

DENSITY CUMULANT THEORY FOR GROUND AND EXCITED ELECTRONIC STATES

by

ANDREAS VICTOR COPAN

(Under the Direction of Henry F. Schaefer III)

ABSTRACT

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INDEX WORDS: Cool stuff, Deep learning, Big data, Crowdsourcing, Computer vision, Computer science

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FOR GROUND AND EXCITED ELECTRONIC STATES

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ANDREAS VICTOR COPAN

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A Dissertation Submitted to the Graduate Faculty
of The University of Georgia in Partial Fulfillment
of the
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DOCTOR OF PHILOSOPHY

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ANDREAS VICTOR COPAN

Approved:

Major Professor: Henry F. Schaefer III

Committee: Gary E. Douberly
Henning Meyer

Electronic Version Approved:

Suzanne Barbour
Dean of the Graduate School
The University of Georgia
December 2018

In memory of Valery Andreiyevich and Valtraut Kirsch Copan



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Chapter 1

Introduction

Here is the introduction. My dissertation introduces *widgets*. If I wish to cite someone, I could refer to them in text as in Pedersen, Fernández, and Koch¹, or parenthetically¹. I can also cite just the year 2001 or mention the author, Pedersen, Fernández, and Koch.

This dissertation template is handy. I like it and use it every time I write a dissertation.

— Abraham Lincoln 2001

1.1 Stuff

Here is a section on stuff.

1.1.1 Artificial Neural Networks

See Figure 1.1 for a neural network.

Cool.

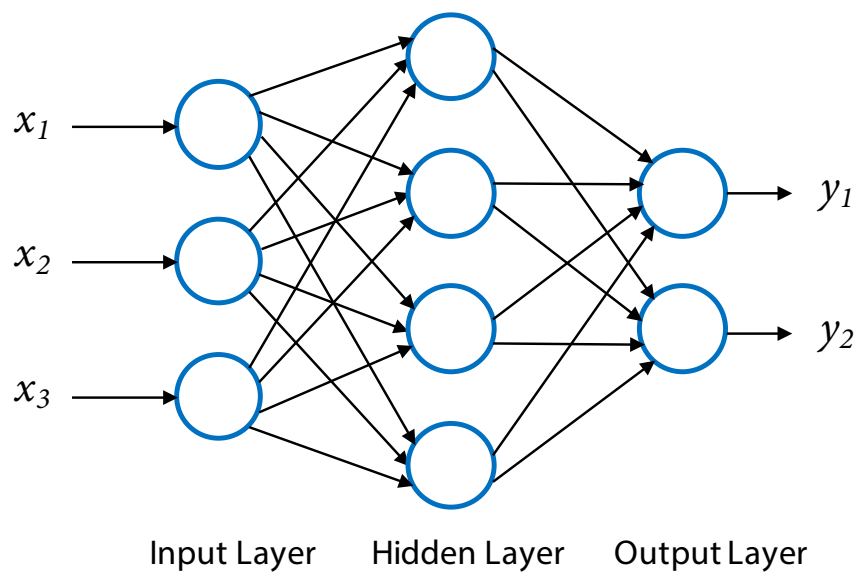


Figure 1.1: An example neural network with two final outputs. Notice how each neuron in one layer connects to each neuron in the following layer. This is called *fully connected*.

Chapter 2

Ground-State Density Cumulant Theory: Thermochemical and Kinetic Benchmark Calculations*

2.1 Abstract

We present an extensive benchmark study of density cumulant functional theory (DCFT) for thermochemistry and kinetics of closed- and open-shell molecules. The performance of DCFT methods (DC-06, DC-12, ODC-06, and ODC-12) is compared to that of coupled-electron pair methods (CEPA₀ and OCEPA₀) and coupled-cluster theory (CCSD and CCSD(T)) for the description of noncovalent interactions (A24 database), barrier heights of hydrogen-transfer reactions (HTBH38), radical stabilization energies (RSE30), adiabatic ionization energies (AIE), and covalent bond stretching in diatomic molecules. Our results indicate that out of four DCFT methods the ODC-12 method is the most reliable and accurate DCFT formulation to date. Compared to CCSD, ODC-12 shows superior results for all benchmark tests employed in our study. With respect to coupled-pair

*A. V. Copan, A. Yu. Sokolov, and H. F. Schaefer., J. Chem. Theory Comput. **10**, 2389 (2014). Adapted with permission of the American Chemical Society.

theories, ODC-12 outperforms CEPA₀, and shows similar accuracy to the orbital-optimized CEPA₀ variant (OCEPA₀) for systems at equilibrium geometries. For covalent bond stretching, ODC-12 is found to be more reliable than OCEPA₀. For the RSE30 and AIE datasets, ODC-12 shows competitive performance with CCSD(T). In addition to benchmark results, we report new reference values for the RSE30 dataset computed using coupled cluster theory with up to perturbative quadruple excitations.

2.2 Introduction

Recent developments in *ab initio* quantum chemistry have resulted in a variety of computational models for studying molecules. Apart from concerns about efficiency and accuracy, several concepts have evolved as criteria for judging the merits of a particular method. Energy-based criteria typically define an “ideal” approximation as one yielding correlation energies that are size-consistent, extensive², well-defined (giving continuous, unique potential surfaces), and variational.³ While it has been argued that the practical benefits of variationality are rather limited,⁴ the efficiency of gradient computations, at least, is improved by formulating a theory in terms of a Hermitian and stationary energy functional.⁵ With respect to scope and stability, methods that show consistent performance for open-shell systems, strongly correlated states, and non-equilibrium geometries are particularly valuable.⁴

The incorrect scaling of truncated configuration interaction (CI) energies with system size has inspired the development of size-extensive alternatives. Among

the earliest formulations, the coupled electron pair approximations (CEPAs)^{6–10} attracted much attention in 1970s,^{11–15} offering rigorous extensivity and size-consistency while retaining much of the linearity¹⁶ of CI in their equations. CEPA methods, however, have been shown to rapidly deteriorate as the molecular geometry deviates from equilibrium¹⁶ and yield energies that vary under the rotation of the occupied orbitals.⁹ Partly in light of such defects, CEPA has been largely displaced by coupled-cluster (CC) theory.^{4;17–23} In addition to size-extensivity, CC offers orbital invariance and improved stability for non-equilibrium structures¹⁶, but has a non-Hermitian energy functional and non-linear equations which are not readily amenable to parallel implementation. Although neither class of methods is strictly variational, VCEPA (variational CEPA) has been shown to be effectively equivalent to its non-variational counterpart.²⁴ Various other modifications to resolve the deficiencies of traditional CEPA have been explored, including self-consistent size-consistent CI,^{25;26} orbital-invariant CEPA,^{27;28} and orbital-optimized CEPA formulations.^{29–32} Recently, the CEPA methods have been revived by Neese and co-workers^{24;33;34} who developed the local pair-natural-orbital CEPA (LPNO-CEPA) methods and have implemented them for massively parallel computer architectures.

It has recently been demonstrated^{35–38} that CEPA methods naturally arise in the context of theories that obtain the molecular energies from density cumulants, the connected and extensive components of the reduced density matrices (RDMs).^{39–44} The advantage of cumulant-based theories is that, unlike their RDM-based counterparts,^{45–47} they are naturally size-extensive and size-consistent.^{42;48}

We have recently achieved the first implementation^{49;50} of density cumulant functional theory (DCFT), proposed by Kutzelnigg in 2006.³⁵ In DCFT, the molecular energy is obtained in terms of a mean-field one-particle RDM and the two-particle density cumulant, constrained to be at least approximately N -representable (*i.e.* to correspond to a physical N -electron wavefunction). Like traditional CC theory, DCFT is size-extensive and orbital-invariant, but it has the additional advantage of a stationary and Hermitian energy functional, which simplifies the computation of molecular properties. In the original DCFT formulation (DC-06)^{35;49;50} N -representability conditions derived from second-order Møller-Plesset perturbation theory (MPPT) were used,⁵¹ yielding equations similar to those of the simplest CEPA model (CEPA₀),^{8;10} but including higher-order terms in the description of one-particle correlation effects. Using the same set of conditions, we have developed new formulations of DCFT that take advantage of an improved description of the one-particle density matrix (DC-12)⁵² and full orbital optimization (ODC-06 and ODC-12 methods).⁵³

Our previous studies^{49;50;52;53} demonstrated for a limited set of systems that the DC-06, DC-12, ODC-06 and ODC-12 methods generally yield molecular energies and properties competitive with those obtained by CCSD and CCSD(T), but may exhibit unstable performance due to imbalances in the description of electron correlation. Herein, we present an extensive benchmark of the DCFT methods with respect to thermochemical and kinetic molecular properties, including noncovalent interactions, barrier heights in hydrogen-transfer reactions, radical stabilization energies, and adiabatic ionization energies for challenging electron-

dense systems. We conclude our benchmark study by testing the performance of DCFT for covalent bond stretching in diatomic molecules.

2.3 Overview of DCFT

In this section a short overview of DCFT is presented. For details on the theory the reader is referred to our earlier publications.^{49;52;53} In the RDM methods⁵⁴ the exact molecular energy is expressed as a functional of the one- and two-particle reduced density matrices, γ_1 and γ_2 (1-RDM and 2-RDM):

$$E = h_p^q \gamma_q^p + \frac{1}{2} g_{pq}^{rs} \gamma_{rs}^{pq}, \quad [\gamma_1]_q^p \equiv \gamma_q^p, \quad [\gamma_2]_{rs}^{pq} \equiv \gamma_{rs}^{pq}. \quad (2.1)$$

In eq. (2.1), h_p^q and g_{pq}^{rs} are the usual one- and two-electron integrals in the orthonormal spin-orbital basis $\{\psi_p\}$ and summation over the repeated indices is implied. Expressing γ_1 through γ_2 via the partial trace relation $\sum_r \gamma_{qr}^{pr} = (N-1)\gamma_q^p$, the energy functional (2.1) can be minimized by varying γ_2 subject to N -representability constraints. This is the essence of the variational 2-RDM approach.⁵⁴

In DCFT, some of the challenges of the 2-RDM approach are circumvented by expanding γ_2 in terms of its irreducible components – the 1-RDM and the two-particle cumulant (denoted by λ_2):

$$\gamma_{rs}^{pq} = \gamma_r^p \gamma_s^q - \gamma_r^q \gamma_s^p + \lambda_{rs}^{pq}. \quad (2.2)$$

In eq. (2.2), λ_2 describes the correlated part of γ_2 that cannot be expressed via γ_1 . The cumulant also determines the correlation contribution to γ_1 , allowing

the 1-RDM to be decomposed as the sum of an idempotent 1-RDM ($\boldsymbol{\kappa}$) and a correlation correction ($\boldsymbol{\tau}$):

$$\boldsymbol{\gamma}_1 = \boldsymbol{\kappa} + \boldsymbol{\tau}. \quad (2.3)$$

The correlation component $\boldsymbol{\tau}$ is fully specified by $\boldsymbol{\lambda}_2$, whereas $\boldsymbol{\kappa}$ is independent of $\boldsymbol{\lambda}_2$. eqs. (2.2) and (2.3) allow us to write an equivalent energy expression with $\boldsymbol{\kappa}$ and $\boldsymbol{\lambda}_2$ as independent functional parameters:

$$\begin{aligned} E[\boldsymbol{\kappa}, \boldsymbol{\lambda}_2] &= \frac{1}{2}(h_p^q + f_p^q)(\kappa_q^p + \tau_q^p) + \frac{1}{4}\bar{g}_{pq}^{rs}\lambda_{pq}^{rs}, \\ f_p^q &= h_p^q + \bar{g}_{pr}^{qs}(\kappa_s^r + \tau_s^r), \quad \bar{g}_{rs}^{pq} = g_{rs}^{pq} - g_{rs}^{qp}. \end{aligned} \quad (2.4)$$

Here, the generalized Fock operator \boldsymbol{f} differs from that of Hartree-Fock theory by the presence of an external potential $\bar{g}_{pr}^{qs}\tau_s^r$ due to electron correlation.³⁵

To date, all DCFT formulations make the energy (2.4) stationary with respect to variations of $\boldsymbol{\lambda}_2$, subject to cumulant N -representability constraints derived from second-order Møller-Plesset perturbation theory (MPPT).⁵¹ To account for orbital relaxation effects, the two earliest DCFT methods, DC-06^{35;49;50} and DC-12⁵², determined the orbitals by diagonalizing the generalized Fock operator \boldsymbol{f} defined in eq. (2.4). These two methods differ in their description of 1-RDM N -representability. Whereas DC-06 employs an approximate expression for $\boldsymbol{\tau}$ in terms of $\boldsymbol{\lambda}_2$, DC-12 uses the exact relationship. Recently, we proposed orbital-optimized variants of DC-06 and DC-12 (ODC-06 and ODC-12),⁵³ which fully account for orbital relaxation effects.

2.4 Computational Details

All computations were performed using the Psi4 package.⁵⁵ The results were benchmarked against coupled cluster theory with single and double excitations (CCSD)^{21–23}, CCSD with perturbative triple excitations [CCSD(T)],^{56;57} coupled electron pair approximation zero (CEPA₀),^{8;10} and the orbital-optimized variant of CEPA₀ (OCEPA₀)³⁰. All electrons were correlated in all computations. The cc-pCVXZ^{58;59} and aug-cc-pVXZ⁶⁰ basis sets (X = T, Q) were used (see text for details). Noncovalent interaction energies, hydrogen-transfer barrier heights, and radical stabilization energies were computed using geometries from the A24⁶¹, HTBH38⁶², and RSE30⁶³ benchmark databases, respectively, available in Psi4. Adiabatic ionization energies were computed from neutral and cation geometries optimized at each level of theory, with added harmonic zero-point vibrational energy corrections. Harmonic frequencies were computed by numerical differentiation of analytic energy gradients. Single-point energies were converged to $10^{-8} E_h$, while the root mean square of the energy gradient was converged to $10^{-6} E_h/a_0$ for geometry optimizations.

2.5 Results and Discussion

2.5.1 Noncovalent Interactions

We begin by testing the accuracy of DCFT methods for the description of noncovalent interactions in 24 closed-shell molecular dimers, which are listed in table 2.1. These molecular complexes comprise the A24 dataset⁶¹ developed by Řezáč and

Table 2.1: Errors in interaction energies (kcal mol^{-1}) for 24 noncovalently bound molecular dimers comprising the A24 database⁶¹ computed using seven methods with the aug-cc-pVTZ basis set. The errors are relative to CCSD(T) reference values (kcal mol^{-1}) shown in the rightmost column. For each method the mean absolute deviations from CCSD(T) (Δ_{MAE} , kcal mol^{-1}) and the standard deviations from the mean signed error (Δ_{SD} , kcal mol^{-1}) are also shown.

Complex (Sym.)	ΔCEPA_0	$\Delta\text{DC-06}$	$\Delta\text{DC-12}$	ΔCCSD	ΔOCEPA_0	$\Delta\text{ODC-06}$	$\Delta\text{ODC-12}$	CCSD(T)
$\text{H}_2\text{O}\cdots\text{NH}_3$ (C_s)	0.26	0.24	0.22	0.36	0.19	0.20	0.18	-7.18
$\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ (C_s)	0.19	0.18	0.16	0.25	0.13	0.14	0.12	-5.71
$\text{HCN}\cdots\text{HCN}$ (C_s)	0.21	0.27	0.16	0.15	0.18	0.26	0.14	-7.12
$\text{HF}\cdots\text{HF}$ (C_s)	0.14	0.13	0.11	0.16	0.08	0.09	0.07	-5.20
$\text{NH}_3\cdots\text{NH}_3$ (C_{2h})	0.15	0.13	0.14	0.26	0.12	0.12	0.12	-3.43
$\text{HF}\cdots\text{CH}_4$ (C_{3v})	0.17	0.16	0.20	0.23	0.12	0.12	0.16	-2.30
$\text{NH}_3\cdots\text{CH}_4$ (C_{3v})	0.07	0.05	0.05	0.13	0.05	0.05	0.04	-1.08
$\text{H}_2\text{O}\cdots\text{CH}_4$ (C_s)	0.06	0.05	0.04	0.11	0.05	0.05	0.04	-1.03
$\text{CH}_2\text{O}\cdots\text{CH}_2\text{O}$ (C_s)	0.89	0.99	0.65	0.46	0.62	0.87	0.46	-5.23
$\text{H}_2\text{O}\cdots\text{C}_2\text{H}_4$ (C_s)	0.15	0.16	0.15	0.31	0.20	0.26	0.21	-3.33
$\text{CH}_2\text{O}\cdots\text{C}_2\text{H}_4$ (C_s)	0.21	0.18	0.14	0.27	0.19	0.24	0.16	-2.24
$\text{HCCH}\cdots\text{HCCH}$ (C_{2v})	0.07	0.05	0.05	0.20	0.10	0.12	0.10	-2.57

Complex (Sym.)	ΔCEPA_0	$\Delta\text{DC-06}$	$\Delta\text{DC-12}$	ΔCCSD	ΔOCEPA_0	$\Delta\text{ODC-06}$	$\Delta\text{ODC-12}$	CCSD(T)
$\text{NH}_3\cdots\text{C}_2\text{H}_4$ (C_s)	0.09	0.06	0.08	0.24	0.12	0.15	0.13	-2.07
$\text{C}_2\text{H}_4\cdots\text{C}_2\text{H}_4$ (C_{2v})	0.10	0.02	0.07	0.33	0.14	0.13	0.15	-1.81
$\text{CH}_4\cdots\text{C}_2\text{H}_4$ (C_s)	0.02	-0.02	0.01	0.14	0.05	0.04	0.06	-0.92
$\text{BH}_3\cdots\text{CH}_4$ (C_s)	0.23	0.18	0.24	0.37	0.18	0.16	0.22	-2.52
$\text{CH}_4\cdots\text{C}_2\text{H}_4$ (C_s)	0.13	0.09	0.13	0.23	0.10	0.09	0.09	-1.37
$\text{CH}_4\cdots\text{C}_2\text{H}_6$ (C_s)	0.09	0.06	0.09	0.17	0.07	0.06	0.09	-1.14
$\text{CH}_4\cdots\text{CH}_4$ (D_{3d})	0.08	0.06	0.08	0.14	0.06	0.05	0.08	-0.93
$\text{Ar}\cdots\text{CH}_4$ (C_{3v})	0.07	0.05	0.07	0.10	0.05	0.05	0.06	-0.78
$\text{Ar}\cdots\text{C}_2\text{H}_4$ (C_{2v})	0.03	-0.01	0.02	0.11	0.05	0.03	0.05	-0.63
$\text{C}_2\text{H}_4\cdots\text{HCCH}$ (C_{2v})	-0.02	-0.19	-0.01	0.38	0.07	-0.06	0.11	0.43
$\text{C}_2\text{H}_4\cdots\text{C}_2\text{H}_4$ (D_{2h})	-0.05	-0.30	-0.03	0.43	0.04	-0.16	0.11	0.41
$\text{HCCH}\cdots\text{HCCH}$ (D_{2h})	0.01	-0.09	0.02	0.34	0.10	0.02	0.12	0.91
$\Delta_{\text{MAE}}:$	0.14	0.16	0.12	0.25	0.13	0.15	0.13	
$\Delta_{\text{SD}}:$	0.18	0.23	0.13	0.11	0.12	0.18	0.09	

Hobza to include a variety of noncovalent interactions, including hydrogen bonding and π - π stacking. Although Řezáč and Hobza reported the interaction energies at the CCSD(T) complete basis set (CBS) limit, we use CCSD(T)/aug-cc-pVTZ energies as reference values in order to effectively exclude basis-set incompleteness error from the comparison.

Figure 2.1 depicts mean absolute error (Δ_{MAE}) relative to CCSD(T) in the binding energies of CEPA₀, OCEPA₀, CCSD, and the four DCFT methods (DC-06, DC-12, ODC-06, and ODC-12), as well as the root mean square deviation from the average signed error (Δ_{SD}). All methods but CCSD give similar Δ_{MAE} values (0.14 ± 0.02 kcal mol⁻¹), and a comparison between CEPA₀, DC-06, and DC-12 and their orbital-optimized variants (OCEPA₀, ODC-06, and ODC-12) shows negligible 0.01 kcal mol⁻¹ differences in each case. CCSD gives a significantly larger Δ_{MAE} (0.25 kcal mol⁻¹) than the other methods, exceeding the DC-12 Δ_{MAE} by a factor of two (0.12 kcal mol⁻¹). The Δ_{SD} values are much more sensitive to the choice of method than the Δ_{MAE} values, and are noticeably affected by orbital optimization. ODC-12 gives the smallest standard deviation ($\Delta_{\text{SD}} = 0.09$ kcal mol⁻¹), while the largest Δ_{SD} value was found for DC-06 (0.23 kcal mol⁻¹). The OCEPA₀, ODC-06, and ODC-12 methods ($\Delta_{\text{SD}} = 0.12, 0.18, \text{ and } 0.09$ kcal mol⁻¹, respectively) exhibit much more consistent performance than their non-orbital-optimized analogues, with Δ_{SD} smaller by 0.05 ± 0.01 kcal mol⁻¹ in each case. CCSD also exhibits a relatively small Δ_{SD} value (0.11 kcal mol⁻¹), possibly due to its inclusion of single excitations which partly account for orbital relaxation.

Errors in interaction energy and CCSD(T) reference values for each molecular

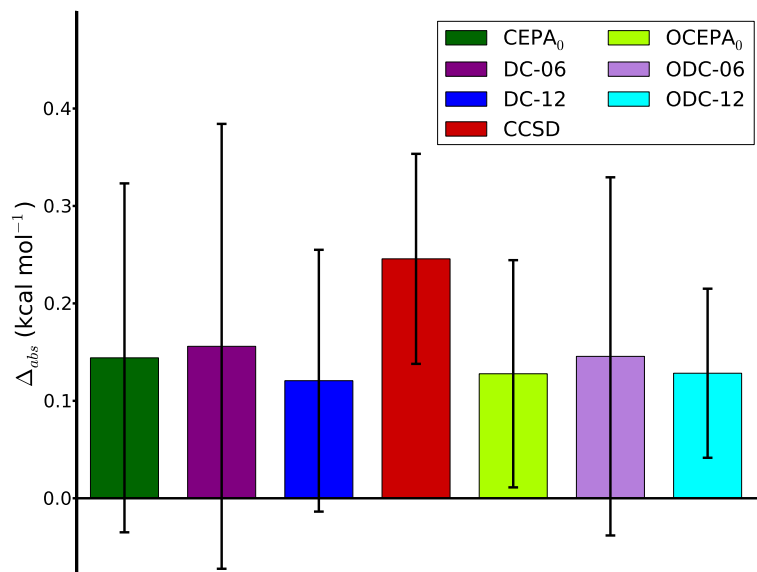


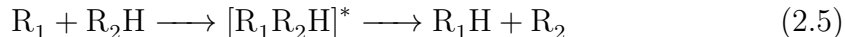
Figure 2.1: Mean absolute deviations (Δ_{MAE} , kcal mol⁻¹) and the standard deviations from the mean signed error (Δ_{SD} , kcal mol⁻¹) of the interaction energies for 24 noncovalently bound molecular dimers (A24 database) computed using seven methods with the aug-cc-pVTZ basis set. The errors are relative to CCSD(T)/aug-cc-pVTZ reference values. The Δ_{MAE} value is represented as a height of each colored box, while the Δ_{SD} value is depicted as a radius of the black vertical bar. See table 2.1 for data on individual database members.

complex are shown in table 2.1. The largest deviations from CCSD(T) were obtained for the formaldehyde dimer ($\text{CH}_2\text{O} \cdots \text{CH}_2\text{O}$, complex 9 in table 2.1), for which DC-06, CEPA₀, and OCEPA₀ yield errors of 0.99, 0.89, and 0.87 kcal mol⁻¹, respectively. For this system, the best performance is shown by CCSD and ODC-12, both of which give an error of 0.46 kcal mol⁻¹. For systems with π -stacking

interactions (complexes 22-24 in table 2.1), CCSD shows large errors (0.38, 0.43, 0.34 kcal mol⁻¹) relative to the magnitude of the interaction energy (0.43, 0.41, 0.91 kcal mol⁻¹, respectively). Here CEPA₀, DC-12, and their orbital-optimized variants offer much better agreement with CCSD(T), with errors ranging from 0.01 to 0.15 kcal mol⁻¹.

2.5.2 Hydrogen-Transfer Reaction Barrier Heights

We continue by assessing the performance of DCFT methods in predicting barrier heights for 18 hydrogen-transfer reactions from the HTBH38 database:⁶²



These reactions[†] involve molecules (R_1 and R_2) and transition states ($[R_1R_2H]^*$) with open-shell character, making their properties more sensitive to electron correlation effects. We employ barrier heights computed at the CCSD(T)/aug-cc-pVTZ level of theory as our reference rather than the values provided by Lynch⁶⁴ in order to effectively exclude basis-set incompleteness effects. We also omit the DC-06 and ODC-06 methods, which encounter frequent convergence problems due to the poor description of N -representability (see Supporting Information for incomplete DC-06 results).

Mean absolute deviations (Δ_{MAE}) and standard deviations (Δ_{SD}) for the hydrogen-transfer barrier heights are presented in table 2.2 and plotted in fig. 2.2. The

[†]Reaction 19 in HTBH38, the cis-trans isomerization of piperylene, is omitted in the present study.

largest Δ_{MAE} values come from CEPA₀ and DC-12 (2.77 and 2.49 kcal mol⁻¹, respectively). Orbital optimization greatly improves the accuracy of these methods, resulting in Δ_{MAE} values of just 0.67 and 0.94 kcal mol⁻¹ for OCEPA₀ and ODC-12, respectively. The CCSD method shows intermediate performance with Δ_{MAE} = 1.84 kcal mol⁻¹. A similar trend is observed for the Δ_{SD} values, with OCEPA₀

Figure 2.2: Mean absolute deviations (Δ_{MAE} , kcal mol⁻¹) and the standard deviations from the mean signed error (Δ_{SD} , kcal mol⁻¹) of barrier heights for 18 hydrogen-transfer reactions ($\text{R}_1 + \text{R}_2\text{H} \rightarrow \text{R}_1\text{H} + \text{R}_2$, HTBH38 database) computed using five methods with the aug-cc-pVTZ basis set. The errors are relative to CCSD(T)/aug-cc-pVTZ reference values. The Δ_{MAE} value is represented as a height of each colored box, while the Δ_{SD} value is depicted as a radius of the black vertical bar. See table 2.2 for data on individual database members.

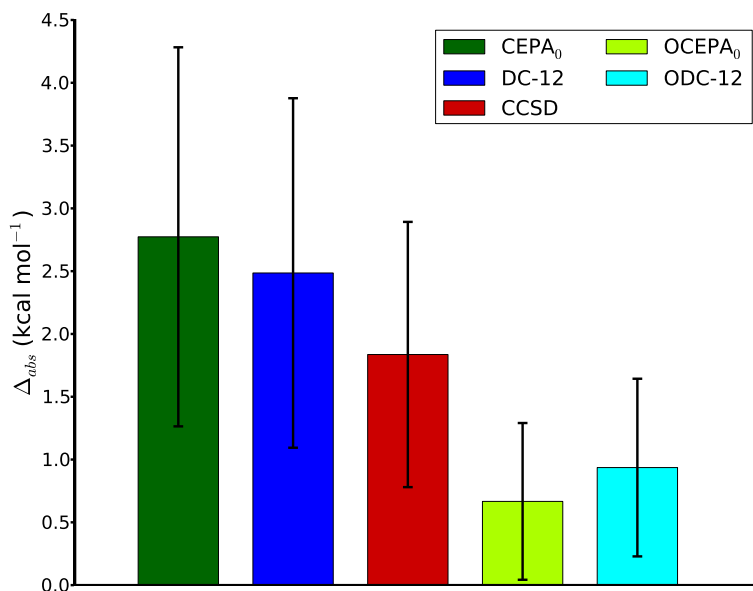


Table 2.2: Errors in barrier heights (kcal mol⁻¹) for 18 hydrogen-transfer reactions ($R_1 + R_2H \rightarrow R_1H + R_2$) comprising the HTBH38 database⁶⁴ computed using five methods with the aug-cc-pVTZ basis set. The errors are relative to CCSD(T) reference values (kcal mol⁻¹) shown in the rightmost column. Each reaction includes barrier heights in the forward ($R_1 + R_2H \rightarrow [R_1R_2H]^*$) and reverse ($[R_1R_2H]^* \leftarrow R_1H + R_2$) directions, respectively, except in the case of $R_1 = R_2 = H$ where they are the same. The mean absolute (Δ_{MAE} , kcal mol⁻¹) and the mean percent (Δ_{rel} , %) errors with respect to CCSD(T), as well as the standard deviations from the mean signed error (Δ_{SD} , kcal mol⁻¹) are also shown.

	Reaction Barrier	$\Delta CEPA_0$	$\Delta DC-12$	$\Delta CCSD$	$\Delta OCEPA_0$	$\Delta ODC-12$	CCSD(T)
1	$H + HCl \rightarrow [HHCl]^*$	0.74	0.49	0.09	-0.41	-0.28	5.22
2	$OH + H_2 \rightarrow [OHH_2]^*$	3.77	3.38	1.82	0.88	1.24	4.99
3	$CH_3 + H_2 \rightarrow [CH_3H_2]^*$	1.60	1.46	1.37	0.46	0.70	11.29
4	$OH + CH_4 \rightarrow [OHCH_4]^*$	4.26	3.85	2.61	1.22	1.65	5.64
5	$H + H_2 \rightarrow [HH_2]^*$	0.80	0.69	0.30	-0.27	-0.05	9.77
6	$OH + NH_3 \rightarrow [OHNH_3]^*$	6.02	5.25	3.54	1.18	1.82	3.17
7	$HCl + CH_3 \rightarrow [HClCH_3]^*$	1.93	1.78	1.79	0.68	0.92	0.10
8	$OH + C_2H_6 \rightarrow [OHC_2H_6]^*$	4.66	4.21	2.69	1.28	1.72	2.69
9	$F + H_2 \rightarrow [FH_2]^*$	3.40	3.14	1.20	0.52	0.78	1.13
10	$O + CH_4 \rightarrow [OHCH_3]^*$	3.40	3.12	2.37	0.70	1.20	13.62
11	$H + PH_3 \rightarrow [HPH_3]^*$	0.93	0.86	0.59	-0.16	0.10	2.29
12	$H + HO \rightarrow [OHH]^*$	2.03	1.59	0.44	-0.61	-0.26	10.25
13	$H + H_2S \rightarrow [HH_2S]^*$	1.01	0.92	0.65	-0.11	0.14	3.17
14	$O + HCl \rightarrow [OHCl]^*$	6.33	6.01	3.58	0.79	1.51	9.74
15	$NH_2 + CH_3 \rightarrow [CH_3NH_2]^*$	2.48	2.22	1.99	0.49	0.86	7.66
16	$NH_2 + C_2H_5 \rightarrow [NH_2C_2H_5]^*$	2.48	2.22	2.09	0.55	0.92	8.21
17	$C_2H_6 + NH_2 \rightarrow [C_2H_6NH_2]^*$	3.30	3.00	2.73	1.23	1.62	10.39
18	$NH_2 + CH_4 \rightarrow [NH_2CH_4]^*$	2.98	2.72	2.55	1.11	1.48	13.23

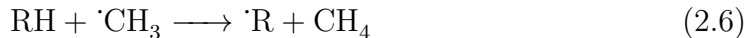
	Reaction Barrier	ΔCEPA_0	$\Delta\text{DC-12}$	ΔCCSD	ΔOCEPA_0	$\Delta\text{ODC-12}$	CCSD(T)
1	$[\text{HHCl}]^* \leftarrow \text{H}_2 + \text{Cl}$	1.44	1.31	1.61	0.53	0.77	7.39
2	$[\text{OHH}_2]^* \leftarrow \text{H} + \text{H}_2\text{O}$	2.09	1.66	0.09	-0.91	-0.58	21.07
3	$[\text{CH}_3\text{H}_2]^* \leftarrow \text{H} + \text{CH}_4$	0.95	0.80	0.38	-0.38	-0.11	14.91
4	$[\text{OHCH}_4]^* \leftarrow \text{CH}_3 + \text{H}_2\text{O}$	3.23	2.80	1.87	0.27	0.65	18.09
6	$[\text{OHNH}_3]^* \leftarrow \text{H}_2\text{O} + \text{NH}_2$	5.46	4.62	3.14	0.79	1.33	13.17
7	$[\text{HClCH}_3]^* \leftarrow \text{Cl} + \text{CH}_4$	1.97	1.94	2.31	0.78	1.16	5.89
8	$[\text{OHC}_2\text{H}_6]^* \leftarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5$	3.34	2.89	1.85	0.28	0.64	18.49
9	$[\text{FH}_2]^* \leftarrow \text{HF} + \text{H}$	1.27	0.88	-0.78	-1.47	-1.33	32.95
10	$[\text{OHCH}_3]^* \leftarrow \text{OH} + \text{CH}_3$	2.62	2.29	1.82	0.32	0.68	7.43
11	$[\text{HPH}_3]^* \leftarrow \text{PH}_2 + \text{H}_2$	1.14	1.11	1.37	0.39	0.63	23.21
12	$[\text{OHH}]^* \leftarrow \text{H}_2 + \text{O}$	3.47	3.08	1.99	0.62	1.07	12.81
13	$[\text{HH}_2\text{S}]^* \leftarrow \text{H}_2 + \text{HS}$	1.51	1.51	1.88	0.65	0.97	16.41
14	$[\text{OHCl}]^* \leftarrow \text{OH} + \text{Cl}$	5.59	5.35	3.55	0.51	1.24	9.35
15	$[\text{CH}_3\text{NH}_2]^* \leftarrow \text{CH}_4 + \text{NH}$	2.77	2.49	2.26	0.73	1.12	21.32
16	$[\text{NH}_2\text{C}_2\text{H}_5]^* \leftarrow \text{C}_2\text{H}_6 + \text{NH}$	3.06	2.75	2.46	0.85	1.26	18.52
17	$[\text{C}_2\text{H}_6\text{NH}_2]^* \leftarrow \text{NH}_3 + \text{C}_2\text{H}_5$	2.54	2.30	2.30	0.63	1.02	16.20
18	$[\text{NH}_2\text{CH}_4]^* \leftarrow \text{CH}_3 + \text{NH}_3$	2.51	2.29	2.21	0.56	0.96	15.69
	$\Delta_{\text{MAE}}:$	2.77	2.49	1.84	0.67	0.94	
	$\Delta_{\text{SD}}:$	1.51	1.39	1.06	0.62	0.71	
	$\Delta_{\text{rel}} \text{ } \%$:	99	90	77	29	40	

(0.62 kcal mol⁻¹) and ODC-12 (0.71 kcal mol⁻¹) significantly improving upon CEPA₀ (1.51 kcal mol⁻¹), DC-12 (1.39 kcal mol⁻¹), and CCSD (1.06 kcal mol⁻¹). In addition to Δ_{MAE} and Δ_{SD} , table 2.2 includes mean percent error (Δ_{rel}) values, which are commonly used to benchmark performance for reaction kinetics. The smallest Δ_{rel} values are 29% and 40% for OCEPA₀ and ODC-12, respectively.

Turning to barrier heights for individual hydrogen-transfer reactions (table 2.2), the largest errors are observed for reactions 6 and 14, both involving the OH radical, for which CEPA₀ and DC-12 give errors of ~ 5 -6 kcal mol⁻¹. The best results for these reactions are obtained from OCEPA₀, with errors ranging from 0.51 to 1.18 kcal mol⁻¹. The ODC-12 method tends to predict larger barrier heights than OCEPA₀, yielding smaller errors only when OCEPA₀ underestimates the barrier heights.

2.5.3 Radical Stabilization Energies

In this section we study the performance of DCFT methods for predicting radical stabilization energies (RSEs). An R-group’s RSE is defined as the enthalpy of a homodesmotic reaction



where exothermic (negative) values indicate that the radical $\cdot\text{R}$ is more thermodynamically stable than $\cdot\text{CH}_3$.⁶⁵ For our benchmark we use the RSE30 dataset⁶³, which provides a diverse variety of $\cdot\text{R}$ species (listed in table 2.3). Since the performance of CCSD(T) is known to deteriorate for strongly spin-contaminated UHF

Table 2.3: Errors in radical stabilization energies (RSEs, kcal mol⁻¹) for 30 open-shell doublet species ([•]R) comprising the RSE30 database⁶³ computed using six methods with the cc-pCVTZ basis set. The errors are relative to CCSD(T) with an added quadruples correction ($\delta Q = E_{\text{CCSDT(Q)}} - E_{\text{CCSD(T)}}$) shown in the rightmost column in kcal mol⁻¹. The δQ correction was computed using the cc-pCVDZ basis set. RSE is defined as the reaction enthalpy for the homodesmotic reaction $^{\bullet}\text{CH}_3 + \text{RH} \rightarrow \text{CH}_4 + ^{\bullet}\text{R}$. To indicate the degree of spin-contamination in the UHF reference, the spin expectation values ($\langle \hat{S}^2 \rangle_{\text{SCF}}$) are also shown in units of \hbar^2 . For each method the mean absolute deviations from CCSD(T)+ δQ (Δ_{MAE} , kcal mol⁻¹) and the standard deviations from the mean signed error (Δ_{SD} , kcal mol⁻¹) are also presented.

[•] R	$\langle \hat{S}^2 \rangle_{\text{SCF}}$	ΔCEPA_0	$\Delta\text{DC-12}$	ΔCCSD	ΔOCEPA_0	$\Delta\text{ODC-12}$	$\Delta\text{CCSD(T)}$	CCSD(T)+ δQ
[•] CH ₂ NO ₂	0.78	1.24	0.95	0.66	0.16	0.27	0.32	-3.50
[•] CH ₂ OCHO	0.76	1.16	1.12	0.63	0.40	0.48	0.10	-4.84
[•] CH ₂ SCH ₃	0.76	1.89	1.70	0.81	0.63	0.72	0.15	-11.01
[•] CF=CH ₂	0.94	6.12	3.71	0.96	0.42	0.64	0.46	6.26
[•] CH ₂ CH ₂ F	0.76	0.30	0.27	0.13	0.08	0.10	0.04	-1.53
[•] CH ₂ CHO	0.93	5.01	2.86	0.32	-0.16	0.02	0.46	-10.11
[•] CH ₂ CN	0.94	6.36	3.52	0.65	-0.02	0.21	0.46	-8.66
[•] CH ₂ F	0.76	1.03	1.00	0.52	0.55	0.57	0.06	-4.22
[•] CH ₂ NH ₂	0.76	1.28	1.18	0.59	0.50	0.52	0.06	-12.06
[•] CH ₂ NH ₃ ⁺	0.76	0.16	0.10	0.08	0.06	0.03	0.02	4.58
[•] CH ₂ NHOH	0.77	1.76	1.57	0.78	0.58	0.64	0.15	-8.81
[•] CH ₂ OH	0.76	1.29	1.23	0.62	0.57	0.60	0.07	-9.27
[•] CH ₂ PH ₃ ⁺	0.76	0.21	0.14	0.01	0.01	-0.02	0.05	0.49
[•] CH ₂ SH ₂ ⁺	0.77	0.41	0.30	0.12	0.11	0.08	0.06	2.29
[•] CH ₂ SH	0.76	1.60	1.43	0.68	0.57	0.63	0.12	-9.68

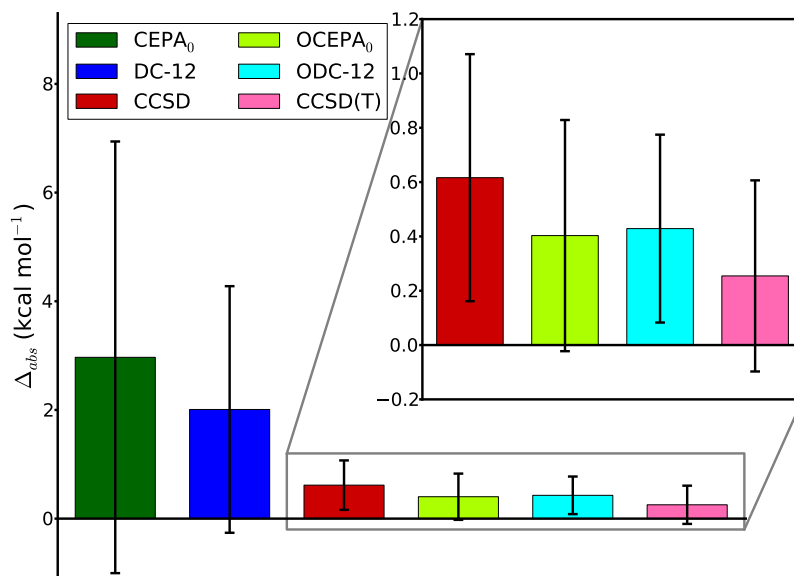
R	$\langle \hat{S}^2 \rangle_{\text{SCF}}$	ΔCEPA_0	$\Delta\text{DC-12}$	ΔCCSD	ΔOCEPA_0	$\Delta\text{ODC-12}$	$\Delta\text{CCSD(T)}$	$\text{CCSD(T)}+\delta\text{Q}$
$\cdot\text{CH}_2\text{C}\equiv\text{CH}$	1.00	6.23	3.47	0.82	-0.03	0.23	0.52	-13.17
$\cdot\text{CH}_2\text{CH}_3$	0.76	0.30	0.26	0.11	0.08	0.10	0.03	-3.36
$\cdot\text{CH}_2\text{Cl}$	0.77	1.13	1.02	0.50	0.48	0.51	0.09	-5.67
$\cdot\text{CH}_2\text{BH}_2$	0.76	0.17	0.17	0.05	0.03	0.04	0.05	-11.66
$\cdot\text{CHO}$	0.77	2.26	2.24	1.48	1.55	1.56	0.20	-17.61
$\cdot\text{CH}_2\text{PH}_2$	0.76	1.17	1.02	0.39	0.36	0.39	0.12	-6.50
$\cdot\text{CHClF}$	0.76	1.61	1.52	0.76	0.78	0.81	0.13	-6.61
$\cdot\text{CHFCH}_3$	0.76	1.07	1.01	0.50	0.51	0.53	0.08	-5.87
$\cdot\text{CH(OH)}_2$	0.76	1.30	1.22	0.60	0.60	0.61	0.08	-6.67
$\cdot\text{CHCl}_2$	0.77	1.78	1.57	0.72	0.72	0.75	0.15	-9.56
$\cdot\text{CHF}_2$	0.76	1.50	1.48	0.78	0.83	0.85	0.10	-4.07
$\text{CH}_2=\text{C}\cdot-\text{CN}$	1.39	19.10	11.50	2.36	-0.31	0.29	1.80	1.98
$\cdot\text{C}\equiv\text{CH}$	1.15	11.20	6.51	0.77	-0.78	-0.07	0.82	26.25
$\cdot\text{CH}=\text{CH}_2$	0.94	5.42	3.01	0.58	0.11	0.31	0.40	5.49
$\cdot\text{CH}_2-\text{CH}=\text{CH}_2$	0.97	4.98	3.17	0.51	0.11	0.31	0.48	-17.53
		$\Delta_{\text{MAE}}:$	2.97	2.01	0.62	0.40	0.43	0.25
		$\Delta_{\text{SD}}:$	3.97	2.27	0.45	0.43	0.35	0.35

references,^{66–70} we augment CCSD(T) energies with a quadruples correction ($\Delta Q = E_{\text{CCSDT(Q)}} - E_{\text{CCSD(T)}}$) and use these as our benchmark. CBS-extrapolated CCSD(T) reference values have been published for this dataset,³¹ but we use CCSD(T) values computed with the cc-pCVTZ basis set to avoid basis-set incompleteness effects. The δQ correction was evaluated using the cc-pCVDZ basis set. As in the previous Section, DC-06 and ODC-06 computations cannot be converged for all database members and are omitted in the analysis below (see Supporting Information for incomplete DC-06 and ODC-06 data).

The relative performance of the DCFT, CEPA, and CC methods for the RSE30 dataset is shown in fig. 2.3. The effect of orbital-optimization on accuracy is now even more pronounced, reducing the large Δ_{MAE} errors of CEPA₀ (2.97 kcal mol⁻¹) and DC-12 (2.01 kcal mol⁻¹) to 0.40 and 0.43 kcal mol⁻¹ for OCEPA₀ and ODC-12, respectively. CCSD has a slightly larger Δ_{MAE} value (0.62 kcal mol⁻¹), while CCSD(T) has the smallest overall Δ_{MAE} (0.25 kcal mol⁻¹). Both CEPA₀ and DC-12 show large standard deviations again (3.97 and 2.27 kcal mol⁻¹, respectively). For OCEPA₀, the standard deviation (0.43 kcal mol⁻¹) is similar to that of CCSD (0.45 kcal mol⁻¹). ODC-12 and CCSD(T) exhibit the most consistent performance with the same Δ_{SD} value of 0.35 kcal mol⁻¹.

Deviations from CCSD(T)+ δQ for individual RSEs predicted by each method are tabulated in table 2.3. In addition, table 2.3 includes expectation values of the square-norm spin operator computed for the UHF wavefunction of $\cdot\text{R}$ ($\langle \hat{S}^2 \rangle_{\text{SCF}}$). The largest errors in computed RSEs were obtained for $\cdot\text{R}$ species with $\langle \hat{S}^2 \rangle_{\text{SCF}} > 0.9 \hbar^2$ (radicals 4, 6, 7, 16, and 27-30 in table 2.3). For these sys-

Figure 2.3: Mean absolute deviations (Δ_{MAE} , kcal mol⁻¹) and the standard deviations from the mean signed error (Δ_{SD} , kcal mol⁻¹) of the radical stabilization energies (RSEs) for 30 open-shell doublet species (RSE30 database) computed using six methods with the cc-pCVTZ basis set. The errors are relative to CCSD(T) with an added quadruples correction ($\delta Q = E_{\text{CCSDT(Q)}} - E_{\text{CCSD(T)}}$). The δQ correction was computed using the cc-pCVDZ basis set. RSE is defined as the reaction enthalpy for the homodesmotic reaction $\cdot\text{CH}_3 + \text{RH} \rightarrow \text{CH}_4 + \cdot\text{R}$. The Δ_{MAE} value is represented as a height of each colored box, while the Δ_{SD} value is depicted as a radius of the black vertical bar. See table 2.3 for data on individual database members.



tems, the average CEPA₀ and DC-12 errors are 8.05 and 4.72 kcal mol⁻¹, and the average CCSD(T) error is 0.68 kcal mol⁻¹. OCEPA₀ and ODC-12 offer remarkably better performance for this subset, with average errors of 0.24 kcal mol⁻¹ and 0.26 kcal mol⁻¹.

Chapter 3

Linear-Response Density Cumulant Theory for Excited States: First Implementation and Benchmark Calculations*

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Chapter 4

Linear-Response Density Cumulant Theory for Excited States: Better Algorithms, Bigger Systems

Check out Table 4.1. You might consider using `longtable` or `tabu` for your tables instead.

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Count	x Error	y Error
4	2.30	2.30
5	2.10	1.97
9	1.92	1.72
13	1.82	1.64

Table 4.1: Effect of count on error using our model. The error reduces as the count increases.

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Chapter 5

Conclusion

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Appendix A

Extended Results

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