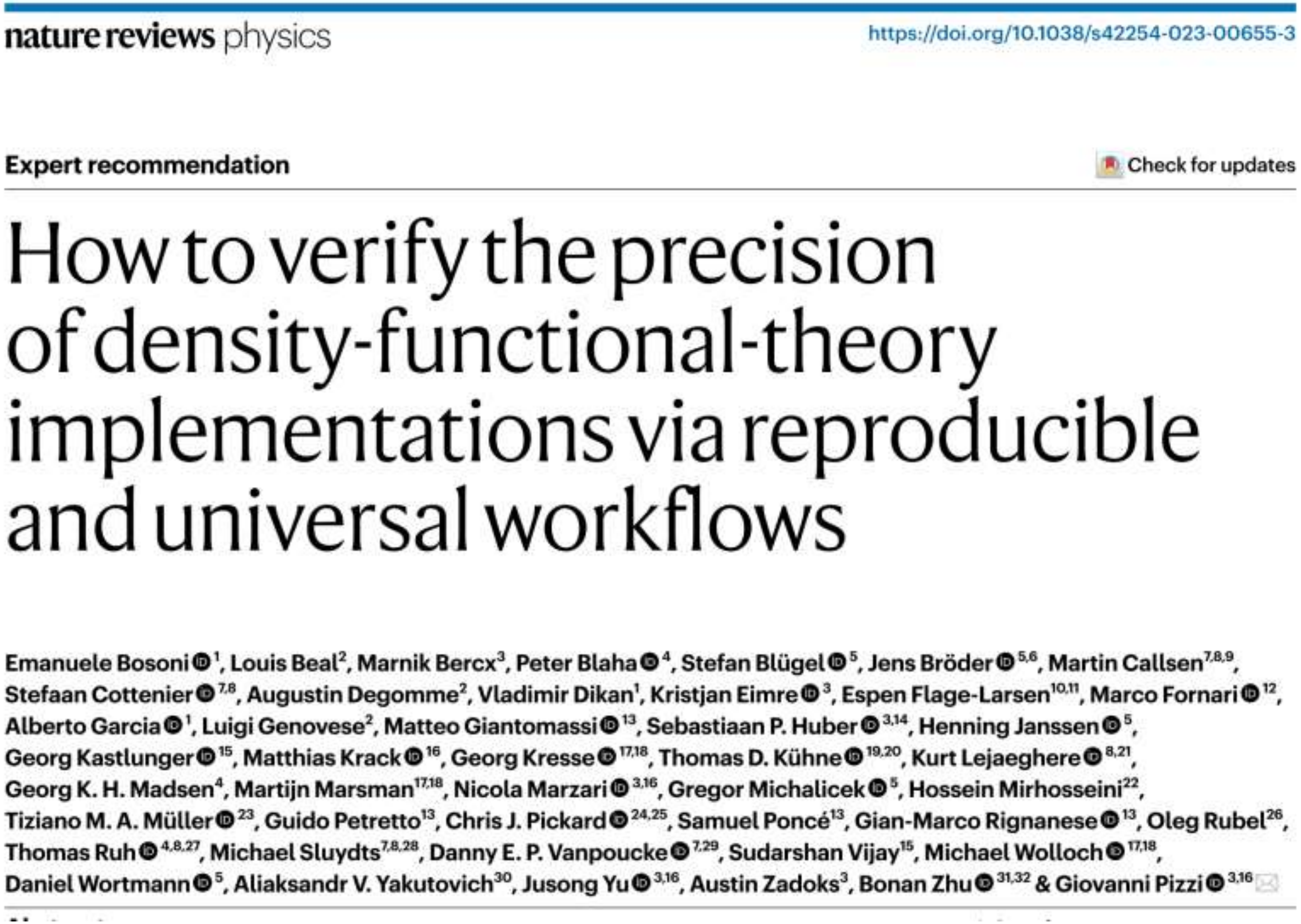

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Expert recommendation

Check for updates

How to verify the precision of density-functional-theory implementations via reproducible and universal workflows

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Density Functional Theory

- Which program should I use ?
- Pseudopotentials
  - Ultrasoft, norm-conserving, …
  - PAW (Projected augmented waves)
  - Scalar relativistic versus full relativistic
  - For spin-orbit calculations
- GW method
- GGA+U
- Time dependent
- ….

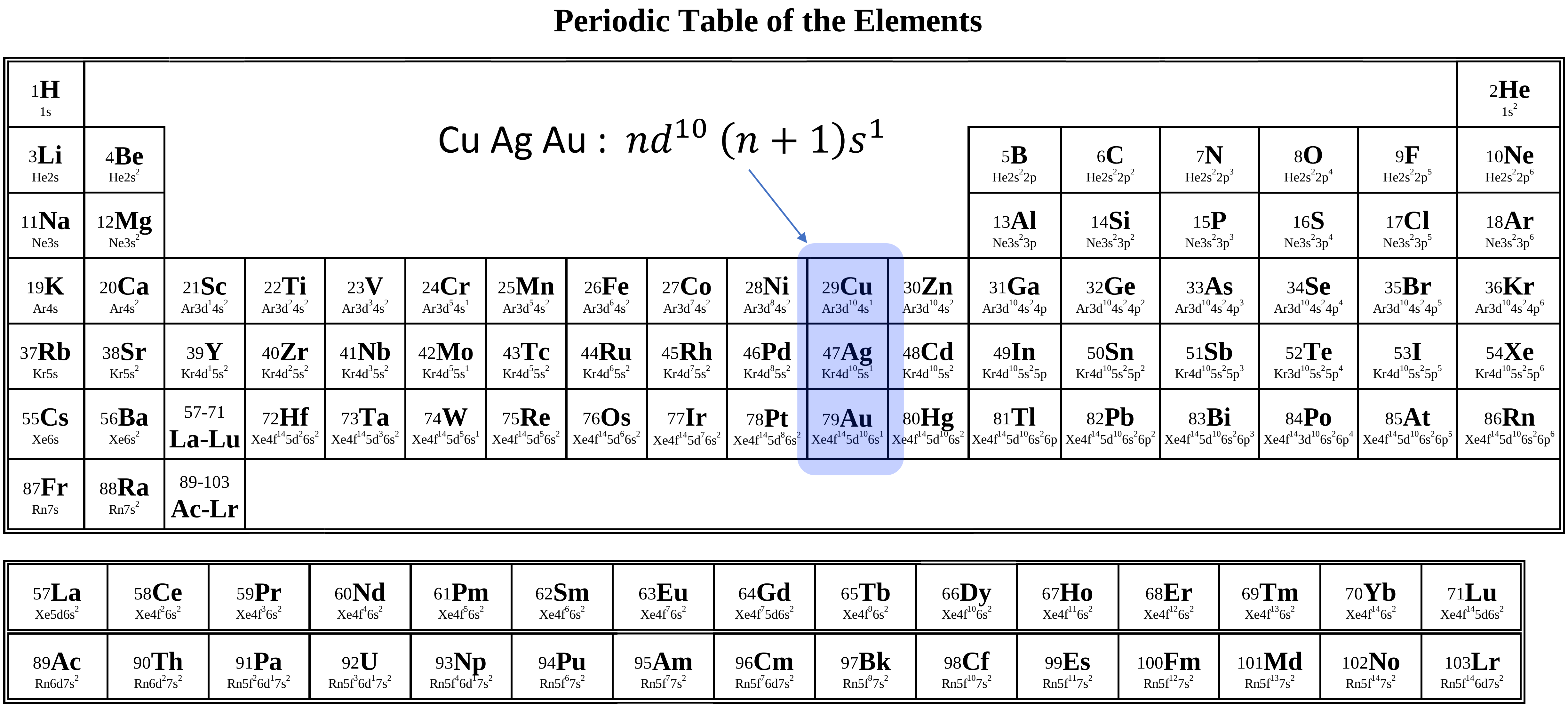
La surprise du chef

Crema Catalana
Quizás sea el postre por excelencia de Cataluña. Esta rica crema es un postre cremoso y crujiente ya que en la parte superior se quema azúcar para crear una capa de crujiente caramelo. Podréis pedirlo en casi cualquier lugar en Cataluña.

Albert Einstein contribution to the Olympic Games

Albert Einstein contribution to the Olympic Games

Cu, Ag, and Au



Periodic Table of the Elements

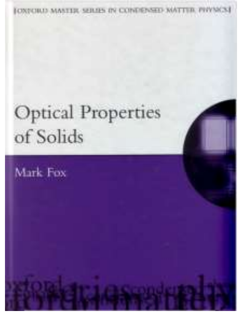
Cu Ag Au : $nd^{10}\ (n+1)s^{1}$

1**H** $1s$																	2**He** $1s^{2}$
3**Li** $\mathrm{He}2s$	4**Be** $\mathrm{He}2s^{2}$											5**B** $\mathrm{He}2s^{2}2p$	6**C** $\mathrm{He}2s^{2}2p^{2}$	7**N** $\mathrm{He}2s^{2}2p^{3}$	8**O** $\mathrm{He}2s^{2}2p^{4}$	9**F** $\mathrm{He}2s^{2}2p^{5}$	10**Ne** $\mathrm{He}2s^{2}2p^{6}$
11**Na** $\mathrm{Ne}3s$	12**Mg** $\mathrm{Ne}3s^{2}$											13**Al** $\mathrm{Ne}3s^{2}3p$	14**Si** $\mathrm{Ne}3s^{2}3p^{2}$	15**P** $\mathrm{Ne}3s^{2}3p^{3}$	16**S** $\mathrm{Ne}3s^{2}3p^{4}$	17**Cl** $\mathrm{Ne}3s^{2}3p^{5}$	18**Ar** $\mathrm{Ne}3s^{2}3p^{6}$
19**K** $\mathrm{Ar}4s$	20**Ca** $\mathrm{Ar}4s^{2}$	21**Sc** $\mathrm{Ar}3d^{1}4s^{2}$	22**Ti** $\mathrm{Ar}3d^{2}4s^{2}$	23**V** $\mathrm{Ar}3d^{3}4s^{2}$	24**Cr** $\mathrm{Ar}3d^{5}4s^{1}$	25**Mn** $\mathrm{Ar}3d^{5}4s^{2}$	26**Fe** $\mathrm{Ar}3d^{6}4s^{2}$	27**Co** $\mathrm{Ar}3d^{7}4s^{2}$	28**Ni** $\mathrm{Ar}3d^{8}4s^{2}$	29**Cu** $\mathrm{Ar}3d^{10}4s^{1}$	30**Zn** $\mathrm{Ar}3d^{10}4s^{2}$	31**Ga** $\mathrm{Ar}3d^{10}4s^{2}4p$	32**Ge** $\mathrm{Ar}3d^{10}4s^{2}4p^{2}$	33**As** $\mathrm{Ar}3d^{10}4s^{2}4p^{3}$	34**Se** $\mathrm{Ar}3d^{10}4s^{2}4p^{4}$	35**Br** $\mathrm{Ar}3d^{10}4s^{2}4p^{5}$	36**Kr** $\mathrm{Ar}3d^{10}4s^{2}4p^{6}$
37**Rb** $\mathrm{Kr}5s$	38**Sr** $\mathrm{Kr}5s^{2}$	39**Y** $\mathrm{Kr}4d^{1}5s^{2}$	40**Zr** $\mathrm{Kr}4d^{2}5s^{2}$	41**Nb** $\mathrm{Kr}4d^{3}5s^{2}$	42**Mo** $\mathrm{Kr}4d^{5}5s^{1}$	43**Tc** $\mathrm{Kr}4d^{5}5s^{2}$	44**Ru** $\mathrm{Kr}4d^{6}5s^{2}$	45**Rh** $\mathrm{Kr}4d^{7}5s^{2}$	46**Pd** $\mathrm{Kr}4d^{8}5s^{2}$	47**Ag** $\mathrm{Kr}4d^{10}5s^{1}$	48**Cd** $\mathrm{Kr}4d^{10}5s^{2}$	49**In** $\mathrm{Kr}4d^{10}5s^{2}5p$	50**Sn** $\mathrm{Kr}4d^{10}5s^{2}5p^{2}$	51**Sb** $\mathrm{Kr}4d^{10}5s^{2}5p^{3}$	52**Te** $\mathrm{Kr}3d^{10}5s^{2}5p^{4}$	53**I** $\mathrm{Kr}4d^{10}5s^{2}5p^{5}$	54**Xe** $\mathrm{Kr}4d^{10}5s^{2}5p^{6}$
55**Cs** $\mathrm{Xe}6s$	56**Ba** $\mathrm{Xe}6s^{2}$	57-71 **La-Lu**	72**Hf** $\mathrm{Xe}4f^{14}5d^{2}6s^{2}$	73**Ta** $\mathrm{Xe}4f^{14}5d^{3}6s^{2}$	74**W** $\mathrm{Xe}4f^{14}5d^{5}6s^{1}$	75**Re** $\mathrm{Xe}4f^{14}5d^{5}6s^{2}$	76**Os** $\mathrm{Xe}4f^{14}5d^{6}6s^{2}$	77**Ir** $\mathrm{Xe}4f^{14}5d^{7}6s^{2}$	78**Pt** $\mathrm{Xe}4f^{14}5d^{8}6s^{2}$	79**Au** $\mathrm{Xe}4f^{14}5d^{10}6s^{1}$	80**Hg** $\mathrm{Xe}4f^{14}5d^{10}6s^{2}$	81**Tl** $\mathrm{Xe}4f^{14}5d^{10}6s^{2}6p$	82**Pb** $\mathrm{Xe}4f^{14}5d^{10}6s^{2}6p^{2}$	83**Bi** $\mathrm{Xe}4f^{14}5d^{10}6s^{2}6p^{3}$	84**Po** $\mathrm{Xe}4f^{14}3d^{10}6s^{2}6p^{4}$	85**At** $\mathrm{Xe}4f^{14}5d^{10}6s^{2}6p^{5}$	86**Rn** $\mathrm{Xe}4f^{14}5d^{10}6s^{2}6p^{6}$
87**Fr** $\mathrm{Rn}7s$	88**Ra** $\mathrm{Rn}7s^{2}$	89-103 **Ac-Lr**															

57**La** $\mathrm{Xe}5d6s^{2}$	58**Ce** $\mathrm{Xe}4f^{2}6s^{2}$	59**Pr** $\mathrm{Xe}4f^{3}6s^{2}$	60**Nd** $\mathrm{Xe}4f^{4}6s^{2}$	61**Pm** $\mathrm{Xe}4f^{5}6s^{2}$	62**Sm** $\mathrm{Xe}4f^{6}6s^{2}$	63**Eu** $\mathrm{Xe}4f^{7}6s^{2}$	64**Gd** $\mathrm{Xe}4f^{7}5d6s^{2}$	65**Tb** $\mathrm{Xe}4f^{9}6s^{2}$	66**Dy** $\mathrm{Xe}4f^{10}6s^{2}$	67**Ho** $\mathrm{Xe}4f^{11}6s^{2}$	68**Er** $\mathrm{Xe}4f^{12}6s^{2}$	69**Tm** $\mathrm{Xe}4f^{13}6s^{2}$	70**Yb** $\mathrm{Xe}4f^{14}6s^{2}$	71**Lu** $\mathrm{Xe}4f^{14}5d6s^{2}$
89**Ac** $\mathrm{Rn}6d7s^{2}$	90**Th** $\mathrm{Rn}6d^{2}7s^{2}$	91**Pa** $\mathrm{Rn}5f^{2}6d^{1}7s^{2}$	92**U** $\mathrm{Rn}5f^{3}6d^{1}7s^{2}$	93**Np** $\mathrm{Rn}5f^{4}6d^{1}7s^{2}$	94**Pu** $\mathrm{Rn}5f^{6}7s^{2}$	95**Am** $\mathrm{Rn}5f^{7}7s^{2}$	96**Cm** $\mathrm{Rn}5f^{7}6d7s^{2}$	97**Bk** $\mathrm{Rn}5f^{9}7s^{2}$	98**Cf** $\mathrm{Rn}5f^{10}7s^{2}$	99**Es** $\mathrm{Rn}5f^{11}7s^{2}$	100**Fm** $\mathrm{Rn}5f^{12}7s^{2}$	101**Md** $\mathrm{Rn}5f^{13}7s^{2}$	102**No** $\mathrm{Rn}5f^{14}7s^{2}$	103**Lr** $\mathrm{Rn}5f^{14}6d7s^{2}$

Albert Einstein contribution to the Olympic Games

Optical properties of Cu



OXFORD MASTER SERIES IN CONDENSED MATTER PHYSICS

Optical Properties of Solids

Mark Fox

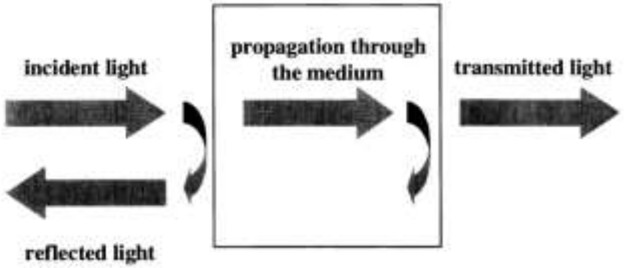
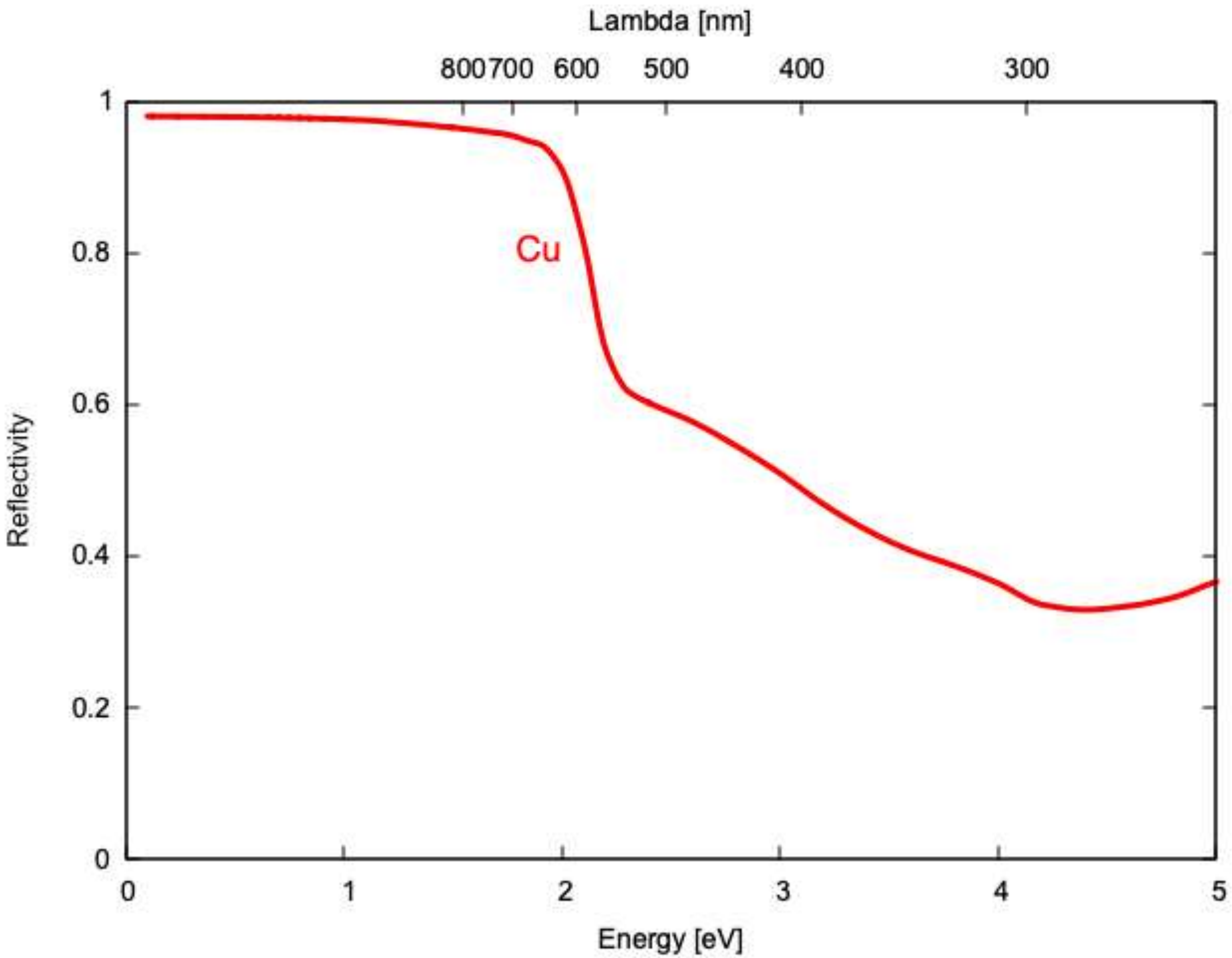
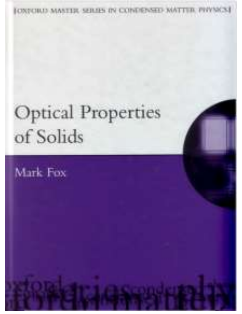


Fig. 1.1 Reflection, propagation and transmission of a light beam incident on an optical medium.



Optical properties of Cu



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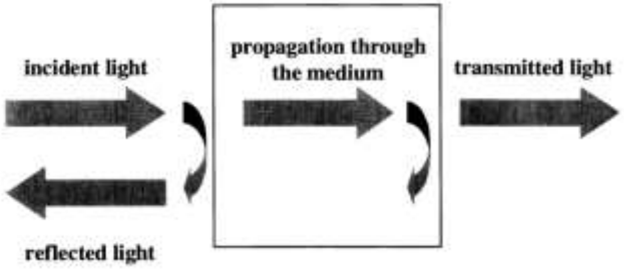
Optical Properties
of Solids

Mark Fox



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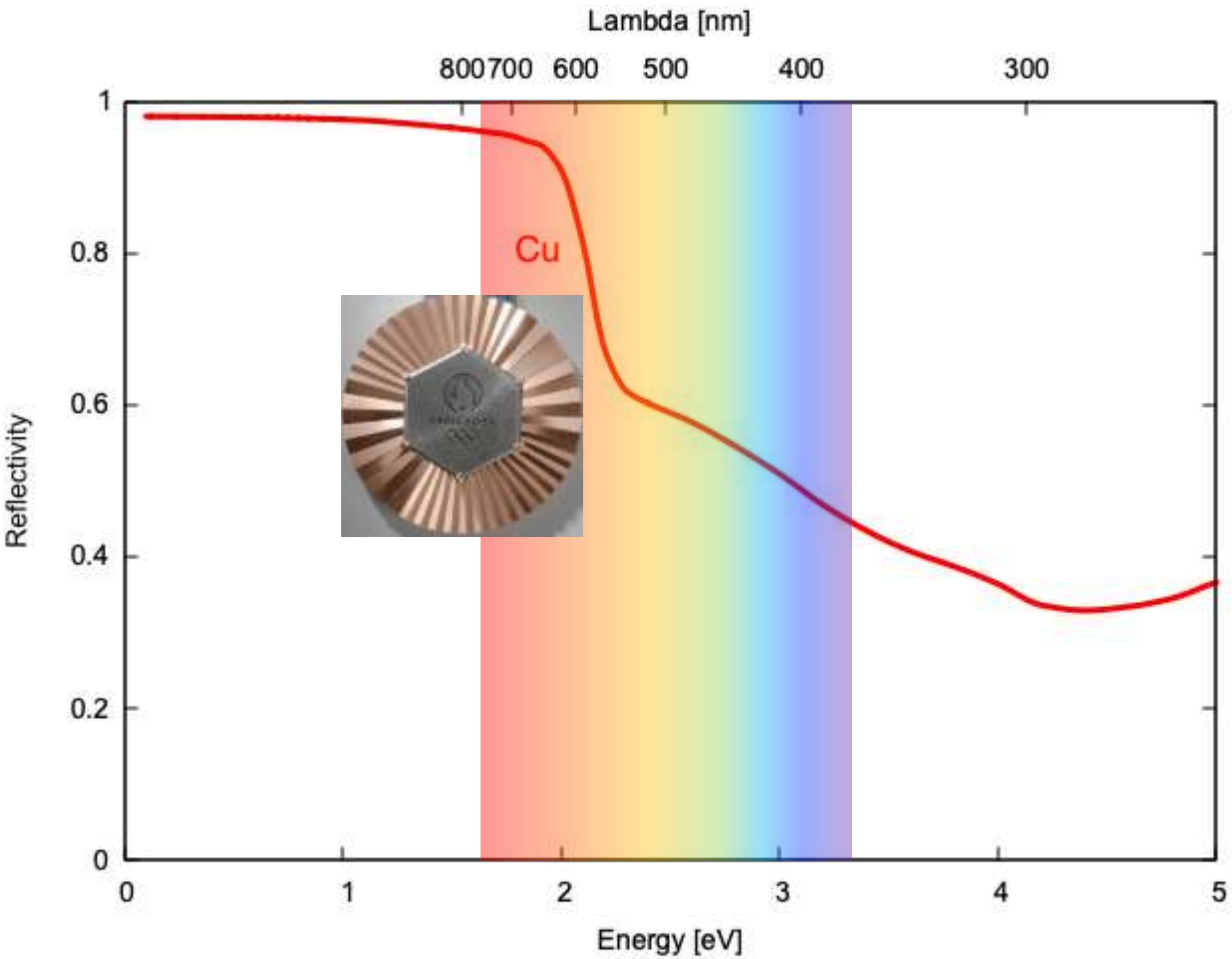
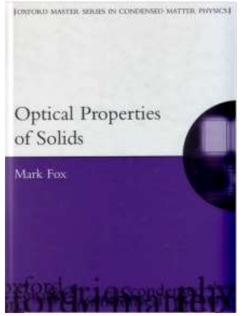


Cu reflects … red

Optical properties of Cu and Ag



OXFORD MASTER SERIES IN CONDENSED MATTER PHYSICS

Optical Properties of Solids

Mark Fox

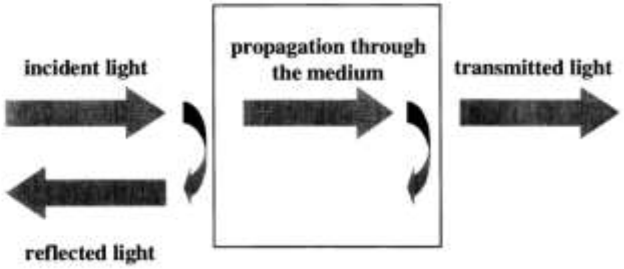
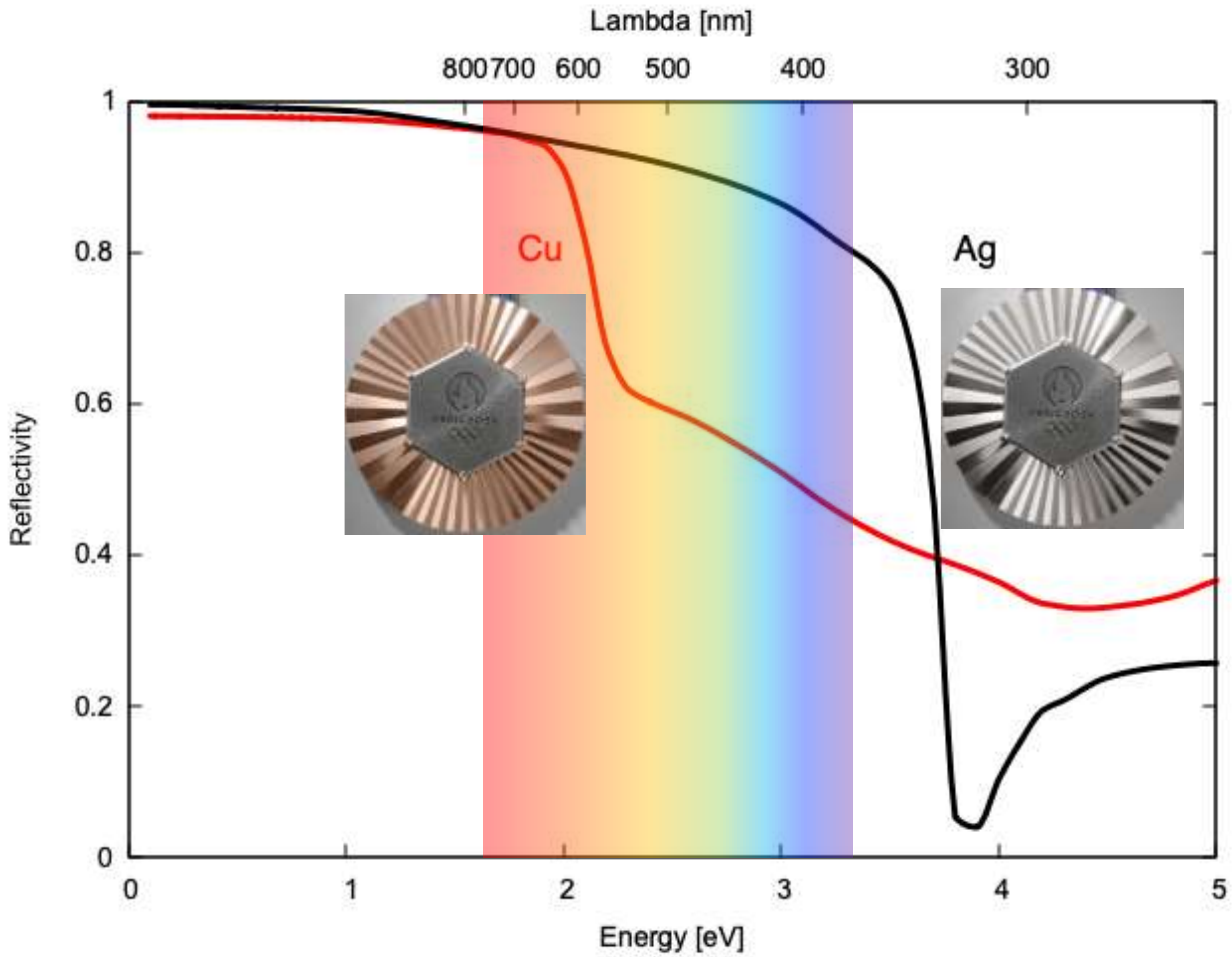
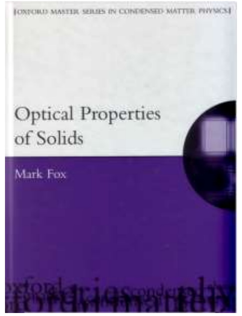


Fig. 1.1 Reflection, propagation and transmission of a light beam incident on an optical medium.



Cu reflects … red
Ag reflects … everything

Optical properties of Cu, Ag, and Au



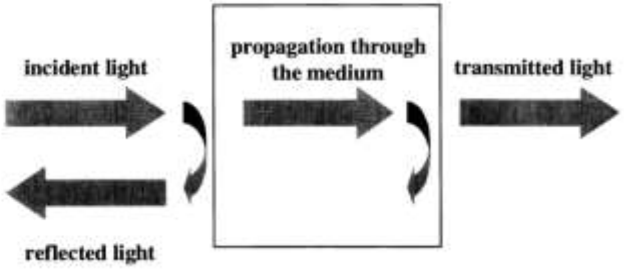
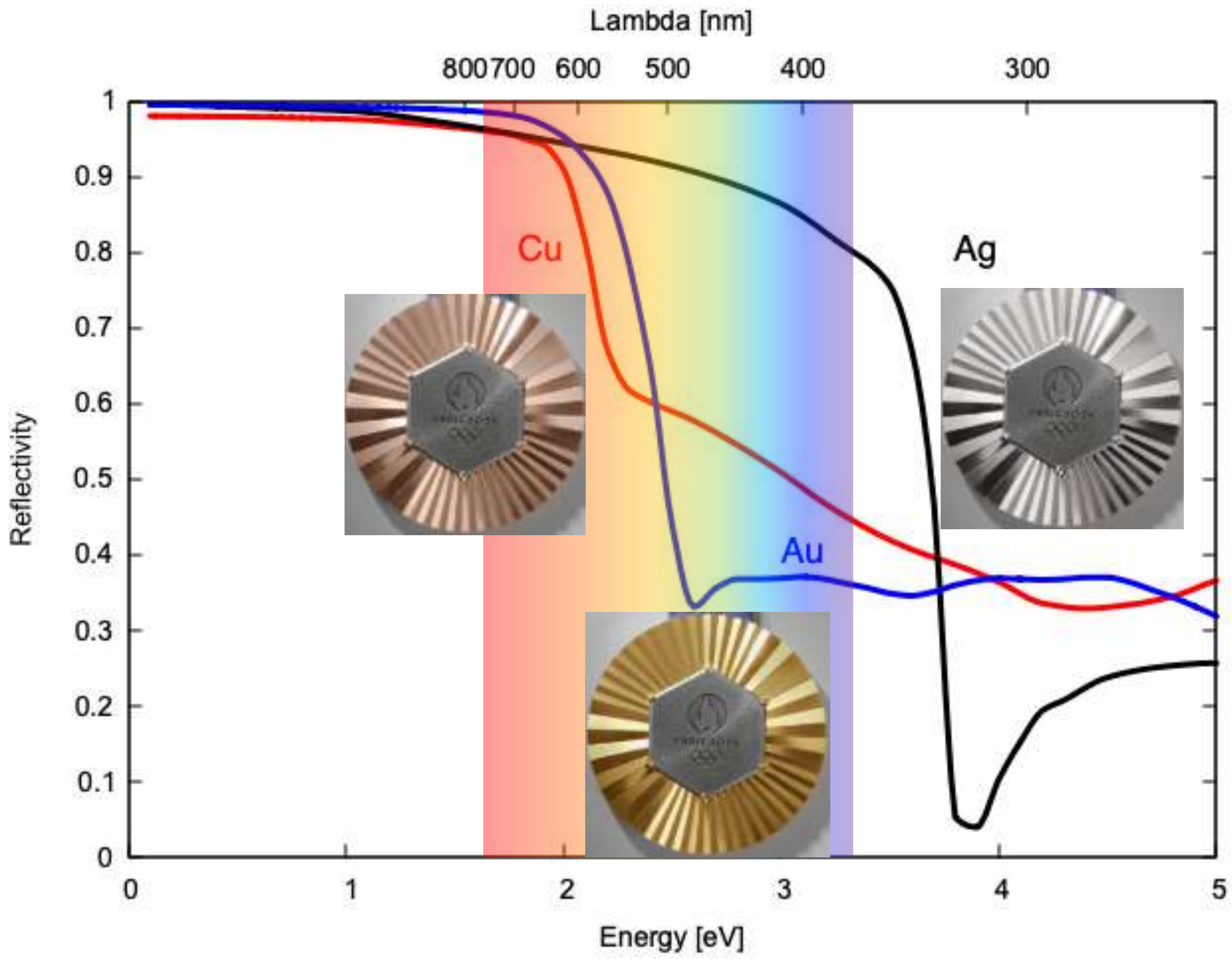


Fig. 1.1 Reflection, propagation and transmission of a light beam incident on an optical medium.

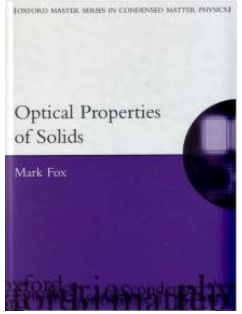


The color of Ag seems to be the “good one” for free electron metals

Cu reflects … red
Ag reflects … everything
Au reflects … red and yellow

1. Why there is a drop in reflectance at around 2eV in Cu and 2.5eV in Au ?
2. Why the energy drop in Au moves up in energy ?

1. Why there is a drop in reflectance ?



A drop in reflectance happens due to electronic inter-band transitions.

The transitions happen from a region with a high density of states (flat bands) to empty state (above the Fermi level)

Cu : $3d^{10}\ 4s^{1}$

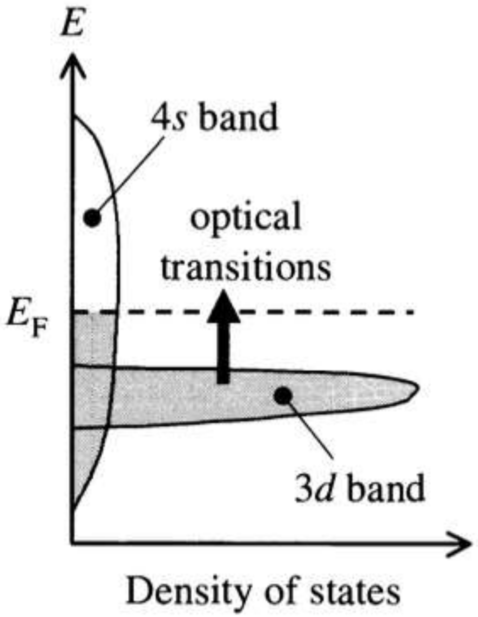
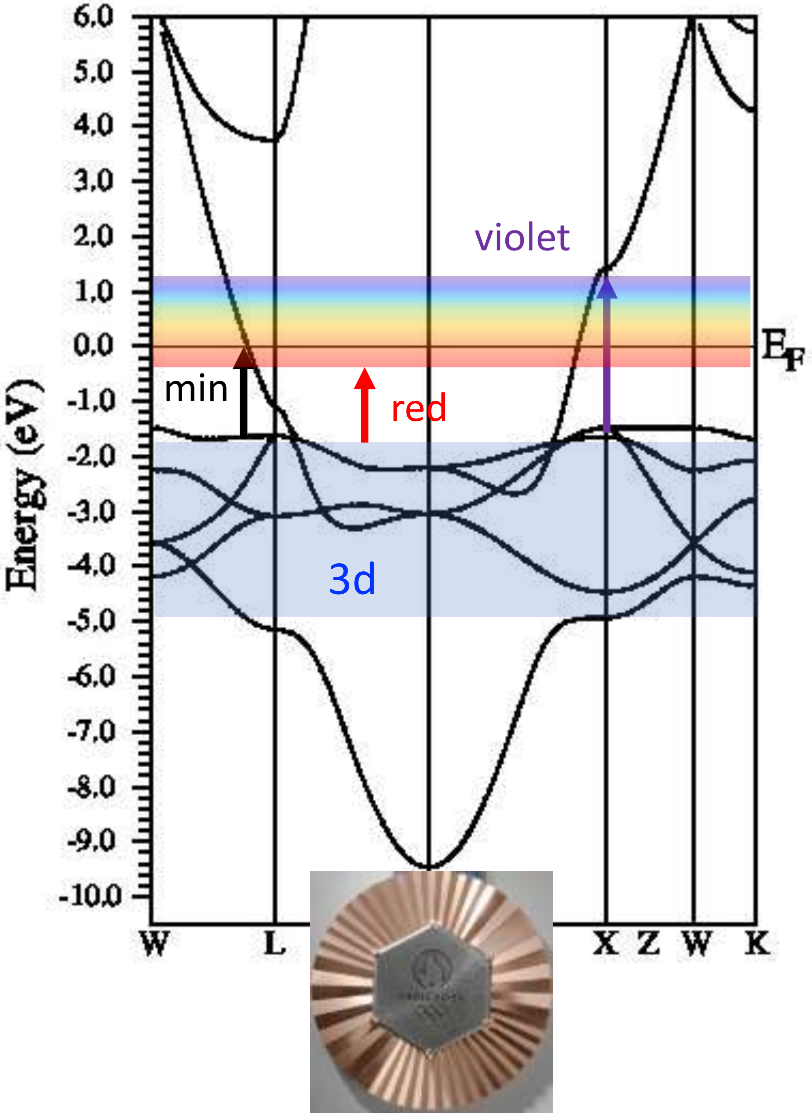


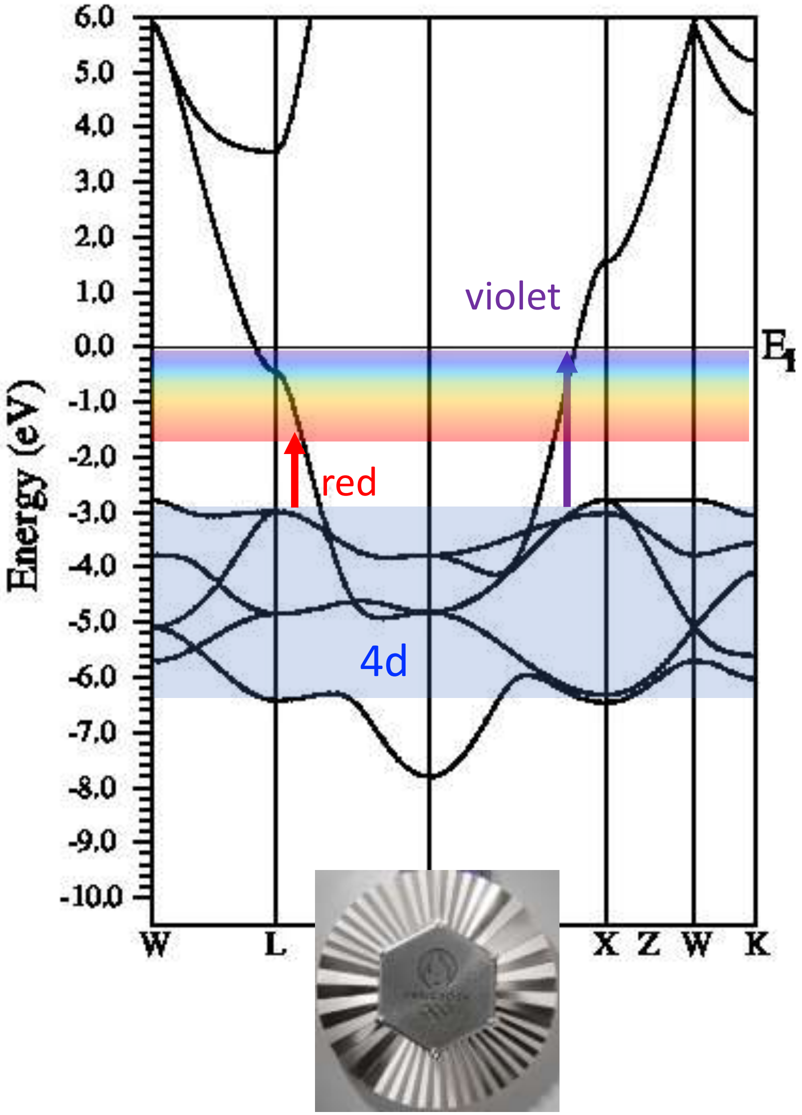
Fig. 7.4 Schematic density of states for the 3d and 4s bands of a transition metal such as copper.

1. Why there is a drop in reflectance ?

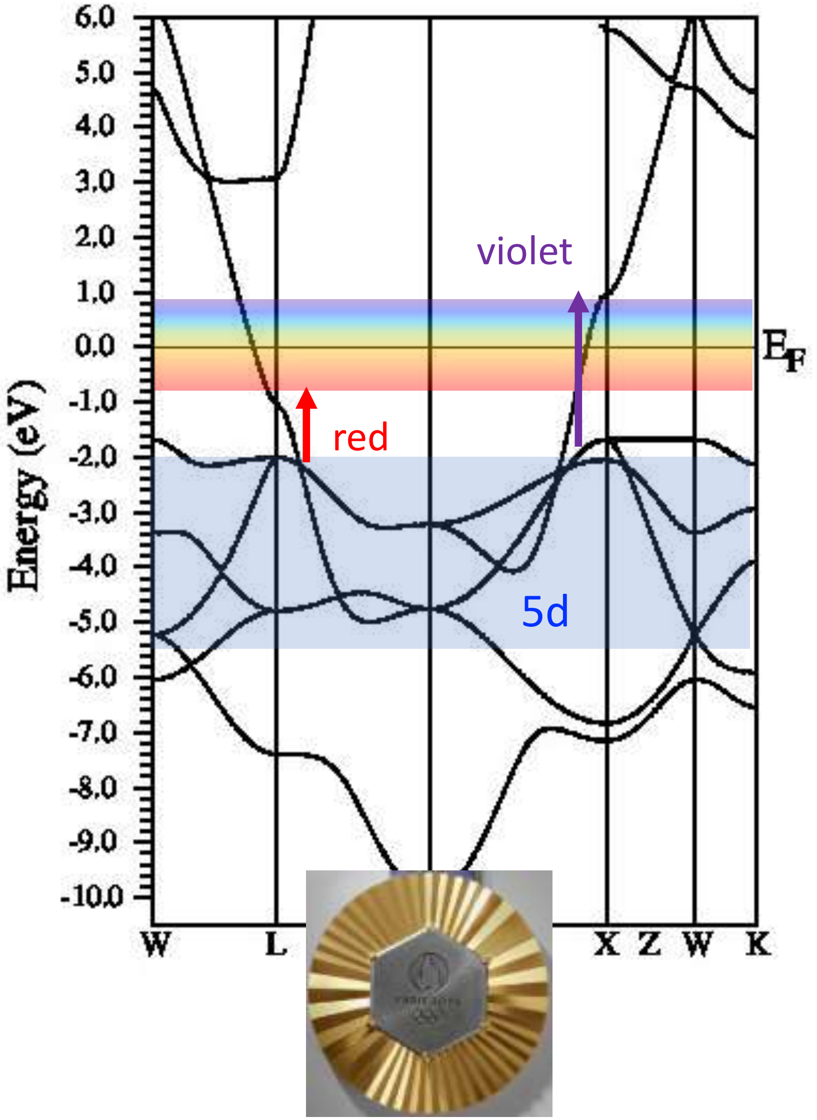
Cu



Ag



Au



Because there are localized d bands just below the Fermi level

2. Why the energy drop in Au move up in energy ? ?

Au is the heaviest atom in the series $Z = 79$

Let's analyse the total, potential and kinetic energies of the orbitals using hydrogenic solutions :

$$E_{nlm} = -\frac{Z^2\ E_0}{n^2} \qquad V_{nlm} = -\frac{2Z^2\ E_0}{n^2} < 0 \qquad T_{nlm} = \frac{Z^2\ E_0}{n^2} > 0$$

The largest kinetic energy happens for the deep $1s$ orbital : $T_{1s} = Z^2\ E_0 > 0$

To decide if relativistic effects are important one has to compare the kinetic energy of the $1s$ state with mc^2.

$$T_{1s} = Z^2\ E_0 \approx mc^2$$

element	Z	T_{1s}/mc^2
Cu	29	2.2 %
Ag	47	6.0 %
Au	79	17 %

Relativistic effects are important for the $1s$ orbital of Au

Optical properties of Cu, Ag, and Au

What is the consequence ?

When the relativistic effects are important the effective mass increases, having the effect to decrease the kinetic energy, (for a given localization, i.e, for a given kinetic moment).

The electron can localize further (approaching the nucleus) and gain potential anf total enegy energy.

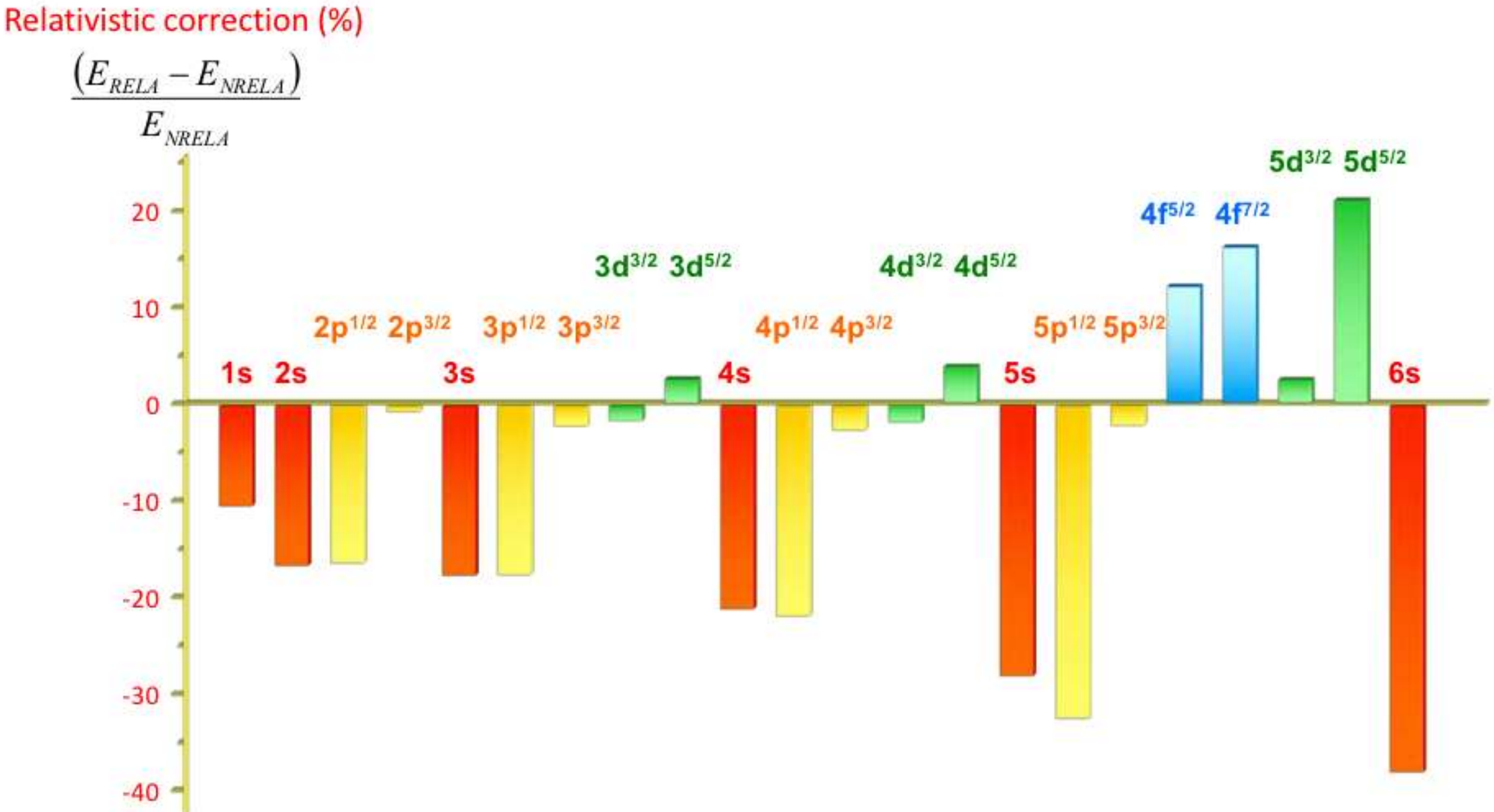
Optical properties of Cu, Ag, and Au

In other words, the total energy of a relativistic 1*s* electron has a lower energy than a non-relativistic one !!

The other *s* electrons (n > 2) also localize because they must be orthonormal to the 1*s*

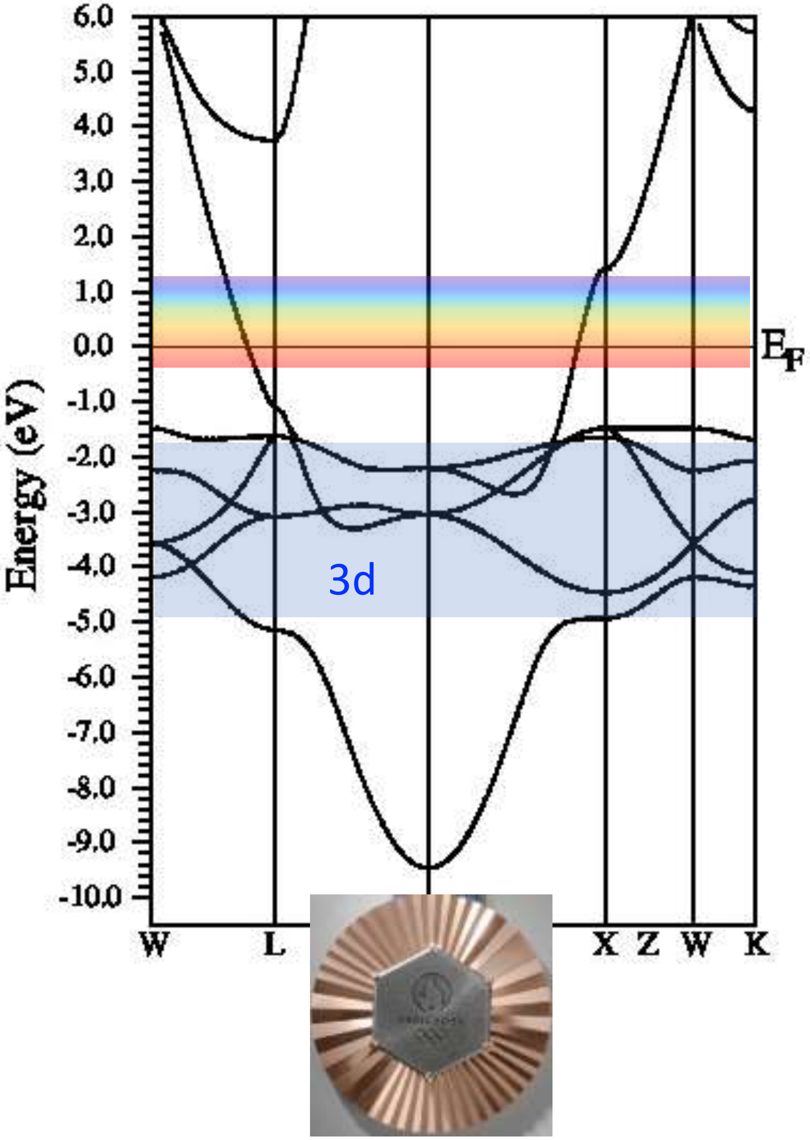
The 5*d* electron delocalizes because the more localized n*s* orbitals screen the nuclei.

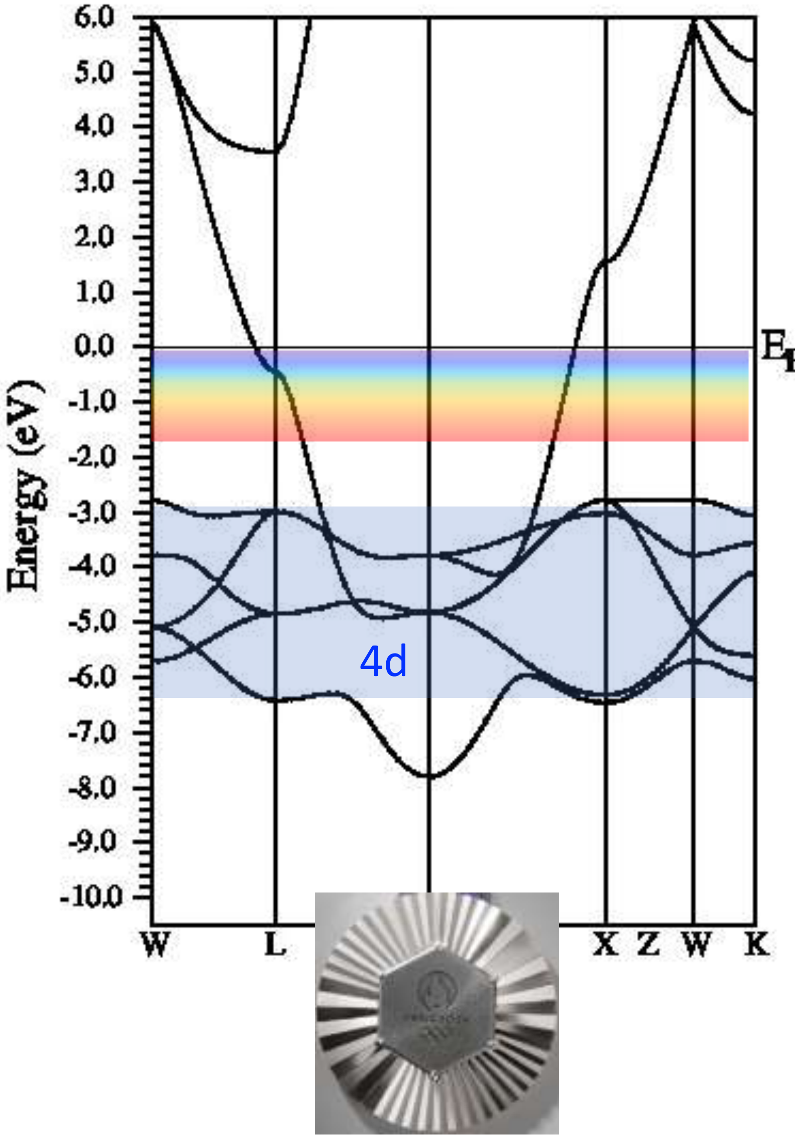
Au: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^{10}\ 6s^1$

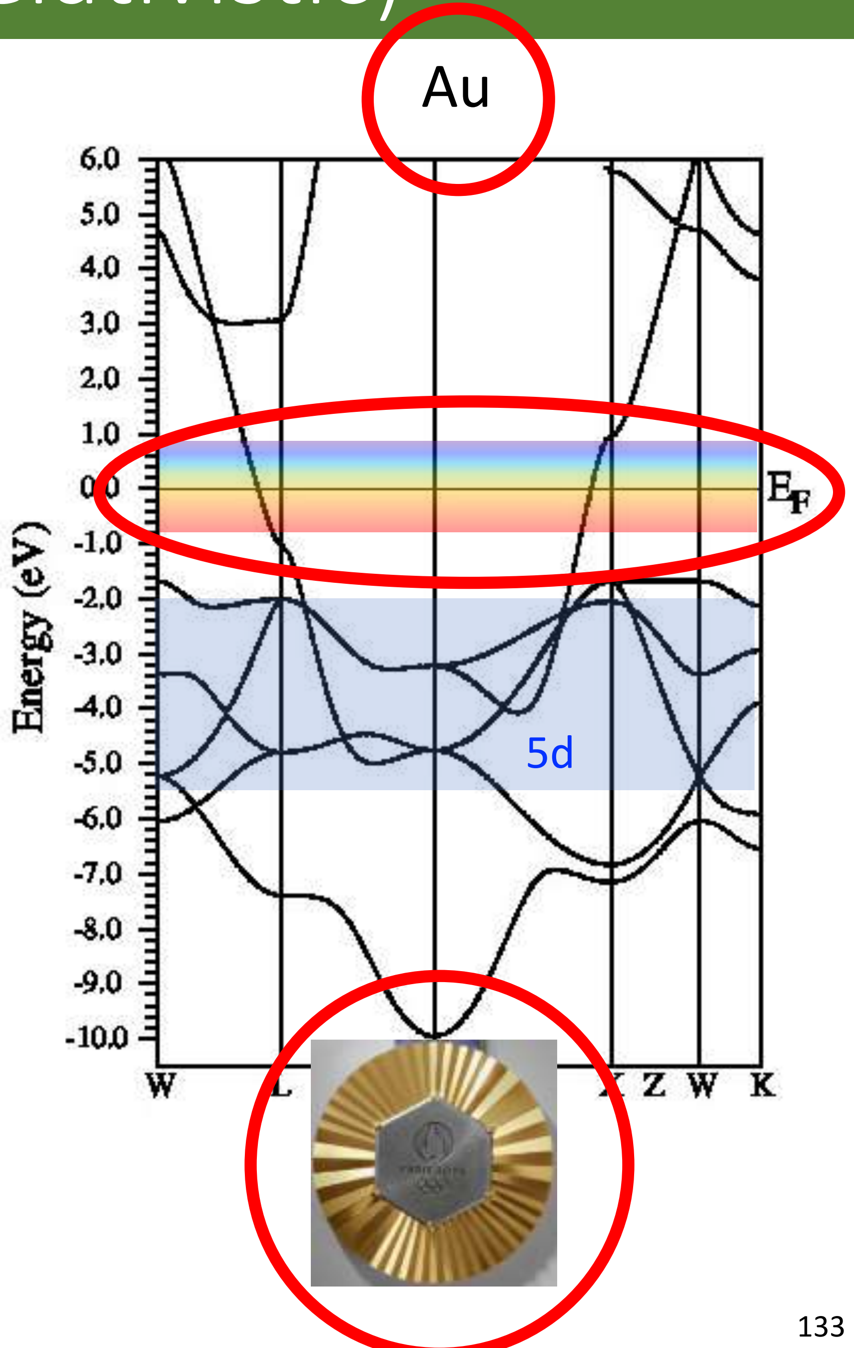


http://susi.theochem.tuwien.ac.at/events/ws24/Rocquefelte-relativity.pdf
Xavier Rocquefelte (ISCR - University of Rennes 1 – CNRS)

Band structure calculation (relativistic)

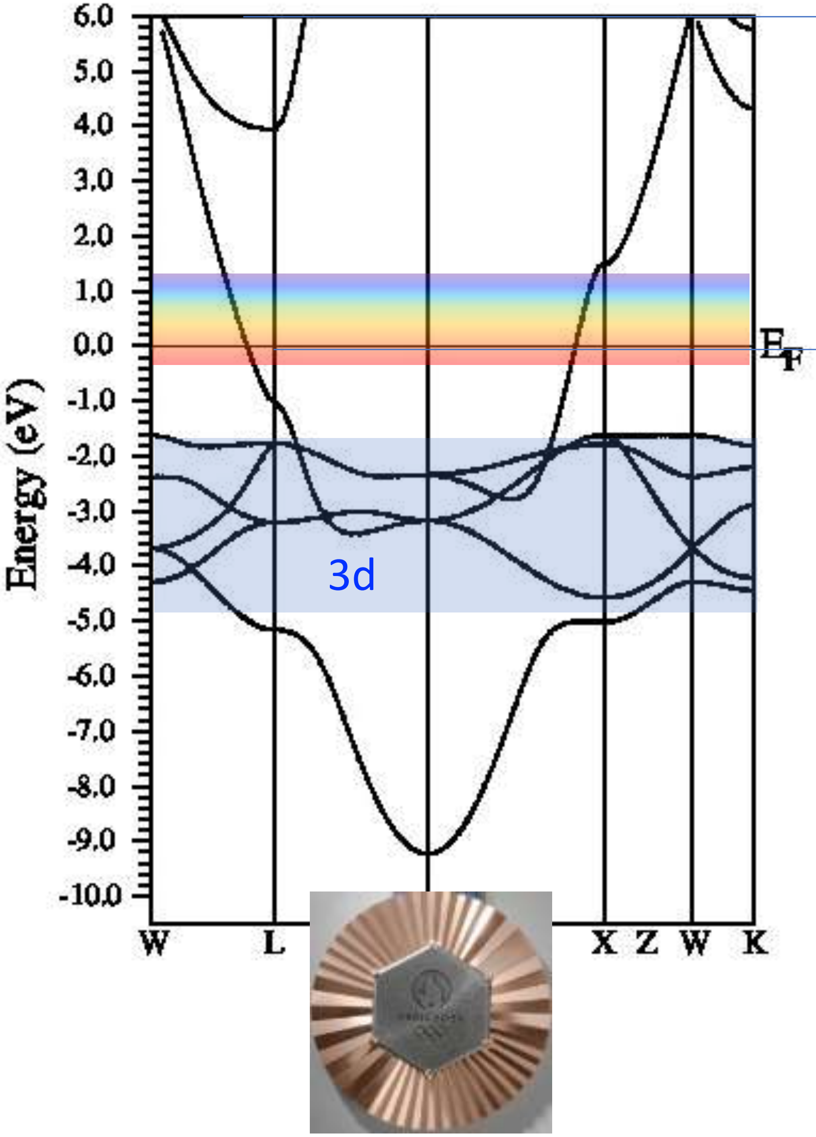

Cu


Ag

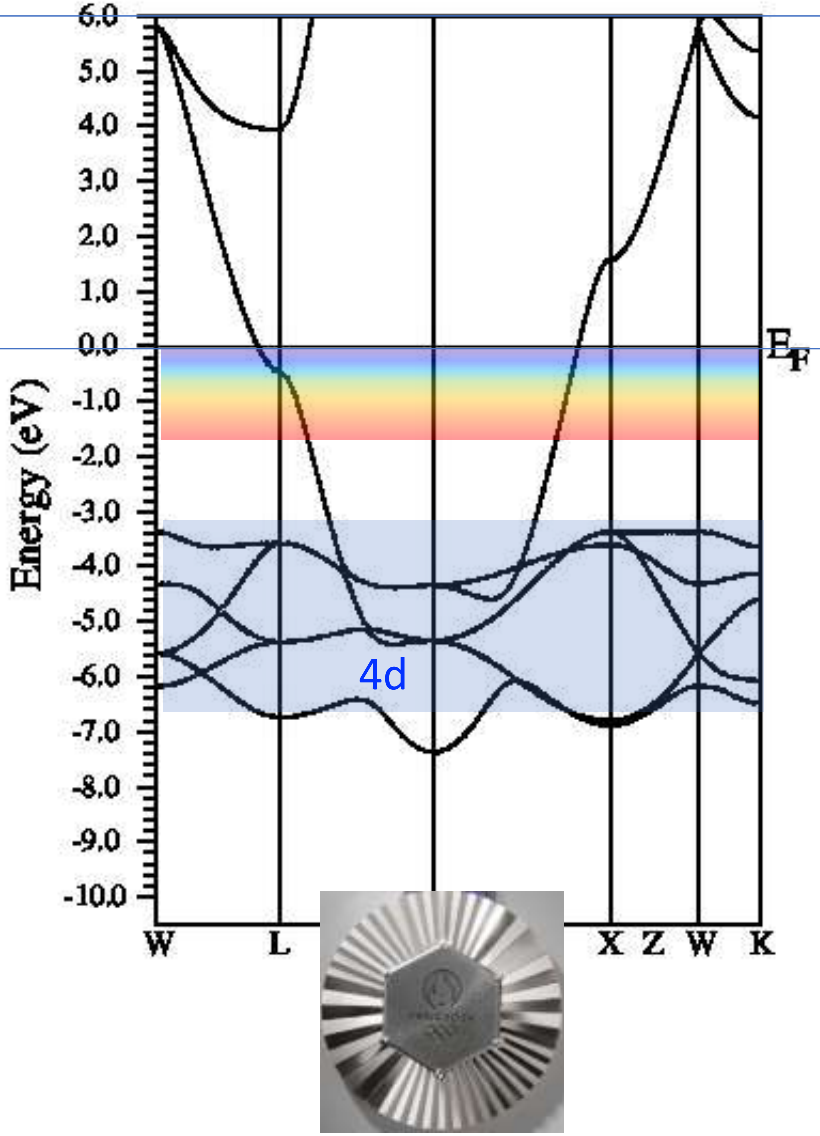

Au

Band structure calculation (non relativistic)

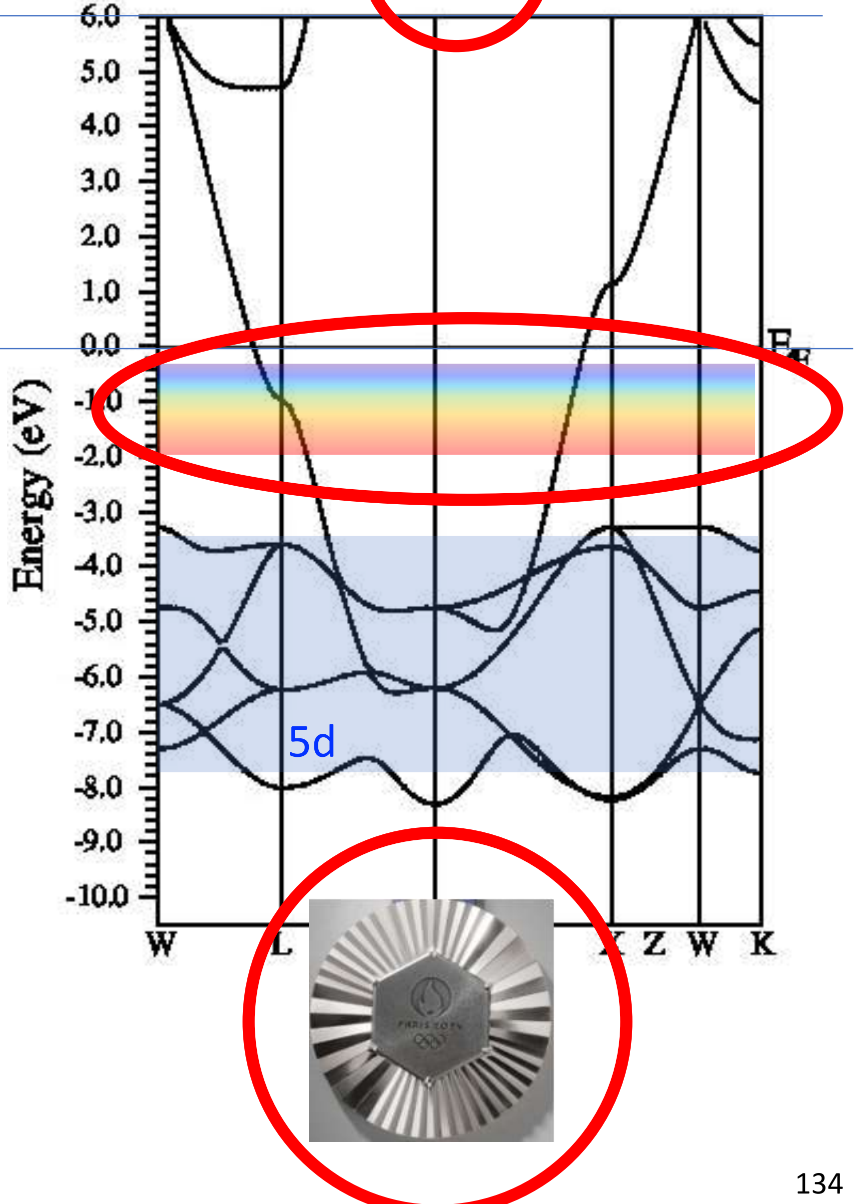
Cu



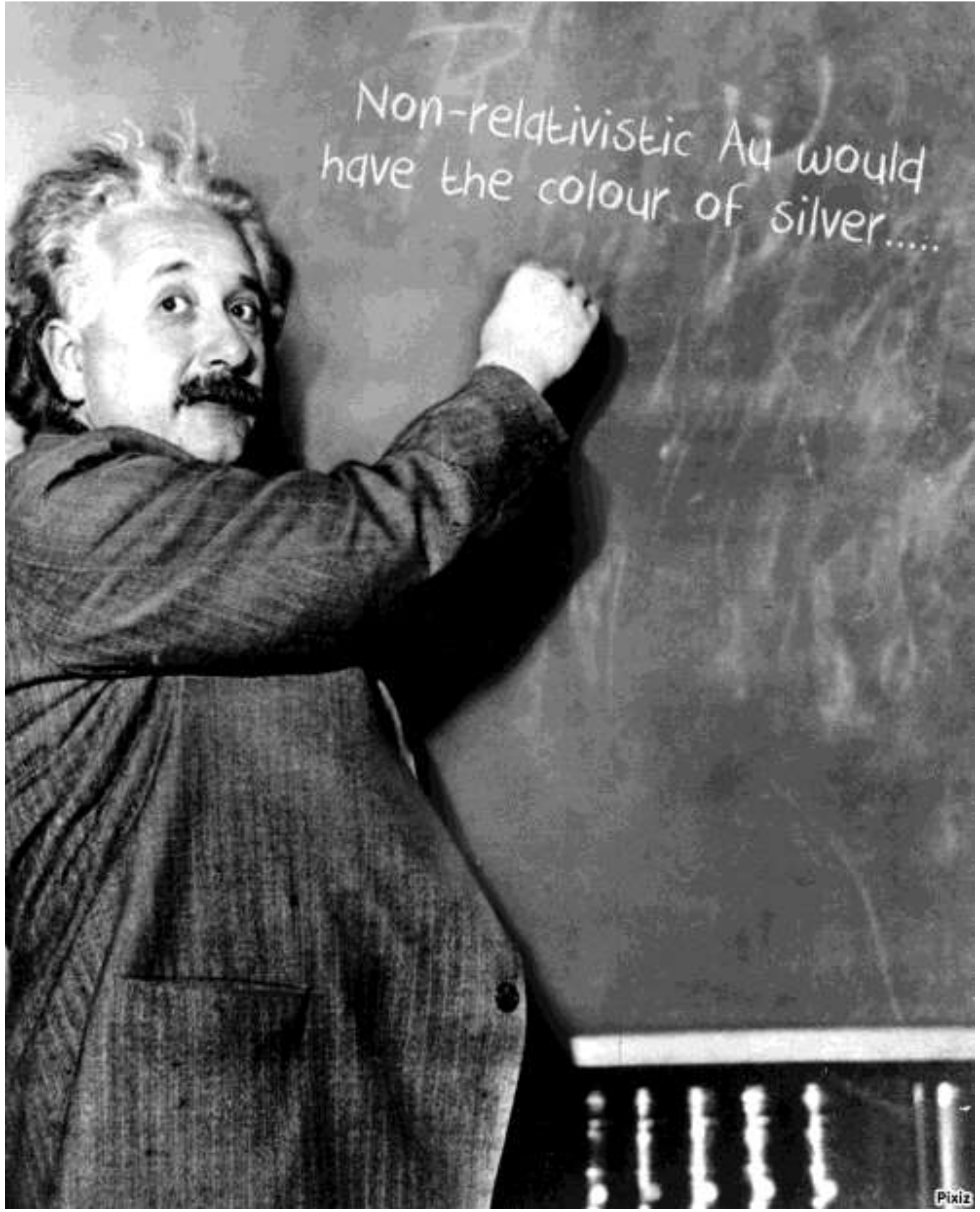
Ag



Au



Einstein …



Optical properties of Cu, Ag, and Au

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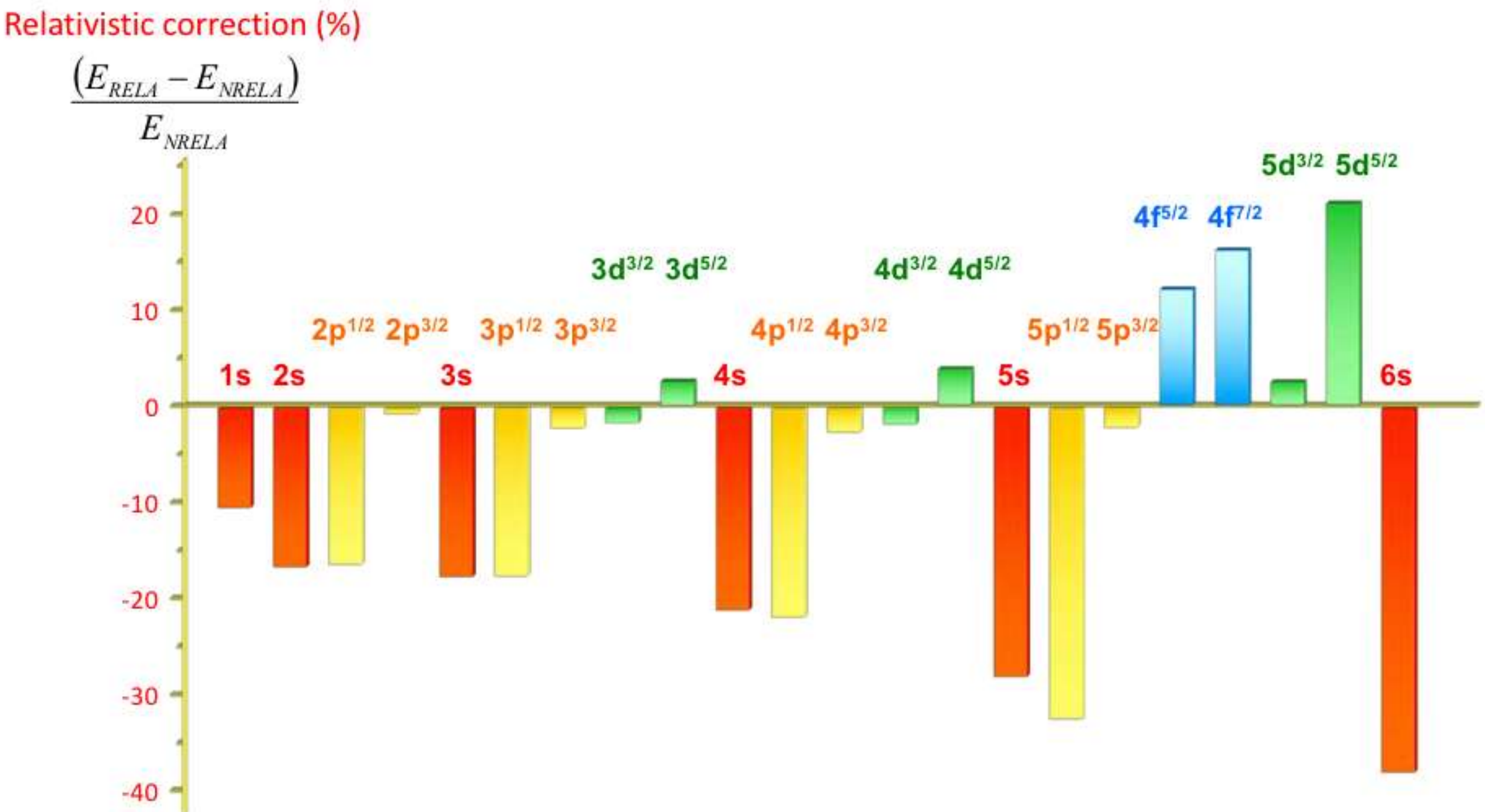
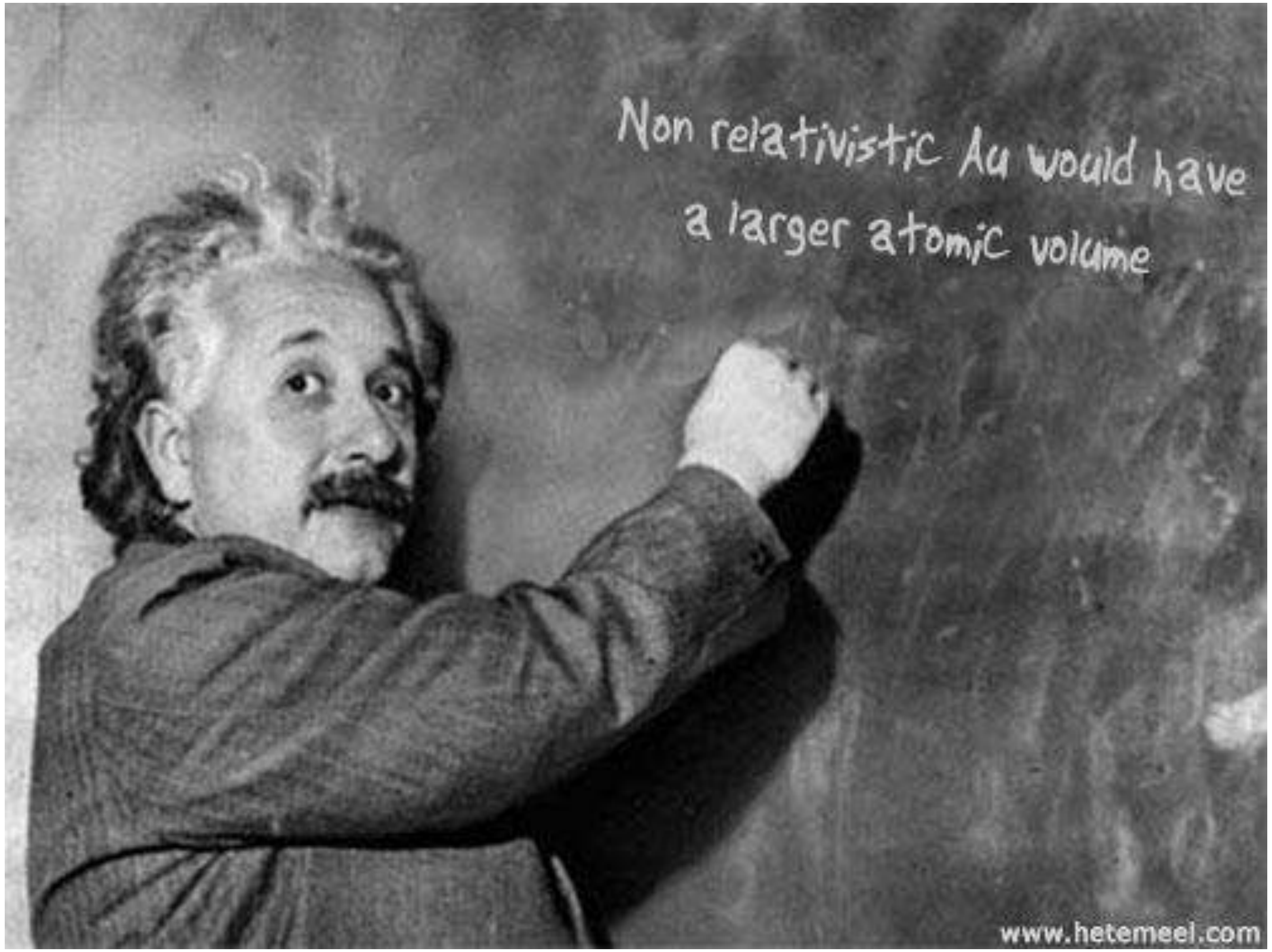
Au: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^{10}\ 6s^1$



http://susi.theochem.tuwien.ac.at/events/ws24/Rocquefelte-relativity.pdf

Xavier Rocquefelte (ISCR - University of Rennes 1 – CNRS)

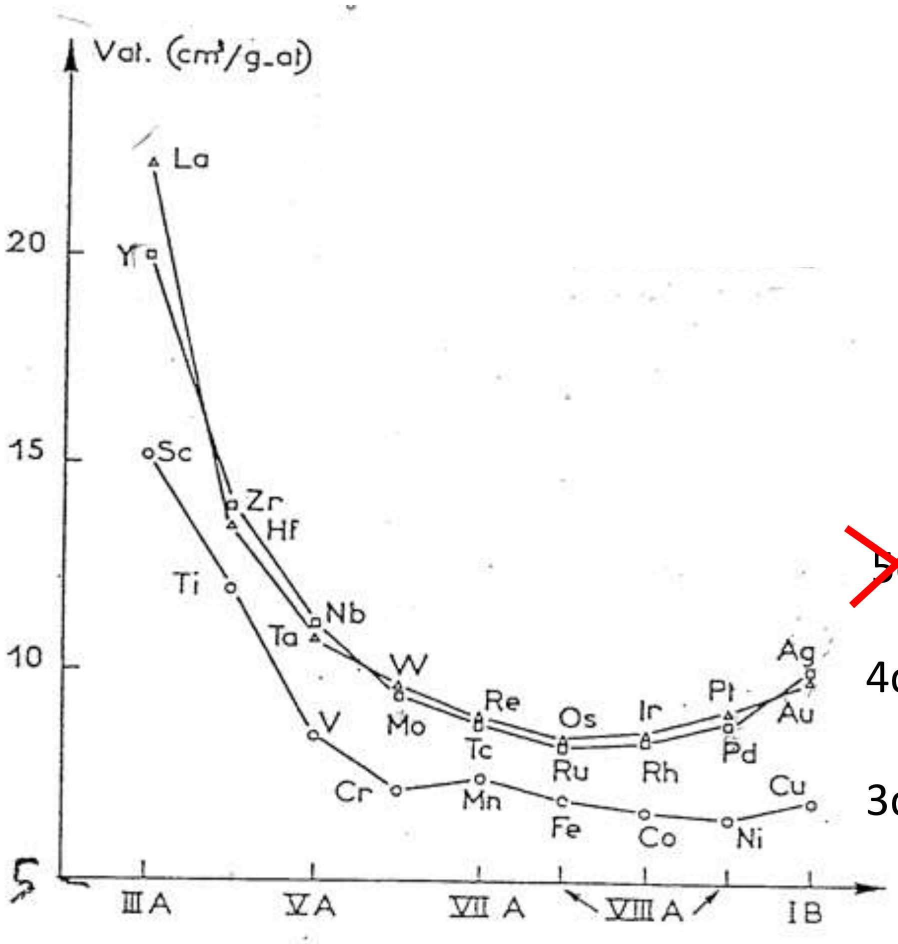
Another interesting relativistic effect



The localization of the core $1s$ orbital, implies the localization of the other ns orbitals due to the orthogonalization.
This effect apply to the $6s$, which is the outermost orbitals.

Atomic volume of the transition metals

The 5d transition metals have the atomic volume of the 4d …..



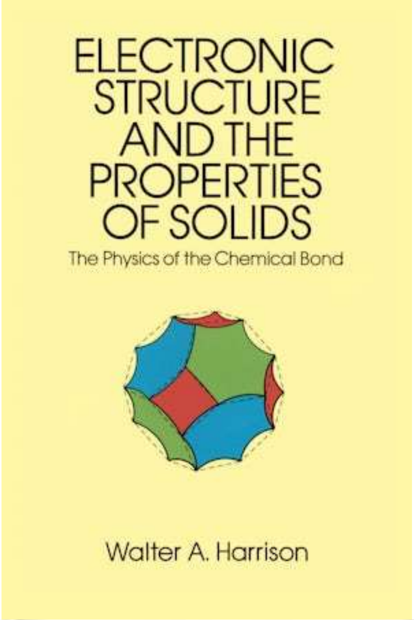
~~5d~~

4d 5d

3d

13 - Volume atomique des métaux de transition (D'après GSCHNEIDNER [59])

Bibliography … pour commencer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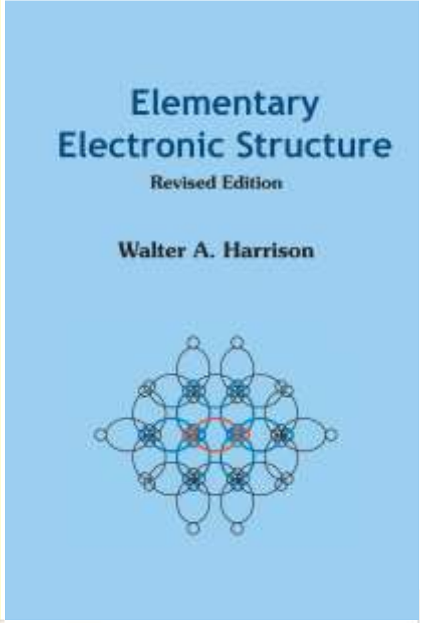
The Physics of the Chemical Bond
Walter A. Harrison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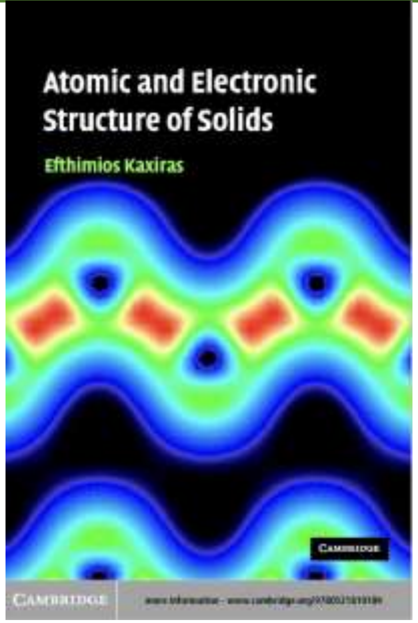
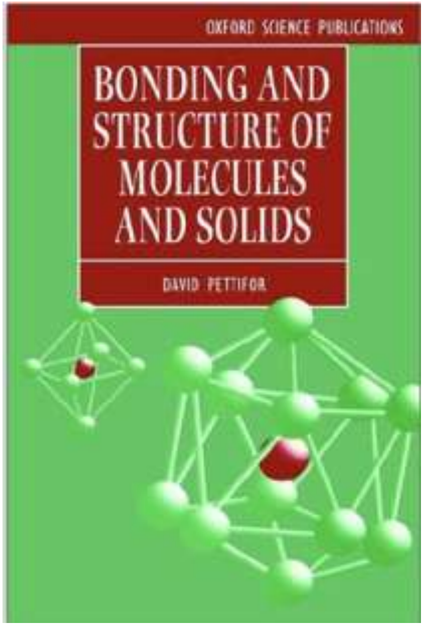

Atomic and Electronic Structure of Solids
Efthimios Kaxiras
CAMBRIDGE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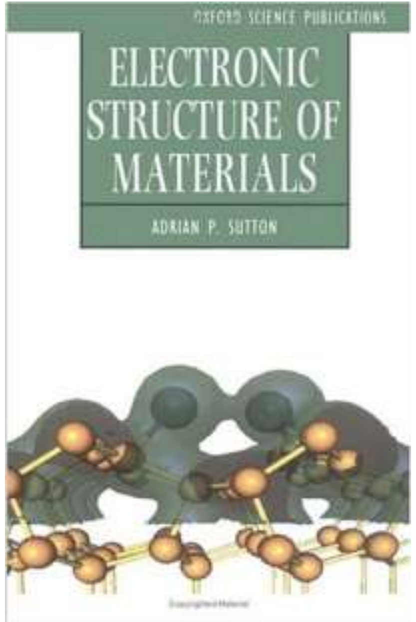
DAVID PETTIFOR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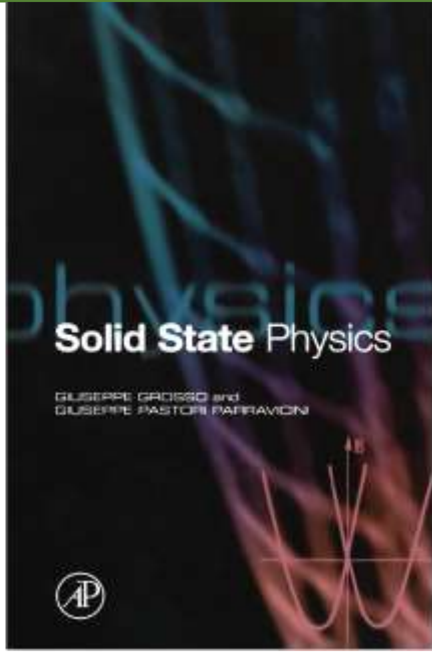
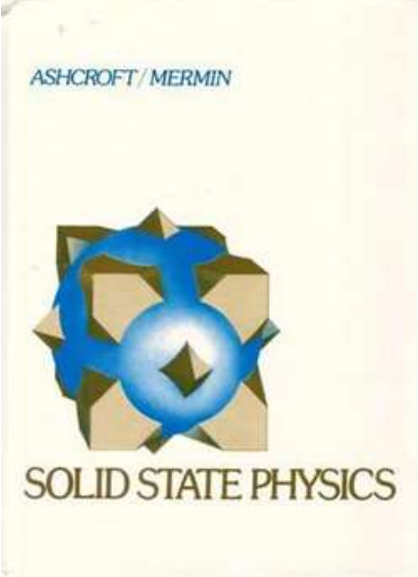
ADRIAN P. SUTTON


Solid State Physics
GIUSEPPE GROSSO and
GIUSEPPE PASTORI PARRAVICINI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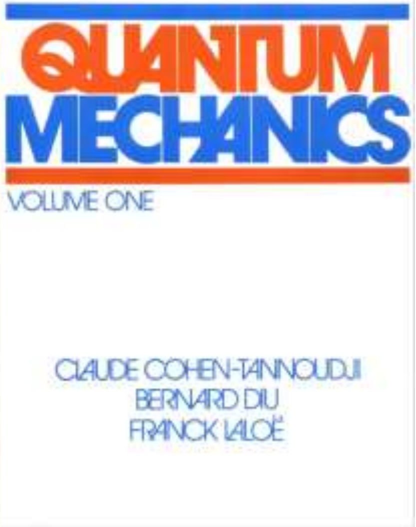
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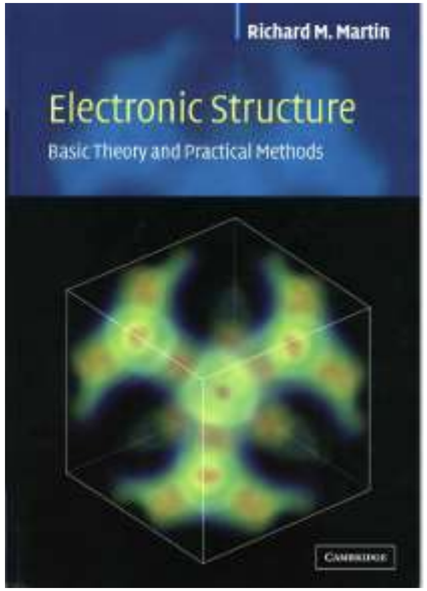
ORDER AND PHASE STABILITY IN ALLOYS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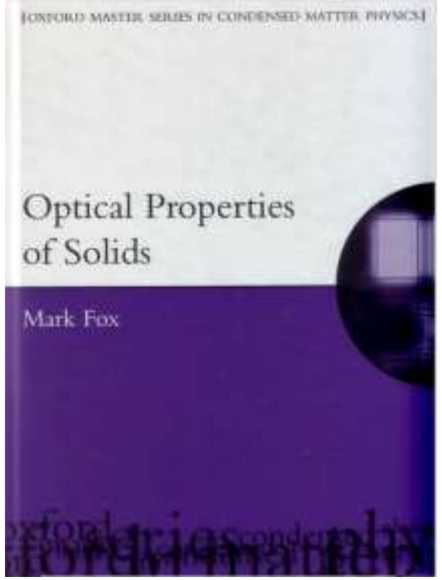
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