5.2 Density Functional Theory and Local Spin Density Approximation

Density functional theory (DFT) is, originally, an approach for calculating ground state properties via a mapping of the full interacting many-body problem onto an effective single-particle problem. It is based on the observation that the ground state energy of any N-electron system can be written as a functional of the electronic density $\rho(\boldsymbol{r})$ alone (Hohenberg and Kohn, 1964). Following Levy's (1979) proof, we split up the full electronic Hamiltonian (1.2) into internal contributions $\hat{T}+\hat{V}_{ee}$ and the external contribution $\hat{V}_{\text{ext}}$ with $\langle\hat{V}_{\text{ext}}\rangle = \int \mathrm{d}\boldsymbol{r} V_{\text{ext}}(\boldsymbol{r})\rho(\boldsymbol{r}) =: E_{\text{ext}}[\rho]$. Since both the kinetic energy $\hat{T}$ and the Coulomb electron-electron interaction $\hat{V}_{ee}$ have a universal form, the functional

$$F[\rho] := \min_{\psi}\left\{\langle\psi|\hat{T}+\hat{V}_{ee}|\psi\rangle \;\middle|\; \langle\psi|\hat{\rho}(\boldsymbol{r})|\psi\rangle = \rho(\boldsymbol{r})\right\}, \tag{5.1}$$

where $\hat{\rho}(\boldsymbol{r})$ measures the density at site $\boldsymbol{r}$ and ψ denotes a fermion many-body wave function, is indeed universal,[4] i.e., a functional of the density alone. In terms of this functional, the basic theorems of DFT read

$$E[\rho] := F[\rho] + \int \mathrm{d}\boldsymbol{r}\, \hat{V}_{\text{ext}}\, \rho(\boldsymbol{r}) \quad \geq \quad E_{\text{GS}}\,, \tag{5.2}$$

$$F[\rho_{\text{GS}}] + \int \mathrm{d}\boldsymbol{r}\, \hat{V}_{\text{ext}}\, \rho_{\text{GS}}(\boldsymbol{r}) \quad = \quad E_{\text{GS}}\,, \tag{5.3}$$

i.e., the energy functional $E[\rho]$ defined in (5.2) is both an upper bound to the true ground state energy E_{GS} for arbitrary density distribution and coincides with E_{GS} for the true ground state density distribution ρ_{GS}.[5] The first theorem (5.2) follows from an application of the usual variational principle $\langle\psi|\hat{T}+\hat{V}_{ee}+\hat{V}_{\text{ext}}|\psi\rangle \geq E_{\text{GS}}$ to the wave function $\psi_{\min}$ which minimizes the r.h.s. expression in (5.1). On the other hand, each ground state wave function ψ_{GS} also minimizes $\hat{T}+\hat{V}_{ee}$ in (5.1) for fixed ground state density which proves (5.3). If the universal functional $F[\rho]$ was known explicitly and could be evaluated efficiently the ground state energy could be obtained in an arbitrary external potential by minimizing $E[\rho]$ defined in (5.2). Other ground state properties could then be obtained using corresponding (possibly multi-valued) functionals. In practice, however, a controlled computation of $F[\rho]$ along the lines of (5.1) (which would require the solution of jellium models with constrained density) is not possible.

In this situation, it is useful to split up the energy functional differently (Kohn and Sham, 1965),

$$E[\rho] = T_0[\rho] + E_{\text{ext}}[\rho] + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho], \tag{5.4}$$

[4] Note that the proof reproduced here implies universality of the functional $F[\rho]$ only for fixed particle number N. Implicitly, one usually assumes that the thermodynamic limit of the formalism is well defined.

[5] One can show that even the external potential is a functional of the ground state density (Hohenberg and Kohn, 1964). This finding is, however, not used in actual calculations and does not extend to spin-resolved DFT with inclusion of magnetic fields (Capelle and Vignale, 2001).