Center for Molecular Modeling

Computational Materials Physics

Department of Materials Science and Engineering

numerical solution methods

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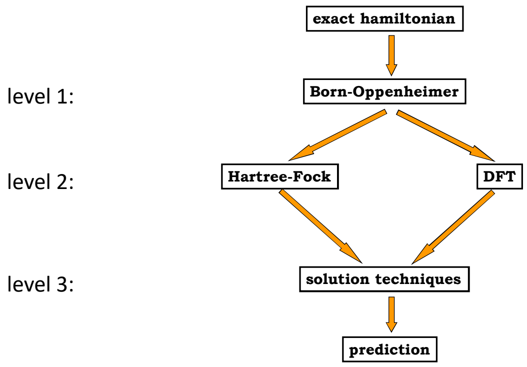
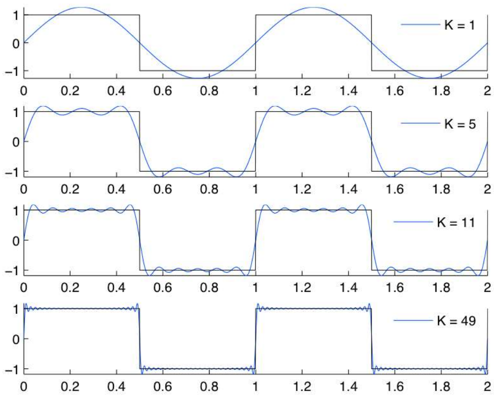
http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

three levels of approximations



numerical solution methods

- ➔ Any numerical method that can solve HF or KS equations
- ➔ Several roads to solution, e.g. solving on a real space grid
- ➔ Most regular applications for solids use **basis set methods**, in combination with reciprocal space.



$\frac{1}{K}\sin(K\pi x)$

(odd terms)

numerical solution methods

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- Several roads to solution, e.g. solving on a real space grid
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$$\phi_i(\vec{r}) = \sum_{\alpha=1}^{\infty} c_\alpha^i \, \chi_\alpha^i(\vec{r})$$

$\phi_i(\vec{r})$: one of the N single-particle functions that will provide the density.

∞: truncation: take enough basis functions for an accurate description, but not more (this limits computer time)

c_α^i: coefficients: this is what we are looking for

$\chi_\alpha^i(\vec{r})$: basis function (known/chosen)

numerical solution methods

Introducing a basis set transforms our problem into matrix algebra :

HC = SCE

H: matrix elements for all basis functions: $\langle \chi_\gamma^i | H_{KS} | \chi_\delta^i \rangle$ can be calculated once and for all

S: overlap matrix: dot products of all basis functions $\langle \chi_\gamma^i | \chi_\delta^i \rangle$ can be calculated once and for all

C: square matrix with all the coefficients we are searching

E: diagonal matrix with all eigenvalues we are searching

numerical solution methods

An important issue is the self-consistent field problem.

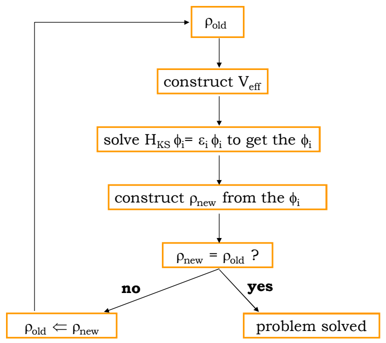
We need to solve the KS-hamiltonian in order to find the ϕ_i (and hence ρ):

$$\begin{aligned}\hat{H}_{KS} &= \hat{T}_0 + \hat{V}_H + \hat{V}_{ext} + \hat{V}_{xc} \\ &= -\frac{\hbar^2}{2m}\vec{\nabla}_i^2 + \frac{e^2}{4\pi\varepsilon_0}\int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,' + \hat{V}_{ext} + \hat{V}_{xc}\end{aligned}$$

But we need to know ρ in order to be able to even write down H_{KS}...!?

➔ an iterative procedure is required (the scf-scheme).

numerical solution methods



numerical solution methods

The choice of the type of basis functions gives its name to
the method (and determines which computer code you can use) :

- localized basis functions: GTO, STO
- plane-wave basis functions (in combination with pseudopotentials)
- augmented plane wave basis functions (LAPW, LMTO, ...)

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