

From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

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Chapter V

Density Functionals

Repetition: The Hartree-Fock algorithm

- i) Set up the atomic information (positions of nuclei, charges of nuclei, number of electrons, basis set)
- ii) Compute $\langle i|\hat{h}|j\rangle$, $\langle ij|\hat{f}|kl\rangle$ and $\langle ij|\hat{K}|kl\rangle$, $\langle i|j\rangle$
- iii) Determine density matrix $\mathbf{P} = 2\mathbf{C}^T\mathbf{C}$
- iv) Compute \mathbf{F}
- v) Diagonalize \mathbf{F} so that $\mathbf{E} = \text{diag}(\mathbf{F})$, and obtain new coefficients \mathbf{C}' as eigenvectors
- vi) Update $\mathbf{P}' = 2\mathbf{C}'^T\mathbf{C}'$
- vii) Compare if $(\mathbf{P}' - \mathbf{P}) < \text{accuracy}$; if yes, go to viii), else go to iv)
- viii) Compute observables

Repetition: Kohn-Sham equations

We know the electronic density

$$(1) \quad \rho(\mathbf{r}) = |\psi^2(\mathbf{r})|$$

which we derive from Kohn-Sham orbitals. These are obtained from the Kohn-Sham equations

$$(2) \quad \left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[\rho(\mathbf{r})] \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

The DFT algorithm

- i) Set up the atomic information (positions of nuclei, charges of nuclei, number of electrons, basis set)
- ii) Compute $\langle i | \hat{h} | j \rangle$, $S_{ij} = \langle i | j \rangle$
- iii) Determine density matrix $\mathbf{P} = 2\mathbf{C}^T\mathbf{C}$ and the density $\mathbf{P}\mathbf{S}$
- iv) Compute $\int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = E_{Coul}$ and $\int d\mathbf{r} \rho(\mathbf{r})v_{xc}[\rho(\mathbf{r})] = E_{xc}$
- v) Compute \mathbf{H}_{KS}
- vi) Diagonalize \mathbf{H}_{KS} so that $\mathbf{E} = \text{diag}(\mathbf{H}_{KS})$, and obtain new coefficients \mathbf{C}' as eigenvectors
- vii) Update $\mathbf{P}' = 2\mathbf{C}'^T\mathbf{C}'$
- viii) Compare if $(\mathbf{P}' - \mathbf{P}) < \text{accuracy}$; if yes, go to ix), else go to iv)
- ix) Compute observables

Local-Density Approximation (LDA)

How can we derive values for E_{xc} ? Of course, we need a good model, which describes electronic density accurately.

Let us consider the following model:

The electrons are free, only limited by the boundaries of the box (which may be periodic). This model yields a uniform, constant density. Now we add nuclei to the model. To make things easier, let the nuclei be distributed homogeneously. Of course, the resulting density of our electrons is not constant any more, but still homogeneous. Now we can have a look at both, exchange and correlation. With electrodynamics (actually quantum electrodynamics) we obtain

$$(3) \quad E_x^{LDA}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \int d\mathbf{r} \rho(\mathbf{r})^{4/3}$$

So, the good news is that we have an analytic expression for the exchange energy as a functional of density.

This is an exchange functional. At this point we could just have stayed with Hartree-Fock. Unfortunately, we do not know an analytic expression for the correlation energy. What we can derive, however, are expressions for the low-density (eq. 4) and high-density (eq. 5) limits of the correlation energy.

$$(4) \quad E_c^{LDA}[\rho_{lo}] = \frac{1}{2} \left(\frac{g_0}{r_s} + \frac{g_1}{r_s^{3/2}} + \frac{g_2}{r_s^2} + \dots \right)$$

$$(5) \quad E_c^{LDA}[\rho_{hi}] = A \ln r_s + B + r_s(C \ln r_s + D)$$

with the Wigner-Seitz radius

$$(6) \quad r_s = \sqrt{\frac{3}{4\pi} \frac{1}{\rho}}$$

We can optimize the low-density formula with the boundary condition of the high-density case. Many solutions exist, but we can always apply the variational principle

$$(7) \quad v_{xc}^{LDA}[\rho] = \frac{\delta E_{xc}^{LDA}}{\delta \rho} = \epsilon_{xc}^{LDA}[\rho] + \rho \frac{\partial \epsilon_{xc}^{LDA}}{\partial \rho}$$

And we obtain the correlation energy from

$$(8) \quad E_{xc} = E_x + E_c$$

One example would be (Vosko, Wilk, Nusair; Perdew, Wang)

$$(9) \quad E_c(r_s, \zeta) = E_c(r_s, 0) + \alpha_c(r_s) \frac{f(\zeta)}{f''(0)} (1 - \zeta^4) + (E_c(r_s, 1) - E_c(r_s, 0)) f(\zeta) \zeta^4$$

with

$$(10) \quad f(\zeta) = \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2^{4/3} - 2}$$

$$(11) \quad \zeta = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta}$$

Generalized Gradient Approximation (GGA)

The LDA works especially well for metals, but as soon as we are getting less uniform in our structures, it yields a wrong behavior. The reason is that the gradient of the density at inhomogeneities influences the exact correlation and exchange. Steepness matters. To overcome these problem, we correct our LDA correlation functional (as exchange is independent of the gradient) by a gradient-depending term, i.e. (Perdew, Burke, Ernzerhof)

$$(12) \quad E_c^{GGA}[\rho] = \int dr \rho \left(\epsilon_c^{unif}(r_s, \zeta) + H(r_s, \zeta, t) \right)$$

t is the density gradient with a factor depending on spin polarization

$$(13) \quad t = \frac{|\nabla\rho|}{\sqrt{\frac{4k_F}{\pi a_0} [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]}}$$

Unfortunately, this also influences exchange, hence we have to correct our LDA exchange functional as well.

Hybrid Functionals

In principle we have good functionals now, but we also know that Hartree-Fock theory yields exact exchange. Unlike DFT exchange functionals, Hartree-Fock is derived directly from our basis functions, and not from the density. So why not reduce Kohn-Sham exchange a little and add some Hartree-Fock exchange?

For example, we could augment the PBE functional (GGA) with HF exchange

$$(14) \quad E_{xc}^{PBE0} = \frac{1}{4} E_x^{HF} + \frac{3}{4} E_x^{PBE} + E_c^{PBE}$$

More widely-used functionals are B3LYP (with Lee-Yang-Parr correlation)

$$(15) \quad E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{LYP}$$

The LDA correlation energy is the Vosko-Wilk-Nusair (VWN) correlation energy, and the factors are $a_0 = 0.2$, $a_x = 0.72$ and $a_c = 0.81$

Double Hybrid Functionals

Finally, we can also add exact correlation to our correlation functional. Exact correlation can be obtained from correlated electronic-structure methods. Of these, second-order perturbation theory is least costly, hence we obtain functionals of type

$$(16) \quad E_{xc} = (1 - a_x)E_x^{DFT} + a_x E_x^{HF} + (1 - a_c)E_c^{DFT} + a_c E_c^{PT2}$$

For example, the B2PLYP functional is

$$(17) \quad E_{xc} = (1 - a_x)E_x^{B88} + a_x E_x^{HF} + bE_c^{LYP} + cE_c^{PT2}$$

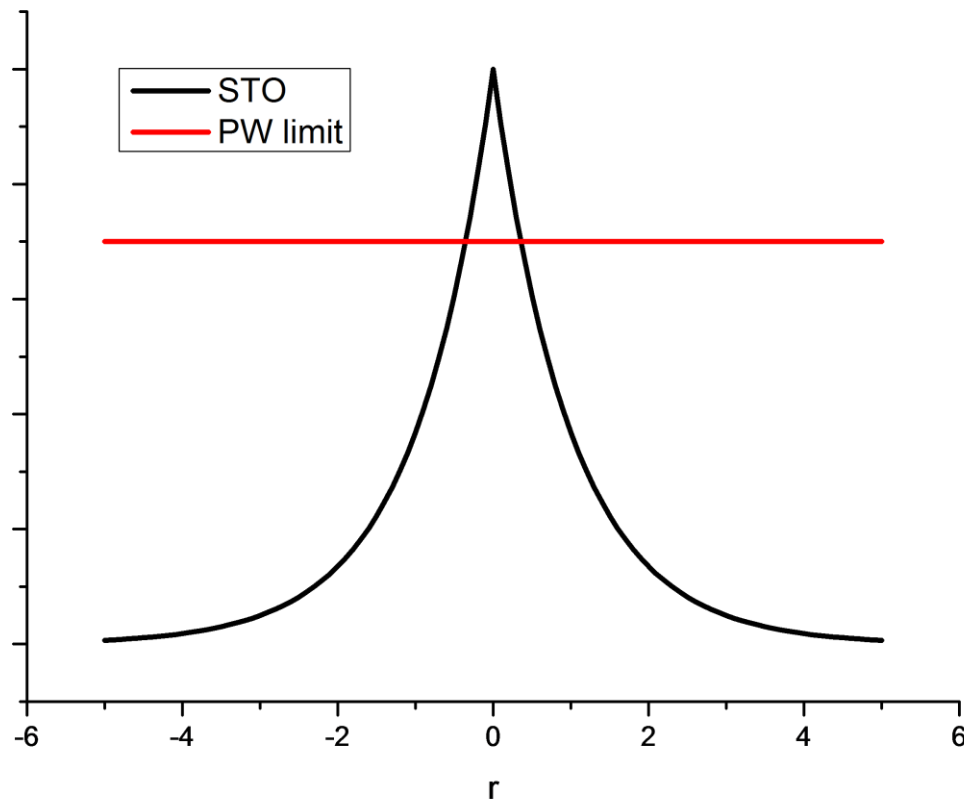
The perturbational term is

$$(18) \quad E_c^{PT2} = \frac{1}{4} \sum_{ij} \sum_{kl} \frac{|\langle ij || kl \rangle|}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l}$$

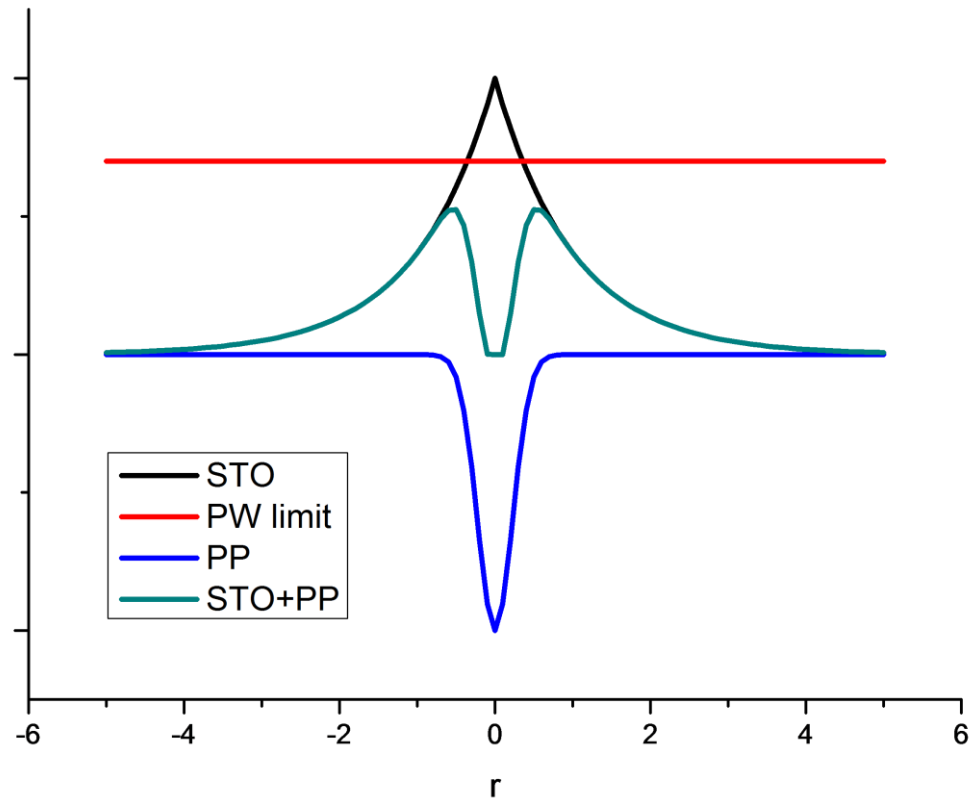
where i, j denote occupied orbitals and k, l denote unoccupied orbitals.

Pseudopotentials

Remember the general form of Slater-type orbitals. If we construct something alike in a plane waves basis, we would in principle need plane waves up to the maximum of the STO.

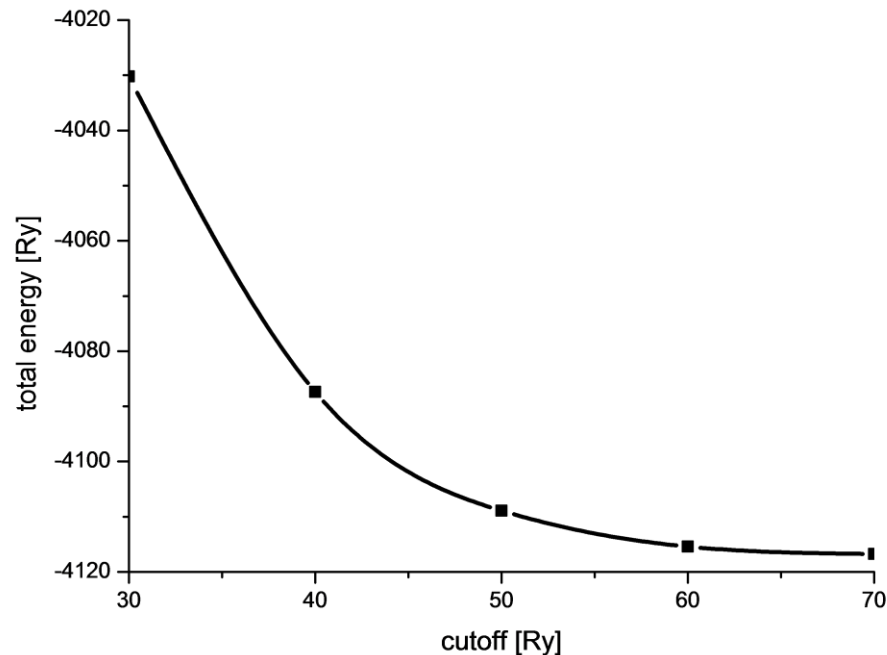


We would obtain artifacts in our description of the density, as we are lacking a part of the electronic description. On the other hand, we do not need an accurate description near the nucleus, as only the bonding region is of interest for chemistry. With a pseudopotential we “tell the electrons” that the core shell is already occupied and yield proper repulsion.



Convergence

To know when our basis is converged is of utmost importance for accurate calculations. The good news is that we only need a single geometry, which does not even have to be converged, and run calculations with different cutoff energies (in the plane waves basis case) and observe when our energy change is below our desired accuracy.



Hands on exercises

1) On the HPC cluster, load the environment for Quantum Espresso
`module load espresso/5.3.0`

2) Prepare your batch script according to

<http://hpc.oit.uci.edu/running-jobs>

Do not forget to load the environment in your batch script!

3) Obtain norm-conserving pseudopotentials from

<http://www.quantum-espresso.org/pseudopotentials/>

4) Modify the example input file so it matches your geometry

5) Run a series of single point runs with different atomic cutoff values

At which cutoff does your calculation converge to less than $1 E_h$?