Another view on XC: the XC hole

$$\begin{split} E_{\text{e-e}} &= \langle \Psi[n] | W | \Psi[n] \rangle = \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tilde{g}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \\ &= \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \left[ \tilde{g}(\mathbf{r}, \mathbf{r}') - 1 \right] \, d\mathbf{r} \, d\mathbf{r}' \\ &= \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + \frac{e^2}{2} \int \int \frac{n(\mathbf{r})\tilde{n}_{\text{XC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \end{split}$$

 $\tilde{g}(\mathbf{r},\mathbf{r}')$ : el-el pair correlation function (draw!).

$$ilde{g}(\mathbf{r},\mathbf{r}')= ilde{g}(\mathbf{r}',\mathbf{r})$$
 and  $\int ilde{g}(\mathbf{r},\mathbf{r}')n(\mathbf{r})\;d\mathbf{r}=N-1$  (normalization)

 $\tilde{n}_{XC}(\mathbf{r}, \mathbf{r}')$ : exchange-correlation hole.

$$\int n(\mathbf{r}) \left[ \tilde{g}(\mathbf{r},\mathbf{r}') - 1 \right] d\mathbf{r} = \int n(\mathbf{r}) \left[ \tilde{g}(\mathbf{r}',\mathbf{r}) - 1 \right] d\mathbf{r} = \int n(\mathbf{r}') \left[ \tilde{g}(\mathbf{r},\mathbf{r}') - 1 \right] d\mathbf{r}' = \int \tilde{n}_{\mathsf{X}\mathsf{C}}(\mathbf{r},\mathbf{r}') d\mathbf{r}' = -1 \quad , \quad \int \tilde{n}_{\mathsf{C}}(\mathbf{r},\mathbf{r}') d\mathbf{r}' = 0$$

The -1 in N-1 comes from the absence of "self-interaction".

The tildes  $(\tilde{g}, \tilde{n}_{XC})$  have to do with the correction for the kinetic energy. We ignore that aspect here.

Help slide:

When the electrons are far apart  $(|\mathbf{r} - \mathbf{r}'| \rightarrow \infty)$ ,  $E_{e-e}$  is just the energy of the (one-particle) densities interacting:  $e^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$ 

So  $\tilde{g}(\mathbf{r},\mathbf{r}')=1$ .

When electrons get closer, they feel each other, Kohanoff: "the probability ... is reduced with respect to finding them at infinite distance", because of Coulomb repulsion (for the same values of the one-electron densities!). So

$$e^2 rac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} g(\mathbf{r},\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \quad ext{with} \quad g(\mathbf{r},\mathbf{r}') < 1$$

The energy is reduced compared to the simple Hartree energy.

In fact, the mere presence of exchange only already pushes electrons with like spins apart and makes it impossible for those to be at the same spot simultaneously. So in pure HF:  $g_X(\mathbf{r}, \mathbf{r}) = 1/2$ . The total pair correlation function also accounts for the electron-electron **correlation** (Kohanoff Fig. 2.3):  $g(\mathbf{r}, \mathbf{r}') < g_X(\mathbf{r}, \mathbf{r}') < 1$ 

The XC energy is:

$$E^{\rm XC} = \frac{e^2}{2} \int n(\mathbf{r}) \left\{ \int \frac{\tilde{n}_{\rm XC}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r}' \right\} d\mathbf{r} \quad \text{with} \quad \tilde{n}_{\rm XC}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}') \big[ \tilde{g}(\mathbf{r},\mathbf{r}') - 1 \big]$$

In the LDA:

$$E_{\text{LDA}}^{\text{XC}}[n(\mathbf{r})] = \int n(\mathbf{r}) \, \epsilon_{\text{XC}}^{\text{LDA}}[n(\mathbf{r})] \, d\mathbf{r}$$

where  $\epsilon_{\text{XC}}^{\text{LDA}}[n(\mathbf{r})]$  is calculated assuming the system is "locally homogeneous", i.e. only determined by  $n(\mathbf{r})$ . This boils down to the LDA approximation of the XC-hole being:

$$\widetilde{n}_{\text{XC}}^{\text{LDA}}(\mathbf{r},\mathbf{r}') = n(\mathbf{r})[\widetilde{g}^{\text{hom}}(|\mathbf{r}'-\mathbf{r}|,n(\mathbf{r}))-1]$$

Here  $n(\mathbf{r}')$  is replaced by  $n(\mathbf{r})$  and the paircorrelation function is that of the homogeneous electron gas at exactly that density. So only the distance  $|\mathbf{r}' - \mathbf{r}|$  matters.

Why does the LDA work? I.e., why isn't it awful, but pretty good (better than HF, but still not good enough for quantum chemists)?

1. We fix **r**,  $\tilde{g}$  is then the g of the uniform electron gas at density  $n(\mathbf{r})$ . This is solved exactly by the LDA, so the xc-hole integrates to -1.

$$\int \tilde{n}_{\mathsf{XC}}(\mathbf{r}',\mathbf{r}) \ d\mathbf{r}' = \int n(\mathbf{r}) [\tilde{g}^{\mathsf{hom}}(\mathbf{r}',\mathbf{r}) - 1] \ d\mathbf{r}' = \int n(\mathbf{r}) [\tilde{g}^{\mathsf{hom}}(|\mathbf{r}'-\mathbf{r}|,n(\mathbf{r})) - 1] \ d\mathbf{r}' = -1$$

note we have  $n(\mathbf{r})$ , not  $n(\mathbf{r}')$ .

.,

2. The exact details of the hole do not matter for the energy, only the spherical average does and that behaves decent.

$$E_{\rm e-e} = \frac{e^2}{2} \int \int \frac{n({\bf r})n({\bf r}')}{|{\bf r}-{\bf r}'|} \, d{\bf r} \, d{\bf r}' + \frac{e^2}{2} \int d{\bf r} \, n({\bf r}) \int \frac{n_{\rm XC}({\bf r},{\bf r}')}{|{\bf r}-{\bf r}'|} \, d{\bf r}'$$

Just do the  $\mathbf{r}'$  integration in spheres centred at  $\mathbf{r}$ , then  $|\mathbf{r} - \mathbf{r}'|$  is constant on the sphere so only the spherical average of the hole matters. Jones & Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989). See Fig. 7, page 703, https://doi.org/10.1103/RevModPhys.61.689

Help slide:

$$\frac{e^2}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int \frac{n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' = \frac{e^2}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int \frac{n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r} + \tilde{\mathbf{r}})}{|\tilde{\mathbf{r}}|} \, d\tilde{\mathbf{r}}$$
$$= \frac{e^2}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int_0^\infty \frac{4\pi \tilde{r}^2}{\tilde{r}} \left[ \frac{1}{4\pi \tilde{r}^2} \int_0^{2\pi} \int_0^\pi n_{\mathsf{XC}}(\mathbf{r}, \mathbf{r} + \tilde{\mathbf{r}}) \sin\theta \, d\theta d\phi \right] d\tilde{r}$$

Center the second integral at **r**:  $\tilde{\mathbf{r}} = \mathbf{r}' - \mathbf{r}$ ,  $\tilde{r} = |\tilde{\mathbf{r}}| = |\mathbf{r}' - \mathbf{r}|$ . The volume element in spherical coordinates:  $d\tilde{\mathbf{r}} = \sin \theta \, d\theta d\phi d\tilde{\mathbf{r}}$ 

The red part is the spherical average, centered at **r**. This works because  $1/\tilde{r}$  can be moved outside the angular integral.

### The Local Spin Density Approximation, LSDA

We split the density in  $\alpha$  and  $\beta$  spin parts (or " $\uparrow$ " and " $\downarrow$ "). Both are represented by their own orbitals (cf. unrestricted open-shell HF).

We add  $T[n^{\alpha}(\mathbf{r})]$  and  $T[n^{\beta}(\mathbf{r})]$ . The Coulomb/Hartree energy depends only on the total density  $n(\mathbf{r}) = n^{\alpha}(\mathbf{r}) + n^{\beta}(\mathbf{r})$ . The XC energy:

$$E_{\rm XC}^{\rm LSDA}[n^{\alpha}(\mathbf{r}), n^{\beta}(\mathbf{r})] = \int (n^{\alpha}(\mathbf{r}) + n^{\beta}(\mathbf{r})) \epsilon_{\rm XC}^{\rm LSDA}[n^{\alpha}(\mathbf{r}), n^{\beta}(\mathbf{r})] d\mathbf{r}$$
$$n(\mathbf{r}) = n^{\alpha}(\mathbf{r}) + n^{\beta}(\mathbf{r}) \text{ and } \xi(\mathbf{r}) = \frac{n^{\alpha}(\mathbf{r}) - n^{\beta}(\mathbf{r})}{n(\mathbf{r})} = \frac{n^{\alpha}(\mathbf{r}) - n^{\beta}(\mathbf{r})}{n^{\alpha}(\mathbf{r}) + n^{\beta}(\mathbf{r})}$$

In practice one interpolates between functionals for unpolarized ( $\xi = 0$ ) and fully polarized ( $\xi = \pm 1$ ,  $n^{\alpha} = 0$  or  $n^{\beta} = 0$ ) electrons.

One cannot build all possible states that are pure eigenfunctions of  $\hat{S}^2$  and  $\hat{S}_z$  (cf. UHF where different  $\alpha$  and  $\beta$  spin determinants are eigenfunctions of  $\hat{S}_z$  but the WF is typically not an eigenstate of  $\hat{S}^2$ , this is called: "spin contamination").

- Too homogeneous electron densities (GGAs can help).
- This results in a tendency to over-bind: overestimate the binding energy of molecules and yield too small bond lengths.
- For covalent and metallic bonds this does not disqualify the method. Errors in bond lengths are typically a few percent.
- ► For weak bonds L(S)DA is really problematic (over-binding...):
  - van der Waals: dynamic, non-local correlation cannot be captured with a local functional. Good results of LDA are unphysical and fortuitous.
  - hydrogen bonds: are described by small, inhomogenous densities.
- Non-perfect cancellation of Coulomb (Hartree) self-interaction and self-exchange. Most acutely felt at *small distances*. E.g., HF does a better job for atoms.
- $\blacktriangleright$  XC has wrong decay into vacuum. Should go as  $\sim 1/{\rm distance}$  for molecules, but goes exponentially, i.e. too fast.
- Negatively charged ions tend to be unstable (see previous bullet).



The Hartree + XC potential for a slab of a Pb crystal with vacuum. The tail is almost entirely due to the XC potential and decays too fast into the vacuum (here vacuum is at  $\approx$  5 eV, in a *molecular* program it would typically be at 0).

This calculation is to determine the work function  $W = \Phi$ : the (minimum) energy needed to extract an electron at the Fermi energy of the metal and bring it into the vacuum. Photoelectric effect:  $\hbar\omega = W$  (Einstein, Nobel price 1921). Calculation by Dr. C. Fang (Brunel University London), with VASP.

Help slide:



Infinite chain:  $(Pb^{2+}[I^{-}]_4)_n$  (formal charges). A lattice of chains at separations d = 11 Å to d = 15 Å.  $d \to \infty$ : Electrons will leave the chains and "drop" into the vacuum. Zero of energy at top of valence band. Calculated with VASP.



With neutralizing positive background. SI of Kamminga et al., https://doi.org/10.1021/acs.inorgchem.7b01096

"Molecular dissociation problem" (Kohanoff: "left-right correlation problem"). Consider, e.g.:

 $H_2 \to H \cdot + \cdot H$ 

In LDA the both radicals are described by the same orbital, localized on both atoms. But they should be come "independent". "cured" to a large extent by the LSDA. Problem also exists in HF (see next week).

"Band gap problem" In semiconductors and insulators the gap between empty and occupied states in the L(S)DA bandstructure is much smaller than the experimental band gap. Often almost by a factor two, sometimes the gap even vanishes.

Experimentally, the gap is the difference between ionization potential (IP) and electron affinity (EA). It can be calculated from energy differences:

$$\epsilon_{gap} = IP - EA = [E(N-1) - E(N)] - [E(N) - E(N+1)]$$

The problem is that the band structure is affected (in a discontinuous) way by the occupation of its levels.

Help slide:

Ionisation potential (IP): the (minimum) energy needed to remove an electron from a (neutral) system, i.e.  $E(N) + IP = E(N-1) \Rightarrow IP = E(N-1) - E(N)$ . (the emitted electron resides at infinity at the zero of energy)

Electron affinity (EA): energy released when an electron is attached to a neutral system, i.e.  $E(N) = E(N+1) + EA \Rightarrow EA = E(N) - E(N+1)$ .



PBE bandstructure of Silicon in (fcc) diamond structure, calculated with VASP. Vertical axis:  $\epsilon_i^{\mathbf{k}}$  (0 eV is top of valence band), horizontal: Brillouin zone path, i.e.  $\mathbf{k}$ . Red lines: experimental band gap. BZ picture from en.wikipedia.org  $\Gamma = (0, 0, 0)$ : KS orbitals have same phase in all unit cells. X and L: KS orbitals have 180° phase change in neighbouring unit cells.

Werkcollege:

$$\frac{\partial E}{\partial n_i} = \epsilon_i$$

Without proof [Jones & Gunnarson, Rev. Mod. Phys. 61, 689 (1989)]:

$$\epsilon_N(n_1 = 1, n_2 = 1, ..., n_{N-1} = 1, n_N = n)$$
  
=  $\epsilon_N(n_1 = 1, n_2 = 1, ..., n_{N-1} = 1, n_N = 1)$  if  $0 < n \le 1$ 

Apply the above for  $\epsilon_N$  and  $\epsilon_{N+1}$ :

$$-IP = E(N) - E(N-1) = \int_{0}^{1} \frac{\partial E}{\partial n_{N}} dn_{N} = \int_{0}^{1} \epsilon_{N}(N-\delta) dn_{N} = \epsilon_{N}(N-\delta) = \epsilon_{N}(N)$$
$$-EA = E(N+1) - E(N) = \int_{0}^{1} \frac{\partial E}{\partial n_{N+1}} dn_{N+1} = \int_{0}^{1} \epsilon_{N+1}(N+\delta) dn_{N+1} = \epsilon_{N+1}(N+\delta) \neq \epsilon_{N+1}(N)$$
$$\epsilon_{g} = \epsilon_{N+1}(N+\delta) - \epsilon_{N}(N) = \underbrace{\epsilon_{N+1}(N+\delta) - \epsilon_{N+1}(N)}_{\epsilon_{N+1}(N+\delta) - \epsilon_{N+1}(N)} + \underbrace{\epsilon_{N+1}(N) - \epsilon_{N}(N)}_{\epsilon_{N}(N)}$$

The discontinuous jump  $\Delta$  arises because of the discontinuity in the real(!) exchange-correlation potential.  $\epsilon_{g}^{DFT}$  comes from the spectrum for neutral system in a single calculation, in principle.



The LDA does not exhibit the discontinuous jump!

In molecules you can still do a reasonable job by calculating the energies for the E(N + 1), E(N) and E(N - 1) systems separately: a so-called  $\Delta$ SCF approach. These are all ground state energies for which DFT is valid. Beware: this is not the  $\Delta$  of the discontinuous jump.

In solids this is more problematic: You have to add a single electron to a system with, in principle,  $N_A$  electrons, i.e. a vanishingly small change of the density in a unit cell...

# Generalized gradient approximation(s)

A systematic, unique expansion of the exchange-correlation energies in terms of the density and its gradients exists:

$$E_{\rm XC} = \int n(\mathbf{r}) \epsilon_{\rm XC}^{\rm LDA}[n(\mathbf{r})] f(n(\mathbf{r}), \boldsymbol{\nabla} n(\mathbf{r}), \boldsymbol{\nabla}^2 n(\mathbf{r}), \boldsymbol{\nabla}^3 n(\mathbf{r}), \dots) d\mathbf{r}$$

Its convergence is bad. No systematic improvement if higher order gradients are included. But gradients do give more information of the density  $n(\mathbf{r})$ , so cannot one use this to improve the functional?

Solution: Generalized gradient approximations. Retain the lowest order gradient information,

$$E_{ ext{XC}}^{ ext{GGA}} = \int \epsilon_{ ext{XC}}[n^{\uparrow}, n^{\downarrow}, | \mathbf{\nabla} n^{\uparrow} |, | \mathbf{\nabla} n^{\downarrow} |] (n^{\uparrow}(\mathbf{r}) + n^{\downarrow}(\mathbf{r})) d\mathbf{r},$$

but construct the functional such that constraints on the exchange-correlation hole are imposed (these are broken when the systematic expansion is interrupted). This is (loosely) what Perdew did.

A "meta-GGA" goes one derivative further, also uses the Laplacian  $\nabla^2 n(\mathbf{r})$ .

# Generalized gradient approximation(s)

GGAs are plural. Making them requires creativity. There is some arbitrariness.

Two "philosophies":

- Fit to (as many) exact properties (as possible).
- Fit to experiment (typically a whole range of molecules with light nuclei).

Features:

- Better thermo chemistry (binding energies), also for quite some H-bonds.
- Better for bond lengths (larger than LDA, GGA sometimes over-corrects).
- Hardly any improvement of the "band gap".

Some important functionals:

- BLYP (1988) Becke exchange (fit to experimental data set) + Lee, Yang & Parr correlation. Used mostly in chemistry.
- PBE (1996) Perdew, Becke & Ernzerhof. Not semi-empirical. Widely used in solid state physics & materials science (a follow-up of "Perdew & Wang 91"). Modifications: rPBE & PBEsol.
- SCAN (2015) Strongly Constrained and Appropriately Normed semi-local density functional Meta-GGA by Sun, Ruszinszky and Perdew. Fulfills as much constraints as possible. To become a new standard?

# Generalized gradient approximation(s)

All GGAs are **semi-local**, i.e. not non-local in that they do not simultaneously depend on the density at two different locations... but they sense how the density locally changes *via* a density derivative (i.e. the gradient).

So GGAs should not work for the weak van der Waals bond, which is inherently non-local. The SCAN appears to work for that too...a story to be continued? ... Indeed.

These mix HF exchange (calculated from the KS orbitals) and DFT exchange:

$$E_{ ext{XC}}^{ ext{hybrid}} = lpha E_{ ext{X}}^{ ext{HF}} + (1 - lpha) E_{ ext{X}}^{ ext{DFT}} + E_{ ext{C}}^{ ext{DFT}}$$

There is a formal basis in HFKS theory.

Heuristic: LDA over-binds and has  $\epsilon_{gap}$  too small, HF under-binds and has  $\epsilon_{gap}$  too large, a mix might improve ...

Some important functionals:

- ▶ B3LYP ( $\neq$  BLYP), Becke 1993, has  $\alpha = 0.2$ . Very popular in chemistry.
- ▶ PBE0 ( $\neq$  PBE) also by PBE. Here  $\alpha = 0.25$ :

$$E_{ ext{xc}}^{ ext{PBE0}} = rac{1}{4}E_{ ext{x}}^{ ext{HF}} + rac{3}{4}E_{ ext{x}}^{ ext{PBE}} + E_{ ext{c}}^{ ext{PBE}}$$

▶ HSE (Heyd, Scuseria & Ernzerhof), a *range-separated* functional.

HSE continued. At short range it mixes in HF exchange, at long range it is a pure DF:

$$E_{\text{XC}}^{\text{HSE}} = \frac{1}{4} E_{\text{X}}^{\text{HF,SR}} + \frac{3}{4} E_{\text{X}}^{\text{PBE,SR}} + E_{\text{X}}^{\text{PBE,LR}} + E_{\text{C}}^{\text{PBE,LR}}$$

Switching is done by splitting 1/r in a short and long range part:

$$\frac{1}{r} = \underbrace{\frac{\operatorname{erfc}(\mu r)}{r}}_{r} + \underbrace{\frac{\operatorname{erf}(\mu r)}{r}}_{r}, \quad \operatorname{erfc}(x) = 1 - \operatorname{erf}(x) \quad , \quad \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^{2}} dt$$

Typical numbers for the "inverse length"  $\mu$ : 0.2 – 0.3 Å<sup>-1</sup>. Beyond  $r = 2/\mu$  typically there is only DF exchange [erf(x) is very close to 1, for x > 2]. The complementary error function is applied to the exchange integrals, the error function to the PBE X hole. HSE06:  $\mu = 0.21$  Å<sup>-1</sup>. Let's have a look at the effect on the band gap.

Help slide:



https://commons.wikimedia.org/wiki/File:Error\_Function.svg



Zero of energy at valence band maximum. Calculated with VASP.



# What we did not do...

We did not talk about:

- ▶ meta-GGAs well, we did...
- orbital dependent functionals Indeed, we did not.
- LDA+U In LSDA strongly localized d and f-electrons are problematic, because too delocalized. LDA+U is an ad hoc on-site fix with a model (Hubbard-like) Hamiltonian, parametrized with a screened on-site electron-electron interaction U. Used mostly for strongly correlated oxides. Computationally convenient, can give good results, but one should know what one is doing.
- van der Waals functionals These are truly non-local functionals and can indeed capture most of the van der Waals bonding reasonably accurate.

exchange	PBE	PBE	optB86b	revPBE	rPW86	QMC	Expt.
correlation	PBE	vdW+LDA	vdW+LDA	vdW+LDA	vdW2+LDA		
a (Å)	2.47	2.47	2.47	2.48	2.48		2.46
d (Å)	4.40	3.44	3.31	3.59	3.51	3.43	3.34
$E_{\rm B}~({\rm meV/C})$	1.0	70.8	69.9	52.7	52.0	$56\pm5$	$52\pm5$

An impression for graphite. d is interlayer distance,  $E_{\rm B}$  is binding energy. 1 eV = 96.5 kJ/mol.

See Hazrati et al., DOI: 10.1103/PhysRevB.90.155448 and references therein.

- van der Waals force fields One patches for the missing interaction with a force field. Methods by Grimme et al. (DFT-D2, DFT-D3, DFT-D4) and Tkatchenko-Scheffler are popular. Works well depending on physical context. So the electronic structure is not corrected, but something is added to the interatomic interaction.
- The (too) many functionals made for specific applications, etc.

#### Practicum

Last week: You actually saw the functionals of today in action. LDA isn't that good. PBE and B3LYP better.

Two assignments:

A simple chemical reaction with an energy barrier

 ${\sf CI}^- + {\sf CH}_3{\sf Br} \longrightarrow {\sf CH}_3{\sf CI} + {\sf Br}^-$ 

Look at:

(a) The fragments at infinite separation: Halogen ions and molecules.

(b) The complexes on either side of the reaction barrier. These are local minima on the potential energy surface (PES).

(c) The **transition state** (TS), i.e. the **saddle** point on the PES. NWChem will have to bring you on the TS. Prepare the initial state for you TS search as a good guess of what you expect it to look like. And keep the halogens and C on a line. A TS search is not trivial.

Spectroscopy i.e. a property calculation for different isomers of a molecule. In this case: NMR chemical shielding.

#### Practicum

Chemical shielding: is minus the ratio between the induced magnetic field at the core (of a nucleus) and the applied magnetic field. Both fields are vectors, so the shielding is a  $3 \times 3$  tensor. One is primarily interested in the isotropic shielding, i.e. the trace/3:

$$\sigma_{
m iso} = (\sigma_{
m xx} + \sigma_{
m yy} + \sigma_{
m zz})/3$$

Preparing & running:

- You can prepare an NWChem job with gmolden, with the MOPAC tool, with Avogrado, or whatever you like (e.g. modify in input file you already have with nano or gedit or vi).
- You can run your NMChem calculation on the PC you are using in the PC room, or, if needed, on lilo8. If cannot run NWChem directly from gmolden, as it will run on lilo7.

You need to write a **report**, see webpage for **guidelines**. We need to fix a **deadline** for submission of the report.

The exam is on Wednesday, January 17, 8.30h, HG00.062 (HG00.071). Please check!

**Q & A** session: Friday, January 12, 8.30-10.15h, HFML0220.

### Practicum

