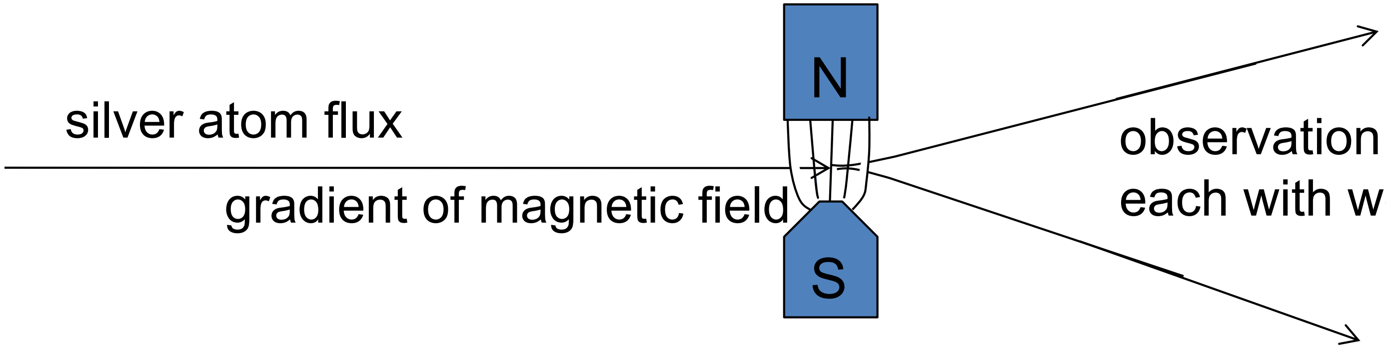
Advanced Materials Modeling
Lecture of 21 april
Part A

+ Spin, magnetism, spin-orbit coupling, spin-density functional theory
+ Forces, and brief introduction to density functional perturbation theory
+ Iterative techniques
+ Troubleshooting

Spin, magnetism, spin-orbit coupling, spin-density functional theory

Intrinsic angular momentum

Spin Notion proposed by Uehlenbeck et Goudsmit (1925)
to explain Stern and Gerlach experiment



silver atom flux

gradient of magnetic field

observation : two beams,
each with well-defined magnetic dipole

Silver Ag = (Kr) + $4d^{10}\,5s^1$

Intrinsic angular momentum

Behaves like an orbital moment, although with only two possible values of the z projection : $m_s\hbar$ $m_s = \pm 1/2$

No intrinsic angular momentum in classical mechanics,
no correspondance principle …

Reminder : orbital momentum

- Vector property $\vec{\ell} = \vec{r} \times \vec{p} \rightarrow \hat{\vec{\ell}} = -i\hbar(\hat{\vec{r}} \times \hat{\vec{\nabla}})$

$$\hat{\ell}_z = -i\hbar\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right)$$

Quantum eigenfunctions and eigenvalues

$$\hat{\ell}_z\varphi = \ell_z.\varphi \qquad -i\hbar\left(x\frac{\partial\varphi}{\partial y} - y\frac{\partial\varphi}{\partial x}\right) = \ell_z\varphi$$

In spherical coordinates

$$\varphi(r,\theta,\Phi) = f(r,\theta)e^{i\ell_z \Phi/\hbar}$$

$\ell_z = m \cdot \hbar$ $\quad m = 0,\pm1,\pm2,\ldots$ Discrete spectrum of $\hat{\ell}_z$

Representation of spin

Representation based on vectors (wavefunction) and matrices (operator) : intrinsic angular momentum cannot be represented using spatially-dependent wavefunction

Spinorial wavefunction: 2-component vector, called "spinor"

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ \psi_{\downarrow}(\mathbf{r}) \end{pmatrix} \quad \text{or} \quad \psi(\mathbf{r},\sigma)$$

σ can take two "values": ↑ or ↓

Other notation : define $|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ et $|\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$\alpha(\uparrow) = 1 \qquad \alpha(\downarrow) = 0 \qquad \beta(\uparrow) = 0 \qquad \beta(\downarrow) = 1$$

$$\psi(\mathbf{r},\sigma)=\psi_{\uparrow}(\mathbf{r})\alpha(\sigma)+\psi_{\downarrow}(\mathbf{r})\beta(\sigma)$$

Norm / scalar product

Norm

$$N^2 = \langle \Psi | \Psi \rangle = \int \begin{pmatrix} \psi_\uparrow(\mathbf{r}) & \psi_\downarrow(\mathbf{r}) \end{pmatrix}^* \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} d\mathbf{r} = \int |\psi_\uparrow(\mathbf{r})|^2 + |\psi_\downarrow(\mathbf{r})|^2 \, d\mathbf{r}$$

Scalar product

$$\langle \Phi | \Psi \rangle = \int \begin{pmatrix} \varphi_\uparrow(\mathbf{r}) & \varphi_\downarrow(\mathbf{r}) \end{pmatrix}^* \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} d\mathbf{r}$$

$$= \int \varphi_\uparrow^*(\mathbf{r}) \psi_\uparrow(\mathbf{r}) + \varphi_\downarrow^*(\mathbf{r}) \psi_\downarrow(\mathbf{r}) \, d\mathbf{r}$$

Pure spin-up or -down wavefunctions

Most often : pure spin up wavefunctions, or pure spin down wavefunctions

Explicitly $\Psi(\mathbf{r}) = \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ 0 \end{pmatrix}$ or $\Psi(\mathbf{r}) = \begin{pmatrix} 0 \\ \psi_{\downarrow}(\mathbf{r}) \end{pmatrix}$

Such pure spin-up or spin-down wavefunctions are orthogonal to each others.
Correspond to different quantum states.

Simply using spin-up or spin-down wavefunctions often referred to "scalar wavefunctions", at variance with "spinorial wavefunctions" or "spinors"

If not pure-up or -down wavefunctions ?

Computation of electronic density, and also spin-density.

Expectation value of electronic density at a point :

$$n(\mathbf{r}) = \left|\psi_\uparrow(\mathbf{r})\right|^2 + \left|\psi_\downarrow(\mathbf{r})\right|^2$$

Expectation value of the spin along z (spin-polarization)

$$s_z(\mathbf{r}) = \left(\left|\psi_\uparrow(\mathbf{r})\right|^2 - \left|\psi_\downarrow(\mathbf{r})\right|^2\right)\frac{\hbar}{2}$$

What about the x- or y- spin-polarization ?
Or expectation along any other direction ?

Pauli matrices : spin along x, y, z + …

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Warning. Potential notation conflict : σ is for ↑ or ↓ , $\sigma_x, \sigma_y, \sigma_z$ are Pauli matrices

Spin-polarization vector (expectation value):

$$s_x(\mathbf{r}) = \left(\psi_\downarrow^*(\mathbf{r})\psi_\uparrow(\mathbf{r}) + \psi_\uparrow^*(\mathbf{r})\psi_\downarrow(\mathbf{r})\right)\frac{\hbar}{2} = \Psi^+(\mathbf{r})\sigma_x\Psi(\mathbf{r})\frac{\hbar}{2}$$

$$s_y(\mathbf{r}) = \left(i\psi_\downarrow^*(\mathbf{r})\psi_\uparrow(\mathbf{r}) - i\psi_\uparrow^*(\mathbf{r})\psi_\downarrow(\mathbf{r})\right)\frac{\hbar}{2} = \Psi^+(\mathbf{r})\sigma_y\Psi(\mathbf{r})\frac{\hbar}{2}$$

$$s_z(\mathbf{r}) = \left(\left|\psi_\uparrow(\mathbf{r})\right|^2 - \left|\psi_\downarrow(\mathbf{r})\right|^2\right)\frac{\hbar}{2} = \Psi^+(\mathbf{r})\sigma_z\Psi(\mathbf{r})\frac{\hbar}{2}$$

Spin-density matrix : $n_{\alpha\beta}(\mathbf{r}) = \psi_\alpha^*(\mathbf{r})\psi_\beta(\mathbf{r})$

$$n(\mathbf{r}) = n_{\uparrow\uparrow}(\mathbf{r}) + n_{\downarrow\downarrow}(\mathbf{r}) \qquad s_z(\mathbf{r}) = \left(n_{\uparrow\uparrow}(\mathbf{r}) - n_{\downarrow\downarrow}(\mathbf{r})\right)\frac{\hbar}{2}$$

Notation, often : $n_\uparrow(\mathbf{r}) \triangleq n_{\uparrow\uparrow}(\mathbf{r})$ $\qquad n_\downarrow(\mathbf{r}) \triangleq n_{\downarrow\downarrow}(\mathbf{r})$

Operators acting on spinors

$$\hat{\mathbb{A}} = \begin{pmatrix} \hat{A}_{\uparrow\uparrow} & \hat{A}_{\uparrow\downarrow} \\ \hat{A}_{\downarrow\uparrow} & \hat{A}_{\downarrow\downarrow} \end{pmatrix}$$

where $\hat{A}_{\uparrow\uparrow}, \hat{A}_{\uparrow\downarrow}, \hat{A}_{\downarrow\uparrow}, \hat{A}_{\downarrow\downarrow}$ are operators acting in usual Hilbert space (=spatial part)

$$\hat{\mathbb{A}}|\Psi\rangle = \begin{pmatrix} \hat{A}_{\uparrow\uparrow}|\psi_{\uparrow}\rangle + \hat{A}_{\uparrow\downarrow}|\psi_{\downarrow}\rangle \\ \hat{A}_{\downarrow\uparrow}|\psi_{\uparrow}\rangle + \hat{A}_{\downarrow\downarrow}|\psi_{\downarrow}\rangle \end{pmatrix}$$

Simple example (simple, because spatial part = unit operator) :

$$\hat{S}_z = \begin{pmatrix} \frac{\hbar}{2}\hat{1} & 0 \\ 0 & -\frac{\hbar}{2}\hat{1} \end{pmatrix} = \frac{\hbar}{2}\sigma_z\hat{1} \qquad \hat{S}_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle \qquad \hat{S}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle$$

Generalization for x and y or other directions using Pauli matrices

Classical treatment of a magnetic field

Now, how does spin relates to magnetic dipole ?

Classical mechanics: for a particle rotating around origin, with mass M and charge q :

Angular momentum $\mathbf{L} = M\mathbf{r} \times \mathbf{v}$

Magnetic momentum $\boldsymbol{\mu} = \frac{q}{2}\mathbf{r} \times \mathbf{v}$

yields $\boldsymbol{\mu} = \frac{q}{2M}\mathbf{L}$

Placed inside a magnetic field, $\mathbf{B}$
a magnetic dipole acquire an energy $E_{\text{int}} = -\boldsymbol{\mu}.\mathbf{B}$

Quantum treatment of a magnetic field

$\boldsymbol{\mu} = \frac{q}{2M}\mathbf{L}$ + Correspondance principle $\Rightarrow$ $\hat{\boldsymbol{\mu}} = \frac{q}{2M}\hat{\mathbf{L}}$

Suppose a magnetic field along z.

For an electron (charge q=-e , mass m_e), observable values for the projection of magnetic moment along z are

$$\mu_z = -\frac{e}{2m_e}L_z = -\frac{e}{2m_e}m\hbar$$

where m = magnetic quantum number (integer)

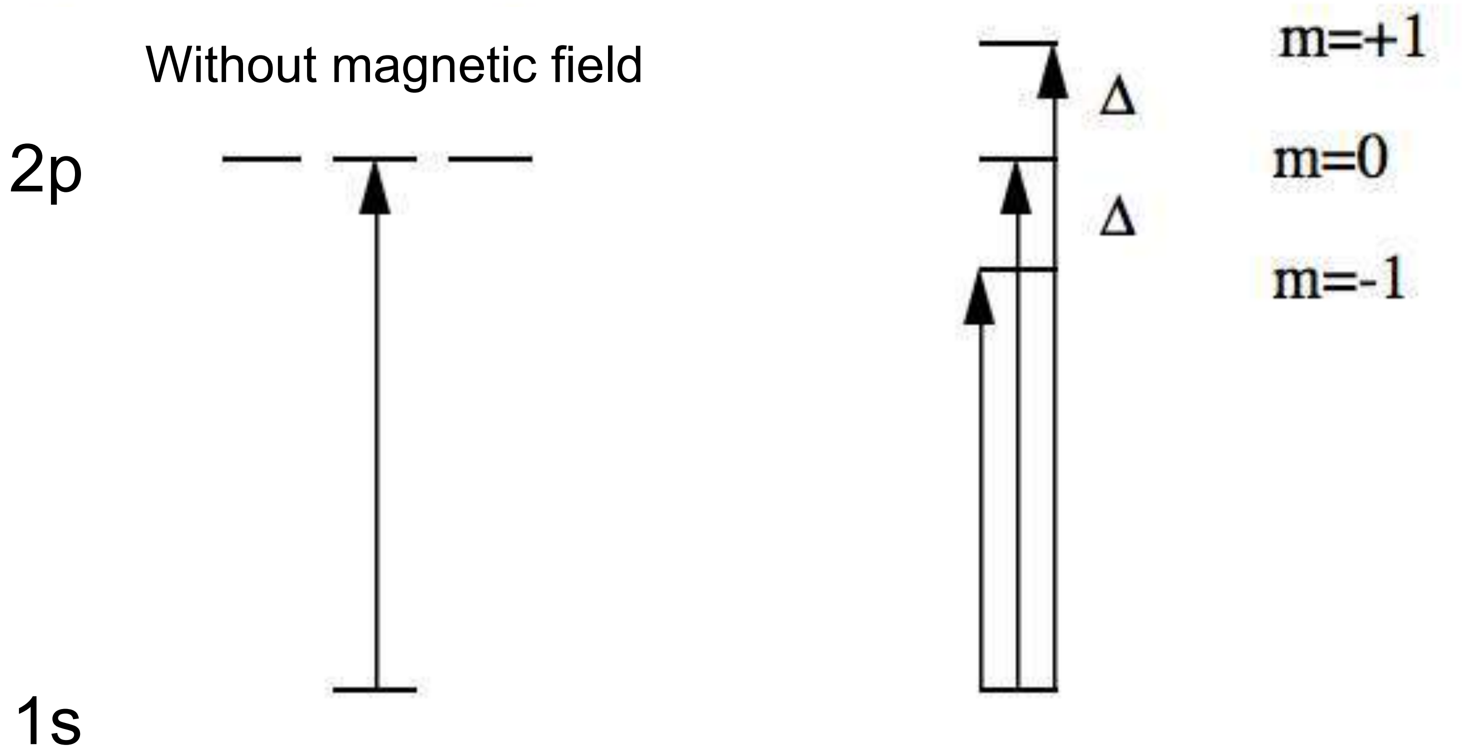
Definition of 'Bohr magneton' $\mu_B = \frac{e\hbar}{2m_e}$

Energy change (first approximation)

$$\boxed{E_{\text{int}} = -\mu_z.B_z = \frac{e}{2m_e}m\hbar B_z = \frac{e\hbar}{2m_e}mB_z = \mu_B m B_z}$$

Zeeman effect : lifting the degeneracy

Atomic levels of same n and ℓ , but different m, are not degenerate anymore in a magnetic field



Without magnetic field

With magnetic field

Intrinsic magnetic moment

Classical relation between orbital moment and magnetic moment :

$$\hat{\boldsymbol{\mu}} = \frac{q}{2M}\hat{\mathbf{L}}$$

There exists also a spin magnetic moment, but the proportionality coefficient is not the same :

$$\hat{\boldsymbol{\mu}}_s = g_e \frac{(-e)}{2m_e}\hat{\mathbf{S}}$$

g-factor : $g_e \cong 2$

$$\boxed{E_{\text{int}} = -\mu_z.B_z = \frac{g_e e}{2m_e} m\hbar B_z = \frac{e\hbar}{2m_e} g_e m B_z = \mu_B g_e m B_z}$$

If gradient of B,
a force appears
=> Stern-Gerlach exp !

Spin-orbit (SOC) coupling (I)

Classically, magnetic dipoles interact with each others.
(magnetic dipole induces a magnetic field, felt by the other dipole)
Magnetic dipole from orbital movement interacts with spin magnetic dipole :

$$E_{SOC} \propto \mathbf{L}.\mathbf{S}$$

Atomic case : degeneracies are lifted.
Example : p levels $m_\ell = -1, 0, +1$ $m_s = -\frac{1}{2}, +\frac{1}{2}$

$$\left\{ \left| p_{m=-1}, \uparrow \right\rangle, \left| p_{m=-1}, \downarrow \right\rangle, \left| p_{m=0}, \uparrow \right\rangle, \left| p_{m=0}, \downarrow \right\rangle, \left| p_{m=+1}, \uparrow \right\rangle, \left| p_{m=+1}, \downarrow \right\rangle \right\}$$

Due to SOC, 6-fold degeneracy becomes doublet+quadruplet

$$m_j \hbar = m_\ell \hbar + m_s \hbar$$

$j = \frac{1}{2}$ with $m_j = -\frac{1}{2}, \frac{1}{2}$ $j = \frac{3}{2}$ with $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

$p_{1/2} - p_{3/2}$ splitting

Spin-orbit interaction (II)

Theory : originates from relativistic corrections (Schrödinger to Dirac Eq.)
Mass-velocity + Darwin term

= modification of kinetic energy and potential

Spin-orbit interaction

= new type of term $E_{SOC} = -\left(\frac{e\hbar}{2m_e c}\right)\boldsymbol{\sigma}.\left[\nabla V\times\left(\frac{\mathbf{p}}{m_e c}\right)\right]$

$\boldsymbol{\sigma}$ = vector of Pauli matrices

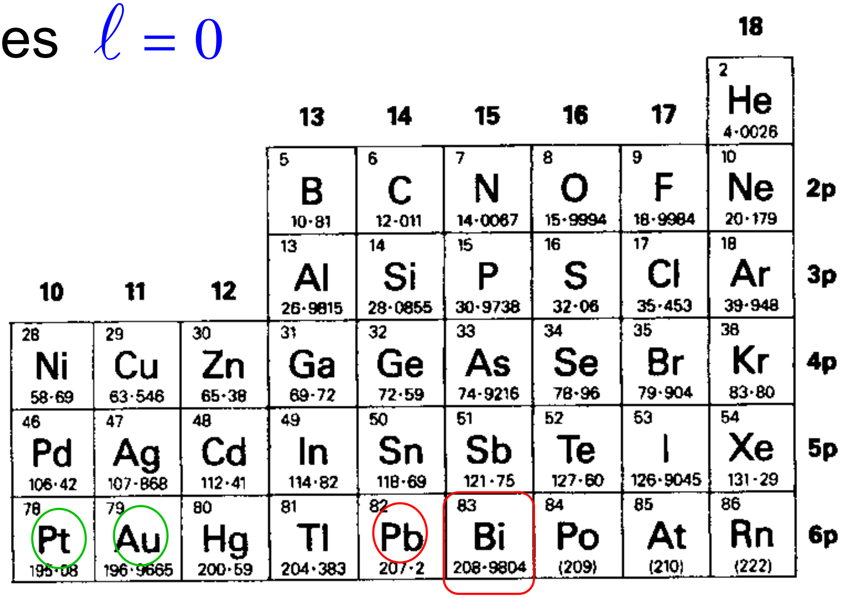
Close to a nucleus, $E_{SOC} \propto \mathbf{L.S}$ with an energy modif proportional to Z^4

Note : vanishes for s electronic states $\ell = 0$

Often NOT taken into account in first-principles calculations, except for electronic properties. Needs spinorial wavefunctions, increase of CPU time > 4.

Z=78 ... 83 →

$6p_{1/2}$-$6p_{3/2}$ splitting in Bi is about 1.5 eV



10	11	12	13	14	15	16	17	18	
								2 **He** 4·0026	
			5 **B** 10·81	6 **C** 12·011	7 **N** 14·0067	8 **O** 15·9994	9 **F** 18·9984	10 **Ne** 20·179	**2p**
			13 **Al** 26·9815	14 **Si** 28·0855	15 **P** 30·9738	16 **S** 32·06	17 **Cl** 35·453	18 **Ar** 39·948	**3p**
28 **Ni** 58·69	29 **Cu** 63·546	30 **Zn** 65·38	31 **Ga** 69·72	32 **Ge** 72·59	33 **As** 74·9216	34 **Se** 78·96	35 **Br** 79·904	36 **Kr** 83·80	**4p**
46 **Pd** 106·42	47 **Ag** 107·868	48 **Cd** 112·41	49 **In** 114·82	50 **Sn** 118·69	51 **Sb** 121·75	52 **Te** 127·60	53 **I** 126·9045	54 **Xe** 131·29	**5p**
78 **Pt** 195·08	79 **Au** 196·9665	80 **Hg** 200·59	81 **Tl** 204·383	82 **Pb** 207·2	83 **Bi** 208·9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)	**6p**

Incomplete p-shell

Exchange-correlation functionals

In principle, exact functional is still a functional of density only !

$$E_{\mathrm{xc}}^{\mathrm{DFT}}\left[n\right]=\int n(\mathbf{r})\varepsilon_{\mathrm{xc}}^{\mathrm{DFT}}(\mathbf{r};n)\mathrm{d}\mathbf{r}$$

However, information on density **+ spin** gives better approximate functionals. "Spin-density functional theory" (SDFT).

O. Gunnarsson and B.I. Lunqvist, *Phys. Rev. B* **13**, 4274 (1976)

If spin-orbit coupling is ignored, most materials have either no spin-polarization (nowhere in space), or their spin-polarization is aligned with only one direction (chosen as z), everywhere in space.

The latter gives the collinear case :

$$E_{\mathrm{xc}}^{\mathrm{SDFT,coll}}\left[n_\uparrow,n_\downarrow\right]=\int n(\mathbf{r})\varepsilon_{\mathrm{xc}}^{\mathrm{SDFT,coll}}(\mathbf{r};\boxed{n_\uparrow,n_\downarrow})\mathrm{d}\mathbf{r}$$

If spin-orbit coupling is taken into account, either there is no spin-polarization (nowhere in space), or spin-polarization is not constrained to be aligned.

The latter gives the non-collinear case :

$$E_{\mathrm{xc}}^{\mathrm{SDFT,non\text{-}coll}}\left[n,\mathbf{s}\right]=\int n(\mathbf{r}_1)\varepsilon_{\mathrm{xc}}^{\mathrm{SDFT,non\text{-}coll}}(\mathbf{r};n\boxed{,\mathbf{s})}\mathrm{d}\mathbf{r}$$

Exchange-correlation potentials

Generalisation of Kohn-Sham equations :

Collinear case : pure spin-up or spin-down wavefunctions $\left|\psi_i^{\alpha}\right\rangle$

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{KS},\alpha}(\mathbf{r})\right)\psi_{i\alpha}(\mathbf{r}) = \varepsilon_{i\alpha}\,\psi_{i\alpha}(\mathbf{r})$$

i and α label the states

$\alpha = \uparrow \text{ or } \downarrow$

$$V_{\mathrm{KS},\alpha}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\,d\mathbf{r}_1 + \frac{\delta E_{\mathrm{xc}}^{\mathrm{SDFT,\,coll}}\left[n_\uparrow, n_\downarrow\right]}{\boxed{\delta n_\alpha(\mathbf{r})}}$$

Spin-dependent XC potential

Non-collinear case : spinorial wavefunctions $\left|\Psi_i\right\rangle$

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r}) + \frac{\hbar}{2}\mathbf{B}_{xc}(\mathbf{r}).\boldsymbol{\sigma}\right)\Psi_i(\mathbf{r}) = \varepsilon_i\,\Psi_i(\mathbf{r})$$

i labels the states

$$V_{\mathrm{KS}}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\,d\mathbf{r}_1 + \frac{\delta E_{\mathrm{xc}}^{\mathrm{SDFT,\,non\text{-}coll}}\left[n, \mathbf{s}\right]}{\delta n(\mathbf{r})}$$

$$B_{\mathrm{xc},j}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{SDFT,\,non\text{-}coll}}\left[n, \mathbf{s}\right]}{\boxed{\delta s_j(\mathbf{r})}}$$

$j = x, y, z$

XC magnetic field

Approximate XC functionals

LDA, GGA, hybrids : can easily be generalized.

E.g. Local spin-density approximation for the collinear case :

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}\left[n_{\uparrow},n_{\downarrow}\right]=\int n(\mathbf{r})\varepsilon_{\mathrm{xc}}^{\mathrm{LSDA}}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r}))\,\mathrm{d}\mathbf{r}$$

$\varepsilon_{\mathrm{xc}}^{\mathrm{LSDA}}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r}))$ parameterized from homogeneous electron gas

Moreover, exchange energy in collinear case has simple general relationship with unpolarized exchange energy :

G.L. Oliver and J.P. Perdew, *Phys. Rev. A* **20**, 397 (1979)

$$E_{\mathrm{x}}^{\mathrm{SDFT,coll}}\left[n_{\uparrow},n_{\downarrow}\right]=\frac{1}{2}\left(E_{\mathrm{x}}^{\mathrm{DFT}}\left[2n_{\uparrow}\right]+E_{\mathrm{x}}^{\mathrm{DFT}}\left[2n_{\downarrow}\right]\right)$$

Indeed, comes from separate contribution of spins to exchange energy:

$$E_{\mathrm{x}}=-\frac{1}{2}\sum_{\sigma}\sum_{i,j}^{occ}\int d\mathbf{r}\,d\mathbf{r}'\frac{\psi_{j\sigma}^{*}(\mathbf{r}')\psi_{i\sigma}^{*}(\mathbf{r}')\psi_{j\sigma}(\mathbf{r})\psi_{i\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}|}$$

For non-collinear case, neglect directional dependence of local spin-polarization => falls back to collinear case.

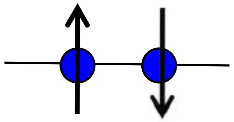
Methodologies : spin+symmetry

In practice … ?

Materials are treated within one of the following methodologies:

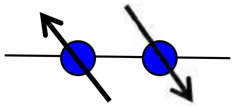
(1) No spin-polarization, scalar wavefunctions

(Many metals/covalent/ionic solids with light nuclei)



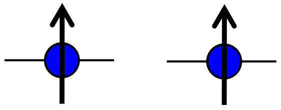
(2) No spin-polarization, spinorial wavefunctions (spin-orbit coupling)

(Many metals/covalent/ionic solids with heavier nuclei ;
the spin-polarization vanishes because of non-broken
time-reversal (TR) symmetry, compensation from TR symmetric states)



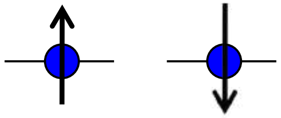
(3) Collinear spin, different spin-up and spin-down wavefunctions

(Ferromagnetic materials with light nuclei, finite systems with net spin,
in particular open shell atoms, and paramagnetic molecules, if light nuclei)



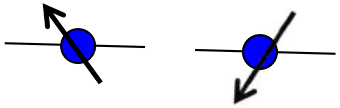
(4) Collinear spin, antiferromagnetic case

(Specific materials, often oxydes – the spin-down density
is space-symmetric to the spin-up density – spin-polarization does not vanish)



(5) Non-collinear spin-polarization

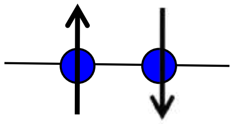
(Heavy nuclei with magnetization, need TR symm. spontaneously broken,
also important for some properties like the magnetocrystalline field,
or spin diffusion)



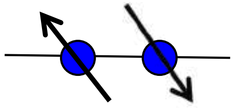
Methodologies : spin+symmetry

In practice … ?
ABINIT input variables nspinor, nspden, nsppol . Also spinat(3,natom).

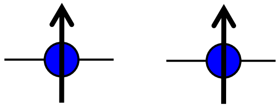
(1) No spin-polarization, scalar wavefunctions
nspinor=1 nspden=1 nsppol=1



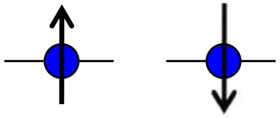
(2) No spin-polarization, spinorial wavefunctions (spin-orbit coupling)
nspinor=2 nspden=1 nsppol=1



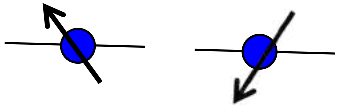
(3) Collinear spin, different spin-up and spin-down wavefunctions
nspinor=1 nspden=2 nsppol=2



(4) Collinear spin, antiferromagnetic case
nspinor=1 nspden=2 nsppol=1



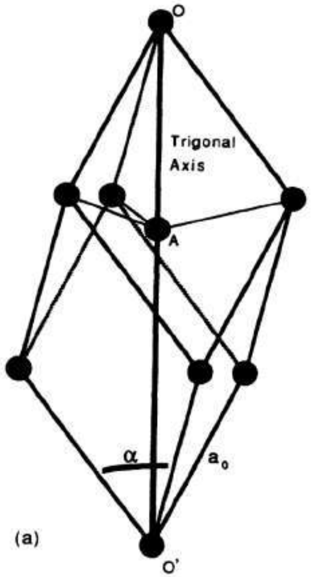
(5) Non-collinear spin-polarization
nspinor=2 nspden=4 nsppol=1

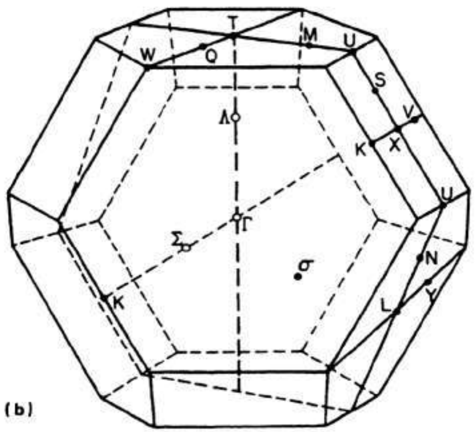


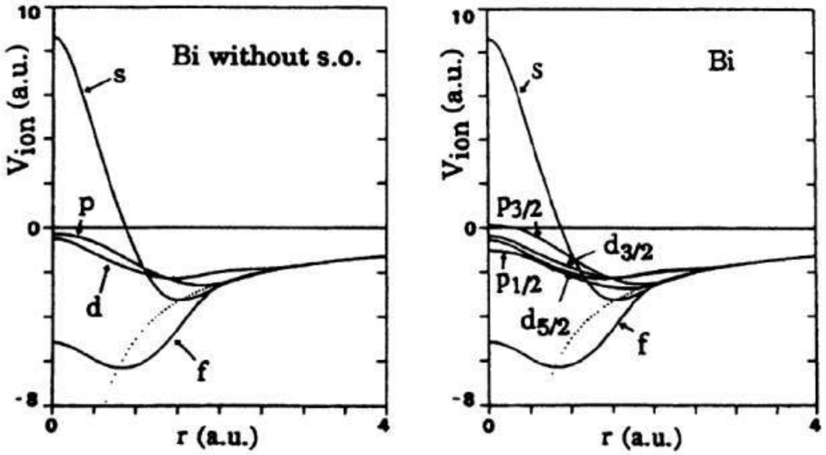
Example : electronic structure of Bismuth

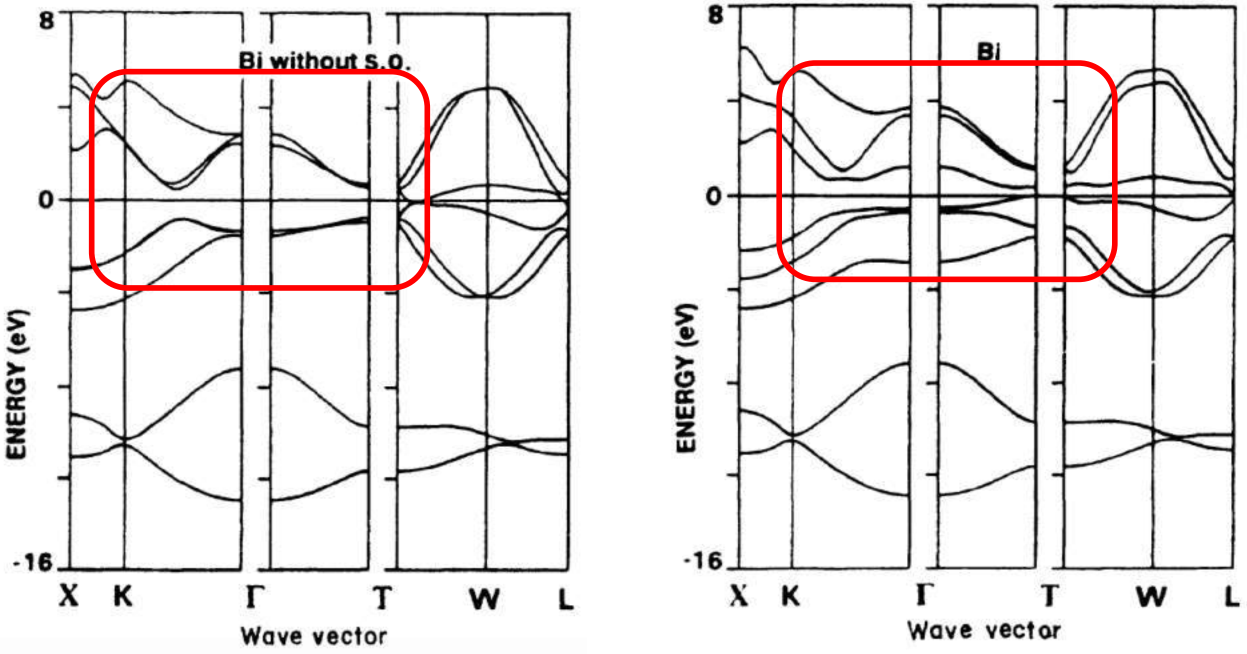
$$Xe+(4f)^{14}(5d)^{10}(6s)^{2}(6p)^{3}$$

$6p_{1/2}$-$6p_{3/2}$ splitting is about 1.5 eV







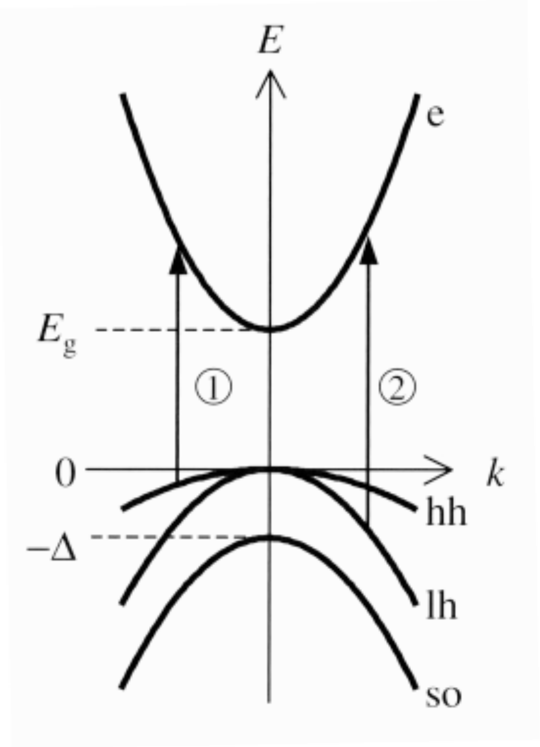


Electronic structure of III-V & II-VI compounds

III-V and II-VI compounds : important for opto-electronic applications (light-emitting diodes, IR and visible photodetectors, solid state lasers)

Crystalline structure : tetrahedrally coordinated (zinc-blende -AlP,AlAs,AlSb,BN,BP,CdTe,GaAs,HgSe,HgTe,InAs,InP,InSb,ZnS ; or wurtzite - AlN,GaN,InN,CdS,CdSe,CdTe, ZnO,ZnS)

ZB Band structure in the vicinity of the Γ point (zone center) : Kane model



<u>Kane model</u>

Band structure of several III-V and II-VI compounds near k=0.

E=0 : top of the valence band

$E = E_g$: bottom of the conduction band.

4 bands :

heavy hole (hh) band, light hole (lh) band, spin-orbit hole (so) band, and electron (e) band.

Two optical transitions are indicated.

Transitions can also take place between spin-orbit hole band and conduction band, but are not shown for the sake of clarity.

Δ ranges from <0.1 eV to 0.33 eV for GaAs and 0.8 eV for InSb

Role of XC functional : the case of Iron

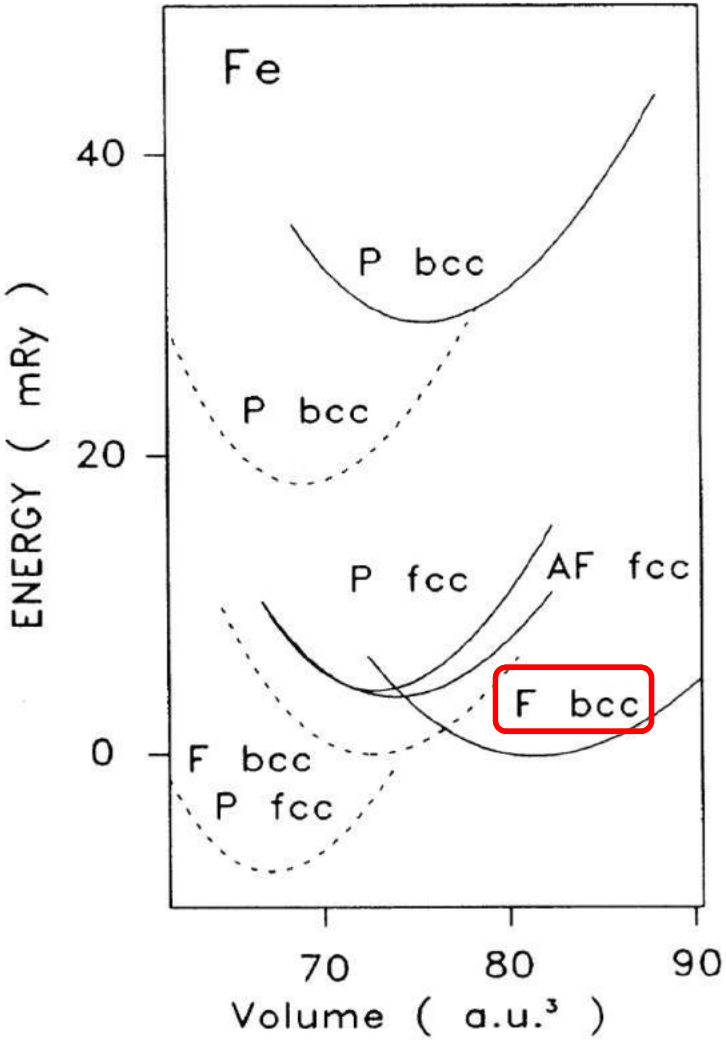
Total energy as a function of volume per atom for Iron.

Dashed lines : Spin-LDA
Full lines : GGA

P = paramagnetic (no spin-polarization)
F = ferromagnetic
AF = antiferromagnetic

FCC= face-centered cubic
BCC= body-centered cubic

The GGA gets the correct phase :
Experimentally Fe is ferromagnetic BCC.



T.C. Leung, C.T. Chan and B.N. Harmon , *Phys. Rev. B* **44**, 2923 (1991)

Time-reversal operator in the scalar case

Many-body electronic Hamiltonian : invariant upon time-reversal symmetry.

$\left[\hat{H}_{el},\hat{T}\right]=0$ with $\hat{T}$ time-reversal operator = simply taking the complex conjugate

(Think to time-dependent Schrödinger equation $\hat{H}\left|\Psi_i(t)\right\rangle = i\hbar\frac{\partial}{\partial t}\left|\Psi_i\right\rangle$)

$\hat{T}^2=\hat{1}$ $\quad\hat{T}^{-1}=\hat{T}$ $\quad\left[\hat{H}_{el},\hat{T}\right]=0 \Rightarrow \hat{T}\hat{H}_{el}\hat{T}=\hat{T}\hat{T}\hat{H}_{el}=\hat{H}_{el}$

Upon time-reversal: $\hat{\mathbf{r}}$ invariant, $\hat{\mathbf{r}}\hat{T}=\hat{T}\hat{\mathbf{r}}$, while $\hat{\mathbf{p}}$ is reversed $\hat{\mathbf{p}}\hat{T}=-\hat{T}\hat{\mathbf{p}}$

If Kohn-Sham Hamiltonian is invariant upon time-reversal symmetry, and if

$\hat{H}_{KS}\left|\Psi_i\right\rangle=\varepsilon_i\left|\Psi_i\right\rangle$ then $\hat{T}\hat{H}_{KS}\hat{T}\left|\Psi_i\right\rangle=\varepsilon_i\left|\Psi_i\right\rangle$

$$\hat{H}_{KS}\left(\hat{T}\left|\Psi_i\right\rangle\right)=\varepsilon_i\left(\hat{T}\left|\Psi_i\right\rangle\right)$$

which means $\hat{T}\left|\Psi_i\right\rangle$ also eigenfunction, with same eigenenergy than $\left|\Psi_i\right\rangle$.

Scalar wavefunctions in periodic boundary conditions and planewave basis

$$\psi_{\mathbf{k}}(\mathbf{r})=\left(N\Omega_0\right)^{-1/2}\sum_{\mathbf{G}}\mathrm{u}_{\mathbf{k}}(\mathbf{G})\,\mathrm{e}^{\mathrm{i}(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

Then there exists n’ such that

$$\boxed{\begin{aligned}\hat{T}\psi_{n\mathbf{k}}(\mathbf{r})=\psi^*_{n\mathbf{k}}(\mathbf{r})&=\psi_{n'-\mathbf{k}}(\mathbf{r})\\ \varepsilon_{n\mathbf{k}}(\mathbf{r})&=\varepsilon_{n'-\mathbf{k}}(\mathbf{r})\end{aligned}}$$

Time-reversal and spin

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

σ_y not invariant upon complex conjugation. Problem with time-reversal symmetry ?

Invariance under complex conjugation AND exchange of spin-up and spin-down.
Time-reversal symmetry exchange spin up and spin down (=angular momentum).

$$\hat{H}_{SOC} = -\left(\frac{e\hbar}{2m_e c}\right)\boldsymbol{\sigma}.\left[\nabla V \times \left(\frac{\hat{\mathbf{p}}}{m_e c}\right)\right]$$

moreover, $\hat{\mathbf{p}}$ changes sign

If Kohn-Sham Hamiltonian including SOC is invariant upon time-reversal symmetry, and if

$$\hat{H}_{KS}\begin{pmatrix} \psi_{\uparrow n\mathbf{k}}(\mathbf{r}) \\ \psi_{\downarrow n\mathbf{k}}(\mathbf{r}) \end{pmatrix} = \varepsilon_{n\mathbf{k}}\begin{pmatrix} \psi_{\uparrow n\mathbf{k}}(\mathbf{r}) \\ \psi_{\downarrow n\mathbf{k}}(\mathbf{r}) \end{pmatrix}$$

Then there exists n' such that $\varepsilon_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n'-\mathbf{k}}(\mathbf{r})$

and $\begin{pmatrix} \psi^{*}_{\downarrow n\mathbf{k}}(\mathbf{r}) \\ -\psi^{*}_{\uparrow n\mathbf{k}}(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \psi_{\uparrow n'-\mathbf{k}}(\mathbf{r}) \\ \psi_{\downarrow n'-\mathbf{k}}(\mathbf{r}) \end{pmatrix}$ is the corresponding eigenfunction.
= Kramers degeneracy

Time-reversal symmetry forbids spin polarization

Compute expectation value of spin polarization from a pair of degenerate Kramers eigenfunctions :

$$\begin{pmatrix} \psi^*_{\downarrow n\mathbf{k}}(\mathbf{r}) \\ -\psi^*_{\uparrow n\mathbf{k}}(\mathbf{r}) \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \psi_{\uparrow n\mathbf{k}}(\mathbf{r}) \\ \psi_{\downarrow n\mathbf{k}}(\mathbf{r}) \end{pmatrix}$$

Reminder $s_j(\mathbf{r}) = \Psi^+(\mathbf{r})\sigma_j\Psi(\mathbf{r})\frac{\hbar}{2}$

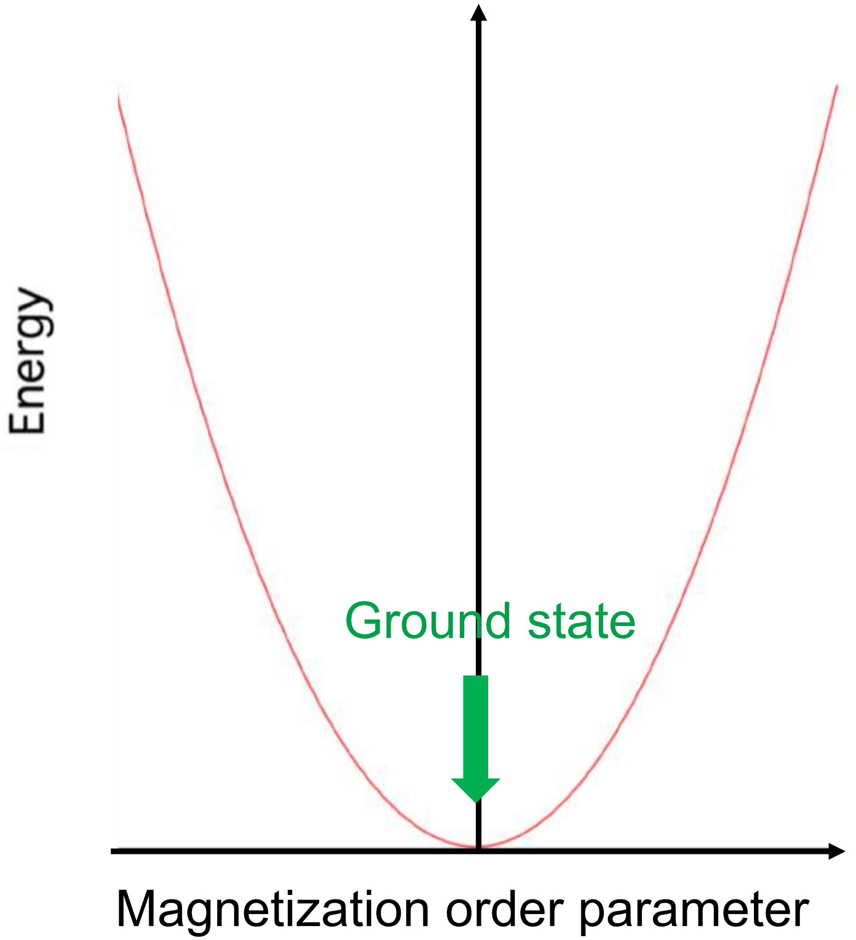
This gives

$$s_x(\mathbf{r}) = \left(-\psi_{\uparrow n\mathbf{k}}(\mathbf{r})\psi^*_{\downarrow n\mathbf{k}}(\mathbf{r}) - \psi_{\downarrow n\mathbf{k}}(\mathbf{r})\psi^*_{\uparrow n\mathbf{k}}(\mathbf{r})\right)\frac{\hbar}{2}$$
$$+\left(\psi^*_{\uparrow n\mathbf{k}}(\mathbf{r})\psi_{\downarrow n\mathbf{k}}(\mathbf{r}) + \psi^*_{\downarrow n\mathbf{k}}(\mathbf{r})\psi_{\uparrow n\mathbf{k}}(\mathbf{r})\right)\frac{\hbar}{2} \qquad = 0$$

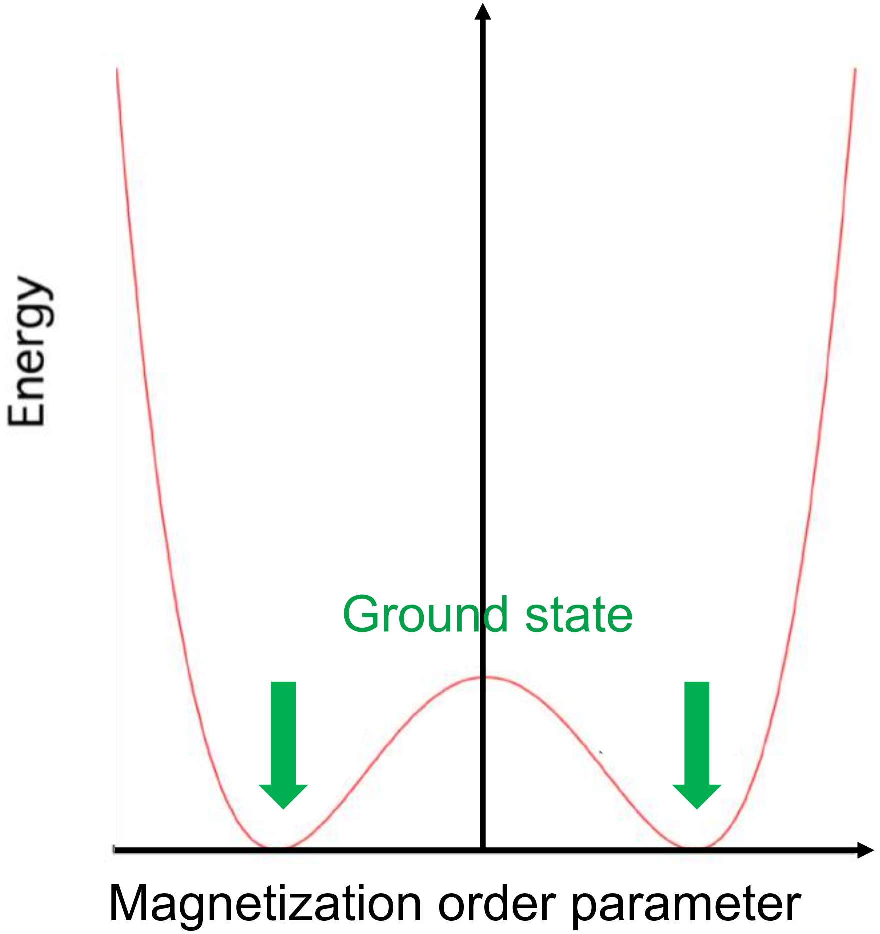
Similarly : $s_y(\mathbf{r}) = 0$ and $s_z(\mathbf{r}) = 0$

So, how can a material be magnetic ?

Spontaneous breaking of time-reversal symmetry



Spin-polarization vanishes,
Time-reversal symmetry not broken
Non-magnetic, possibly spin texture



Spin-polarization does not vanish
Time-reversal symmetry broken
Magnetic materials

Computing the forces

Basic equations in DFT

Solve self-consistently the Kohn-Sham equation

$$\begin{cases} \hat{H}\left|\psi_n\right\rangle = \varepsilon_n\left|\psi_n\right\rangle \\ \hat{H} = \hat{T} + \hat{V} + \hat{V}_{Hxc}[n] \\ n(\mathbf{r}) = \sum_{n}^{occ} \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}) \end{cases}$$

$$\begin{tikzcd} \hat{H} \arrow[rr, bend left] & & \psi_n(\mathbf{r}) \arrow[dl, bend left] \\ & n(\mathbf{r}) \arrow[ul, bend left] & \end{tikzcd}$$

$$\delta_{mn} = \left\langle \psi_m \middle| \psi_n \right\rangle \text{for m,n} \in \text{occupied set}$$

or minimize

$$E_{el}\{\psi\} = \sum_{n}^{occ} \left\langle \psi_n \middle| \hat{T} + \hat{V} \middle| \psi_n \right\rangle + E_{Hxc}[n]$$

with

$$\hat{V}(\mathbf{r}) = \sum_{\kappa} -\frac{Z_\kappa}{\left|\mathbf{r} - \mathbf{R}_\kappa\right|}$$

Exchange-correlation functional might be LDA, GGA (e.g. PBE, PBESol), or hybrids, van der waals, etc

Computing the forces (I)

Born - Oppenheimer approx. ⇨ find electronic ground state in potential created by nuclei.

A starting configuration of nuclei $\{\mathbf{R}_\kappa\}$ is usually NOT in equilibrium geometry.

$$F_{\kappa,\alpha} = - \left.\frac{\partial E}{\partial R_{\kappa,\alpha}}\right|_{\{\mathbf{R}_\kappa\}}$$

(principle of virtual works)

Forces are first derivatives of total energy.
Can be computed by finite differences.

Better approach : compute the response to a perturbation

⇨ What is the energy change ?

$$\left\{R_{\kappa,\alpha}\right\} \rightarrow \left\{R_{\kappa,\alpha} + \lambda \delta R_{\kappa,\alpha}\right\}$$

Small parameter

Computing the forces (II)

To simplify, let's compute the derivative of an electronic eigenvalue

Perturbation theory : Hellmann - Feynman theorem

$\hat{H}(\lambda)$ $\varepsilon_n(\lambda)$ $\psi_n(\lambda)$ normalized $\hat{H}\left|\psi_n\right\rangle = \varepsilon_n\left|\psi_n\right\rangle$ for all λ

$$\boxed{\frac{d\varepsilon_n}{d\lambda}} = \frac{d}{d\lambda}\left(\left\langle\psi_n\middle|\hat{H}\middle|\psi_n\right\rangle\right)$$

$$= \left\langle\frac{d\psi_n}{d\lambda}\middle|\hat{H}\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|\frac{d\hat{H}}{d\lambda}\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|\hat{H}\middle|\frac{d\psi_n}{d\lambda}\right\rangle$$

$$= \left\langle\frac{d\psi_n}{d\lambda}\middle|\varepsilon_n\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|\frac{d\hat{H}}{d\lambda}\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|\varepsilon_n\middle|\frac{d\psi_n}{d\lambda}\right\rangle \quad \boxed{= \left\langle\psi_n^{(0)}\middle|\frac{d\hat{H}}{d\lambda}\middle|\psi_n^{(0)}\right\rangle}$$

Indeed $\left\langle\frac{d\psi_n}{d\lambda}\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|\frac{d\psi_n}{d\lambda}\right\rangle = \frac{d}{d\lambda}\left\langle\psi_n\middle|\psi_n\right\rangle = \frac{d}{d\lambda}(1) = 0$

$\frac{d\psi_n}{d\lambda}$ not needed !

Computing the forces (III)

Application to the derivative of
with respect to an atomic displacement :

$$\hat{H} = \hat{T} + \hat{V}_{ext}\{\hat{R}\} \Rightarrow \frac{\partial \hat{H}}{\partial R_{\kappa,\alpha}} = \frac{\partial \hat{V}_{ext}}{\partial R_{\kappa,\alpha}}$$

$$\frac{\partial \varepsilon_n}{\partial R_{\kappa,\alpha}} = \left\langle \psi_n \middle| \frac{\partial \hat{H}}{\partial R_{\kappa,\alpha}} \middle| \psi_n \right\rangle = \int \frac{\partial \hat{V}_{ext}(\mathbf{r})}{\partial R_{\kappa,\alpha}} n(\mathbf{r}) d\mathbf{r}$$

Computing the forces (IV)

Generalisation to density functional theory

Reminder :
$$E[\psi\ ] = \sum_n \langle \psi_n | \hat{\mathrm{T}} | \psi_n \rangle + \int n(\mathbf{r})\, V_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} + E_{\mathrm{Hxc}}[n]$$

If change of atomic positions ...

$$V_{\mathrm{ext}}(\mathbf{r}) = \sum_{\mathrm{k}} -\frac{Z_{\mathrm{k}}}{|\mathbf{r}-\mathbf{R}_{\mathrm{k}}|}$$

(can be generalized to pseudopotential case)

$$\frac{\partial V_{\mathrm{ext}}(\vec{\mathrm{r}})}{\partial R_{\mathrm{k},\alpha}} = +\frac{Z_{\mathrm{k}}}{|\mathbf{r}-\mathbf{R}_{\mathrm{k}}|^2} \cdot \frac{\partial |\mathbf{r}-\mathbf{R}_{\mathrm{k}}|}{\partial R_{\mathrm{k},\alpha}} = -\frac{Z_{\mathrm{k}}}{|\mathbf{r}-\mathbf{R}_{\mathrm{k}}|^3} \cdot (\mathbf{r}-\mathbf{R}_{\mathrm{k}})_\alpha$$

$$\boxed{\frac{\partial E}{\partial R_{\mathrm{k},\alpha}} = \int n(\mathbf{r}) \frac{\partial V_{\mathrm{ext}}(\mathbf{r})}{\partial R_{\mathrm{k},\alpha}} d\mathbf{r} = -\int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_{\mathrm{k}}|^3} \, . \, (\mathbf{r}-\mathbf{R}_{\mathrm{k}})_\alpha \, d\mathbf{r}}$$

Forces can be computed directly from the density !
Also, similarly, stresses.
=> Optimization of geometry (lattice parameters and atomic positions)

Density Functional Perturbation Theory

Many physical properties = derivatives of total energy
(or suitable thermodynamic potential) with respect to perturbations.

Consider :

- atomic displacements (phonons)
- dilatation/contraction of primitive cell
- homogeneous external field (electric field, magnetic field ...)

Derivatives of total energy (electronic part + nuclei-nuclei interaction) :

1st order derivatives : forces, stresses, dipole moment ...

2nd order derivatives : dynamical matrix, elastic constants, dielectric susceptibility
atomic polar tensors or Born effective charge tensors
piezoelectricity, internal strains ...

3rd order derivatives : non-linear dielectric susceptibility, Raman susceptibilities
electro-optic effect, phonon - phonon interaction, Grüneisen parameters, ...

Further properties obtained by integration over phononic degrees of freedom :
entropy, thermal expansion, phonon-limited thermal conductivity ...

Iterative algorithms, troubleshooting

Algorithmics : problems to be solved

(1) Kohn - Sham equation

$$\boxed{\underline{\underline{A}}\ \underline{x}_i = \lambda_i \underline{x}_i}$$

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r})$$

$$\{\mathbf{G}_j\} \qquad \{\mathbf{r}_j\}$$

Size of the system	[2 atoms…	600 atoms…]	+ vacuum ?
Dimension of the vectors $\underline{x}_i$	300…	100 000…	(if planewaves)
# of (occupied) eigenvectors	4…	1200…	

(2) Self-consistency

$$\begin{tikzcd}
V_{KS}(\mathbf{r}) \arrow[rr, bend left] & & \psi_i(\mathbf{r}) \arrow[dl, bend left] \\
& n(\mathbf{r}) \arrow[ul, bend left] &
\end{tikzcd}$$

(3) Geometry optimization

Find the positions $\{\mathbf{R}_\kappa\}$ of ions such that the forces $\{\mathbf{F}_\kappa\}$ vanish
[= Minimization of energy]

Current practice : iterative approaches

The ‘steepest-descent’ algorithm

Forces are gradients of the energy : moving the atoms along gradients is the steepest descent of the energy surface.

=> Iterative algorithm.
Choose a starting geometry, then a parameter λ ,
and iterately update the geometry, following the forces :

$$\boxed{R_{\kappa,\alpha}^{(n+1)} = R_{\kappa,\alpha}^{(n)} + \lambda F_{\kappa,\alpha}^{(n)}}$$

Equivalent to the simple mixing algorithm
of SCF (see later)

Energy+forces around equilib. geometry

Let us denote the equilibrium geometry as $R^*_{\kappa,\alpha}$

Analysis of forces close to the equilibrium geometry, at which forces vanish, thanks to a Taylor expansion :

$$F_{\kappa,\alpha}(R_{\kappa',\alpha'}) = \cancel{F_{\kappa,\alpha}(R^*_{\kappa',\alpha'})} + \sum_{\kappa',\alpha'} \left.\frac{\partial F_{\kappa,\alpha}}{\partial R_{\kappa',\alpha'}}\right|_{\{R^*\}} \left(R_{\kappa',\alpha'} - R^*_{\kappa',\alpha'}\right) + O\left(R_{\kappa',\alpha'} - R^*_{\kappa',\alpha'}\right)^2$$

Moreover, $F_{\kappa,\alpha} = -\dfrac{\partial E^{BO}}{\partial R_{\kappa,\alpha}}$

$$\frac{\partial F_{\kappa',\alpha'}}{\partial R_{\kappa,\alpha}} = -\frac{\partial^2 E^{BO}}{\partial R_{\kappa,\alpha} \partial R_{\kappa',\alpha'}}$$

Vector and matrix notation

$$R^*_{\kappa,\alpha} \rightarrow \underline{R}^*$$

$$R_{\kappa,\alpha} \rightarrow \underline{R}$$

$$F_{\kappa,\alpha} \rightarrow \underline{F}$$

$$\left.\frac{\partial^2 E^{BO}}{\partial R_{\kappa,\alpha} \partial R_{\kappa',\alpha'}}\right|_{\{R^*_{\kappa,\alpha}\}} \rightarrow \underline{\underline{H}}$$

(the Hessian)

Steepest-descent : analysis (I)

$$\boxed{R_{\kappa,\alpha}^{(n+1)} = R_{\kappa,\alpha}^{(n)} + \lambda F_{\kappa,\alpha}^{(n)}}$$

Analysis of this algorithm, in the linear regime :

$$\underline{F}(\underline{R}) = \cancel{\underline{F}(\underline{R}^{*})} - \underline{\underline{H}}\left(\underline{R} - \underline{R}^{*}\right) + \cancel{O\left(\underline{R} - \underline{R}^{*}\right)^{2}}$$

$$\underline{R}^{(n+1)} = \underline{R}^{(n)} + \lambda \underline{F}^{(n)} \Longrightarrow \left(\underline{R}^{(n+1)} - \underline{R}^{*}\right) = \left(\underline{R}^{(n)} - \underline{R}^{*}\right) - \lambda \underline{\underline{H}}\left(\underline{R}^{(n)} - \underline{R}^{*}\right)$$

$$\boxed{\left(\underline{R}^{(n+1)} - \underline{R}^{*}\right) = \left(\underline{\underline{1}} - \lambda \underline{\underline{H}}\right)\left(\underline{R}^{(n)} - \underline{R}^{*}\right)}$$

For convergence of the iterative procedure, the "distance" between trial geometry and equilibrium geometry must decrease.

1) Can we predict conditions for convergence ?
2) Can we make convergence faster ?

Need to understand the action of the matrix (or operator) $\boxed{\underline{\underline{1}} - \lambda \underline{\underline{H}}}$

Steepest-descent : analysis (II)

What are the eigenvectors and eigenvalues of $\underline{\underline{H}}$?

$\underline{\underline{H}}$ symmetric,
positive definite matrix

$$\left(= \frac{\partial^2 E^{BO}}{\partial R_{\kappa,\alpha} \partial R_{\kappa',\alpha'}} \Bigg|_{\left\{R^*_{\kappa,\alpha}\right\}} \right)$$

$\underline{\underline{H}}\,\underline{f}_i = h_i\,\underline{f}_i$ where $\left\{\underline{f}_i\right\}$ form a complete, orthonormal, basis set

Discrepancy decomposed as $\left(\underline{R}^{(n)} - \underline{R}^*\right) = \sum_i c_i^{(n)} \underline{f}_i$

and $\left(\underline{R}^{(n+1)} - \underline{R}^*\right) = \left(\underline{\underline{1}} - \lambda \underline{\underline{H}}\right) \sum_i c_i^{(n)} \underline{f}_i = \sum_i c_i^{(n)} \left(1 - \lambda h_i\right) \underline{f}_i$

The coefficient of $\underline{f}_i$ is multiplied by 1- λ h_i

Iteratively : $\left(\underline{R}^{(n)} - \underline{R}^*\right) = \sum_i c_i^{(0)} \left(1 - \lambda h_i\right)^{(n)} \underline{f}_i$

Steepest-descent : analysis (III)

$$\left(\underline{R}^{(n)} - \underline{R}^{*}\right) = \sum_{i} c_i^{(0)} \left(1 - \lambda h_i\right)^{(n)} \underline{f}_i$$

The size of the discrepancy decreases if $|1- \lambda h_i| < 1$

Is it possible to have $|1- \lambda h_i| < 1$, for all eigenvalues ?

$\underline{\underline{H}}$ positive definite => all h_i are positive

Yes ! If λ positive, sufficiently small ...

Steepest-descent : analysis (IV)

$$\left(\underline{R}^{(n)} - \underline{R}^{*}\right) = \sum_{i} c_i^{(0)} \left(1 - \lambda h_i\right)^{(n)} \underline{f}_i$$

How to determine the optimal value of λ ?

The maximum of all $|1-\lambda h_i|$ should be as small as possible.
At the optimal value of λ , what will be the convergence rate ?
(= by which factor is reduced the worst component of $\left(\underline{R}^{(n)} - \underline{R}^{*}\right)$?)

As an exercise : suppose
$$\left.\begin{aligned} h_1 &= 0.2 \\ h_2 &= 1.0 \\ h_3 &= 5.0 \end{aligned}\right\}$$
=> what is the best value of λ ?

\+ what is the convergence rate ?

Hint : draw the three functions $|1-\lambda h_i|$ as a function of λ . Then, find the location of λ where the largest of the three curves is the smallest.
Find the coordinates of this point.

Steepest-descent : analysis (V)

Minimise the maximum of $|1-\lambda h_i|$

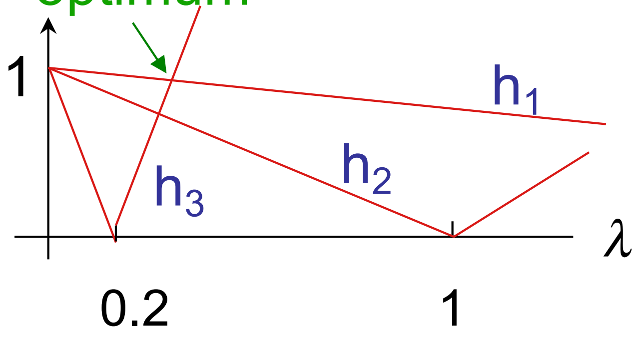
$h_1 = 0.2 \quad |1-\lambda .0.2| \quad$ optimum => $\lambda = 5$

$h_2 = 1.0 \quad |1-\lambda . 1| \quad$ optimum => $\lambda = 1$

$h_3 = 5.0 \quad |1-\lambda . 5| \quad$ optimum => $\lambda = 0.2$

$\}$?

optimum



$$\mu = |\underbrace{1-\lambda\, 0.2}_{\text{positive}}| = |\underbrace{1-\lambda\, 5}_{\text{negative}}|$$

$$1-\lambda . 0.2 = -(1-\lambda .5)$$

$$2-\lambda(0.2+5)=0 \Rightarrow \lambda = 2/5.2$$

$$\mu = 1 - 2. (0.2 / 5.2)$$

Only ~ 8% decrease of the error, per iteration ! Hundreds of iterations will be needed to reach a reduction of the error by 1000 or more.

Note : the second eigenvalue does not play any role.
The convergence is limited by the extremal eigenvalues : if the parameter is too large, the smallest eigenvalue will cause divergence, but for that small parameter, the largest eigenvalue lead to slow decrease of the error...

The condition number

In general, $\lambda_{\text{opt}} = 2 / (h_{\min} + h_{\max})$

$\mu_{\text{opt}} = 2 / [1+ (h_{\max}/h_{\min})] - 1 = [(h_{\max}/h_{\min}) -1] / [(h_{\max}/h_{\min}) +1]$

Perfect if $h_{\max} = h_{\min}$. Bad if $h_{\max} >> h_{\min}$.
$h_{\max}/h_{\min}$ called the "condition" number. A problem is "ill-conditioned" if the condition number is large. It does not depend on the intermediate eigenvalues.

Suppose we start from a configuration with forces on the order of 1 Ha/Bohr, and we want to reach the target 1e-4 Ha/Bohr. The mixing parameter is optimal. How many iterations are needed ?
For a generic decrease factor Δ , with "n" the number of iterations.

$$\left\|\underline{F}^{(n)}\right\| \approx \left(\frac{h_{\max}/h_{\min} - 1}{h_{\max}/h_{\min} + 1}\right)^n \left\|\underline{F}^{(0)}\right\| \qquad \Delta \approx \left(\frac{h_{\max}/h_{\min} - 1}{h_{\max}/h_{\min} + 1}\right)^n$$

$$\boxed{n \approx \left[\ln\left(\frac{h_{\max}/h_{\min} + 1}{h_{\max}/h_{\min} - 1}\right)\right]^{-1} \ln\Delta \approx 0.5\left(h_{\max}/h_{\min}\right)\ln\frac{1}{\Delta}}$$

(The latter approximate equality supposes a large condition number)

Analysis of self-consistency

$$\begin{tikzcd}
\mathrm{v}_{\mathrm{KS}}(\mathbf{r}) \arrow[rr, bend left] & & \psi_i(\mathbf{r}) \arrow[dl, bend left] \\
& \mathrm{n}(\mathbf{r}) \arrow[ul, bend left] &
\end{tikzcd}$$

Natural iterative methodology (KS : in => out) :

$$\mathrm{v}_{\mathrm{in}}(\mathbf{r}) \rightarrow \psi_i(\mathbf{r}) \rightarrow \mathrm{n}(\mathbf{r}) \rightarrow \mathrm{v}_{\mathrm{out}}(\mathbf{r})$$

Which quantity plays the role of a force, that should vanish at the solution ?

The difference $\mathrm{v}_{\mathrm{out}}(\mathbf{r}) - \mathrm{v}_{\mathrm{in}}(\mathbf{r})$ (generic name : a "residual")

Simple mixing algorithm
(≈ steepest - descent)

$$\boxed{\underline{\mathrm{v}}_{\mathrm{in}}^{(\mathrm{n}+1)} = \underline{\mathrm{v}}_{\mathrm{in}}^{(\mathrm{n})} + \lambda\left(\underline{\mathrm{v}}_{\mathrm{out}}^{(\mathrm{n})} - \underline{\mathrm{v}}_{\mathrm{in}}^{(\mathrm{n})}\right)}$$

Analysis ... $\underline{\mathrm{v}}_{\mathrm{out}}\left[\underline{\mathrm{v}}_{\mathrm{in}}\right] = \underline{\mathrm{v}}_{\mathrm{out}}\left[\underline{\mathrm{v}}^{*}\right] + \dfrac{\delta \underline{\mathrm{v}}_{\mathrm{out}}}{\delta \underline{\mathrm{v}}_{\mathrm{in}}}\left(\underline{\mathrm{v}}_{\mathrm{in}} - \underline{\mathrm{v}}^{*}\right)$

$$\searrow \underline{\underline{\mathrm{H}}}$$

Like the steepest-descent algorithm, this leads to the requirement to minimize $|1-\lambda h_i|$ where h_i are eigenvalues of $\dfrac{\delta \underline{\mathrm{v}}_{\mathrm{out}}}{\delta \underline{\mathrm{v}}_{\mathrm{in}}}$

(actually, the dielectric matrix)

Modify the condition number (II)

$$\boxed{\underline{R}^{(n+1)} = \underline{R}^{(n)} + \lambda\left(\underline{\underline{H}}^{-1}\right)_{\text{approx}} \underline{F}^{(n)}}$$

$$\underline{F}(\underline{R}) = -\underline{\underline{H}}\left(\underline{R} - \underline{R}^{*}\right) \Longrightarrow \left(\underline{R}^{(n+1)} - \underline{R}^{*}\right) = \left(1 - \lambda\left(\underline{\underline{H}}^{-1}\right)_{\text{approx}} \underline{\underline{H}}\right)\left(\underline{R}^{(n)} - \underline{R}^{*}\right)$$

Notes : 1) If approximate inverse Hessian perfect, optimal geometry is reached in one step, with λ =1. Steepest-descent NOT the best direction.

2) Non-linear effects not taken into account. For geometry optimization, might be quite large. Even with perfect hessian, need 5-6 steps to optimize a water molecule.

3) Approximating inverse hessian by a multiple of the unit matrix is equivalent to changing the λ value.

4) Eigenvalues and eigenvectors of $\left(\underline{\underline{H}}^{-1}\right)_{\text{approx}} \underline{\underline{H}}$ govern the convergence : the condition number can be changed. $\left(\underline{\underline{H}}^{-1}\right)_{\text{approx}}$ often called a "pre-conditioner".

5) Generalisation to other optimization problems is trivial.

(The Hessian is referred to as the Jacobian if it is not symmetric.)

Modify the condition number (III)

Approximate Hessian can be generated on a case-by-case basis.

Selfconsistent determination of the Kohn-Sham potential :

Jacobian = dielectric matrix.
Lowest eigenvalue close to 1.
Largest eigenvalue :
= 1.5 ... 2.5 for small close-shell molecules, and small unit cell solids
(Simple mixing will sometimes converge with parameter set to 1 !)
= the macroscopic dielectric constant (e.g. 12 for silicon),
forlarger close-shell molecules and large unit cell insulators,
= diverge for large-unit cell metals, or open-shell molecules !

Model dielectric matrices known for rather homogeneous systems.
Knowledge of approx. macroscopic dielectric constant
=> efficient preconditioner
Work in progress for inhomogeneous systems
(e.g. metals/vacuum systems).

Advanced algorithms : using the history

Instead of using only previously computed forces,
take into account past forces for past positions

Large class of methods :

- Broyden (quasi-Newton-type),
- Davidson,
- conjugate gradients,
- Lanczos ...

+Approximate Hessian can be combined with usage of history

For geometry optimization : current practice
Broyden ionmov 22
First without cell relaxation optcell 0
then optimizing the cell optcell 2 (or 1, or 3…9)

Iterative algorithms always working ?

No !

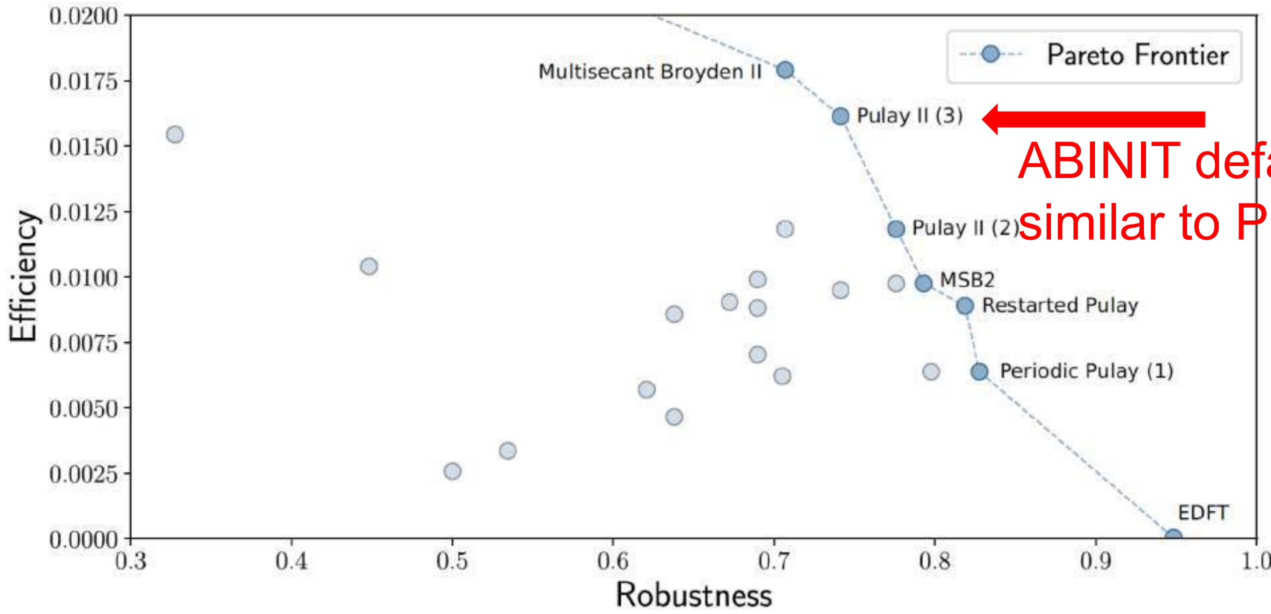
Hypothesis of harmonic energy can be problematic

Many hard cases where iterations go on, without reaching SCF convergence or vanishing forces / stresses.

Trade-off between speed and robustness.

Example : test of 24 iterative algorithms/settings for a set of 56 hard systems

N.D. Woods, M.C. Payne and P.J. Hasnip, *J. Phys.: Condens. Matt.* **31**, 453001 (2019)



ABINIT default algo+settings similar to PULAY II (3)

Iterative algorithms always working ?

SCF default iscf 7 or 17
    try changing iscf, diemac, dielng
    is the solution of KS equation accuracte ? nline, nnsclo, tolrde

Geometry optimization default ionmov 22
    try improving underlying SCF accuracy using tolrff, nstep
    try changing ionmov
    if optimizing primitive lattice vectors, beware about ecutsm,

Other troubleshooting ?

Read ABINIT error messages !

Possibly also warnings and comments.

In log file, or in error file, or in the __ABI_MPIABORTFILE__ file if parallel

Problems with the initial geometry (cell, atom type, nuclei positions)

Many mistakes done by beginners !

Check the units (reminder : ABINIT uses atomic units by default)

Check whether natom is coherent with xred (or xcart)

Check that you have not switched atom types

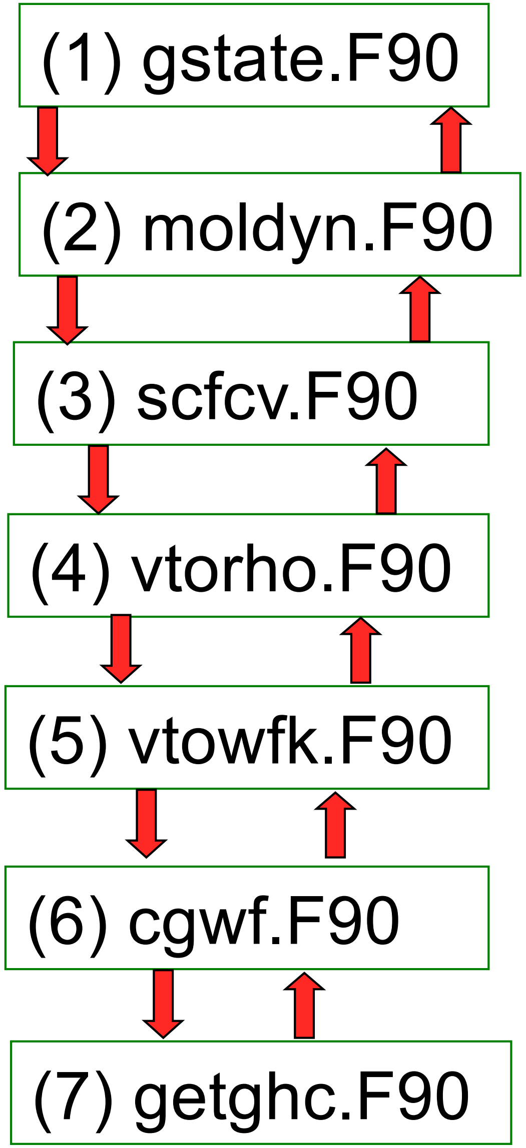
Relax first the atomic positions **at fixed primitive vectors** before optimizing the cell. Read optcell documentation

ABINIT can read VASP POSCAR external files containing unit cell parameters and atomic positions. See the input variable structure.

Possibly try to visualize your input geometry using Abipy, VESTA, XCrysDEN, see docs.abinit.org/tutorial/analysis_tools to produce .xsf files for XCrysDEN

More on troubleshooting at wiki.abinit.org/doku.php?id=howto:troubleshooting

ABINIT : levels in main processing unit



(1) gstate.F90	Ground-state
(2) moldyn.F90	Molecular dynamics
(3) scfcv.F90	Self-consistent field convergence
(4) vtorho.F90	From a potential (v) to a density (rho)
(5) vtowfk.F90	From a potential (v) to a wavefunction at some k-point
(6) cgwf.F90	Conjugate-gradient on one wavefunction
(7) getghc.F90	Get the application of the Hamiltonian

An example run : tbase1_1

- First run in tutorial base1 (https://docs.abinit.org/tutorial/base1)
- Very quick (less than 1 sec)
- Look at `tbase1_1.files`, `tbase1_1.in`, `01h.pspgth`
- `abinit < tbase1_1.files > log`
- Look at `tbase1_1.out` (such *.out file will usually be much longer)
- Look at `log` (such log file is mainly for finding errors or debugging)
- Issue: (-A3 might not be enough for more atoms)

```
grep –i –B1 –A3 ETOT tbase1_1.out
grep –i –A3 forces      tbase1_1.out
grep –i –A3 stress      tbase1_1.out
grep –i –A3 energy      tbase1_1.out
grep –i –A3 coordinates tbase1_1.out
grep –i –A3 density     tbase1_1.out
```

Additional slides

Exact result for exchange-correlation energy

(without demonstration)

The exchange-correlation energy, functional of the density is the integral over the whole space of the density times the local exchange-correlation energy per particle

$$E_{\mathrm{xc}}\left[n\right]=\int n(\mathbf{r}_1)\varepsilon_{xc}(\mathbf{r}_1;n)\,\mathrm{d}\mathbf{r}_1$$

while the local exchange-correlation energy per particle is the electrostatic interaction energy of a particle with its DFT exchange-correlation hole.

$$\varepsilon_{xc}(\mathbf{r}_1;n)=\int\frac{1}{2}\frac{\overline{n^{xc}}(\mathbf{r}_2|\mathbf{r}_1;n)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_2$$

Sum rule : $\int\overline{n^{xc}}(\mathbf{r}_2|\mathbf{r}_1;n)\,\mathrm{d}\mathbf{r}_2=-1$

Local density approximation (I)

Hypothesis :

- the local XC energy per particle only depend on the local density
- and is equal to the local XC energy per particle of an homogeneous electron gas of same density (in a neutralizing background - « jellium »)

$$\varepsilon_{xc}^{LDA}(\mathbf{r}_1; n) = \varepsilon_{xc}^{hom}(\, n(\mathbf{r}_1)\,)$$

Gives excellent numerical results ! Why ?

1) Sum rule is fulfilled

2) Characteristic screening length indeed depend on local density

Local density approximation (II)

Actual function : exchange part + correlation part

$\varepsilon_x^{\mathrm{hom}}(n) = Cn^{1/3}$ with $C = -\frac{3}{4\pi}\left(3\pi^2\right)^{1/3}$

for the correlation part, one resorts to accurate numerical simulations beyond DFT (e.g. Quantum Monte Carlo)

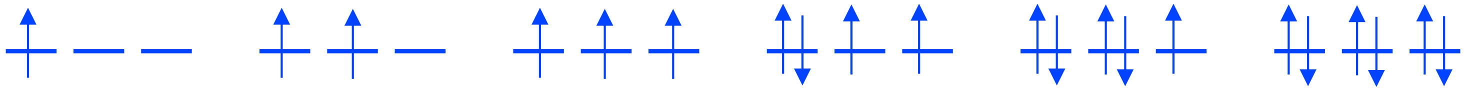
Corresponding exchange-correlation potential $V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}$

$V_{\mathrm{xc}}^{\mathrm{approx}}(\mathbf{r}) = \mu_{\mathrm{xc}}\left(n(\mathbf{r})\right)$ $\mu_{xc}(n) = \frac{\mathrm{d}\left(n\varepsilon_{xc}^{approx}(n)\right)}{\mathrm{d}n}$

$$\mu_x(n) = C\frac{4}{3}n^{1/3} = \frac{4}{3}\varepsilon_x^{\mathrm{hom}}(n)$$

Hund’s rule

Example: p levels

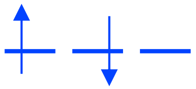


$|S|_{\text{total}}$ 1/2 1 3/2 1 1/2 0

Suppose frozen spherically symmetric effective potential

created by nuclei and core electrons

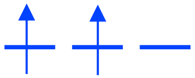
favored over



Indeed, density identical => Hartree energy identical
However, exchange energy more negative

$$E_H[n] = \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

$$E_x = -\frac{1}{2}\sum_{\sigma} \sum_{i,j}^{occ} \int d\mathbf{r}\, d\mathbf{r}' \frac{\psi^*_{j\sigma}(\mathbf{r}')\psi^*_{i\sigma}(\mathbf{r}')\psi_{j\sigma}(\mathbf{r})\psi_{i\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}|}$$



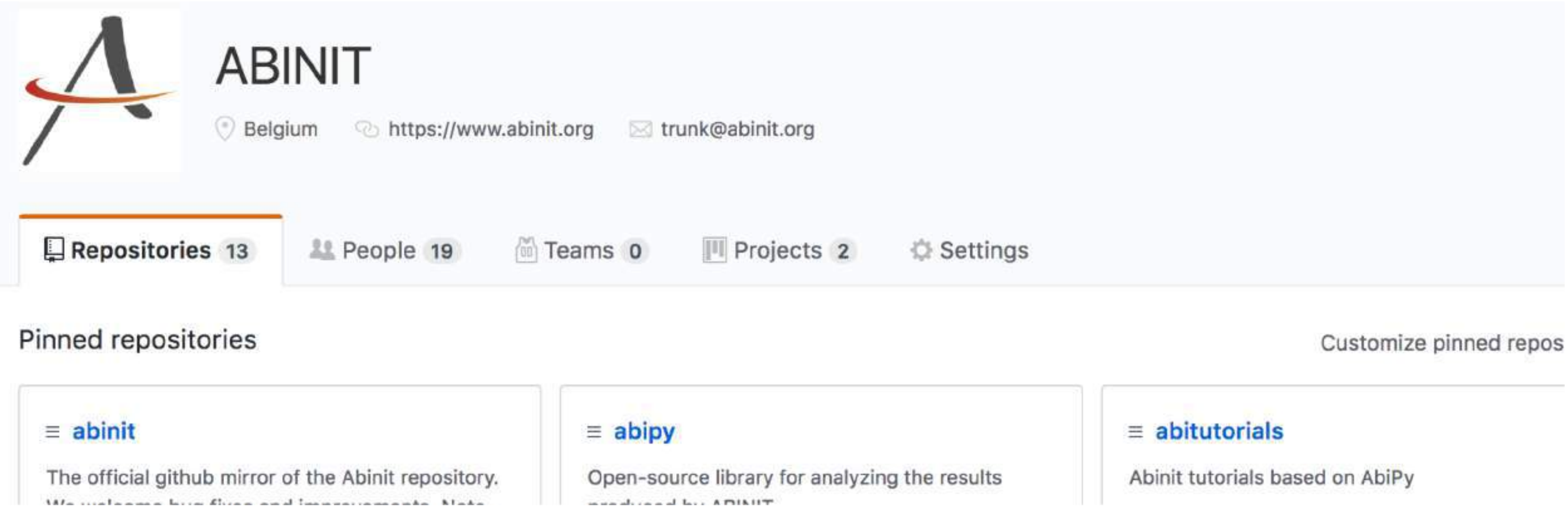
favored over

Indeed, density in the same orbital (same spatial location)
increase Hartree energy (also E_x energy less negative !)

ABINIT + python : Abipy, Abitutorials …

ABINIT organization on GitHUB https://github.com/abinit

Abipy : python library for launching ABINIT jobs,
and analysing/plotting the results http://pythonhosted.org/abipy
=> e.g. connecting ABINIT with tools for high-throughput calculations developed in the Materials Project context (like Pymatgen, Fireworks).
Abitutorials : tutorial based on Jupyter notebooks ABINIT+python


ABINIT

Belgium https://www.abinit.org trunk@abinit.org

Pinned repositories

abinit
The official github mirror of the Abinit repository.

abipy
Open-source library for analyzing the results

abitutorials
Abinit tutorials based on AbiPy

Advanced Materials Modeling
Lecture of 21 april
Part B

+ Many-body physics
+ The total energy : Quantum monte Carlo
+ Experiments : total energy, band gap, spectroscopies ?
+ Charged excitations and Green's function G
+ GW approximation (incl. self-consistency and miscellaneous tricks)

A basic reference on first-principles simulations of Interacting electrons

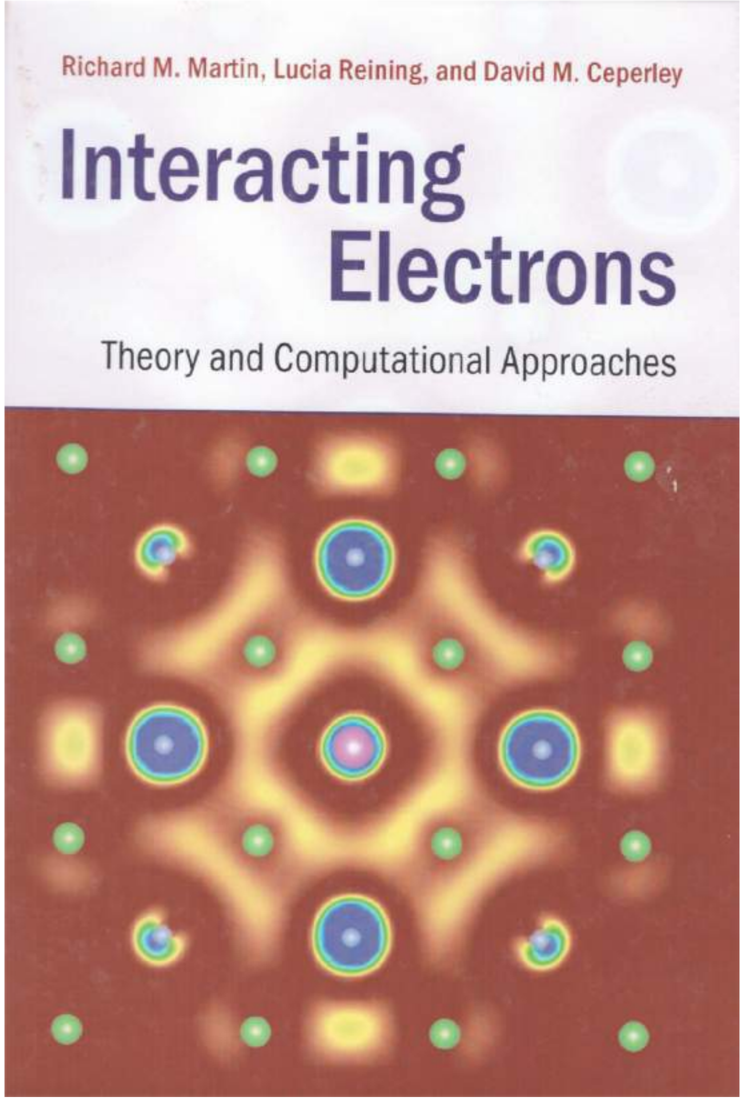
Richard M. Martin, L. Reining, and D.M. Cepreley

Cambridge University Press, 2016

Interacting electrons:

Theory and computational approaches

(ISBN: 978-0-521)87150-1)



Richard M. Martin, Lucia Reining, and David M. Ceperley

Interacting Electrons

Theory and Computational Approaches

Many-body physics

Systems with n electrons and N nuclei

- Born-Oppenheimer approximation.
- Nuclei are treated as distinct particles, without spin. Internal structure is neglected. Only charge, mass and (classical) position taken into account.

Wavefunction :

$$\Psi_e(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,\ldots,\mathbf{r}_n,\sigma_n;\mathbf{R}_1,\mathbf{R}_2,\ldots\mathbf{R}_N)$$

+ antisymmetry for electron exchange

Electronic Hamiltonian, in atomic units (without spin-orbit) :

$$\hat{T}_e=\sum_{i=1}^{n}-\frac{\nabla_{r_i}^2}{2} \qquad \hat{V}_{eN}=\sum_{A}^{N}\sum_{i}^{n}\frac{-Z_A}{|\mathbf{r}_i-\mathbf{R}_A|} \qquad \hat{V}_{ee}=\sum_{\substack{(i,j)\\ i<j}}^{(n,n)}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

$$\hat{H}_e=\hat{T}_e+\hat{V}_{eN}+\hat{V}_{ee}$$

$$\boxed{\hat{H}_e|\Psi_e\rangle=E_e|\Psi_e\rangle}$$

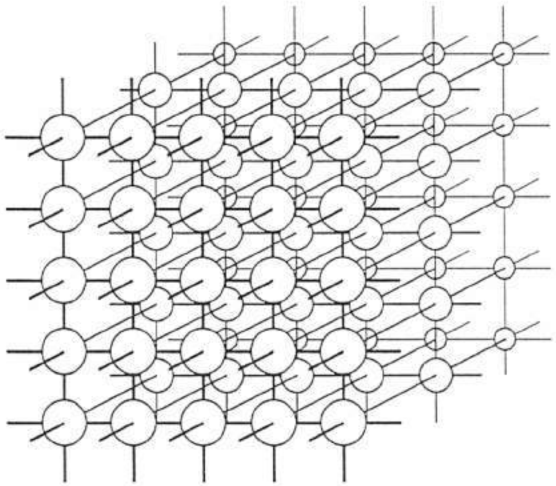
Many-body wavefunction representation

Classical objets : fields $p(\mathbf{r},t), V(\mathbf{r},t), T(\mathbf{r},t), \mathbf{E}(\mathbf{r},t), \ldots$

or trajectories $\mathbf{R}_1(t), \mathbf{R}_2(t), \mathbf{R}_3(t), \ldots \mathbf{R}_N(t)$

Quantum objects : wavefunctions

for interacting particles $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N, t)$



Classical position and speed of 8 objects
2x3x8=48 real numbers.

Oxygen atom : 8 electrons.
Quantum description, on a cubic grid of 10x10x10 points.
24-dimensional object => 10^{24} complex numbers

HF, DFT : set of wavefunctions for non-interacting particles

For the oxygen atom, back to 8x10x10x10 real numbers,
but with an approximate treatment ...

Simplified notations

(1) Arguments of wavefunction :

$$\Psi_e(\boxed{\mathbf{r}_1,\sigma_1};\mathbf{r}_2,\sigma_2;\ldots;\mathbf{r}_n,\sigma_n) \Longrightarrow \Psi_e(\boxed{1}, 2, \ldots, n)$$

"1" becomes a symbol to denote $\mathbf{r}_1,\sigma_1$

(2) Define also $r_{ij} \triangleq |\mathbf{r}_i - \mathbf{r}_j|$

$$\hat{V}_{ee} = \sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{r_{ij}}$$

and "one-particle" part of Hamitonian

$$\hat{V}_{eN} = \sum_{A}^{N} \sum_{i}^{n} \frac{-Z_A}{r_{iA}} = \sum_{i}^{n} \hat{V}_N(\mathbf{r}_i) \qquad \hat{h}^N(i) \triangleq -\frac{\nabla_{r_i}^2}{2} + \hat{V}_N(\mathbf{r}_i)$$

Hamitonian becomes :

$$\left(\sum_{i}^{n} \hat{h}^N(i) + \sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{r_{ij}} \right) \Psi_e(1,2,\ldots,n) = E_e \Psi_e(1,2,\ldots,n)$$

Separation of variables

$$\left(\sum_{i}^{n}\hat{h}^{N}(i)+\boxed{\sum_{\substack{(i,j)\\ i<j}}^{(n,n)}\frac{1}{r_{ij}}}\right)\Psi_{e}(1,2,\dots,n)=E_{e}\,\Psi_{e}(1,2,\dots,n)$$

+ antisymmetry for electron exchange

Interelectronic coupling does not
allow to separate electronic coordinates

Mean-field approximation (like DFT)

$\sum_{\substack{(i,j)\\ i<j}}^{(n,n)}\frac{1}{r_{ij}}$ replaced by $\sum_{i}\hat{V}_{Hxc}(i)$

$$\hat{h}^{N}_{MF}(i)=\hat{h}^{N}(i)+\hat{V}_{Hxc}(i)$$

$$\left(\sum_{i}^{n}\hat{h}^{N}_{MF}(i)\right)\Psi_{MF,e}(1,2,\dots,n)=E_{MF}\,\Psi_{MF,e}(1,2,\dots,n)$$

+ antisymmetry for electron exchange

gives solutions as
Slater determinants of 1-particle wavefunctions
mean-field energy=sum of 1-particle eigenenergies,
must be corrected to give electronic energy (avoid double-counting)

Monte Carlo approaches

$$\left(\sum_{i}^{n}\hat{h}^{N}(i)+\boxed{\sum_{\substack{(i,j)\\ i<j}}^{(n,n)}\frac{1}{r_{ij}}}\right)\Psi_{e}(1,2,\ldots,n)=E_{e}\Psi_{e}(1,2,\ldots,n)$$

Variational Monte Carlo
Diffusion Monte Carlo
Diagrammatic Monte Carlo
Green’s function Monte Carlo
…

“Monte Carlo” refers to stochastic evaluation of high-dimensional integrals using random sampling, and generation of such samplings using random walks

Usually : target evaluation of the ground-state energy

Monte Carlo approaches (brief overview)

Variational Monte Carlo (VMC)

$$\hat{H}_e \Psi_e(1,2,\ldots,n) = \left(\sum_{i}^{n} \hat{h}^N(i) + \boxed{\sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{r_{ij}}} \right) \Psi_e(1,2,\ldots,n) = E_e \Psi_e(1,2,\ldots,n)$$

Use the variational principle to approximate ground-state energy

$$E_{e,GS} = \min_{\Psi_e \text{ normalized}} \left\langle \Psi_e \middle| \hat{H}_e \middle| \Psi_e \right\rangle < E_{e,trial} = \left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle$$

Simplest form of VMC : use trial wavefunctions of the type

$$\Psi_{e,trial}(1,2,\ldots,n) = \left(\prod_{\substack{(i,j)\\ i<j}}^{(n,n)} f(r_{ij}) \right) \Psi_{SD}(1,2,\ldots,n)$$

Jastrow-Slater

Jastrow factor, symmetric upon electron exchange, builds-in correlation between electrons

f tends to 1 at large separation, and to zero at small separation

Slater determinant, antisymmetric upon electron exchange

Challenge : multi-dimensional integrals

$$\left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle \quad \text{with} \quad \hat{H}_e = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}$$

$$\hat{T}_e = \sum_{i=1}^{n} -\frac{\nabla_{r_i}^2}{2} \qquad \hat{V}_{eN} = \sum_{A}^{N} \sum_{i}^{n} \frac{-Z_A}{\left|\mathbf{r}_i - \mathbf{R}_A\right|} \qquad \hat{V}_{ee} = \sum_{\substack{(i,j) \\ i<j}}^{(n,n)} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

and $\Psi_e(1,2,\ldots,n) = \left(\prod_{\substack{(i,j) \\ i<j}}^{(n,n)} f(r_{ij}) \right) \Psi_{SD}(1,2,\ldots,n)$

$$\left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle = \int \ldots \int \Psi^*_{e,trial}(1,\ldots N) \hat{H}_e \Psi^*_{e,trial}(1,\ldots N) d1 \ldots dN$$

No simple expression for the expectation value,
unlike with Slater determinants

Evaluation of Jastrow-Slater wavefunction energy expectation,
then optimization of orbitals of Slater determinant and Jastrow factor ?

Stochastic evaluation

$$\left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle = \int \ldots \int \Psi^*_{e,trial}(1,\ldots N) \hat{H}_e \Psi^*_{e,trial}(1,\ldots N) d1 \ldots dN$$

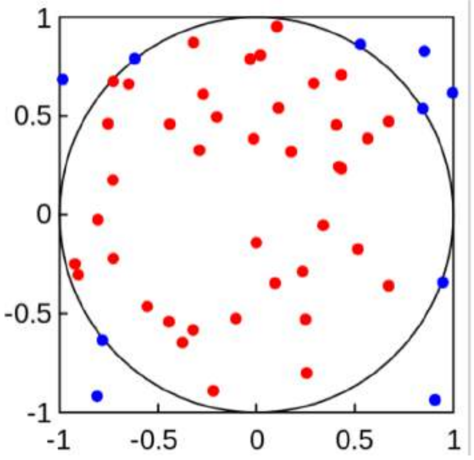
Standard multi (few) dimensional integration of dimention d :
sample with homogeneous grid of L points in each dimension,
with step h inversely proportional to L .

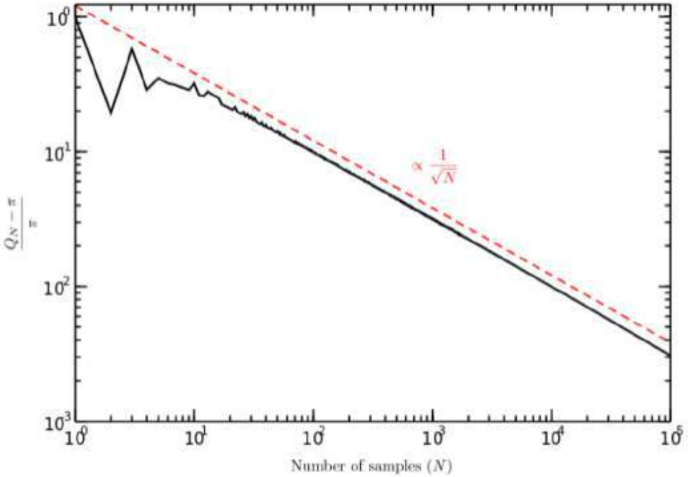
Total number of points $M=L^d$

Convergence of Simpson rule error $\varepsilon = (1/L)^4 = M^{-4/d}$

Random sampling $\varepsilon = M^{-1/2}$

Better than fixed grid technique for $d > 8$!





Importance sampling

Sampling point distribution : generated from the trial wavefunction, to favour the configurations that have higher probability

$$\Pi(1\ldots N)=\frac{\left|\Psi_{e,trial}(1\ldots N)\right|^2}{\int\left|\Psi_{e,trial}(1\ldots N)\right|^2 d1\ldots dN}$$

Metropolis algorithm to generate a random walk in the multi-dimensional space $(1\ldots N)_i$ for $i=1 \ldots M$,
whose probability distribution tends to $\Pi(1\ldots N)$
by randomly generating new configurations and accepting/rejecting them

Then evaluate $\left\langle\Psi_{e,trial}\middle|\hat{H}_e\middle|\Psi_{e,trial}\right\rangle=\lim_{M\to\infty}\frac{1}{M}\sum_{i=1}^{M}E_L\left((1\ldots N)_i\right)$

where $E_L\left((1\ldots N)\right)=\mathrm{Re}\frac{\hat{H}_e\Psi_{e,trial}(1\ldots N)}{\Psi_{e,trial}(1\ldots N)}$

Diffusion Monte Carlo

Consider time-dependent Schrödinger equation in imaginary time

$$i\hbar\frac{\partial}{\partial t}\left|\Psi_e(t)\right\rangle = \hat{H}_e\left|\Psi_e(t)\right\rangle \qquad \Rightarrow \qquad -\hbar\frac{\partial}{\partial\tau}\left|\Psi_e(\tau)\right\rangle = \hat{H}_e\left|\Psi_e(\tau)\right\rangle$$

Propagate initial trial wavefunction $\left|\Psi_{e,trial}(\tau=0)\right\rangle$ using such Eq.

Complete set of eigenfunctions of Hamiltonian $\hat{H}_e\left|\Psi_i\right\rangle = E_i\left|\Psi_i\right\rangle$

Solve imaginary-time Schrödinger equation $\left|\Psi_i(\tau)\right\rangle = e^{-E_i\tau}\left|\Psi_i\right\rangle$

Decomposition of $\left|\Psi_{e,trial}(\tau=0)\right\rangle = \sum_{i=1} c_i\left|\Psi_i\right\rangle$

$$\left|\Psi_{e,trial}(\tau)\right\rangle = \sum_{i=1} c_i e^{-E_i\tau}\left|\Psi_i\right\rangle$$

Hence, in the large-time limit $\left|\Psi_{e,trial}(\tau)\right\rangle \rightarrow \left|\Psi_{e,i=\text{Ground State}}\right\rangle$

Diffusion Monte-Carlo = generate a random walk using imaginary-time Schrödinger equation

Accuracy of Quantum Monte Carlo

Variational Monte Carlo :

quality of Energy estimate depends directly on trial wavefunction

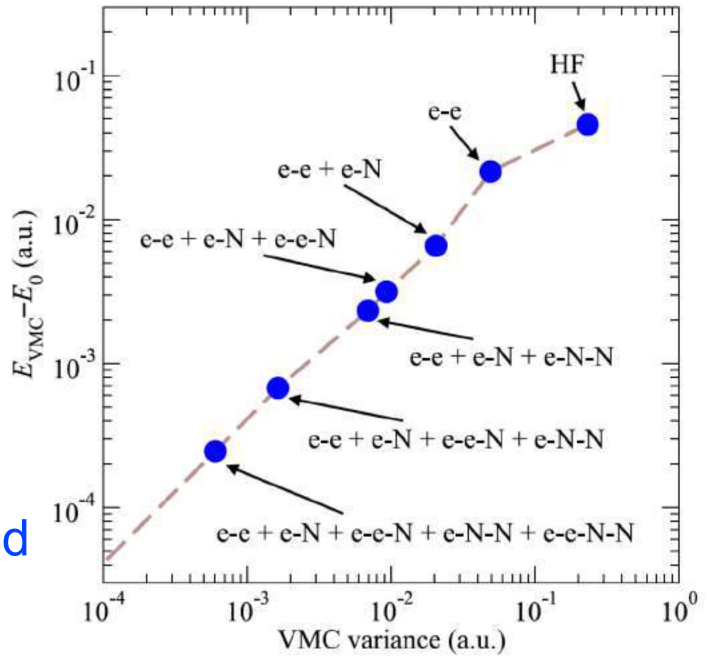
Diffusion Monte Carlo :

quality of Energy is partly dependent on trial wavefunction

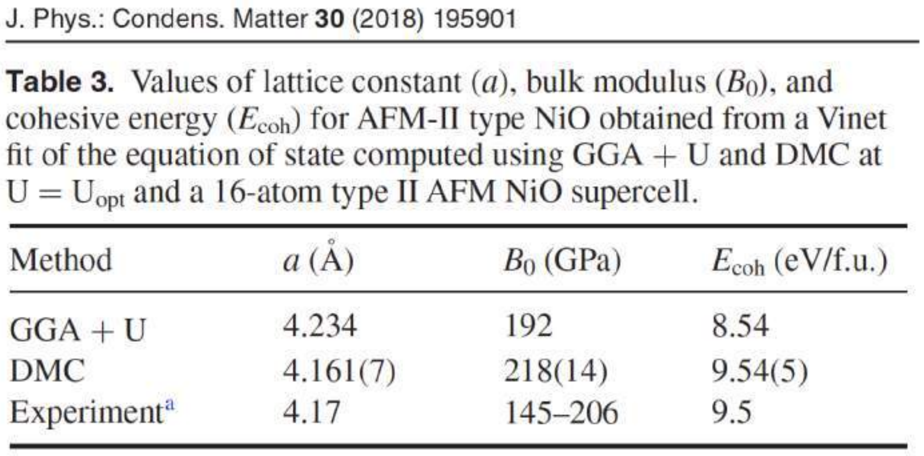
Still not exact !

Indeed, the antisymmetry of the sampling of the random walk is hard to maintain => fixed-node approximation (and fixed-node error)

VMC H_2 benchmark : total energy difference wrt numerically exact results With improved Jastrow



NiO lattice parameter, cohesive energy



J. Phys.: Condens. Matter **30** (2018) 195901

Table 3. Values of lattice constant (a), bulk modulus (B_0), and cohesive energy (E_{coh}) for AFM-II type NiO obtained from a Vinet fit of the equation of state computed using GGA + U and DMC at U = U_{opt} and a 16-atom type II AFM NiO supercell.

Method	a (Å)	B_0 (GPa)	E_{coh} (eV/f.u.)
GGA + U	4.234	192	8.54
DMC	4.161(7)	218(14)	9.54(5)
Experiment[a]	4.17	145–206	9.5

Quantum Monte Carlo codes

QMCPACK

https://qmcpack.org

Jeongnim Kim et al , J. Phys.: Condens. Matter 30, 195901 (2018)

CASINO

https://vallico.net/casinoqmc

RJ Needs, MD Towler, ND Drummond and P Lopez Rios
J. Phys.: Condens. Matter 22, 195901 (2010)