Universal Generalization of Density Functional Theory for Static Correlation

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A major challenge for density functional theory (DFT) is its failure to treat static correlation, yielding errors in predicted charges, band gaps, van der Waals forces, and reaction barriers. Here we combine one- and two-electron reduced density matrix (1- and 2-RDM) theories with DFT to obtain a universal $O(N^3)$ generalization of DFT for static correlation. Using the lowest unitary invariant of the cumulant 2-RDM, we generate a 1-RDM functional theory that corrects the convexity of any DFT functional to capture static correlation in its fractional orbital occupations. Importantly, the unitary invariant yields a predictive theory by revealing the dependence of the correction's strength upon the trace of the two-electron repulsion matrix. We apply the theory to the barrier to rotation in ethylene, the relative energies of the benzynes, as well as an 11-molecule, dissociation benchmark. By inheriting the computational efficiency of DFT without sacrificing the treatment of static correlation, the theory opens new possibilities for the prediction and interpretation of significant quantum molecular effects and phenomena.

Introduction: The success of density functional theory (DFT) [1–3] lies in its ability to improve upon the energies and properties of mean-field theories like Hartree-Fock while retaining the computational scaling of a one-electron theory. Nonetheless, the exact energy functional of DFT, originally postulated by Hohenberg and Kohn [4], is not known in a practical form, which leads to limitations in the prediction of charges [5, 6], van der Waals forces [7], barrier heights [8], and bi- and multi-radicals [9]. These limitations largely arise from the inability of DFT to provide a complete description of static (or multi-reference) electron correlation, which occurs when two or more Slater determinants contribute equally or nearly equally to the wave function. Recently, it has been shown that modern density functionals typically improve the energy over more established functionals at the expense of other properties including electron density [10, 11], implying that such improvements may be arising in part from an overfitting of the energy rather than a fundamental enhancement of the underlying functional.

In this Letter we combine DFT [1–3] and its extensions [12–22] with 1-RDM [23–40] and 2-RDM [41–68] theories to obtain a universal $O(N^3)$ generalization of DFT for static correlation. We consider the invariants of the cumulant part of the 2-RDM [45–48] with respect to one-body unitary transformations [69, 70]. Using the lowest order invariant, we derive a universal transformation of DFT into a 1-RDM functional theory (1-RDMFT) whose convexity naturally allows the orbital occupations to become fractional upon correlation. Critically, the correction, derived from the cumulant invariant, has an explicit dependence on the trace of the electron-repulsion matrix that correctly determines the magnitude of the correction, removing a significant limitation of previous work [21, 38], to realize a predictive theory. The quadratic dependence of the functional on the 1-RDM produces a quadratic semidefinite program that we solve using an efficient boundary-point algorithm for semidefinite programming [63] developed for variational 2-RDM theory [41, 42, 57–68]. To demonstrate, we apply the functional theory to examining the barrier to rotation in ethylene [71], the relative energies of the benzynes [72], as well as a benchmark based on the dissociation energies of 11 molecules [73]. The cumulant-based generalization of DFT has the potential to extend the reach of DFT to treat a broader range of molecules and materials including those whose properties are significantly influenced by static correlation.

Theory: Consider the energy of any many-electron atom or molecule in a finite basis of r spin orbitals as a functional of the 1- and 2-RDMs [28]

$$E_{\rm 2RDM}[{}^1D,{}^2D] = {\rm Tr}({}^1H\,{}^1D) + {\rm Tr}({}^2V\,{}^2D) \tag{1}$$

in which ${}^1H$ is the matrix representation of the one-electron kinetic energy and nuclear-electron Coulomb terms, ${}^2V$ is the matrix representation of the two-electron repulsion term, and ${}^1D$ and ${}^2D$ are the 1- and 2-RDMs, normalized to N and $N(N-1)/2$, respectively. We can re-express the 2-RDM in terms of its cumulant expansion [45–48]

$${}^2D = {}^1D \wedge {}^1D + {}^2\Delta \tag{2}$$

where $\wedge$ denotes the antisymmetric (or Grassmann) tensor product [45] and ${}^2\Delta$ is the cumulant (or connected) part of the 2-RDM. Hence, the energy can also be written as a functional of the 1-RDM and the cumulant 2-RDM

$$E_{\rm 2RDM}[{}^1D,{}^2\Delta] = E[{}^1D] + E^{\Delta}[{}^2\Delta] \tag{3}$$

in which

$$E[{}^1D] = {\rm Tr}({}^1H\,{}^1D) + {\rm Tr}({}^2V\,{}^1D \wedge {}^1D) \tag{4}$$
$$E^{\Delta}[{}^2\Delta] = {\rm Tr}({}^2V\,{}^2\Delta). \tag{5}$$

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Because the cumulant 2-RDM can be decomposed into three orthogonal subspaces based on the unitary group [69], known as the unitary decomposition [70], we have

$$ {}^2\Delta = {}^2\Delta_0 + {}^2\Delta_1 + {}^2\Delta_2 \tag{6} $$

or

$$ E^{\Delta}[{}^2\Delta] = E^{\Delta}_0[{}^2\Delta_0] + E^{\Delta}_1[{}^2\Delta_1] + E^{\Delta}_2[{}^2\Delta_2] \tag{7} $$

where

$$ E^{\Delta}_k[{}^2\Delta_k] = \mathrm{Tr}({}^2V\,{}^2\Delta_k). \tag{8} $$

Because the zeroth component of the unitary decomposition of the cumulant 2-RDM is [69]

$$ {}^2\Delta_0 = \frac{2}{r(r-1)}\mathrm{Tr}({}^2\Delta)\,{}^2I \tag{9} $$

in which ${}^2I$ is the two-electron identity matrix, we can express the zeroth component of the cumulant correction to the energy as follows

$$ E^{\Delta}_0[{}^2\Delta_0] = \frac{2}{r(r-1)}\mathrm{Tr}({}^2V)\mathrm{Tr}({}^2\Delta). \tag{10} $$

However, the trace of the cumulant 2-RDM can be expressed in terms of the 1-RDM's idempotency [74–77]

$$ \mathrm{Tr}({}^2\Delta) = -\frac{1}{2}\mathrm{Tr}({}^1D - {}^1D^2) \tag{11} $$

in which ${}^1D^2$ denotes the square of the 1-RDM, and the trace of ${}^2V$ can be expressed in terms of the two-electron repulsion integrals in physics notation

$$ \mathrm{Tr}({}^2V) = 2\sum_{\tilde{i},\tilde{j}}\left(2\langle\tilde{i}\tilde{j}||\tilde{i}\tilde{j}\rangle - \langle\tilde{i}\tilde{j}||\tilde{j}\tilde{i}\rangle\right) \tag{12} $$

where the tilde denotes the index of the spatial part of the spin orbital. Therefore, using Eqs. (11) and (12) in Eq. (10), we can express the zeroth component of the cumulant energy correction as a functional of the 1-RDM

$$ E^{\Delta}_0[{}^2\Delta_0] = -\gamma\mathrm{Tr}({}^1D - {}^1D^2) \tag{13} $$

where

$$ \gamma = \frac{2}{r(r-1)}\sum_{\tilde{i},\tilde{j}}\left(2\langle\tilde{i}\tilde{j}||\tilde{i}\tilde{j}\rangle - \langle\tilde{i}\tilde{j}||\tilde{j}\tilde{i}\rangle\right). \tag{14} $$

Approximating the cumulant energy with its zeroth-order component yields a 1-RDM functional theory that corrects the Hartree-Fock energy.

The correction mainly accounts for static correlation. To see this, we consider the contribution of energetically low-lying excitations to the electron correlation, known as dynamic correlation. The largest contribution arises from the double excitations in which two electrons in occupied orbitals are promoted to two unoccupied orbitals. These excitations appear in off-diagonal terms of the cumulant 2-RDM in which both upper indices correspond to unoccupied orbitals and both lower indices correspond to occupied orbitals [55]. These elements, however, only contribute to the final energy term from the unitary decomposition. Consequently, the zeroth energy term, arising from the trace of the cumulant 2-RDM, primarily accounts for static correlation. We can alternately establish the relationship between this correction and static correlation from directly evaluating the trace of the cumulant 2-RDM. The cumulant's trace equals the trace of the idempotency relation for the 1-RDM [74–77]. The 1-RDM only deviates significantly from idempotency when its occupation numbers are highly fractional—far from zero and one, which occurs primarily when an atom or molecule possesses significant static correlation.

Previous work showed that we can transform DFT into a 1-RDMFT by adding a correction functional [21, 38]

$$ E_{\mathrm{RDMFT}}[{}^1D] = E_{\mathrm{DFT+T}}[{}^1D] + C[{}^1D] \tag{15} $$

in which

$$ E_{\mathrm{DFT+T}}[{}^1D] = E_{\mathrm{DFT}}[\rho] + \left(T[{}^1D] - T_{\mathrm{s}}[\rho]\right) \tag{16} $$

$$ E_{\mathrm{DFT}}[\rho] = T_{\mathrm{s}}[\rho] + V[\rho] + F_{\mathrm{xc}}[\rho] \tag{17} $$

where ρ is the one-electron density, $T_{\mathrm{s}}[\rho]$ is the non-interacting kinetic energy functional, $T[{}^1D]$ is the interacting kinetic energy functional, $V[\rho]$ is the sum of the external and Hartree potentials, $F_{\mathrm{xc}}[\rho]$ is the exchange-correlation functional, and $C[{}^1D]$ is the correction functional. An approximate form for $C[{}^1D]$ we derived to be [38]

$$ C[{}^1D] = -w\mathrm{Tr}({}^1D - {}^1D^2) \tag{18} $$

in which w was an unknown parameter whose value, we showed, depends on the molecular system. Comparing Eq. (18) with Eqs. (13) and (14), however, we find that $w = \gamma$ or that w depends on a subset of the electron repulsion integrals. We introduce a damping factor $\kappa \in [0, 1]$ such that $w = \kappa\gamma$ to account for the fact that the density functional already includes some of the static correlation. Importantly, κ, we observe, is largely independent of the molecular system because the system-dependent behavior is captured by the trace of the two-body interaction matrix, and hence, for a given approximate density functional a single value for the damping parameter can be used across molecules. While the damping parameter does vary with the choice of the density functional, its optimal magnitude increases linearly with the amount of Hartree-Fock exchange. Consequently, we find that a greater correction for electron correlation is required for DFT functionals with a greater degree of Hartree-Fock exchange. Using the correction with DFT rather than Hartree-Fock theory has the important advantage that DFT already has a good approximation to the dynamic correlation.

The cumulant-based correction can also be viewed as a correction to the convexity of the energy functional [78]. The Hartree-Fock energy is a concave functional of the 1-RDM [79, 80]. This concave property causes the solutions of Hartree-Fock theory to occur at extreme points along the boundary of the convex set of 1-RDMs that correspond to Slater determinant wave functions [80]. The correct 1-RDM energy functional is convex which causes its solutions, when correlated, to lie inside the convex set of 1-RDMs [81]. Incorporation of the cumulant-based energy correction, which is a convex functional of the 1-RDM, increases the convexity of both the Hartree-Fock and DFT-based energy functionals. This enhancement of convexity generates a movement, described by Schilling and Schilling as a force [33], arising from correlation that drives the 1-RDM into the convex set and away from its boundary.

Results: We apply the 1-RDMFT to treat the barrier to rotation in ethylene [71], the relative energies of the benzynes [72], as well as a benchmark based on the atomization energies of 11 molecules [73]. We use the formula $w = \kappa\gamma$ with γ in Eq. (14) and $\kappa = 0.158$ for correcting both SCAN-DFT [82] and PBE-DFT [83], which we denote as SCAN-RDMFT and PBE-RDMFT, respectively (see Table S1 in the Supplemental Material (SM)). Previous work showed empirically that the ratio of the optimal weight for correcting the Hartree-Fock method to the optimal weight for correcting the SCAN-DFT functional is a constant [21], which determines the value of κ. The fact that κ is significantly less than unity indicates that the SCAN and PBE functionals already account for a significant percentage of ${}^2\Delta_0$; nonetheless, as shown below, the missing part is critical to both generating the fractional occupations and correcting the energy errors. Because the degree to which a functional accounts for this term should be independent of the molecule, we can understand why a single value of κ for a given functional is likely to be accurate across a wide range of molecules. All calculations use the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set [84]. We solve the 1-RDMFT by an $O(N^3)$ self-consistent-field method, detailed in Refs. [21, 38], that solves a semidefinite program by the boundary-point algorithm developed in Ref. [63] for variational 2-RDM theory [57–68]. In general, the 1-RDMFT can be readily implemented on top of existing self-consistent-field implementations of DFT. While DFT can in principle employ only the occupied molecular orbitals, the 1-RDMFT can also exploit just the non-negligible fractionally occupied orbitals, which will be a small fraction of the total number of orbitals. Calculations with the complete-active-space self-consistent-field method (CASSCF) [85] and the anti-Hermitian contracted Schrödinger equation (ACSE) [49, 51] are performed with the Quantum Chemistry Package in Maple [86], and calculations with coupled cluster with single, double, and pertubative triple excitations [CCSD(T)] [87] and multi-configuration pair density functional theory (MC-PDFT) [14] are performed with PySCF [88].

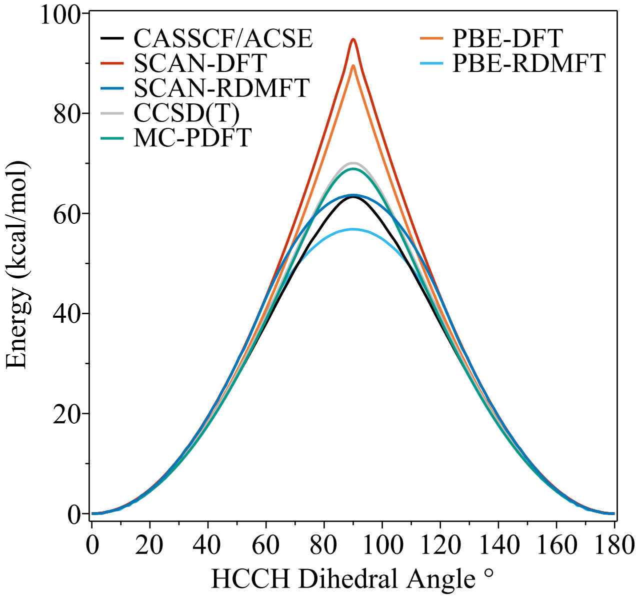

FIG. 1. C_2H_4 rotational barrier potential energy surfaces obtained from CASSCF(12,12)/ACSE, CCSD(T), PBE-RDMFT, SCAN-RDMFT, PBE-DFT, SCAN-DFT, and CASSCF(12,12)/tPBE calculations with a cc-pVDZ basis set.

First, we calculate the potential energy surface for the C-C bond rotation in C_2H_4, which corresponds to a transition from a double bond well captured by a single reference approach at a 0° dihedral angle to a strongly correlated biradical at a 90° dihedral angle. The results, plotted in Fig. 1, reveal a general overestimation of the barrier height in single-reference methods, with errors of 26.21, 31.50, and 6.70 kcal/mol for PBE-DFT, SCAN-DFT, CCSD(T) respectively, as compared to a CASSCF(12,12)/ACSE reference (here we use the $(N,r/2)$ convention where N is the number of electrons and $r/2$ is the number of spatial orbitals in the active space). 1-RDMFT yields significant improvements with errors of -6.51, and 0.33 kcal/mol for PBE-RDMFT and SCAN-RDMFT, respectively. These results compare favorably to tPBE MC-PDFT, which yields an error of 5.72 kcal/mol. (The "t" in the acronym tPBE denotes the translation of the conventional PBE exchange-correlation functional in DFT to an on-top functional for use in MC-PDFT [14].) The DFT and 1-RDMFT potential energy surfaces reveal identical relative energies along the HCCH dihedral angle until the 1-RDMFTs yield fractionally occupied orbitals,

TABLE I. Dissociation errors in kcal/mol for a subset of the MR-MGN-BE17 test set compared to the CASSCF(valence)/ACSE energies. Dissociation data taken at 5Å internuclear distances.

	Dissociation errors				
	DFT		RDMFT		MC-PDFT
	PBE	SCAN	PBE	SCAN	tPBE
$B_2 \longrightarrow 2\,B$	19.53	23.01	-2.12	-0.87	10.73
$C_2 \longrightarrow 2\,C$	101.47	85.63	12.12	23.38	7.80
$CN \longrightarrow C + N$	125.34	139.02	29.47	48.28	17.69
$CO_2 \longrightarrow C + 2\,O$	172.11	205.46	8.17	46.22	35.37
$F_2 \longrightarrow 2\,F$	73.84	84.91	-19.13	-17.53	22.51
$NF_3 \longrightarrow N + 3\,F$	184.18	205.46	71.10	96.94	68.28
$NO \longrightarrow N + O$	142.28	156.00	36.58	57.72	22.81
$S_2 \longrightarrow 2\,S$	58.21	153.34	-40.02	-27.79	17.41
$SiO \longrightarrow Si + O$	67.55	251.27	-36.07	-15.28	8.77
$CO \longrightarrow C + O$	94.62	359.51	-26.09	-0.47	12.27
$N_2 \longrightarrow 2\,N$	219.93	213.67	43.61	71.57	20.08
MSE	114.46	127.85	7.06	25.65	22.15
MUE	114.46	127.85	29.50	36.91	22.15

starting at the 54° and 57° dihedral angles, for PBE and SCAN respectively, owing to increasingly strong static correlation. A plot of the orbital occupations along the dihedral angle is available in Fig. S1 of the SM. Both PBE-RDMFT and SCAN-RDMFT are able to remove correctly the energetic discontinuity observed in DFT at the 90° dihedral angle caused by the degeneracy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) resulting in a smooth potential energy surface. CCSD(T) and tPBE MC-PDFT, however, increasingly deviate from the reference CASSCF(12,12)/ACSE curve with a maximal error at the 90° dihedral angle, where they both fail to fully resolve the multi-reference character, resulting in the overestimation of the barrier height compared to the ACSE and the 1-RDMFTs.

Next, we apply PBE-RDMFT and SCAN-RDMFT to a subset of the multi-reference main group non-metal bond energy molecular test set (MR-MGN-BE17) [73], previously developed as set of systems for testing the accuracy of density functionals on bond dissociations. Equilibrium geometries and reference dissociation energies are obtained by scanning over the molecules' limited degrees of freedom using the ACSE seeded with a valence CASSCF calculation. The results, displayed in Table I, yield mean unsigned errors (MUEs) of 29.50 and 36.91 kcal/mol for PBE-RDMFT and SCAN-RDMFT, respectively, compared to the reference CASSCF/ACSE energies. Here, CASSCF calculations utilize active spaces encompassing all valence electrons and orbitals. These results present significant improvements over traditional PBE-DFT and SCAN-DFT's MUEs of 114.46 and 127.85 kcal/mol with an approximate 4-fold reduction in error. This is the result of 1-RDMFT fractionally occupying the valence orbitals as the molecules dissociate which corrects DFT's overestimation of the dissociated limit. The 1-RDMFT MUEs also compare favorably to the explicitly correlated tPBE MC-PDFT calculations' MUE of 22.15 kcal/mol. Finally, consideration of the mean signed error (MSE) for PBE-RDMFT of 7.06 kcal/mol, reveals a nearly equal over and underestimation of the dissociation energies, while SCAN-RDMFT's MSE of 25.65 kcal/mol shows a stronger tendency to overestimate the dissociation energies. As PBE-DFT, SCAN-DFT, and tPBE never underestimate the dissociation energy their MSEs match their MUEs with values of 114.46, 127.85, and 22.15 kcal/mol respectively.

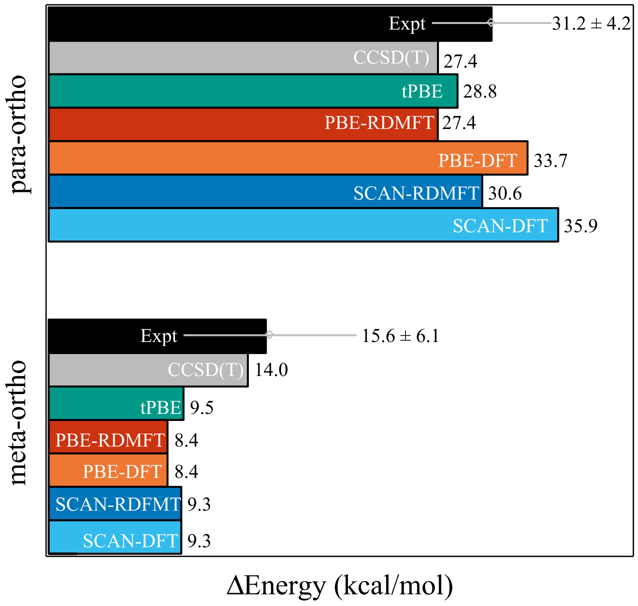

FIG. 2. Relative energies of meta and para-benzyne with respect to ortho-benzyne from RDMFT and DFT with the SCAN and PBE functionals, MC-PDFT using the tPBE functional, and CCSD(T).

Finally, we investigate the relative energy differences between the three geometric isomers of benzyne with ground-state geometries obtained from Ref. [72], which become increasingly strongly correlated with increasing distance between the radical centers (ortho-benzyne < meta-benzyne < para-benzyne) [89]. As both meta- and ortho-benzyne have weak static correlation effects, the 1-RDMFTs are expected to remain idempotent, recovering traditional DFT's energies. This is, indeed, observed, with SCAN-RDMFT and SCAN-DFT both producing energy differences of 9.34 kcal/mol between the two isomers while PBE-RDMFT and PBE-DFT yield 8.4 kcal/mol. These results are both within 1.1 kcal/mol of CASSCF(4,4)/tPBE's predicted energy difference of 9.5 kcal/mol. CCSD(T) deviates more significantly from the previous results, yielding the largest energy difference at 14.03 kcal/mol, which is in good agreement with the experimentally predicted energy gap of 15.6 kcal/mol. Calculation of the more strongly correlated para-isomer yields more significant deviations between 1-RDMFT and DFT, resulting in decreases in the para-ortho energy differences obtained from SCAN-DFT and PBE-DFT of 35.89 and 33.73 kcal/mol respectively to 30.62 and 27.41 kcal/mol from SCAN-RDMFT and PBE-RDMFT. These 1-RDMFT values are within the experimental error range and give significantly better agreement with CCSD(T) and tPBE's energy differences of 27.42 and 28.80 kcal/mol, respectively, compared to DFT.

Conclusions: We present a universal 1-RDMFT functional for the treatment of strongly correlated systems, based on a transformation of traditional DFT. While the development of density-, 1-RDM-, and 2-RDM-based theories often occur separately, here we combine aspects of DFT and 2-RDM theory to develop a 1-RDMFT that retains DFT's $O(N^3)$ efficiency while realizing the ability to capture static correlation. Importantly, by using the unitary invariants of the cumulant 2-RDM, we derive a general formula for the magnitude of the correction—the w parameter—in terms of the diagonal part of two-electron interaction matrix, which overcomes a limitation of earlier work, arising from the need to define a system specific w value [21, 38]. The derived formula for w can also be used to systematize related approaches, such as information density-matrix functional theory (iDMFT) [37] and thermally-assisted-occupation DFT (TAO-DFT) [13, 22], which rely on unknown fictitious temperatures in Fermi-Dirac distributions. We can potentially improve the functional further by approximating the remaining terms of the unitary decomposition, which we will investigate in future work. We demonstrate the applicability of 1-RDMFT by investigating a set of small molecular dissociations in the MR-MGN-BE17 test set, as well as the rotational barrier height of ethylene and the relative energy differences of the benzyne isomers. Due to the 1-RDM correction in the energy functional, 1-RDMFT yields significant improvements over DFT in the presence of strong correlation while recovering the DFT energy in the single-reference limit. The 1-RDMFT opens new possibilities for the treatment of static correlation in the accurate prediction of molecular structures and processes.

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