where $T_0[\rho]$ is not the true kinetic energy (Jones and Gunnarsson, 1989), but the kinetic energy of a noninteracting N-particle system with density distribution $\{\rho(\boldsymbol{r})\}$; E_{ext} was defined above and the Hartree energy is given by

$$E_{\text{Hartree}} = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\,V_{ee}(\boldsymbol{r}-\boldsymbol{r}')\rho(\boldsymbol{r})\rho(\boldsymbol{r}')\,. \tag{5.5}$$

The first three terms in (5.4) can be treated exactly, so that the methodological problem is reduced to finding a good approximation for the exchange-correlation energy for which (5.4) is a defining equation in connection with (5.1), (5.2), and (5.5). This energy functional can be assumed to be much less dependent on details of the density distribution than the full functional which includes very large kinetic energy terms. Given an (approximate) explicit expression for $E_{\text{xc}}[\rho]$, the ground state properties E_{GS} and $\{\rho_{\text{GS}}\}$ of some specified system are then found numerically by a self-consistent solution of the Kohn-Sham equations,

$$\Big[-\frac{\hbar^2}{2m_e}\nabla + V_{ext}(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}'\rho(\boldsymbol{r}')\,V_{\text{ee}}(\boldsymbol{r}-\boldsymbol{r}') + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\boldsymbol{r})}\Big]\,\varphi_i(\boldsymbol{r}) = \epsilon_i\,\varphi_i(\boldsymbol{r})\,, \tag{5.6}$$

i.e., a Schrödinger-like equation for a set of single-particle wave functions $\{\varphi_i\}_{i=1}^N$ which reproduce the density $\rho(\boldsymbol{r}) = \sum_{i=1}^N |\varphi_i(\boldsymbol{r})|^2$. Note that these wave functions and the associated eigenvalues ϵ_i have no direct meaning in the context of the original many-body problem.

In the DFT calculations presented in this work we follow the usual approach of treating the functional E_{xc} in local spin density approximation (LDA or LSDA),[6]

$$E_{\text{xc}}[\rho] \approx \int \mathrm{d}\boldsymbol{r}\;\rho(\boldsymbol{r})\;v_{\text{xc}}^{\text{LDA}}\big(\rho_\uparrow(\boldsymbol{r}),\rho_\downarrow(\boldsymbol{r})\big), \tag{5.7}$$

where the functional dependence of $v_{\text{xc}}^{\text{LDA}}$ is usually taken from parameterizations of solutions of simplified jellium models (von Barth and Hedin, 1972; Gunnarsson and Lundqvist, 1976) or from the QMC solution by Ceperley and Alder (1980) of the jellium model (Vosko and Wilk, 1980; Perdew and Zunger, 1981). Different parameterizations lead to slightly different results, but are all free from adjustable parameters. For exact properties of $E_{\text{xc}}[\rho]$ and possible general approximations beyond LDA see, e.g., the review by Jones and Gunnarsson (1989).

Even though the LDA problem (5.6) with (5.7) is conceptually much simpler than the original many-body problem, its numerically stable solution in the presence of singular ion potentials and for a relatively large number of electrons is still a non-trivial task. For condensed matter problems[7] one may distinguish full-potential from

[6] It is easy to check that the above derivations directly generalize to functionals $F[\rho_\uparrow,\rho_\downarrow]$ and $E[\rho_\uparrow,\rho_\downarrow]$ of the spin density. While in principle the approaches with and without explicit spin resolution are equivalent (cf. footnote 5 on page 249) since $\{\rho_\uparrow\}$ and $\{\rho_\downarrow\}$ are functionals of $\{\rho\}$, it is found that better approximations to the exchange-correlation energy are available in terms of the spin resolved densities.

[7] Specialized methods and, in particular, basis sets for the single-particle wave functions φ_i exist for quantum chemistry problems.