Chapter 3

Approximations for $E_{xc}[\Gamma^{(1)}]$

In the following Chapter we introduce currently known and extensively explored approximations for the exchange-correlation energy functional $E_{xc}[\Gamma^{(1)}]$. Before describing the different approximations, we give an overview over properties of the *exact* exchange-correlation functional in Section 3.1. All approximations are then analyzed with respect to these properties.

Since the interaction energy can be exactly expressed in terms of the diagonal of the two-body density matrix, our goal is to approximate $\Gamma^{(2)}$ in terms of $\Gamma^{(1)}$ or, in most cases, in terms of the occupation numbers n_j and natural orbitals φ_j. In addition, we give the explicit formula for the exchange-correlation energy because all approximations presented in this chapter share the Hartree part. The combined exchange- and correlation energy is notationally less difficult than the correlation part alone. Therefore, despite the fact that E_x can be given exactly, we state the approximation for the total exchange-correlation energy. We start with the Hartree-Fock approximation in Section 3.2 and continue with increasingly ambitious approximations in Sections 3.3 to 3.5.

3.1 Properties of the Exact Exchange-Correlation Energy Functional

An important guidance in the construction of approximate functionals is provided by known properties of the exact functional. Several of these properties are simply consequences of properties of the two-body density matrix. In addition, one can derive properties from the definition of the exchange-correlation energy itself or from applying the RDMFT formalism to specific systems, like the homogeneous electron gas or the hydrogen atom, where the exact solution is known. An extended compilation of properties of the exact E_{xc} was given by Cioslowski, Pernal, and Ziesche in [24].

From Eq. (2.12) we can directly conclude that finding a good approximation for $\Gamma^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$ in terms of $\Gamma^{(1)}$ results in a good approximation for E_{total} or E_{xc}.

As a consequence, the following properties of $\Gamma^{(2)}$ directly lead to restrictions for possible approximations.

(1) The two-body density matrix is antisymmetric

$$\begin{aligned}\Gamma^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') &= -\Gamma^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_2',\mathbf{x}_1') &(3.1)\\ &= -\Gamma^{(2)}(\mathbf{x}_2,\mathbf{x}_1;\mathbf{x}_1',\mathbf{x}_2') &(3.2)\end{aligned}$$

and hermitian

$$\Gamma^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \Gamma^{(2)\dagger}(\mathbf{x}_1',\mathbf{x}_2';\mathbf{x}_1,\mathbf{x}_2). \tag{3.3}$$

(2) The partial sum rule, Eq. (2.14), should be respected when $\Gamma^{(2)}$ is approximated.

(3) The Carlson-Keller theorem [25] states that the non-zero eigenvalues of $\Gamma^{(p)}$ and $\Gamma^{(N-p)}$ are identical. For $N = 3$ this leads to the fact that the non-vanishing eigenvalues of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are identical.

In addition to properties of $\Gamma^{(2)}$, there are also known properties of the exchange-correlation energy itself. Since the exchange energy E_x is known exactly, most of these properties can be formulated in terms of the correlation energy E_c alone.

(4) The correlation energy for idempotent 1-RDMs vanishes, i.e.

$$E_c[\Gamma^{(1)}] = 0, \quad \text{for idempotent } \Gamma^{(1)}. \tag{3.4}$$

(5) Due to a theorem by Lieb [26] the correlation energy is strictly non-positive [27], i.e.

$$E_c[\Gamma^{(1)}] \leq 0. \tag{3.5}$$

Scaling the coordinate with a constant λ, i.e. $\mathbf{x} \to \lambda\mathbf{x} = (\lambda\mathbf{r}, \sigma)$, the one-body density matrix has to preserve its normalization and therefore

$$\Gamma^{(1)}(\mathbf{x};\mathbf{x}') \to \Gamma^{(1)}_\lambda(\mathbf{x};\mathbf{x}') = \lambda^3\Gamma^{(1)}(\lambda\mathbf{x};\lambda\mathbf{x}'). \tag{3.6}$$

(6) The correlation energy shows a very simple scaling behavior [27], namely,

$$E_c[\Gamma^{(1)}_\lambda] = \lambda E_c[\Gamma^{(1)}]. \tag{3.7}$$

The linear scaling is due to the fact that the kinetic energy is treated exactly in RDMFT and does not pollute the exchange-correlation energy. One can show that both the exact interaction energy, Eq. (2.43), as well as the Hartree-exchange part, $E_{\mathrm{H}x} = E_{\mathrm{H}} + E_x$, scale linearly with λ. Hence, the correlation energy, $E_c = E_{\mathrm{int}} - E_{Hx}$, has to scale in the same way.

(7) Due to its definition, Eq. (2.43), as a minimum, the interaction energy must be a convex functional, i.e.

$$E_{\text{int}}[c_1\Gamma_1^{(1)} + c_2\Gamma_2^{(1)}] \leq c_1 E_{\text{int}}[\Gamma_1^{(1)}] + c_2 E_{\text{int}}[\Gamma_2^{(1)}] \tag{3.8}$$

for any two positive constants c_1 and c_2 with $c_1 + c_2 = 1$ and N-representable one-body density matrices $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$.

(8) For the correlation energy, property (7) implies that, for systems where $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$ are localized in distant regions,

$$E_c[c_1\Gamma_1^{(1)} + c_2\Gamma_2^{(1)}] = c_1 E_c[\Gamma_1^{(1)}] + c_2 E_c[\Gamma_2^{(1)}]. \tag{3.9}$$

This property is known as size-consistency.

(9) As an additional property, shown by Yasuda [28], the correlation energy is invariant under an exchange of particles and holes, i.e.

$$E_c[\Gamma^{(1)}] = E_c[\mathbb{1} - \Gamma^{(1)}], \tag{3.10}$$

where $\mathbb{1}$ is a unit matrix of the same rank as $\Gamma^{(1)}$. If the correlation energy is given as a functional of the natural orbitals and occupation numbers this property can be written as

$$E_c[\{n_j\}, \{\varphi_j\}] = E_c[\{n'_j\}, \{\varphi_j\}], \quad \text{with } n_j + n'_j = 1 \quad \forall j\ . \tag{3.11}$$

For orbital functionals the invariance under a certain class of unitary transformations is required. In Chapter 2 we discussed the existence of a one-to-one mapping between $\Gamma^{(1)}$ and the sets of natural orbitals and occupation numbers as long as the latter are non-degenerate, i.e. as long as there are no two natural orbitals with the same eigenvalue. If there is at least one degenerate eigenvalue one can apply a unitary transformation to the orbitals in that subspace without changing the one-body density matrix $\Gamma^{(1)}$. Therefore, the energy functional $E_{Hxc} = E_H + E_{xc}$ being a functional of $\Gamma^{(1)}$ according to Gilbert's theorem, has to be invariant under the very same unitary transformation. The Hartree and exchange parts, both explicit functionals of the one-body density matrix, certainly fulfill this requirement. Hence, the correlation energy also has to be invariant under this unitary transformation. In other words:

(10) The one-body density matrix $\Gamma^{(1)}$ and the exact correlation energy E_c are invariant under the same set of unitary transformations.

(11) For the special case of two-particle closed-shell systems the exact two-body density matrix is known in terms of the natural orbitals [29, 30, 31], namely

$$\Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = 2 \sum_{j,k=1}^{\infty} c_j c_k \varphi_j^*(\mathbf{r}'_1)\varphi_j^*(\mathbf{r}'_2)\varphi_k(\mathbf{r}_1)\varphi_k(\mathbf{r}_2) \tag{3.12}$$

with real coefficients $c_j = \pm\sqrt{n_j/2}$ which satisfy $\sum_j c_j^2 = 1$.

Kollmar and Heß [32] therefore suggested to include the reproduction of this result in the list of desired properties of an approximation for $\Gamma^{(2)}$. However, any approximation in terms of the occupation numbers and natural orbitals looses the information on the phase factor in the coefficients c_j, $n_j = 2c_j^2$, unless the sign is determined correctly for each j. Therefore, all functionals introduced in the next sections violate (3.12), although BBC1 corrects some signs [31] (see Section 3.4).

For the different approximations discussed in the following sections, we state which of the above properties are fulfilled. A compilation of the approximations and obeyed properties can be found in Appendix B.

3.2 Hartree-Fock approximation

A well-known and still simple approximation is the Hartree-Fock approximation [33, 34], where the two-body density matrix is approximated by

$$\Gamma^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \frac{1}{2}\Gamma^{(1)}(\mathbf{x}_1;\mathbf{x}_1')\Gamma^{(1)}(\mathbf{x}_2;\mathbf{x}_2') - \frac{1}{2}\Gamma^{(1)}(\mathbf{x}_1;\mathbf{x}_2')\Gamma^{(1)}(\mathbf{x}_2;\mathbf{x}_1') \; . \quad (3.13)$$

The first term leads to the Hartree energy, Eq. (2.45), while the second yields the approximate exchange-correlation energy functional

$$E_{xc}^{HF} = -\frac{1}{2}\iint d\mathbf{x}d\mathbf{x}' \, \frac{\Gamma^{(1)}(\mathbf{x};\mathbf{x}')\Gamma^{(1)}(\mathbf{x}';\mathbf{x})}{\mid \mathbf{r}-\mathbf{r}' \mid} = E_x[\Gamma^{(1)}] \; , \quad (3.14)$$

which is also known as the Fock term. Comparing Eq. (3.14) with (2.46), the Fock term is identical, as a functional of $\Gamma^{(1)}$, to the exchange energy of RDMFT. However, we emphasize that in a traditional HF calculation the 1-RDMs are restricted to occupation numbers identical to either zero or one. If we allow for non-idempotent $\Gamma^{(1)}$ in Eqs. (3.13) and (3.14) and do not add any correlation contribution, one can show that the minimum is actually obtained for an idempotent $\Gamma^{(1)}$ [26].

Concerning the properties described in the previous section, the two-body density matrix (3.13) is antisymmetric and hermitian. The partial sum rule, however, is violated unless the one-body density matrix is idempotent, hence, it is fulfilled at the solution but not during the minimization process. Since $E_c \equiv 0$ properties (4-6) and (8-10) are trivially fulfilled.

3.3 The Müller functional with and without self-interaction

Most of the functionals currently in use can be traced back to an approximation by Müller [35] who suggested to approximate the two particle density matrix $\Gamma^{(2)}$,

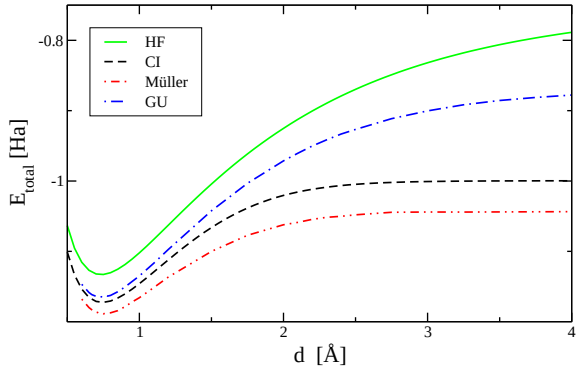

Figure 3.1: The ground-state energy of H_2 as a function of the distance between the two nuclei for Hartree-Fock (HF), the Müller and the Goedecker/Umrigar (GU) functionals. For comparison we also give the configuration interaction (CI) result. All results are obtained using the cc-pVTZ basis set [36].

using three parameters β_1, β_2, and p, as

$$\begin{aligned}\Gamma^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2',\beta_1,\beta_2,p) &= \beta_1\Gamma^{(1)}(\mathbf{x}_1;\mathbf{x}_1')\Gamma^{(1)}(\mathbf{x}_2;\mathbf{x}_2') \\ &+ \beta_2\sum_{j,k} n_j^{1/2+p} n_k^{1/2-p}\varphi_j^*(\mathbf{x}_2')\varphi_j(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_1')\varphi_k(\mathbf{x}_2).\end{aligned} \tag{3.15}$$

The parameters β_1 and β_2 are chosen such that the Hartree-Fock case is recovered whenever all occupation numbers are either zero or one, i.e.

$$\beta_1 = \frac{1}{2}, \quad \beta_2 = -\frac{1}{2}. \tag{3.16}$$

As was shown by Müller, the probability of finding two particles at the same position, $n_2(\mathbf{r}\sigma,\mathbf{r}\sigma') \propto \Gamma^{(2)}(\mathbf{x},\mathbf{x}';\mathbf{x},\mathbf{x}')\delta(\mathbf{r}-\mathbf{r}')$, is negative if at least one occupation number is fractional. Of course, it should be positive for two particles with different spins, $\sigma \neq \sigma'$, and exactly zero for $\sigma = \sigma'$. This catastrophe is minimized by choosing $p = 0$ in the sense that the absolute value of the still negative probability is minimized. Therefore, the functional proposed by Müller reads

$$\begin{aligned}\Gamma_M^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') &= \frac{1}{2}\sum_{j,k=1}^{\infty} n_j n_k\, \varphi_j^*(\mathbf{x}_1')\varphi_j(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_2')\varphi_k(\mathbf{x}_2) \\ &\quad -\sqrt{n_j n_k}\, \varphi_j^*(\mathbf{x}_2')\varphi_j(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_1')\varphi_k(\mathbf{x}_2).\end{aligned} \tag{3.17}$$

Buijse and Baerends arrived at the same functional by approximating the exchange-correlation hole as the square of a so-called hole amplitude [37]. In DFT the quality of a functional is often measured by the quality of the approximation of the exchange-correlation hole. Therefore, Buijse's and Baerends' derivation sheds some light on the reason for the great success of Müller's functional. Due to this alternative

derivation, Müller's functional is often called Buijse/Baerends (BB) functional in the literature. The exchange-correlation energy for the Müller or BB functional is given by

$$E_{xc}^{M} = -\frac{1}{2}\sum_{j,k=1}^{\infty}\sqrt{n_j n_k}\iint d\mathbf{x}d\mathbf{x}'\,\frac{\varphi_j(\mathbf{x})\varphi_j^*(\mathbf{x}')\varphi_k(\mathbf{x}')\varphi_k^*(\mathbf{x})}{\mid \mathbf{r}-\mathbf{r}' \mid}. \tag{3.18}$$

Due to the appearance of the square root in the exchange-correlation energy and the fractional nature of the occupation numbers the electron self-interaction, present in both the Hartree and the exchange-correlation energies, is only partially cancelled. Therefore, Goedecker and Umrigar [16] introduced a small but important variation of Müller's functional by explicitly removing all terms with $j = k$ from the summation. The resulting two-body density matrix is given by

$$\begin{aligned}\Gamma_{GU}^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') &= \frac{1}{2}\sum_{\substack{j,k=1\\ j\neq k}}^{\infty} n_j n_k\,\varphi_j^*(\mathbf{x}_1')\varphi_j(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_2')\varphi_k(\mathbf{x}_2) \\ &\quad -\sqrt{n_j n_k}\,\varphi_j^*(\mathbf{x}_2')\varphi_j(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_1')\varphi_k(\mathbf{x}_2).\end{aligned} \tag{3.19}$$

We emphasize that this procedure leads to a functional without *orbital* self-interaction, i.e. any interaction of orbital j with itself is excluded. However, because the distribution of a specific electron over several natural orbitals (fractional occupation numbers) is unknown the exclusion of the complete self-interaction of the electron is not possible. The exclusion of orbital self-interaction is the best one can do. In practical applications, however, the occupation numbers are often close to either zero or one such that the orbital self-interaction resembles a large part of the total self-interaction.

The exchange-correlation energy for the Goedecker/Umrigar approximation explicitly reads

$$\begin{aligned}E_{xc}^{GU} &= -\frac{1}{2}\sum_{\substack{j,k=1\\ j\neq k}}^{\infty}\sqrt{n_j n_k}\iint d\mathbf{x}d\mathbf{x}'\,\frac{\varphi_j(\mathbf{x})\varphi_j^*(\mathbf{x}')\varphi_k(\mathbf{x}')\varphi_k^*(\mathbf{x})}{\mid \mathbf{r}-\mathbf{r}' \mid} \\ &\quad -\frac{1}{2}\sum_{j=1}^{\infty} n_j^2\iint d\mathbf{x}d\mathbf{x}'\,\frac{\mid \varphi_j(\mathbf{x})\mid^2 \mid \varphi_j(\mathbf{x}')\mid^2}{\mid \mathbf{r}-\mathbf{r}' \mid}\,,\end{aligned} \tag{3.20}$$

where we have removed the $j = k$ term from the first sum and the second term removes the self-interaction of the Hartree energy.

As one can see in Fig. 3.1, the dissociation of H_2 is best described by the Müller functional. It reproduces the convergence to a constant energy although it still misses the correct asymptotic value of twice the energy of the hydrogen atom. At the equilibrium position, however, the GU performs better than the Müller functional. For other small molecules it was found that the exclusion of self-interaction also improves the dissociation results [38, 31]. A detailed analysis of the performance of

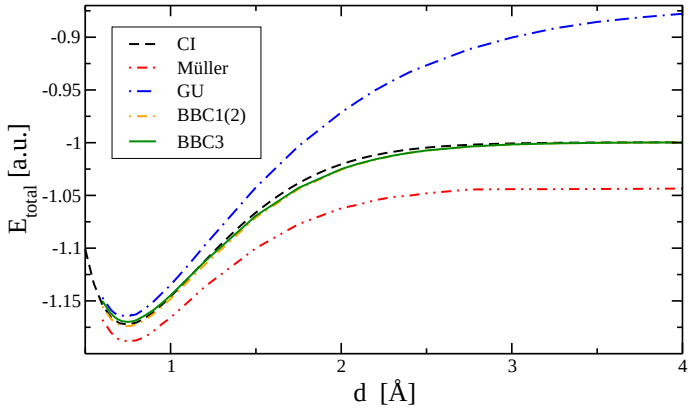

Figure 3.2: The ground-state energy of H_2 as a function of the distance of the two hydrogen atoms for the original Müller functional, the GU correction and the three corrections BBC1, BBC2, and BBC3. For comparison we also give the CI result. The cc-pVTZ basis set [36] is used in all calculations.

different functionals for the dissociation of several small molecules can be found in [38].

The removal of the self-interaction leads to the violation of several exact properties. Contrary to the original Müller functional the GU approximation violates the partial sum rule and also property (10). Both the Müller as well as the GU functional satisfy the hermiticity but not the anti-symmetry of the two-body density matrix. Also properties (4-6), and (8) are obeyed in both cases.

3.4 Corrections to the Müller functional

Recently, Baerends and co-workers introduced a series of improvements to the original Müller/BB functional, which they baptized BBC1, BBC2, and BBC3 [31]. They wanted mainly to correct for the over-binding of the original functional which consistently overestimates the absolute value of the total energy in the dissociation of H_2 (see Fig. 3.1). Hence, the corrections increase the repulsion between the electrons guided by physical arguments. They distinguish between strongly and weakly occupied orbitals. All orbitals with occupation number equal to 1 in a Hartree-Fock treatment of the system are strongly occupied, all orbitals with occupation number zero are weakly occupied. In the RDMFT treatment these orbitals are then modified and have, in most cases, occupation numbers close to one or zero, respectively.

Starting from the approximation (3.17), for BBC1 the sign for the exchange-correlation part for all products between two different weakly occupied orbitals is changed. The approximation then reads

$$\Gamma^{(1)}_{BBC1}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) = \Gamma^{(1)}_{M}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) + \Gamma^{(1)}_{C1}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) \tag{3.21}$$

with

$$\Gamma^{(1)}_{C1}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) = \sum_{\substack{j\neq k\\ j,k>N}} \sqrt{n_j n_k}\varphi^*_j(\mathbf{x}'_2)\varphi_j(\mathbf{x}_1)\varphi^*_k(\mathbf{x}'_1)\varphi_k(\mathbf{x}_2). \tag{3.22}$$

This approximation improves especially the results for two-electron closed-shell systems, where the product of two weakly occupied orbitals enters $\Gamma^{(2)}$ with a positive sign [31].

BBC2 restores the exchange-only term for terms containing two different strongly occupied orbitals, i.e.

$$\Gamma^{(1)}_{BBC2}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) = \Gamma^{(1)}_{BBC1}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) + \Gamma^{(1)}_{C2}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) \tag{3.23}$$

with

$$\Gamma^{(1)}_{C2}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) = \frac{1}{2}\sum_{\substack{j\neq k\\ j,k\leq N}} \left(\sqrt{n_j n_k} - n_j n_k\right)\varphi^*_j(\mathbf{x}'_2)\varphi_j(\mathbf{x}_1)\varphi^*_k(\mathbf{x}'_1)\varphi_k(\mathbf{x}_2). \tag{3.24}$$

This correction can be physically motivated because correlation mainly occurs between strongly and weakly occupied orbitals while two strongly occupied orbitals interact mainly via exchange.

BBC3 mostly concerns the bonding and anti-bonding natural orbitals. Firstly, the self-interaction correction, as in the GU functional, is applied to all natural orbitals except the bonding and anti-bonding ones. Secondly, the correction C2 is applied to the interaction of the anti-bonding orbitals (one for each spin) with all strongly occupied natural orbitals except the corresponding bonding orbitals. Hence, if we denote the anti-bonding orbitals with indices r and r' and the corresponding bonding orbitals with N and $N-1$ we obtain

$$\Gamma^{(1)}_{BBC3}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) = \Gamma^{(1)}_{BBC2}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) + \Gamma^{(1)}_{C3}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) \tag{3.25}$$

with

$$\begin{aligned}
\Gamma^{(1)}_{C3}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) &= \frac{1}{2}\sum_{j<N}\left(\sqrt{n_j n_r} - n_j n_r\right)\varphi^*_j(\mathbf{x}'_2)\varphi_j(\mathbf{x}_1)\varphi^*_r(\mathbf{x}'_1)\varphi_r(\mathbf{x}_2) + c.c.\\
&+ \frac{1}{2}\sum_{j<N-1}\left(\sqrt{n_j n_{r'}} - n_j n_{r'}\right)\varphi^*_j(\mathbf{x}'_2)\varphi_j(\mathbf{x}_1)\varphi^*_{r'}(\mathbf{x}'_1)\varphi_{r'}(\mathbf{x}_2) + c.c.\\
&+ \frac{1}{2}\sum_{\substack{j\neq N,N-1\\ j\neq r,r'}}\left(n_j - n_j^2\right)\varphi^*_j(\mathbf{x}'_2)\varphi_j(\mathbf{x}_1)\varphi^*_j(\mathbf{x}'_1)\varphi_j(\mathbf{x}_2)\,.
\end{aligned} \tag{3.26}$$

The first two sums are the correction C2 applied to the anti-bonding states and the last term removes the self-interaction of all orbitals which are neither bonding nor anti-bonding.

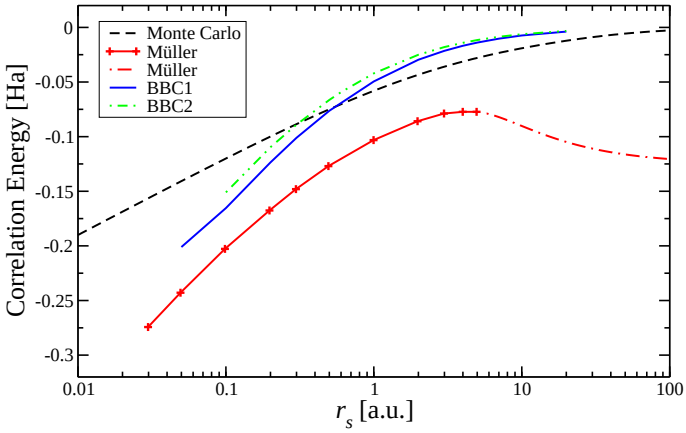

Figure 3.3: The correlation energy of the homogeneous electron gas calculated from the original Müller functional as well as the BBC1 and BBC2 corrections. For comparison the Monte-Carlo results of Ortiz and Ballone [4, 40] are also given. For the Müller functional analytical results are given above $r_s \approx 5.77$ [41] and numerical results below this value [42]. ($r_s = (3n/4\pi)^{1/3}$)

The distinction between bonding and anti-bonding orbitals, of course, is somewhat problematic for extended systems. Also, one can show that the self-interaction is proportional to the inverse of the volume for periodic systems and hence vanishes for infinite systems. Hence, for solids, the correction C3 coincides with C2. The bonding/anti-bonding pair is treated differently from the rest of the orbitals because it is this pair which is mainly responsible for the proper dissociation of a bond. Removing the self-interactions for this pair results in a distortion of the energy curve in the dissociation region [31]. Fig. 3.2 shows the success of the three different corrections for the H_2 dissociation compared to the original Müller functional, the Goedecker/Umrigar approximation and the quasi-exact CI result. As one can see, BBC1 and BBC2 coincide for a 2 electron closed-shell system since there are no two different strongly occupied natural orbitals in that case. All three approximations improve the dissociation curve significantly lying almost on top of the CI result. This is not too surprising since the corrections aimed at improving exactly this dissociation curve. However, applications to other small systems show a large improvement of the dissociation curves as well [31]. More surprisingly, the corrections also result in a significant improvement of the correlation energy of the homogeneous electron gas (HEG) [39], as shown in Fig. 3.3. However, as discussed in [39], there are other properties of the HEG which are not properly reproduced.

Regarding the properties of the exact functional all three corrections still lead to a hermitian two-body density matrix which is however not anti-symmetric. The partial sum rule is violated in all three cases. The three approximations fulfill properties (4-6), and (8), but only BBC1 and BBC2 satisfy (10). BBC3 violates (10) due to the removal of the self-interaction terms.

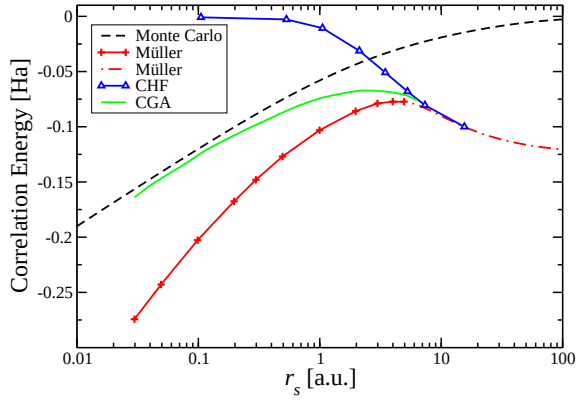

Figure 3.4: The correlation energy of the homogeneous electron gas for the CHF and CGA functionals as a function of $r_s = (3n/4\pi)^{1/3}$. For comparison the original Müller functional [41, 42] and the fit to the Monte-Carlo data of Ortiz and Ballone [4, 40] are given.

3.5 Functionals from tensor product expansion

While all functionals presented so far have been constructed by optimizing their performance for finite systems, Csányi, Goedecker, and Arias were concerned with the homogeneous electron gas (HEG). As we have seen in Fig. 3.3, the Müller/BB functional does not give satisfactory results for the HEG [39, 41]. The results are improved by the BBC1 and BBC2 corrections but important features of the exact solution are still not captured [39].

Csányi and Arias [42] started from a tensor product expansion of the two-body density matrix

$$\Gamma^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \frac{1}{2}\left(\Gamma^{(1)}(\mathbf{x}_1;\mathbf{x}_1')\Gamma^{(1)}(\mathbf{x}_2;\mathbf{x}_2') + \sum_j u_j \otimes v_j\right), \tag{3.27}$$

where $\otimes$ denotes the tensor product

$$[u \otimes v]\,(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = u(\mathbf{x}_1;\mathbf{x}_2')v(\mathbf{x}_2;\mathbf{x}_1'). \tag{3.28}$$

u_j and v_j represent functions of two variables and the sum in Eq. (3.27) can in principle be infinite. One possible approximation in this framework coincides with the Müller/BB functional but is called corrected Hartree (CH) in [42]. A second approximation, corrected Hartree-Fock (CHF), is given by

$$\begin{aligned}\Gamma^{(2)}_{CHF}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = {}& \frac{1}{2}\Gamma^{(1)}(\mathbf{x}_1;\mathbf{x}_1')\Gamma^{(1)}(\mathbf{x}_2;\mathbf{x}_2') \\ & -\frac{1}{2}\sum_{j,k=1}^{\infty}\left(n_j n_k + \sqrt{n_j(1-n_j)n_k(1-n_k)}\right)\varphi_j^*(\mathbf{x}_2')\varphi_j(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_1')\varphi_k(\mathbf{x}_2).\end{aligned} \tag{3.29}$$

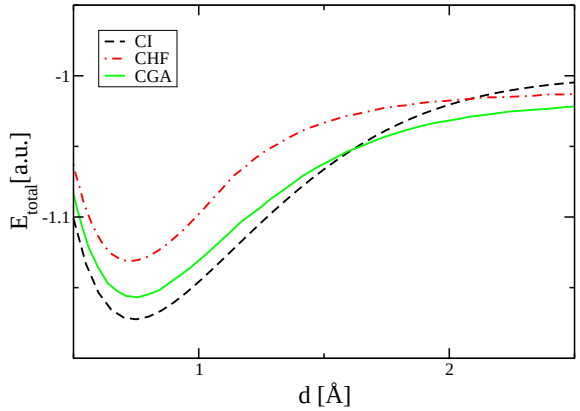

Figure 3.5: The ground-state energy of H_2 as a function of the distance of the two nuclei for the CHF and CGA functionals.

When applied to the HEG the Müller/BB functional overestimates the absolute value of the correlation energy for all r_s while the CHF undercorrelates for small r_s and overcorrelates for $r_s > 6$ [42], as can be seen in Fig. 3.4. This finding prompted Csányi, Goedecker, and Arias to suggest a somewhat intermediate approximation [43]

$$\Gamma^{(2)}_{CGA}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \frac{1}{2}\Gamma^{(1)}(\mathbf{x}_1;\mathbf{x}_1')\Gamma^{(1)}(\mathbf{x}_2;\mathbf{x}_2') \tag{3.30}$$
$$-\frac{1}{4}\sum_{j,k=1}^{\infty}\left(n_j n_k + \sqrt{n_j(2-n_j)n_k(2-n_k)}\right)\varphi_j^*(\mathbf{x}_2')\varphi_j(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_1')\varphi_k(\mathbf{x}_2)$$

which improves the results dramatically for very small r_s and still performs quite well at metallic densities ($1 < r_s < 6$), see Fig. 3.4 [43].

The exchange-correlation energies for the two new functionals read

$$E_{xc}^{CHF} = -\frac{1}{2}\sum_{j,k}\left(n_j n_k + \sqrt{n_j(1-n_j)n_k(1-n_k)}\right) \iint d\mathbf{x}d\mathbf{x}' \frac{\varphi_j^*(\mathbf{x}')\varphi_j(\mathbf{x})\varphi_k^*(\mathbf{x})\varphi_k(\mathbf{x}')}{\mid \mathbf{r}-\mathbf{r}' \mid}, \tag{3.31}$$

$$E_{xc}^{CGA} = -\frac{1}{4}\sum_{j,k}\left(n_j n_k + \sqrt{n_j(2-n_j)n_k(2-n_k)}\right) \iint d\mathbf{x}d\mathbf{x}' \frac{\varphi_j^*(\mathbf{x}')\varphi_j(\mathbf{x})\varphi_k^*(\mathbf{x})\varphi_k(\mathbf{x}')}{\mid \mathbf{r}-\mathbf{r}' \mid}. \tag{3.32}$$

Applying the two functionals to finite systems [38] shows remarkably good predictions if one keeps in mind that they were designed for the homogeneous electron

gas. Fig. 3.5 shows the dissociation of H_2 calculated from the CHF and CGA functionals compared to the CI calculation.

Both the CHF and the CGA approximations lead to a hermitian two-body density matrix which is, however, not anti-symmetric and violates the partial sum rule. The correlation energy vanishes for idempotent one-body density matrices, it is strictly non-positive, and has the correct scaling, i.e. properties (4-6) are obeyed. Also the size consistency property (8) and the invariance property (10) are satisfied for both functionals. CHF is the only approximation presented here which is invariant under particle-hole exchange, i.e. it fulfills property (9). (HF also fulfills it but only because correlation is neglected completely.)

In addition to the two specific functionals discussed here, Csányi's and Arias' tensor product expansion (3.27) also provides an idea for the systematic improvement of functionals in the future.