

2. Density functional theory

The widely used and extremely successful density functional theory is based on the exact theorem that the ground state energy is determined only by the density. In particular, the theorem guarantees that all ground state properties are unique functionals of the electron density and that the electron density can be obtained from a Schrödinger equation in an effective potential. Thus the interacting electron system is mapped onto a system of noninteracting electrons in an effective potential. This potential depends on the electron distribution and describes the interactions between the electrons in an effective way.

Density functional theory provides a total energy functional of the form

$$E[n(\vec{r})] = \underbrace{\sum_n \left\langle \phi_n \left| \frac{\hat{p}^2}{2m_e} \right| \phi_n \right\rangle}_{T_s[n(\vec{r})]} + \int d^3r n(\vec{r}) v_{\text{ext}}(\vec{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{4\pi\epsilon_0|\vec{r} - \vec{r}'|} \quad (2.1)$$

T_s is the kinetic energy of the noninteracting reference system, not that of the many body system. It can be written as a functional of the density. $E_{\text{xc}}[n(\vec{r})]$ is the exchange and correlation functional which is not known and has to be approximated.

The minimum principle leads to the Kohn-Sham equations for the one particle orbitals

$$\left[\frac{\hat{p}^2}{2m_e} + v_{\text{eff}}(\vec{r}) - \epsilon_n \right] |\phi_n\rangle = 0 \quad (2.2)$$

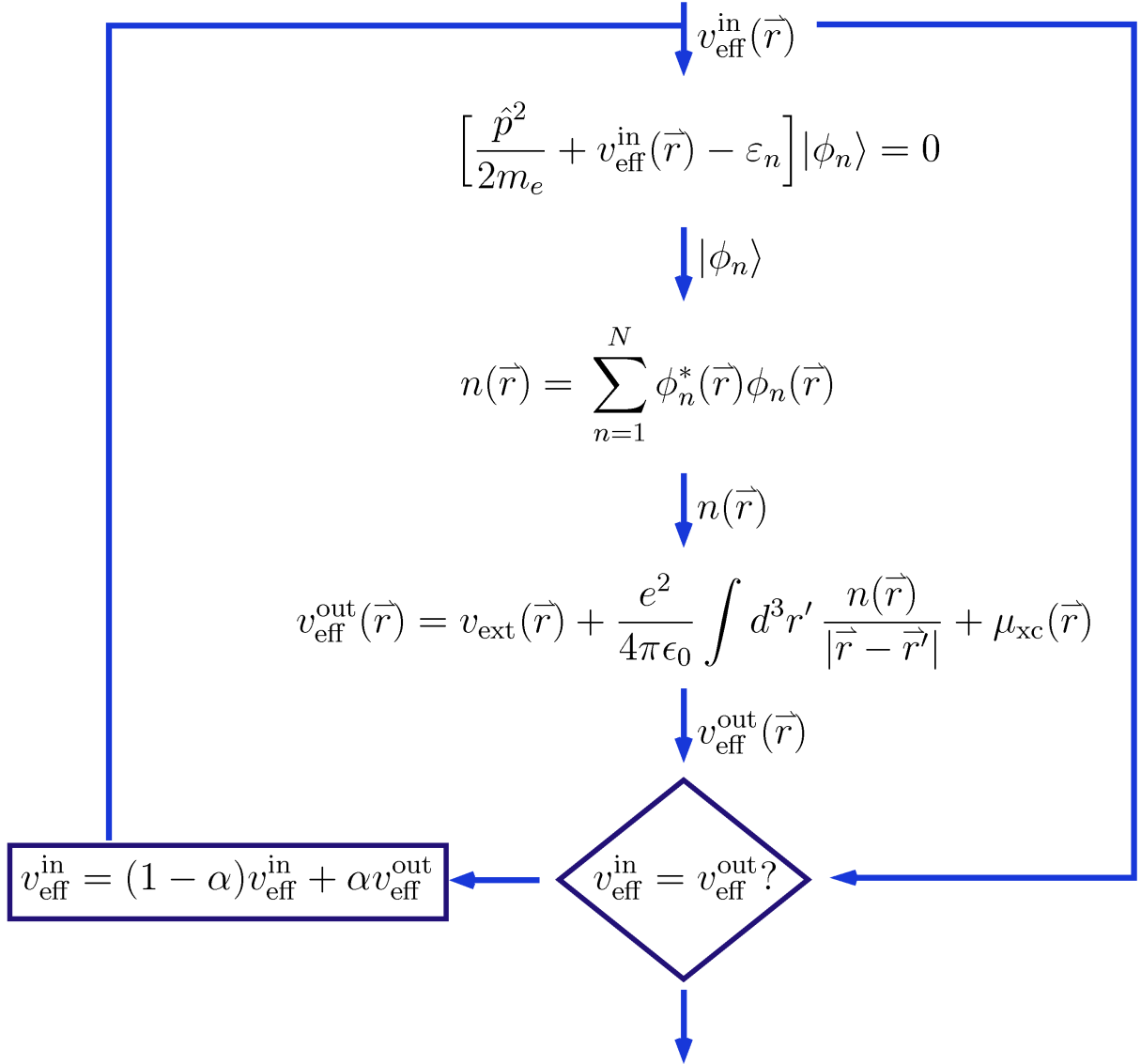
with the effective potential

$$v_{\text{eff}}(\vec{r}) = v_{\text{ext}}(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \underbrace{\frac{\partial E_{\text{xc}}}{\partial n(\vec{r})}}_{\mu_{\text{xc}}(\vec{r})} \quad (2.3)$$

and the density

$$n(\vec{r}) = \sum_{n=1}^N \phi_n^*(\vec{r}) \phi_n(\vec{r}) \quad (2.4)$$

Thus, a conventional selfconsistency cycle to solve this system of equations looks like this:



2.1 Local spin density approximation

In order to describe magnetic systems (called open shell molecules by chemists), one uses the local spin density approximation where the spin dependent density $n(\vec{r}, \sigma)$ is used instead of the total density $n(\vec{r}) =$

$\sum_{\sigma} n(\vec{r}, \sigma)$. This leads to one-particle wave functions with spin up and spin down character and to two effective potentials, one for spin up electrons and one for spin down electrons. The difference between the effective potentials acts like a magnetic field even though its origin is purely electrostatic, *i.e.* exchange and correlation; it is called the **exchange interaction**.

2.2 Interpretation of Kohn-Sham energies

The Kohn-Sham eigenvalues, introduced as Lagrange multipliers, have no direct physical meaning, at least not that of the energies to add or subtract electrons from the interacting manybody system (in analogy to Koopmans theorem for Hartree Fock). The exception is the highest eigenvalue in a finite system which is minus the ionization energy.

Nevertheless, the eigenvalues have a well defined meaning within the theory and can be used to construct physically meaningful quantities. For example, they can be used to develop perturbation expressions for excitation energies, either in the form of a functional or in the form of explicit many-body calculations that use the Kohn-Sham eigenfunctions and eigenvalues as an input.

Within the Kohn-Sham formalism, the meaning of the eigenvalues, known as Janak theorem, is that the eigenvalue is the derivative of the total energy with respect to the occupation of a state:

$$\varepsilon_i = \frac{dE_{\text{total}}}{dn_i} = \int d^3r \frac{dE_{\text{total}}}{dn(\vec{r})} \frac{dn(\vec{r})}{dn_i}. \quad (2.5)$$

2.3 Basis sets

Here we give a very brief overview over the different basis sets that are in use for the solution of the Kohn Sham equations.

1) Plane waves

Plane waves are conceptionally very simple but they are not well adapted to describe strongly varying potentials. Therefore, they are usually used in conjunction with pseudopotentials or their more recent generalization, projector augmented waves (PAW).

2) Augmented functions

Mixed basis sets that treat the region close to the atomic cores differently from the interstitial region are often computationally efficient as they lead to a small (or even minimal) basis. Examples are augmented plane wave

(APW), muffin tin orbital (MTO) and the Korringa-Kohn-Rostoker (KKR) multiple scattering Green function method. Linear augmented function methods were invented to deal with the energy dependence of the basis functions.

3) Localized orbitals

Here, we give slightly more detail about methods using localized orbitals as we will use one of them in this course.

The following expansion theorem is important for the usefulness of analytical basis functions:

$$\chi_{\alpha}(\vec{r} - \vec{R}) = \sum_{\alpha'} B_{\alpha\alpha'}(\vec{R}, \vec{R}') \chi_{\alpha'}(\vec{r} - \vec{R}') \quad (2.6)$$

This is an expansion in terms of basis functions on neighbouring sites. Examples are: Gaussians times polynomials $\mathbf{r}^{\beta} e^{-\alpha r^2}$, Slater type orbitals (STO) $\mathbf{r}^{\beta} e^{-\alpha r}$, Bessel, Neumann and Hankel functions.

a) Gaussians

Gaussians have the nice property that the product of any two Gaussians is a Gaussian:

$$e^{-\alpha|\vec{r}-\vec{R}_A|} e^{-\beta|\vec{r}-\vec{R}_B|} = K_{AB} e^{-\gamma|\vec{r}-\vec{R}_C|}$$

with

$$\gamma = \alpha + \beta, \quad \vec{R}_C = \frac{\alpha \vec{R}_A + \beta \vec{R}_B}{\alpha + \beta}, \quad K_{AB} = \left[\frac{2\alpha\beta}{\pi(\alpha + \beta)} \right]^{3/4} e^{\frac{\alpha\beta}{\gamma} |\vec{R}_A - \vec{R}_B|^2} \quad (2.7)$$

Thus, all multicenter integrals can be done analytically. This is why most molecular calculations and quantum chemistry codes use Gaussians. They are also very suitable for Coulomb integrals which is important for Hartree Fock and hybrid functionals. Many commercial codes based on Gaussians exist.

b) Numerical atomic orbitals

These basis sets rely on the solution of the atomic Schrödinger equation with spherically symmetric potentials; confining potentials are used for compression (*i.e.* for limiting the range of the overlap of the basis functions). An example is the SIESTA code which has rather low precision due to its use of pseudopotentials.

The full potential local orbital (FPLO) minimum basis band structure code

uses the crystal potential decomposition

$$\mathbf{v}(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{R}}+\vec{\boldsymbol{\tau}}, \mathbf{L}} \mathbf{v}_{\vec{\boldsymbol{\tau}}, \mathbf{L}}(|\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\boldsymbol{\tau}}|) \mathbf{Y}_{\mathbf{L}}(\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\boldsymbol{\tau}}) \quad (2.8)$$

where $\mathbf{L} = \mathbf{l}, \mathbf{m}$ and $\mathbf{Y}_{\mathbf{L}}$ are spherical harmonics. Extended states are expanded in localized atomic basis orbitals

$$\langle \vec{\mathbf{r}} | \vec{\mathbf{R}} \vec{\boldsymbol{\tau}} \mathbf{L} \rangle = \phi_{\vec{\boldsymbol{\tau}}}^{\mathbf{l}}(|\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\boldsymbol{\tau}}|) \mathbf{Y}_{\mathbf{L}}(\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\boldsymbol{\tau}}) \quad (2.9)$$

The basis orbitals solve the Schrödinger equation with spherical potential

$$\mathbf{v}^{\text{atom}}(\mathbf{r}) = \frac{1}{4\pi} \int d\Omega \mathbf{v}(\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\boldsymbol{\tau}}) + \mathbf{v}^{\text{confinement}} \quad (2.10)$$

FPLO uses a confinement potential growing as \mathbf{r}^4 ,

$$\mathbf{v}^{\text{confinement}} = \left(\frac{\mathbf{r}}{\mathbf{r}_0} \right)^4 \quad (2.11)$$

but there are several other choices in the literature.