# Appendix B

# Approximations for $E_{xc}$ and their properties

In the following appendix we state all the approximations introduced in Chapter 3 and the respective properties of the exact functional they fulfil. It should serve as a quick reference, for a more detailed discussion of the functionals we refer the reader to Chapter 3.

All approximations presented in this thesis can be written as

$$E_{xc} = -\frac{1}{2}\sum_{j,k=1}^{\infty} f(n_j, n_k) \iint d\mathbf{x}d\mathbf{x}' \frac{\varphi_j^*(\mathbf{x}')\varphi_j(\mathbf{x})\varphi_k^*(\mathbf{x})\varphi_k(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} \tag{B.1}$$

with different functions $f(n_j, n_k)$. For the Hartree-Fock approximation this function is given as

$$f_{HF}(n_j, n_k) = n_j n_k. \tag{B.2}$$

For the Müller functional the dependence is changed into

$$f_M(n_j, n_k) = \sqrt{n_j n_k}, \tag{B.3}$$

while for the Goedecker/Umrigar functional we have to remove the self-interaction which leads to

$$f_{GU}(n_j, n_k) = \sqrt{n_j n_k} - (n_j - n_j^2)\delta_{jk}. \tag{B.4}$$

The three different corrections, BBC1, BBC2, and BBC3, are more complicated due to their distinction between strongly and weakly occupied orbitals. The first correction is given as

$$f_{BBC1}(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & j \neq k \text{ both weakly occupied} \\ \sqrt{n_j n_k} & \text{otherwise.} \end{cases} \tag{B.5}$$

The second correction changes the form of $f$ for two different strongly occupied orbitals

$$f_{BBC2}(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & j \neq k \text{ both weakly occupied} \\ n_j n_k & j \neq k \text{ both strongly occupied} \\ \sqrt{n_j n_k} & \text{otherwise.} \end{cases} \tag{B.6}$$

| Approximation | Fulfilled Properties |
|---|---|
| Hartree-Fock (HF) | (1) (4-6) (8-10) |
| Müller (M,BB) | (1*) (2) (4-6) (8) (10) |
| Goedecker, Umrigar (GU) | (1*) (4-6) (8) |
| BBC1 | (1*) (4-6) (8) (10) |
| BBC2 | (1*) (4-6) (8) (10) |
| BBC3 | (1*) (4-6) (8) |
| Corrected Hartree-Fock (CHF) | (1*) (4-6) (8) (9) (10) |
| Csányi, Goedecker, Arias (CGA) | (1*) (4-6) (8) (10) |

Table B.1: Various approximations in RDMFT and the exact properties which they fulfil. (1*) denotes the fulfilment of hermiticity but the violation of antisymmetry.

Finally, the BBC3 correction reads as

$$f_{BBC3}(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & j \neq k \text{ both weakly occupied} \\ n_j n_k & \begin{cases} j \neq k \text{ both strongly occupied} \\ j(k) \text{ anti}-\text{bonding }, k(j) \text{ not the bonding orbital} \end{cases} \\ n_j^2 & j = k \\ \sqrt{n_j n_k} & \text{otherwise.} \end{cases} \tag{B.7}$$

The approximations from the tensor product expansion, CHF and CGA, are given by

$$f_{CHF}(n_j, n_k) = n_j n_k + \sqrt{n_j(1-n_j)n_k(1-n_k)}, \tag{B.8}$$

$$f_{CGA}(n_j, n_k) = n_j n_k + \sqrt{n_j(2-n_j)n_k(2-n_k)}. \tag{B.9}$$

Table B.1 states which of the properties of the exact functional each of these approximations fulfils. The numbers refer to Section 3.1.