

# Static correlated functionals for reduced density matrix functional theory<sup>\*</sup>

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**Abstract.** Based on recent progress on fermionic exchange symmetry we propose a way to develop new functionals for reduced density matrix functional theory. For some settings with an odd number of electrons, by assuming saturation of the inequalities stemming from the generalized Pauli principle, the many-body wave-function can be written explicitly in terms of the natural occupation numbers and the natural orbitals. This leads to an expression for the two-particle reduced density matrix and therefore for the correlation energy functional. This functional is tested for a three-electron Hubbard model where it shows excellent performance both in the weak and strong correlation regimes.

## 1 Introduction

The quantum many-body problem (the problem of computing the ground-state features of a system of many interacting electrons) is at the very heart of quantum chemistry and condensed matter physics. The complexity of such a problem is so striking that its simplification is the main goal of electronic modeling. Hartree-Fock (HF), density-functional (DFT) and reduced-density-matrix functional (RDMFT) theories attempt to achieve this goal by using, respectively, one Slater determinant, the electron density or the one-body reduced density matrix as the basic variable.

The one-body reduced density matrix is obtained by tracing out  $N - 1$  particles, and reads, for a  $N$ -fermion quantum state  $|\Psi\rangle$ ,

$$\hat{\gamma} \equiv N \text{Tr}_{N-1} [|\Psi\rangle\langle\Psi|]. \quad (1)$$

In the quantum-chemistry jargon, the *natural occupation numbers* are the eigenvalues (organized in decreasing order  $n_1 \geq n_2 \geq \dots$ ) and the *natural spin-orbitals* are the eigenvectors  $\{|\varphi_i\rangle\}$  of  $\hat{\gamma}$ . The theoretical framework of RDMFT is based on a variational principle stating that the ground-state energy of a fermionic system can be obtained by minimizing some energy functional on the set of  $N$ -representable one-body reduced density matrices [1,2]. The (ensemble)  $N$ -representability conditions of  $\hat{\gamma}$  (the famous Pauli exclusion principle) depend on its

eigenvalues only, reading simply [3]:

$$0 \leq n_i \leq 1 \quad \text{and} \quad \sum_i n_i = N, \quad (2)$$

where  $N$  is the number of electrons of the system under consideration.

For pure quantum systems the occupation numbers meet also additional requirements with tremendous physical implications [4–13]. This so-called *generalized* Pauli exclusion principle provides a (large) set of constraints on the natural occupation numbers. These are much more stringent than the ordinary Pauli principle, and take the form of independent linear inequalities, namely,

$$\mathcal{D}_j(\vec{n}) \equiv \kappa_j^0 + \sum_{i=1}^d \kappa_j^i n_i \geq 0, \quad (3)$$

where  $d$  is the dimension of the one-particle Hilbert space. The coefficients  $\kappa_j^i$  are integers.

In RDMFT the  $N$ -representability conditions (2) can be easily taken into account. Yet, the exact correlation functional is, by and large, not available and therefore the predicted RDMFT energy can be either lower or higher than the exact ground-state energy. An exception of this is the Müller functional [14], for it is believed that it constitutes an universal lower bound for quantum mechanics. So far, this statement has been rigorously proved only for two-electron systems [15,16]. To write a correlation functional one often starts by engineering an approximate expression for the two-body reduced density matrix

$$\hat{\Gamma} \equiv \binom{N}{2} \text{Tr}_{N-2} [|\Psi\rangle\langle\Psi|]. \quad (4)$$

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This is normally accomplished by writing  $\hat{\Gamma}$  in terms of the exchange-correlation hole, defined by the following relation:

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2) \equiv \frac{1}{2}\rho(\mathbf{x}_1)[\rho(\mathbf{x}_2) - \rho_{\text{xc}}^{\text{hole}}(\mathbf{x}_1, \mathbf{x}_2)]. \quad (5)$$

We used the customary compact notation  $\mathbf{x} \equiv (\mathbf{r}, \varsigma)$ . The electronic density, the main object in DFT, is of course the diagonal of the one-body reduced density matrix. The Müller (also called Buijse-Baerends) functional describes the exchange-correlation hole as the square of a *hole amplitude* [17,18], reading  $|\gamma^{1/2}(\mathbf{x}_1, \mathbf{x}_2)/\sqrt{\rho(\mathbf{x}_1)}|^2$ . The functional then reads:

$$\Gamma_{\text{BB}}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2}\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \frac{1}{2}\sum_{ij}\sqrt{n_i n_j}\chi_{ij}(\mathbf{x}_1)\chi_{ji}(\mathbf{x}_2), \quad (6)$$

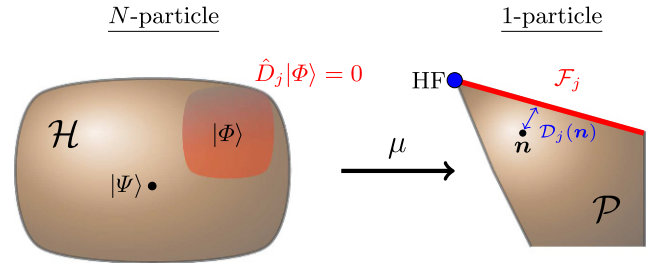
where  $\chi_{ij}(\mathbf{x}) \equiv \varphi_i(\mathbf{x})\varphi_j(\mathbf{x})$ , assuming from now on real natural orbitals. Further developments in RDMFT were inspired by this functional. Chief among them, the Goedecker-Umrigar functional is an extension of (6), excluding self-interactions in the exchange-correlation and the direct Coulomb terms [19]. Another example is the “power” functional [20], proposed by Hardy Gross and collaborators, that replaces the square root by a general fractional power. Cioslowski and Pernal [21] and Csányi et al. [22] have all proposed different generalizations based on a distinction between strongly and weakly occupied natural orbitals. A different perspective is given by the study of the cumulant part of  $\Gamma$  (i.e.,  $\Gamma - \frac{1}{2}\gamma \wedge \gamma$ ) under some of its known representability conditions [23,24].

In all these functionals, the exchange-correlation term of the energy functional can be cast into the simple form

$$\mathcal{E}_{\text{xc}}[\gamma] = -\frac{1}{2}\sum_{ij\varsigma}\int d^3r d^3r' f_{ij}^{\varsigma}(\vec{n})\frac{\chi_{ij}(\mathbf{r}, \varsigma)\chi_{ji}(\mathbf{r}', \varsigma)}{|\mathbf{r} - \mathbf{r}'|}. \quad (7)$$

Almost all functionals fare quite well in benchmarking tests, yielding errors for the correlation at least an order of magnitude [25] smaller than B3LYP [26], perhaps the most used DFT functional. RDMFT has also succeeded in predicting more accurate gaps of conventional semiconductors than semi-local DFT does and has demonstrated insulating behavior for Mott-type insulators [27,28], another major result stemming from the research group of Hardy Gross.

Unfortunately, most RDMFT functionals were designed having in mind singlet ground states. Furthermore, at zero temperature one can argue that the representability conditions (2) are unsatisfactory, and that different results could be obtained if more (pure-representability) constraints were imposed [29]. This is especially true in the framework of finite basis sets [30]. For this reason, the enforcement of additional constraints can only improve the total energy [31,32]. Based on recent progress on fermionic exchange symmetry and, in particular, on the generalization of Pauli exclusion principle, our aim in



**Fig. 1.** Schematic view of the reconstruction of  $N$ -particle states based on one-particle information only.  $\mathcal{H}$  is the fermionic Hilbert space of wave functions of  $N$  fermions.  $\mathcal{P}$  is the polytope of pure-representable one-particle states. The Hartree-Fock point is represented as a dot on one of vertexes of the polytope. The arrow goes then from  $\mathcal{H}$  to  $\mathcal{P}$  ( $\mu: \mathcal{H} \rightarrow \mathcal{P}$ ). The image of the state  $|\Psi\rangle$  is then  $\mu(|\Psi\rangle) = \vec{n}$ . The spectra lying on one of the facets  $\mathcal{F}_j$  (i.e. the sets of occupation numbers with  $\mathcal{D}_j(\vec{n}) = 0$ ) correspond to states satisfying  $\hat{D}_j|\Phi\rangle = 0$ .

this paper is to introduce functionals motivated by pure representability considerations.

The paper is organized as follows: Section 2 discusses the recent solution of the pure  $N$ -representability solution of the one-body reduced density matrix, and some of its remarkable physical implications. Section 3 presents two RDMFT functionals for the Borland–Dennis state, i.e. the pinned state for three fermions in a six dimensional one-particle Hilbert space (say, three fermions in six modes). In Section 4, we generalize our results for a system with three active (valence) electrons and an arbitrary number of modes. In Section 5, we test the functionals for Hubbard models and discuss the numerical quality of the results. The paper ends with a conclusion and two appendixes.

## 2 Pure representability conditions and stability of the selection rules

For pure systems, the fermionic natural occupation numbers satisfy sets of generalized Pauli constraints of the form (3). Together with the non-increasing ordering of these numbers, these constraints define a polytope  $\mathcal{P}_{N,d}$  in  $\mathbb{R}^d$  for the occupation numbers compatible with pure states of  $N$  fermions in an one-particle Hilbert space of dimension  $d$  [33]. The Hartree-Fock point, i.e.  $|\varphi_1, \dots, \varphi_N\rangle$ , lies in one of the vertexes of the polytope. The asymptotic properties of such polytopes are actively being researched [34]. For a recent review of the generalized Pauli exclusion principle and its growing impact in quantum chemistry and condensed matter physics we refer to [35].

The generalized Pauli principle is particularly relevant whenever the set of natural occupation numbers of a given fermionic state “saturates” a generalized Pauli constraint, i.e., the equality holds in equation (3). This so-called *pinning* effect is connected with a remarkable simplification of the global structure of the many-body wave function. In fact, any  $N$ -fermion state  $|\Phi\rangle$ , with

occupation numbers  $\vec{n} = (n_1, n_2, \dots)$ , compatible with the pinning condition  $\mathcal{D}_j(\vec{n}) = 0$ , belongs to the null eigenspace of the operator

$$\hat{D}_j \equiv \kappa_j^0 + \sum_i \kappa_j^i \hat{n}_i, \quad (8)$$

where  $\hat{n}_i$  denotes the number operator of the natural orbital  $|\varphi_i\rangle$  of  $|\Phi\rangle$ . For non-degenerate natural occupation numbers, the condition  $\hat{D}_j|\Phi\rangle = 0$  amounts to a simple selection rule for the configurations present in the expansion of the quantum state. Indeed, the configuration interaction expansion of a *pinned* wave function

$$|\Phi\rangle = \sum_{(i_1, \dots, i_N) \in \mathcal{I}_j} c_{i_1, \dots, i_N} |\varphi_{i_1}, \dots, \varphi_{i_N}\rangle, \quad (9)$$

where  $|\varphi_{i_1}, \dots, \varphi_{i_N}\rangle$  denotes a normalized Slater determinant, is restricted to configurations belonging to  $\mathcal{I}_j$ , namely, the set of determinants fulfilling the selection rule

$$\hat{D}_j|\varphi_{i_1}, \dots, \varphi_{i_N}\rangle = 0. \quad (10)$$

For a schematic view of the wave-function reconstruction see Figure 1. To give an example of these representability constraints, the rank-six approximation (i.e., six modes or six natural spin-orbitals) for the three-electron system (the so-called Borland–Dennis *setting*) is completely characterized by four such constraints [36], namely, the equalities  $n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1$  and the inequality:

$$\mathcal{D}_{\text{BD}}(\vec{n}) = 2 - n_1 - n_2 - n_4 \geq 0. \quad (11)$$

This latter inequality together with the non-increasing ordering of the natural occupation numbers defines a polytope in  $\mathbb{R}^6$ , called the “Borland–Dennis Paulitope”. These conditions imply that, in the natural orbital basis, every Slater determinant  $|\varphi_i\varphi_j\varphi_k\rangle$ , built up from three natural spin-orbitals, showing up in the configuration interaction expansion of the Borland–Dennis setting, satisfies

$$|\varphi_i\varphi_j\varphi_k\rangle = (\hat{n}_{7-s} + \hat{n}_s)|\varphi_i\varphi_j\varphi_k\rangle, \quad (12)$$

for  $s \in \{1, 2, 3\}$ . The Borland–Dennis *state*, in addition, fulfills  $\mathcal{D}_{\text{BD}}(\vec{n}) = 0$ , and therefore according to (9), reads:

$$|\Phi_{\text{BD}}\rangle = \alpha|\varphi_1\varphi_2\varphi_3\rangle + \beta|\varphi_1\varphi_4\varphi_5\rangle + \gamma|\varphi_2\varphi_4\varphi_6\rangle. \quad (13)$$

Noticeably, the selection rule for pinned states is stable in the sense that being in the vicinity of the Paulitope boundary ( $\mathcal{D}_j(\vec{n}) \approx 0$ ) implies approximately the simplified structure (9). This important result states that, in other words, any many-fermion quantum state  $|\Psi\rangle$  can be approximated by the structural simplified form (9), corresponding to saturation of the generalized Pauli constraint  $\mathcal{D}_j$ , up to an error bounded by the distance of  $\vec{n}$  to the corresponding polytope facet [37]:

$$1 - \|\hat{P}_j\Psi\|^2 \leq 2\mathcal{D}_j(\vec{n}). \quad (14)$$

Here  $\hat{P}_j$  is the projector on the zero-eigenspace of  $\hat{D}_j$ .

There is a growing corpus of theoretical and numerical evidence that indicate that, for some systems, ground states are quasipinned to one or more boundaries of the pertinent polytope [10, 38–41]. It is therefore reasonable to assume that such ground states have approximately a simplified structure due to pinning. Inspired by this result, our main aim in this paper is to produce systematically functionals for RDMFT for quantum systems very close to the boundary of the polytope.

A word of caution is in order here. To some extent, the interplay between RDMFT functionals and pure  $N$ -representability is not a happy tale. Some time ago, Pernal [42] discovered that the so-called PNOF5 functional [43] is strictly pure  $N$ -representable. Although this result displayed the mathematical quality of the functional, it also showed that for this reason it underestimated seriously dynamic electron correlation. Our functionals are inspired on the structural simplification (9) but we do not require that the final result is representable. We are just orienting our search for a RDMFT functional in order to capture correctly strong correlation, at least for finite Hilbert spaces.

### 3 Three active electrons

We consider here the Borland–Dennis wave function  $|\Phi_{\text{BD}}\rangle$  given in equation (13), which in terms of the natural occupation numbers reads:

$$|\Phi_{\text{BD}}[\vec{n}, \vec{\varphi}]\rangle = \sqrt{n_3} |\varphi_1\varphi_2\varphi_3\rangle - \sqrt{n_5} |\varphi_1\varphi_4\varphi_5\rangle + \sqrt{n_6} |\varphi_2\varphi_4\varphi_6\rangle, \quad (15)$$

with  $\vec{\varphi} \equiv (\varphi_1, \varphi_2, \dots)$ . By normalization,  $n_3 + n_5 + n_6 = 1$ . Remarkably, just like in the famous Löwdin–Shull functional, exact for two-fermion systems [44], the wave function (15) – only exact for a pinned three-electron system within the rank-six approximation – is explicitly written in terms of both the natural occupation numbers and the natural orbitals. Hence, the Borland–Dennis state is by itself a functional of these quantities. Likewise, any sign dilemma that may occur when writing the amplitudes of the states (15) can be circumvented by absorbing the possible phases into the spin-orbitals. In addition, only doubly excited configurations are permitted.

Remember that the occupation numbers also satisfy the pinning constraints  $n_i + n_{7-i} = 1$ . Just for convenience we choose a negative sign in front of the second Slater determinant, which can be viewed, without loss of generality, as a rotation of the fifth natural orbital. The two-body reduced-density matrix for the Borland–Dennis state can be separated in two terms: the diagonal part

$$\hat{\Gamma}_{\text{BD}}^{(d)}[\vec{n}, \vec{\varphi}] = \sum_{k \in \{3, 5, 6\}} n_k \sum_{i < j \in \mathcal{Z}_k} |\varphi_i\varphi_j\rangle \langle \varphi_i\varphi_j|, \quad (16)$$

where  $\mathcal{Z}_3 = \{1, 2, 3\}$ ,  $\mathcal{Z}_5 = \{1, 4, 5\}$  and  $\mathcal{Z}_6 = \{2, 4, 6\}$ , and the non-diagonal one

$$\begin{aligned} \hat{\Gamma}_{\text{BD}}^{(nd)}[\vec{n}, \vec{\varphi}] = & -\sqrt{n_3 n_5}(|\varphi_2 \varphi_3\rangle\langle\varphi_4 \varphi_5| + h.c.) \\ & -\sqrt{n_5 n_6}(|\varphi_1 \varphi_5\rangle\langle\varphi_2 \varphi_6| + h.c.) \\ & -\sqrt{n_3 n_6}(|\varphi_1 \varphi_3\rangle\langle\varphi_4 \varphi_6| + h.c.). \end{aligned} \quad (17)$$

This latter term is responsible, so to speak, for the pure character of  $\hat{\Gamma}_{\text{BD}}$ . In fact, without this term, the Borland–Dennis state would reduce to an incoherent superposition of Slater determinants; therefore, a mixed state. The appearance of the terms

$$\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_1)\varphi_k(\mathbf{x}_2)\varphi_l(\mathbf{x}_2), \quad (18)$$

in (17) is by no means new in the realm of RDMFT. Recently, Gebauer, Cohen and Car introduced a linear scaling functional containing such terms [45]. These new terms lead us to represent the exchange-correlation functional (7) in a more general fashion:

$$\mathcal{E}_{\text{xc}}[\vec{n}, \vec{\varphi}] = -\frac{1}{2} \sum_{ijkl} \int d^3x d^3x' f_{ijkl}^{s's'}(\vec{n}) \frac{\chi_{ij}(\mathbf{x})\chi_{kl}(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (19)$$

Obviously,  $f_{ijkl}^{s's'}(\vec{n}) = f_{klij}^{s's'}(\vec{n})$ . It is worth mentioning that there is an important physical motivation in writing  $\mathcal{E}_{\text{xc}}$  in this way. In fact, the new functional (19) is in principle spin inseparable, namely,  $\mathcal{E}_{\text{xc}}[\gamma] \neq \mathcal{E}_{\text{xc}}[\gamma^\uparrow] + \mathcal{E}_{\text{xc}}[\gamma^\downarrow]$ . It is known that spin separability is not able to reproduce spin polarizations and is therefore physically inexact [46].

For the doublet, the two-body reduced density matrix can be regarded as a  $4 \times 4$  matrix in spin space [47], but due to particle conservation only four terms are different from zero:

$$\hat{\Gamma} = \begin{pmatrix} \hat{\Gamma}^{\uparrow\uparrow} & \hat{\Gamma}^{\uparrow\downarrow} \\ \hat{\Gamma}^{\downarrow\uparrow} & \hat{\Gamma}^{\downarrow\downarrow} \end{pmatrix}. \quad (20)$$

For the three-particle system, the  $\hat{\Gamma}^{\downarrow\downarrow}$  term is zero. By symmetry,  $\Gamma^{\downarrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2) = \Gamma^{\uparrow\downarrow}(\mathbf{r}_2, \mathbf{r}_1)$ .

### 3.1 One frozen electron

A natural spin orbital is a direct product of a spatial orbital and a spinor  $|\zeta\rangle \otimes |\phi_i^\zeta\rangle$ . The active space is then described by two sets of orthonormal spatial functions, namely,  $\{\phi_i^\uparrow\}$  and  $\{\phi_i^\downarrow\}$ . Let us first consider one electron frozen in the doublet spin configuration of the three-electron system. Save a sign indeterminacy, which in principle cannot be removed, the wave function reads:

$$|\Psi_2[\vec{n}, \vec{\phi}^s]\rangle = \sum_{\mu>0} (\pm) \sqrt{n_\mu} |\uparrow\phi_0^\uparrow, \uparrow\phi_\mu^\uparrow, \downarrow\phi_\mu^\downarrow\rangle. \quad (21)$$

It is easy to show that the corresponding elements of the two-body density matrix read:

$$\hat{\Gamma}_2^{\uparrow\uparrow}[\vec{n}, \vec{\phi}^s] = \sum_{\mu>0} n_\mu |\phi_0^\uparrow \phi_\mu^\uparrow\rangle\langle\phi_0^\uparrow \phi_\mu^\uparrow|, \quad (22)$$

and

$$\begin{aligned} \Gamma_2^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{2} \sum_{\mu>0} n_\mu \chi_{00}^\uparrow(\mathbf{r}_1) \chi_\mu^\downarrow(\mathbf{r}_2) \\ & + \frac{1}{2} \sum_{\mu, \nu>0} (\pm) \sqrt{n_\mu n_\nu} \chi_{\mu\nu}^\uparrow(\mathbf{r}_1) \chi_{\nu\mu}^\downarrow(\mathbf{r}_2). \end{aligned} \quad (23)$$

It is instructive to realize that the last term of equation (23) is the Löwdin–Shull functional for two active electrons. The final expression of the exchange-correlation functional can be written using similar approximations as Buijse and Baerends used for their functional [17]. The first approximation uses the fact that the coefficients  $\sqrt{n_\mu}$  are usually very small for  $\mu > 1$ , allowing us to neglect the product of two such terms. The second approximation addresses the sign undeterminacy by choosing a negative sign in front of these small coefficients and a positive one in front of the first dominant term. This choice is justified by the positivity of the Coulomb potential which ensures that the off-diagonal terms ( $p > 1$ )

$$\int \frac{\chi_{1p}(r)\chi_{p1}(r')}{|r - r'|} dr dr', \quad (24)$$

are positive. By the Rayleigh principle, a lower value of the ground-state energy will be reached only if the sign of the first small coefficient is negative [16]. In this way, the exchange-correlation functional reads

$$\begin{aligned} f_{2,0\mu\mu 0}^{\uparrow\uparrow}(\vec{n}) = f_{2,\mu 00\mu}^{\uparrow\uparrow}(\vec{n}) = n_\mu, \quad & \forall \mu \geq 0, \\ f_{2,\mu\mu\nu\nu}^{\uparrow\uparrow}(\vec{n}) = n_\mu n_\nu, \quad & \forall \mu, \nu > 0, \end{aligned} \quad (25)$$

with  $n_0 = 1$ . Furthermore, like in the Müller functional,

$$f_{2,\mu\nu\nu\mu}^{\uparrow\downarrow}(\vec{n}) = \sqrt{n_\mu n_\nu}, \quad \forall \mu, \nu > 0. \quad (26)$$

Finally, to correctly cancel the spurious self-interaction contribution of the Coulomb term  $f_{2,\mu\mu\nu\nu}^{\uparrow\downarrow}(\vec{n}) = n_\mu n_\nu$ . The remaining terms are zero.

### 3.2 Borland–Dennis functional

In this section we write the doublet configuration of the Borland–Dennis state (15) in terms of the spatial orbitals explicitly:

$$\begin{aligned} |\Psi_{\text{BD}}[\vec{n}, \vec{\phi}^s]\rangle = & \sqrt{n_1} |\uparrow\phi_0^\uparrow, \downarrow\phi_1^\downarrow, \uparrow\phi_1^\uparrow\rangle - \sqrt{n_2} |\uparrow\phi_0^\uparrow, \downarrow\phi_2^\downarrow, \uparrow\phi_2^\uparrow\rangle \\ & + \sqrt{n_3} |\uparrow\phi_1^\uparrow, \downarrow\phi_3^\downarrow, \uparrow\phi_2^\uparrow\rangle. \end{aligned} \quad (27)$$

The corresponding two-body reduced density matrix is

$$\hat{\Gamma}_{\text{BD}}^{\uparrow\uparrow} = n_1 |\phi_0^\uparrow \phi_1^\uparrow\rangle \langle \phi_0^\uparrow \phi_1^\uparrow| + n_2 |\phi_0^\uparrow \phi_2^\uparrow\rangle \langle \phi_0^\uparrow \phi_2^\uparrow| + n_3 |\phi_1^\uparrow \phi_2^\uparrow\rangle \langle \phi_1^\uparrow \phi_2^\uparrow|. \quad (28)$$

Notice that the first two terms of (28) also appear in the density matrix for the rank-five approximation  $\hat{\Gamma}_2^{\uparrow\uparrow}$ . The non-diagonal parts of  $\hat{\Gamma}_{\text{BD}}$  are given by

$$\begin{aligned} \Gamma_{\text{BD}}^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{n_1}{2} [\chi_{00}^\uparrow(\mathbf{r}_1) + \chi_{11}^\uparrow(\mathbf{r}_1)] \chi_{11}^\downarrow(\mathbf{r}_2) \\ &+ \frac{n_2}{2} [\chi_{00}^\uparrow(\mathbf{r}_1) + \chi_{22}^\uparrow(\mathbf{r}_1)] \chi_{22}^\downarrow(\mathbf{r}_2) \\ &+ \frac{n_3}{2} [\chi_{11}^\uparrow(\mathbf{r}_1) + \chi_{22}^\uparrow(\mathbf{r}_1)] \chi_{33}^\downarrow(\mathbf{r}_2) \\ &- \Delta^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (29)$$

The last term contains the following exchange terms:

$$\begin{aligned} \Delta^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2) &= \sqrt{n_1 n_2} \chi_{12}^\uparrow(\mathbf{r}_1) \chi_{21}^\downarrow(\mathbf{r}_2) \\ &+ \sqrt{n_1 n_3} \chi_{02}^\uparrow(\mathbf{r}_1) \chi_{13}^\downarrow(\mathbf{r}_2) \\ &+ \sqrt{n_2 n_3} \chi_{01}^\uparrow(\mathbf{r}_1) \chi_{23}^\downarrow(\mathbf{r}_2). \end{aligned} \quad (30)$$

It is interesting to note that only the first term appearing in equation (30) appears also in (23). The other two correspond to the exchange terms of the Borland–Dennis wave function. The functional then reads (see Appendix A):

$$f_{\text{BD},ijji}^{\uparrow\uparrow}(\vec{n}) = \begin{cases} n_{i+j} & \text{if } i \neq j \\ (n_1 + n_{i+2})^2 & \text{if } i = j \in \{0, 1\}, \end{cases} \quad (31)$$

with  $i, j \in \{0, 1, 2\}$ . Also,  $f_{\text{BD},1122}^{\uparrow\uparrow} = f_{\text{BD},2211}^{\uparrow\uparrow} = n_1 n_3$ . To correctly cancel the spurious self-interaction contribution of the Coulomb term,

$$f_{\text{BD},\mu\mu\nu\nu}^{\downarrow\downarrow}(\vec{n}) = n_\mu n_\nu, \quad (32)$$

with  $\mu, \nu \in \{1, 2, 3\}$ . Furthermore,

$$f_{\text{BD},ii\mu\mu}^{\uparrow\downarrow}(\vec{n}) = \begin{cases} -n_{3-i} n_\mu & \text{if } i + \mu \neq 3 \\ (1 - n_\mu) n_\mu & \text{if } i + \mu = 3. \end{cases} \quad (33)$$

Finally, the exchange term of  $\hat{\Gamma}^{\uparrow\downarrow}$  is nothing more than the “twisted” exchange term  $\Delta^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2)$ .

### 3.3 New functional

In this paper we seek a good compromise between the dynamical-correlated functional  $\hat{\Gamma}_2$  and the static-correlated functional  $\hat{\Gamma}_{\text{BD}}$ . A linear superposition of these two density matrices would be a good starting point. Although the result would be not representable, it would fulfill the sum rule  $\int \Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) d\mathbf{x}_2 = \gamma(\mathbf{x}_1, \mathbf{x}'_1)$ . For engineering the exchange-correlation functional we proceed, however, in the following way. Notice that the final outcome of the Sections 3.1 and 3.2 is the proposal of two

exchange-correlation functionals which share one common term:

$$\begin{aligned} \mathcal{E}_2[\vec{n}, \vec{\phi}^s] &= \mathcal{F}[\vec{n}, \vec{\phi}^s] + \mathcal{F}_2[\vec{n}, \vec{\phi}^s] \\ \mathcal{E}_{\text{BD}}[\vec{n}, \vec{\phi}^s] &= \mathcal{F}[\vec{n}, \vec{\phi}^s] + \mathcal{F}_{\text{BD}}[\vec{n}, \vec{\phi}^s]. \end{aligned} \quad (34)$$

Typically these functionals undercorrelate, each representing just a fraction of the correlation energy. Assume that the functional  $\mathcal{F}[\vec{n}, \vec{\phi}^s] + \mathcal{F}_2[\vec{n}, \vec{\phi}^s] + \mathcal{F}_{\text{BD}}[\vec{n}, \vec{\phi}^s]$  overcorrelates. We seek a constant  $\alpha$  such that the new functional

$$\begin{aligned} \mathcal{E}_\alpha[\vec{n}, \vec{\phi}^s] &= \mathcal{F}[\vec{n}, \vec{\phi}^s] \\ &+ \alpha(\mathcal{F}_2[\vec{n}, \vec{\phi}^s] + \mathcal{F}_{\text{BD}}[\vec{n}, \vec{\phi}^s]), \end{aligned} \quad (35)$$

gives an energy close to the one of the ground state. We call this the “ $\alpha$ -functional”. The terms of the new functional can be easily written. For instance,  $\forall \mu, \nu > 0$

$$\begin{aligned} f_{\mu\nu\nu\mu}^{\uparrow\downarrow}(\vec{n}) &= \\ &[\alpha + (\delta_\mu^1 \delta_\nu^2 + \delta_\nu^1 \delta_\mu^2 + \delta_\mu^1 \delta_\nu^1 + \delta_\mu^2 \delta_\nu^2)(1 - \alpha)] \sqrt{n_\mu n_\nu}, \end{aligned} \quad (36)$$

as well as  $f_{0213}^{\uparrow\downarrow}(\vec{n}) = \alpha \sqrt{n_1 n_3}$  and  $f_{0123}^{\uparrow\downarrow}(\vec{n}) = \alpha \sqrt{n_2 n_3}$ . In Appendix B we give an argument on how to compute  $\alpha$ .

It is worth mentioning that the fully polarized case can be easily tackled for the Borland–Dennis state by separating the natural orbitals in two sets, namely  $\{1, 2, 4\}$ , for which we use latin letters ( $a, b, \dots$ ), and  $\{3, 5, 6\}$ , for which we use greek letters ( $\mu, \nu, \dots$ ). Similar expressions to (31) and (33) can be easily obtained.

## 4 Generalizations

### 4.1 Higher-rank representability conditions

In rank seven there are four generalized Pauli constraints

$$\begin{aligned} \mathcal{D}_1(\vec{n}) &= 2 - n_2 - n_3 - n_4 - n_5 \geq 0, \\ \mathcal{D}_2(\vec{n}) &= 2 - n_1 - n_3 - n_4 - n_6 \geq 0, \\ \mathcal{D}_3(\vec{n}) &= 2 - n_1 - n_2 - n_4 - n_7 \geq 0, \\ \mathcal{D}_4(\vec{n}) &= 2 - n_1 - n_2 - n_5 - n_6 \geq 0. \end{aligned} \quad (37)$$

The saturation of the four constraints ( $\mathcal{D}_j(\vec{n}) = 0$ ) implies the saturation of the lower-rank Borland–Dennis relation  $\mathcal{D}_{\text{BD}}(\vec{n}) = 0$ . This can be explained in the following way: for the settings of  $N$  fermions in a  $d$ -dimensional one-particle Hilbert space and  $N$  fermions in a  $d'$ -dimensional one-particle Hilbert space, such that  $d < d'$ , the corresponding polytopes satisfy:  $\mathcal{P}_{N,d} = \mathcal{P}_{N,d'}|_{n_{d+1}=\dots=n_{d'}=0}$ . It means that, intersected with the hyperplane given by  $n_{d+1} = \dots = n_{d'} = 0$ , the polytope  $\mathcal{P}_{N,d'}$  coincides with  $\mathcal{P}_{N,d}$ . Therefore  $\mathcal{P}_{3,6} = \mathcal{P}_{3,7}|_{n_7=0}$ . In this case  $\mathcal{D}_1(\vec{n}) = \mathcal{D}_2(\vec{n}) = \mathcal{D}_4(\vec{n}) = 0$  implies  $n_7 = 0$  and therefore  $\mathcal{D}_3(\vec{n}) = \mathcal{D}_{\text{BD}}(\vec{n}) = 0$ .

If one generalized constraint is not fixed, one Slater determinant is added to the Borland–Dennis wave function. The rule to add such a determinant is simple: the

natural orbitals in the configuration correspond to the occupation numbers not appearing in the unsaturated generalized Pauli constraint. For instance, if  $\mathcal{D}_4(\vec{n}) \neq 0$  the new Slater determinant is  $|\varphi_3\varphi_4\varphi_7\rangle$ . We do not consider here the unsaturation of the third constraint, because we would end up in a six-rank wave function. Let us consider that  $\mathcal{D}_2(\vec{n}) = \mathcal{D}_3(\vec{n}) = \mathcal{D}_4(\vec{n}) = 0$  and  $\mathcal{D}_1(\vec{n}) \neq 0$ , the structure of the wave function then reads:

$$|\Phi_7[\vec{n}, \vec{\varphi}]\rangle = \sqrt{n_3} |\varphi_1\varphi_2\varphi_3\rangle + \sqrt{n_5} |\varphi_1\varphi_4\varphi_5\rangle + \sqrt{\lambda} |\varphi_2\varphi_4\varphi_6\rangle + \sqrt{n_7} |\varphi_1\varphi_6\varphi_7\rangle, \quad (38)$$

where  $\lambda = 1 - n_3 - n_5 - n_7$ . This shows that  $|\Phi_7\rangle$ , as for the Borland–Dennis state, can be written in terms of the natural orbitals and the natural occupation numbers.

## 4.2 Frozen electrons

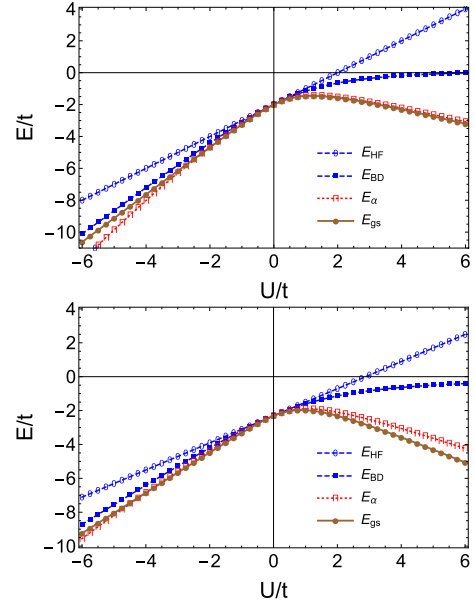
In quantum chemistry it is customary to separate the one-particle Hilbert space in core (fully occupied), active (partially occupied) and virtual (empty) spin-orbitals. The core spin-orbitals are pinned (completely populated) and are not treated as correlated. For the case of  $r$  core (and consequently  $d - r$  active orbitals) the Hilbert space is isomorphic to the wedge product between a Hilbert space of  $r$  electrons in a  $r$ -dimensional one-particle Hilbert space and a Hilbert space of  $d - r$  electrons in a  $d - r$ -dimensional one-particle Hilbert space. Hence, the wave function can be written as  $|\Psi_r\rangle = |\varphi_1, \dots, \varphi_r\rangle \wedge |\Psi^{\text{active}}\rangle$ , where  $|\Psi^{\text{active}}\rangle$  is the part of the wave function belonging to the space of fractional occupied natural orbitals. While the first  $r$  natural occupation numbers are saturated to 1, the remaining  $d - r$  natural occupation numbers ( $n_{r+1}, \dots, n_d$ ) satisfy a set of generalized Pauli constraints and lie therefore inside the polytope  $\mathcal{P}_{N-r, d-r}$  [37]. For the “active” Borland–Dennis state we can apply the same considerations discussed in the last section, namely: if the corresponding constraint (11) is saturated, the wave function fulfills  $(\hat{n}_{r+1} + \hat{n}_{r+2} + \hat{n}_{r+4})|\Psi\rangle = 2|\Psi\rangle$ , and the set of possible Slater determinants reduces to just three. Following our preceding reasoning, the corresponding two-body density matrix reads

$$\hat{\Gamma}_{r+\text{BD}} = \sum_{i=1}^r \sum_{j=1}^{r+6} n_j |\varphi_i\varphi_j\rangle \langle \varphi_i\varphi_j| + \hat{\Gamma}_{\text{BD}},$$

where we use the fact that  $n_1 = \dots = n_r = 1$ .

## 5 Numerical investigations

To illustrate our results we use a simple but non-trivial fermionic system, namely the few-site Hubbard model. This model is capable of exhibiting both weak and strong (static) correlation. Besides its importance for solid-state physics, the Hubbard model is one of the paradigmatic instances used to simplify the description of strongly correlated quantum many-body systems and to test RDMFT functionals [48]. The Hamiltonian (in second quantization) of the one-dimensional  $r$ -site Hubbard



**Fig. 2.** For the three-electron Hubbard model we present the energy predicted for the Borland–Dennis and the  $\alpha$ -functionals. The upper and bottom panels correspond to the four- and the five-site Hubbard model, respectively. The Hartree-Fock and ground-state energies are also shown (see text).

model reads:

$$\hat{H} = -\frac{t}{2} \sum_{i,\zeta} (c_{i\zeta}^\dagger c_{(i+1)\zeta} + h.c.) + 2U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \quad (39)$$

$i \in \{1, 2, \dots, r\}$ . The operators  $c_{i\zeta}^\dagger$  and  $c_{i\zeta}$  are the fermionic creation and annihilation operators for a particle on the site  $i$  with spin  $\zeta$  and  $\hat{n}_{i\zeta}$  is the particle-number operator. The first term in equation (39) describes the hopping between two neighboring sites while the second represents the on-site interaction.

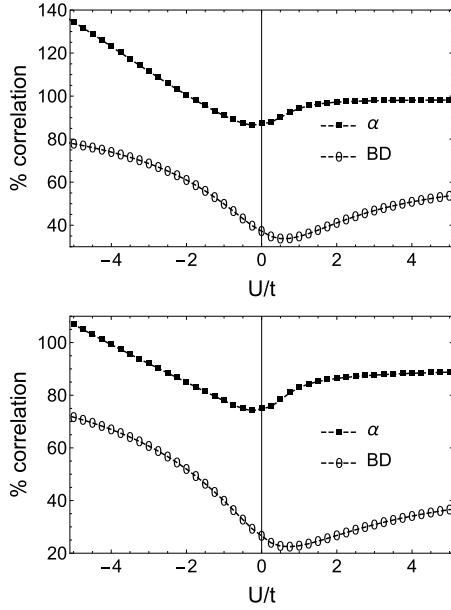
The one-body reduced density matrix inherits the symmetries of the corresponding wave function. For the Hubbard model with periodic boundary conditions, the lattice translation and the  $z$ -component of the spin define such symmetries. The spatial part of the natural orbitals is nothing more than a Bloch state that satisfies

$$\hat{T}_1 |q\rangle = e^{i\varphi q} |q\rangle, \quad (40)$$

where  $\varphi = 2\pi/r$  and  $\hat{T}_1$  is the one-particle translation operator. Using the basis of natural orbitals, the energy can be computed analytically for the rank five approximation for the three-electron Hubbard model [38,49]. For  $r = 4$  the result turns out to only depend on the first occupation number

$$E_{r_5}(t, U) = -\frac{1}{2}(t - 2U + \sqrt{9t^2 + U^2}). \quad (41)$$

This result is important because it allows us to compute the value of  $\alpha$ . Indeed, for  $r = 4$  in equation (B.2) we



**Fig. 3.** For the three-electron Hubbard model we present the percentage of the correlation energy recovered by the Borland–Dennis and the  $\alpha$ -functionals. The percentage is plotted as a function of the relative coupling.

approximate  $\mathcal{G}[\vec{n}_*, \vec{\varphi}_*] - \mathcal{F}[\vec{n}_*, \vec{\varphi}_*] = E_{r_5}(t, U)$ . We computed the best  $\alpha$  for 4- and 5-site three-fermion Hubbard model by averaging equation (B.2) for  $U/t \in [-6, 6]$ . This value turns out to be  $\approx 0.72$ , which we used from now on.

In Figure 2 we present the performance of the two functionals introduced in this paper (Borland–Dennis and the  $\alpha$ -functional) and compare them with the ground-state and Hartree-Fock energies for the four- and five-site Hubbard model. For the three-electron problem in the three-site Hubbard model, the Borland–Dennis functional is exact. It is worth mentioning the striking performance of the Borland–Dennis functional for negative values of the relative strength. With our new functional we recovered almost the full correlation energy. Although it slightly overcorrelates for large negative values of the relative strength, its performance is still remarkable (see Fig. 3). Part of the reason for the overcorrelation for negative values is the very low value of the correlation energy for this sector of interaction.

## 6 Conclusions

Inspired by the recent solution of the pure representability problem for the one-body reduced density matrix, we proposed a new way of producing RDMFT functionals. Our approach is based on the specific simplified structure exhibited by the many-body wave functions whose occupation numbers are pinned to one or more boundaries of the polytope of physical states. Some of the states reconstructed in this way depend explicitly on the natural occupation numbers as well as the natural orbitals yielding explicit expressions for the two-body reduced density matrix. Although this kind of expressions can only be written for Hilbert spaces of low dimensionality it is

possible to combine this information with other known functionals to derive a general purpose formula.

Our method leads to a hierarchy of exchange correlation functionals, depending to the degree of correlation one wishes to reach. In our example, we produced a cross-breed functional by combining a dynamical-correlated and a static-correlated functional. The results are remarkable even in the highly correlated regime. Last but not least, the Borland–Dennis functional contains twisted exchange-correlation terms of the type  $\chi_{kl}^S(\mathbf{r}_1)\chi_{ij}^E(\mathbf{r}_2)$ . These terms, not new but anyhow not common in the realm of RDMFT, are crucial, for example, for capturing correctly the time evolution of the system [50].

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## Author contribution statement

Both authors contributed equally to this manuscript.

## Appendix A: Borland–Dennis functional

The one-body reduced density matrix corresponding to the Borland–Dennis state (27) is given by the following expressions:

$$\hat{\gamma}_{\text{BD}}^{\uparrow} = (n_1 + n_2)|\phi_0^{\uparrow}\rangle\langle\phi_0^{\uparrow}| + (n_1 + n_3)|\phi_1^{\uparrow}\rangle\langle\phi_1^{\uparrow}| + (n_2 + n_3)|\phi_2^{\uparrow}\rangle\langle\phi_2^{\uparrow}|,$$

and  $\hat{\gamma}_{\text{BD}}^{\downarrow} = \sum_i n_i |\phi_i^{\downarrow}\rangle\langle\phi_i^{\downarrow}|$ . Notice that

$$\begin{aligned} \rho_{\text{BD}}^{\uparrow}(\mathbf{r}_1)\rho_{\text{BD}}^{\uparrow}(\mathbf{r}_2) &= (n_1 + n_2)^2\chi_{00}^{\uparrow}(\mathbf{r}_1)\chi_{00}^{\uparrow}(\mathbf{r}_2) \\ &+ (n_1 + n_3)^2\chi_{11}^{\uparrow}(\mathbf{r}_1)\chi_{11}^{\uparrow}(\mathbf{r}_2) + (n_2 + n_3)^2\chi_{22}^{\uparrow}(\mathbf{r}_1)\chi_{22}^{\uparrow}(\mathbf{r}_2) \\ &+ (n_1 + n_2n_3)[\chi_{00}^{\uparrow}(\mathbf{r}_1)\chi_{11}^{\uparrow}(\mathbf{r}_2) + \chi_{11}^{\uparrow}(\mathbf{r}_1)\chi_{00}^{\uparrow}(\mathbf{r}_2)] \\ &+ (n_2 + n_2n_3)[\chi_{00}^{\uparrow}(\mathbf{r}_1)\chi_{22}^{\uparrow}(\mathbf{r}_2) + \chi_{22}^{\uparrow}(\mathbf{r}_1)\chi_{00}^{\uparrow}(\mathbf{r}_2)] \\ &+ (n_3 + n_1n_3)[\chi_{11}^{\uparrow}(\mathbf{r}_1)\chi_{22}^{\uparrow}(\mathbf{r}_2) + \chi_{22}^{\uparrow}(\mathbf{r}_1)\chi_{11}^{\uparrow}(\mathbf{r}_2)], \end{aligned}$$

where we used the normalization condition  $n_1 + n_2 + n_3 = 1$ . Self interaction should be canceled, so that

$$\begin{aligned} f_{\text{BD},0000}^{\uparrow\uparrow} &= (n_1 + n_2)^2, f_{\text{BD},1111}^{\uparrow\uparrow} = (n_1 + n_3)^2, \\ f_{\text{BD},2222}^{\uparrow\uparrow} &= (n_2 + n_3)^2. \end{aligned}$$

Notice that, by taking  $n_2n_3 \approx 0$ , almost all the prefactors of the remaining terms of  $\rho_{\text{BD}}^{\uparrow}(\mathbf{r}_1)\rho_{\text{BD}}^{\uparrow}(\mathbf{r}_2)$  show up in (28) so that the only important term to be added is

$$f_{\text{BD},1122}^{\uparrow\uparrow} = f_{\text{BD},2211}^{\uparrow\uparrow} = n_1n_3. \quad (\text{A.1})$$

Furthermore,

$$\rho_{\text{BD}}^{\downarrow}(\mathbf{r}_1)\rho_{\text{BD}}^{\downarrow}(\mathbf{r}_2) = \sum_{ij} n_in_j\chi_{ii}^{\downarrow}(\mathbf{r}_1)\chi_{jj}^{\downarrow}(\mathbf{r}_2). \quad (\text{A.2})$$

and therefore  $f_{\text{BD},ijj}^{\uparrow\downarrow} = -n_i n_j$ . Finally,  $\rho_{\text{BD}}^{\uparrow}(\mathbf{r}_1)\rho_{\text{BD}}^{\downarrow}(\mathbf{r}_2)$  contains terms like

$$(n_1 + n_2)n_1\chi_{00}^{\uparrow}(\mathbf{r}_1)\chi_{11}^{\downarrow}(\mathbf{r}_2) = (1 - n_3)n_1\chi_{00}^{\uparrow}(\mathbf{r}_1)\chi_{11}^{\downarrow}(\mathbf{r}_2).$$

A quick inspection teaches us that  $f_{\text{BD},ii\mu\mu}^{\uparrow\downarrow} = -n_{3-i}n_{\mu}$ , provided that  $i + \mu \neq 3$ . Whenever  $i + \mu = 3$ ,

$$f_{\text{BD},ii\mu\mu}^{\uparrow\downarrow} = (1 - n_{\mu})n_{\mu}. \quad (\text{A.3})$$

## Appendix B: Calculation of $\alpha$

In this Appendix we provide an argument for choosing  $\alpha$ . Remember that, for the best value of  $\alpha$ , the minimization of the functional (35) should be approximatively the ground-state energy. Therefore, the functional evaluated on the minimizers ( $\vec{n}_*$  and  $\vec{\varphi}_*$ ) satisfies

$$\mathcal{G}[\vec{n}_*, \vec{\varphi}_*] - \mathcal{E}_{\text{new}}[\vec{n}_*, \vec{\varphi}_*] = E_{\text{gs}}, \quad (\text{B.1})$$

where

$$\begin{aligned} \mathcal{G}[\vec{n}_*, \vec{\varphi}_*] &= \int \delta(\mathbf{x} - \mathbf{x}') \hat{h}\gamma[\vec{n}_*, \vec{\varphi}_*](\mathbf{x}, \mathbf{x}') d\mathbf{x} \\ &+ \frac{1}{2} \int \frac{\gamma[\vec{n}_*, \vec{\varphi}_*](\mathbf{x}_1, \mathbf{x}_1)\gamma[\vec{n}_*, \vec{\varphi}_*](\mathbf{x}_2, \mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2. \end{aligned}$$

Therefore,

$$\alpha = \frac{\mathcal{G}[\vec{n}_*, \vec{\varphi}_*] - \mathcal{F}[\vec{n}_*, \vec{\varphi}_*] - E_{\text{gs}}}{\mathcal{F}_2[\vec{n}_*, \vec{\varphi}_*] + \mathcal{F}_{\text{BD}}[\vec{n}_*, \vec{\varphi}_*]}. \quad (\text{B.2})$$

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