Density Cumulant Theory for Ground and Excited Electronic states

by

Andreas Victor Copan

(Under the Direction of Henry F. Schaefer III)

Abstract

Here is my abstract. Here is my abstract. Here is my abstract. Here is my abstract. Here is my abstract. Here is my abstract. Here is my abstract. Here is my abstract. Here is my abstract. Here is my abstract.

Index words: Cool stuff, Deep learning, Big data, Crowdsourcing, Computer vision, Computer science

Density Cumulant Theory for Ground and Excited Electronic states

by

Andreas Victor Copan

B.A., Bethel University, 2013

A Dissertation Submitted to the Graduate Faculty
of The University of Georgia in Partial Fulfillment
of the
Requirements for the Degree

Doctor of Philosophy

Athens, Georgia

2018

Density Cumulant Theory for Ground and Excited Electronic states

by

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

Acknowledgments

All of your acknowledgments should go here. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

Nam dui ligula, fringilla a, euismod sodales, sollicitudin vel, wisi. Morbi auctor lorem non justo. Nam lacus libero, pretium at, lobortis vitae, ultricies et, tellus. Donec aliquet, tortor sed accumsan bibendum, erat ligula aliquet magna, vitae ornare odio metus a mi. Morbi ac orci et nisl hendrerit mollis. Suspendisse ut massa. Cras nec ante. Pellentesque a nulla. Cum sociis natoque penatibus et

magnis dis parturient montes, nascetur ridiculus mus. Aliquam tincidunt urna. Nulla ullamcorper vestibulum turpis. Pellentesque cursus luctus mauris.

Nulla malesuada porttitor diam. Donec felis erat, congue non, volutpat at, tincidunt tristique, libero. Vivamus viverra fermentum felis. Donec nonummy pellentesque ante. Phasellus adipiscing semper elit. Proin fermentum massa ac quam. Sed diam turpis, molestie vitae, placerat a, molestie nec, leo. Maecenas lacinia. Nam ipsum ligula, eleifend at, accumsan nec, suscipit a, ipsum. Morbi blandit ligula feugiat magna. Nunc eleifend consequat lorem. Sed lacinia nulla vitae enim. Pellentesque tincidunt purus vel magna. Integer non enim. Praesent euismod nunc eu purus. Donec bibendum quam in tellus. Nullam cursus pulvinar lectus. Donec et mi. Nam vulputate metus eu enim. Vestibulum pellentesque felis eu massa.

Quisque ullamcorper placerat ipsum. Cras nibh. Morbi vel justo vitae lacus tincidunt ultrices. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. In hac habitasse platea dictumst. Integer tempus convallis augue. Etiam facilisis. Nunc elementum fermentum wisi. Aenean placerat. Ut imperdiet, enim sed gravida sollicitudin, felis odio placerat quam, ac pulvinar elit purus eget enim. Nunc vitae tortor. Proin tempus nibh sit amet nisl. Vivamus quis tortor vitae risus porta vehicula.

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a faucibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis port-

titor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetuer.

Suspendisse vel felis. Ut lorem lorem, interdum eu, tincidunt sit amet, laoreet vitae, arcu. Aenean faucibus pede eu ante. Praesent enim elit, rutrum at, molestie non, nonummy vel, nisl. Ut lectus eros, malesuada sit amet, fermentum eu, sodales cursus, magna. Donec eu purus. Quisque vehicula, urna sed ultricies auctor, pede lorem egestas dui, et convallis elit erat sed nulla. Donec luctus. Curabitur et nunc. Aliquam dolor odio, commodo pretium, ultricies non, pharetra in, velit. Integer arcu est, nonummy in, fermentum faucibus, egestas vel, odio.

Sed commodo posuere pede. Mauris ut est. Ut quis purus. Sed ac odio. Sed vehicula hendrerit sem. Duis non odio. Morbi ut dui. Sed accumsan risus eget odio. In hac habitasse platea dictumst. Pellentesque non elit. Fusce sed justo eu urna porta tincidunt. Mauris felis odio, sollicitudin sed, volutpat a, ornare ac, erat. Morbi quis dolor. Donec pellentesque, erat ac sagittis semper, nunc dui lobortis purus, quis congue purus metus ultricies tellus. Proin et quam. Class aptent taciti sociosqu ad litora torquent per conubia nostra, per inceptos hymenaeos. Praesent sapien turpis, fermentum vel, eleifend faucibus, vehicula eu, lacus.

Contents

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 Koch[1], or parenthetically[1]. 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.

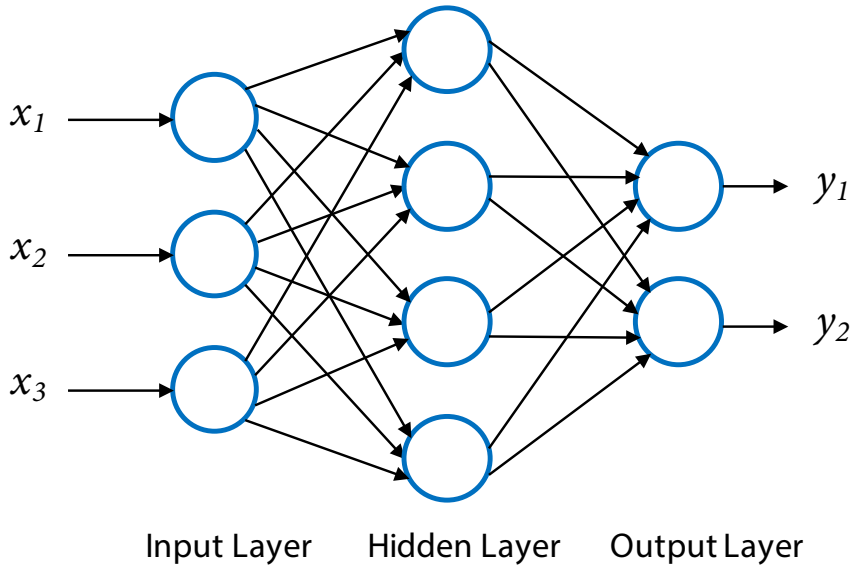

Figure 1.1: An example neural network with two final outputs. Notice how each neuron in one layer connects to each neuron in the following layer. This is called *fully connected*.

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 ($CEPA_0$ and $OCEPA_0$) 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 $CEPA_0$, and shows similar accuracy to the orbital-optimized $CEPA_0$ variant ($OCEPA_0$) for systems at equilibrium geometries. For covalent bond stretching, ODC-12 is found to be more reliable than $OCEPA_0$. 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, extensive[2], 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 linearity[16] of CI in their equations. CEPA methods, however, have been shown to rapidly deteriorate as the molecular geometry deviates from equilibrium[16] 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 structures[16], 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 ($CEPA_0$),[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 methods[54] the exact molecular energy is expressed as a functional of the one- and two-particle reduced density matrices, $\boldsymbol{\gamma}_1$ and $\boldsymbol{\gamma}_2$ (1-RDM and 2-RDM):

$$E = h^q_p \gamma^p_q + \tfrac{1}{2} g^{rs}_{pq} \gamma^{pq}_{rs} \ , \qquad [\boldsymbol{\gamma}_1]^p_q \equiv \gamma^p_q \ , \qquad [\boldsymbol{\gamma}_2]^{pq}_{rs} \equiv \gamma^{pq}_{rs} \, . \tag{2.1}$$

In eq. (2.1), h^q_p and g^{rs}_{pq} 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 $\boldsymbol{\gamma}_1$ through $\boldsymbol{\gamma}_2$ via the partial trace relation $\sum_r \gamma^{pr}_{qr} = (N-1)\gamma^p_q$, the energy functional (2.1) can be minimized by varying $\boldsymbol{\gamma}_2$ 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 $\boldsymbol{\gamma}_2$ in terms of its irreducible components – the 1-RDM and the two-particle cumulant (denoted by $\boldsymbol{\lambda}_2$):

$$\gamma^{pq}_{rs} = \gamma^p_r \gamma^q_s - \gamma^q_r \gamma^p_s + \lambda^{pq}_{rs} \, . \tag{2.2}$$

In eq. (2.2), $\boldsymbol{\lambda}_2$ describes the correlated part of $\boldsymbol{\gamma}_2$ that cannot be expressed via $\boldsymbol{\gamma}_1$. The cumulant also determines the correlation contribution to $\boldsymbol{\gamma}_1$, allowing

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

$$\boldsymbol{\gamma}_1 = \boldsymbol{\kappa} + \boldsymbol{\tau}\,. \tag{2.3}$$

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:

$$\begin{aligned} E[\boldsymbol{\kappa}, \boldsymbol{\lambda}_2] &= \tfrac{1}{2}(h^q_p + f^q_p)(\kappa^p_q + \tau^p_q) + \tfrac{1}{4}\overline{g}^{rs}_{pq}\lambda^{rs}_{pq}, \\ f^q_p &= h^q_p + \overline{g}^{qs}_{pr}(\kappa^r_s + \tau^r_s), \quad \overline{g}^{pq}_{rs} = g^{pq}_{rs} - g^{qp}_{rs}\,. \end{aligned} \tag{2.4}$$

Chapter 3

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

Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

Nam dui ligula, fringilla a, euismod sodales, sollicitudin vel, wisi. Morbi auctor lorem non justo. Nam lacus libero, pretium at, lobortis vitae, ultricies et, tellus.

*A. V. Copan and A. Yu. Sokolov (to be submitted in J. Chem. Theory Comput).

Donec aliquet, tortor sed accumsan bibendum, erat ligula aliquet magna, vitae ornare odio metus a mi. Morbi ac orci et nisl hendrerit mollis. Suspendisse ut massa. Cras nec ante. Pellentesque a nulla. Cum sociis natoque penatibus et magnis dis parturient montes, nascetur ridiculus mus. Aliquam tincidunt urna. Nulla ullamcorper vestibulum turpis. Pellentesque cursus luctus mauris.

Nulla malesuada porttitor diam. Donec felis erat, congue non, volutpat at, tincidunt tristique, libero. Vivamus viverra fermentum felis. Donec nonummy pellentesque ante. Phasellus adipiscing semper elit. Proin fermentum massa ac quam. Sed diam turpis, molestie vitae, placerat a, molestie nec, leo. Maecenas lacinia. Nam ipsum ligula, eleifend at, accumsan nec, suscipit a, ipsum. Morbi blandit ligula feugiat magna. Nunc eleifend consequat lorem. Sed lacinia nulla vitae enim. Pellentesque tincidunt purus vel magna. Integer non enim. Praesent euismod nunc eu purus. Donec bibendum quam in tellus. Nullam cursus pulvinar lectus. Donec et mi. Nam vulputate metus eu enim. Vestibulum pellentesque felis eu massa.

Quisque ullamcorper placerat ipsum. Cras nibh. Morbi vel justo vitae lacus tincidunt ultrices. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. In hac habitasse platea dictumst. Integer tempus convallis augue. Etiam facilisis. Nunc elementum fermentum wisi. Aenean placerat. Ut imperdiet, enim sed gravida sollicitudin, felis odio placerat quam, ac pulvinar elit purus eget enim. Nunc vitae tortor. Proin tempus nibh sit amet nisl. Vivamus quis tortor vitae risus porta vehicula.

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a fau-

cibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis porttitor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetuer.

Suspendisse vel felis. Ut lorem lorem, interdum eu, tincidunt sit amet, laoreet vitae, arcu. Aenean faucibus pede eu ante. Praesent enim elit, rutrum at, molestie non, nonummy vel, nisl. Ut lectus eros, malesuada sit amet, fermentum eu, sodales cursus, magna. Donec eu purus. Quisque vehicula, urna sed ultricies auctor, pede lorem egestas dui, et convallis elit erat sed nulla. Donec luctus. Curabitur et nunc. Aliquam dolor odio, commodo pretium, ultricies non, pharetra in, velit. Integer arcu est, nonummy in, fermentum faucibus, egestas vel, odio.

Sed commodo posuere pede. Mauris ut est. Ut quis purus. Sed ac odio. Sed vehicula hendrerit sem. Duis non odio. Morbi ut dui. Sed accumsan risus eget odio. In hac habitasse platea dictumst. Pellentesque non elit. Fusce sed justo eu urna porta tincidunt. Mauris felis odio, sollicitudin sed, volutpat a, ornare ac, erat. Morbi quis dolor. Donec pellentesque, erat ac sagittis semper, nunc dui lobortis purus, quis congue purus metus ultricies tellus. Proin et quam. Class aptent taciti sociosqu ad litora torquent per conubia nostra, per inceptos hymenaeos. Praesent sapien turpis, fermentum vel, eleifend faucibus, vehicula eu, lacus.

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.

Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem.

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.

Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

Nam dui ligula, fringilla a, euismod sodales, sollicitudin vel, wisi. Morbi auctor lorem non justo. Nam lacus libero, pretium at, lobortis vitae, ultricies et, tellus. Donec aliquet, tortor sed accumsan bibendum, erat ligula aliquet magna, vitae ornare odio metus a mi. Morbi ac orci et nisl hendrerit mollis. Suspendisse ut massa. Cras nec ante. Pellentesque a nulla. Cum sociis natoque penatibus et magnis dis parturient montes, nascetur ridiculus mus. Aliquam tincidunt urna. Nulla ullamcorper vestibulum turpis. Pellentesque cursus luctus mauris.

Nulla malesuada porttitor diam. Donec felis erat, congue non, volutpat at, tincidunt tristique, libero. Vivamus viverra fermentum felis. Donec nonummy pellentesque ante. Phasellus adipiscing semper elit. Proin fermentum massa ac quam. Sed diam turpis, molestie vitae, placerat a, molestie nec, leo. Maecenas lacinia. Nam ipsum ligula, eleifend at, accumsan nec, suscipit a, ipsum. Morbi blandit ligula feugiat magna. Nunc eleifend consequat lorem. Sed lacinia nulla vitae enim. Pellentesque tincidunt purus vel magna. Integer non enim. Praesent euismod nunc eu purus. Donec bibendum quam in tellus. Nullam cursus pulvinar lectus. Donec et mi. Nam vulputate metus eu enim. Vestibulum pellentesque felis eu massa.

Quisque ullamcorper placerat ipsum. Cras nibh. Morbi vel justo vitae lacus tincidunt ultrices. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. In hac habitasse platea dictumst. Integer tempus convallis augue. Etiam facilisis. Nunc elementum fermentum wisi. Aenean placerat. Ut imperdiet, enim sed gravida sollicitudin, felis odio placerat quam, ac pulvinar elit purus eget enim. Nunc vitae tortor. Proin tempus nibh sit amet nisl. Vivamus quis tortor vitae risus porta vehicula.

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a faucibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis porttitor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetuer.

Suspendisse vel felis. Ut lorem lorem, interdum eu, tincidunt sit amet, laoreet vitae, arcu. Aenean faucibus pede eu ante. Praesent enim elit, rutrum at, molestie non, nonummy vel, nisl. Ut lectus eros, malesuada sit amet, fermentum eu, sodales cursus, magna. Donec eu purus. Quisque vehicula, urna sed ultricies auctor, pede lorem egestas dui, et convallis elit erat sed nulla. Donec luctus. Curabitur et nunc. Aliquam dolor odio, commodo pretium, ultricies non, pharetra in, velit. Integer arcu est, nonummy in, fermentum faucibus, egestas vel, odio.

Sed commodo posuere pede. Mauris ut est. Ut quis purus. Sed ac odio. Sed vehicula hendrerit sem. Duis non odio. Morbi ut dui. Sed accumsan risus eget odio. In hac habitasse platea dictumst. Pellentesque non elit. Fusce sed justo eu urna porta tincidunt. Mauris felis odio, sollicitudin sed, volutpat a, ornare ac, erat. Morbi quis dolor. Donec pellentesque, erat ac sagittis semper, nunc dui lobortis purus, quis congue purus metus ultricies tellus. Proin et quam. Class aptent taciti sociosqu ad litora torquent per conubia nostra, per inceptos hymenaeos. Praesent sapien turpis, fermentum vel, eleifend faucibus, vehicula eu, lacus.

Chapter 5

Conclusion

Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

Nam dui ligula, fringilla a, euismod sodales, sollicitudin vel, wisi. Morbi auctor lorem non justo. Nam lacus libero, pretium at, lobortis vitae, ultricies et, tellus. Donec aliquet, tortor sed accumsan bibendum, erat ligula aliquet magna, vitae ornare odio metus a mi. Morbi ac orci et nisl hendrerit mollis. Suspendisse ut

massa. Cras nec ante. Pellentesque a nulla. Cum sociis natoque penatibus et magnis dis parturient montes, nascetur ridiculus mus. Aliquam tincidunt urna. Nulla ullamcorper vestibulum turpis. Pellentesque cursus luctus mauris.

Nulla malesuada porttitor diam. Donec felis erat, congue non, volutpat at, tincidunt tristique, libero. Vivamus viverra fermentum felis. Donec nonummy pellentesque ante. Phasellus adipiscing semper elit. Proin fermentum massa ac quam. Sed diam turpis, molestie vitae, placerat a, molestie nec, leo. Maecenas lacinia. Nam ipsum ligula, eleifend at, accumsan nec, suscipit a, ipsum. Morbi blandit ligula feugiat magna. Nunc eleifend consequat lorem. Sed lacinia nulla vitae enim. Pellentesque tincidunt purus vel magna. Integer non enim. Praesent euismod nunc eu purus. Donec bibendum quam in tellus. Nullam cursus pulvinar lectus. Donec et mi. Nam vulputate metus eu enim. Vestibulum pellentesque felis eu massa.

Quisque ullamcorper placerat ipsum. Cras nibh. Morbi vel justo vitae lacus tincidunt ultrices. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. In hac habitasse platea dictumst. Integer tempus convallis augue. Etiam facilisis. Nunc elementum fermentum wisi. Aenean placerat. Ut imperdiet, enim sed gravida sollicitudin, felis odio placerat quam, ac pulvinar elit purus eget enim. Nunc vitae tortor. Proin tempus nibh sit amet nisl. Vivamus quis tortor vitae risus porta vehicula.

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a faucibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue

quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis porttitor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetuer.

Suspendisse vel felis. Ut lorem lorem, interdum eu, tincidunt sit amet, laoreet vitae, arcu. Aenean faucibus pede eu ante. Praesent enim elit, rutrum at, molestie non, nonummy vel, nisl. Ut lectus eros, malesuada sit amet, fermentum eu, sodales cursus, magna. Donec eu purus. Quisque vehicula, urna sed ultricies auctor, pede lorem egestas dui, et convallis elit erat sed nulla. Donec luctus. Curabitur et nunc. Aliquam dolor odio, commodo pretium, ultricies non, pharetra in, velit. Integer arcu est, nonummy in, fermentum faucibus, egestas vel, odio.

Sed commodo posuere pede. Mauris ut est. Ut quis purus. Sed ac odio. Sed vehicula hendrerit sem. Duis non odio. Morbi ut dui. Sed accumsan risus eget odio. In hac habitasse platea dictumst. Pellentesque non elit. Fusce sed justo eu urna porta tincidunt. Mauris felis odio, sollicitudin sed, volutpat a, ornare ac, erat. Morbi quis dolor. Donec pellentesque, erat ac sagittis semper, nunc dui lobortis purus, quis congue purus metus ultricies tellus. Proin et quam. Class aptent taciti sociosqu ad litora torquent per conubia nostra, per inceptos hymenaeos. Praesent sapien turpis, fermentum vel, eleifend faucibus, vehicula eu, lacus.

Appendix A

Extended Results

Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

Nam dui ligula, fringilla a, euismod sodales, sollicitudin vel, wisi. Morbi auctor lorem non justo. Nam lacus libero, pretium at, lobortis vitae, ultricies et, tellus. Donec aliquet, tortor sed accumsan bibendum, erat ligula aliquet magna, vitae ornare odio metus a mi. Morbi ac orci et nisl hendrerit mollis. Suspendisse ut

massa. Cras nec ante. Pellentesque a nulla. Cum sociis natoque penatibus et magnis dis parturient montes, nascetur ridiculus mus. Aliquam tincidunt urna. Nulla ullamcorper vestibulum turpis. Pellentesque cursus luctus mauris.

Nulla malesuada porttitor diam. Donec felis erat, congue non, volutpat at, tincidunt tristique, libero. Vivamus viverra fermentum felis. Donec nonummy pellentesque ante. Phasellus adipiscing semper elit. Proin fermentum massa ac quam. Sed diam turpis, molestie vitae, placerat a, molestie nec, leo. Maecenas lacinia. Nam ipsum ligula, eleifend at, accumsan nec, suscipit a, ipsum. Morbi blandit ligula feugiat magna. Nunc eleifend consequat lorem. Sed lacinia nulla vitae enim. Pellentesque tincidunt purus vel magna. Integer non enim. Praesent euismod nunc eu purus. Donec bibendum quam in tellus. Nullam cursus pulvinar lectus. Donec et mi. Nam vulputate metus eu enim. Vestibulum pellentesque felis eu massa.

Quisque ullamcorper placerat ipsum. Cras nibh. Morbi vel justo vitae lacus tincidunt ultrices. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. In hac habitasse platea dictumst. Integer tempus convallis augue. Etiam facilisis. Nunc elementum fermentum wisi. Aenean placerat. Ut imperdiet, enim sed gravida sollicitudin, felis odio placerat quam, ac pulvinar elit purus eget enim. Nunc vitae tortor. Proin tempus nibh sit amet nisl. Vivamus quis tortor vitae risus porta vehicula.

Fusce mauris. Vestibulum luctus nibh at lectus. Sed bibendum, nulla a faucibus semper, leo velit ultricies tellus, ac venenatis arcu wisi vel nisl. Vestibulum diam. Aliquam pellentesque, augue quis sagittis posuere, turpis lacus congue

quam, in hendrerit risus eros eget felis. Maecenas eget erat in sapien mattis porttitor. Vestibulum porttitor. Nulla facilisi. Sed a turpis eu lacus commodo facilisis. Morbi fringilla, wisi in dignissim interdum, justo lectus sagittis dui, et vehicula libero dui cursus dui. Mauris tempor ligula sed lacus. Duis cursus enim ut augue. Cras ac magna. Cras nulla. Nulla egestas. Curabitur a leo. Quisque egestas wisi eget nunc. Nam feugiat lacus vel est. Curabitur consectetuer.

Suspendisse vel felis. Ut lorem lorem, interdum eu, tincidunt sit amet, laoreet vitae, arcu. Aenean faucibus pede eu ante. Praesent enim elit, rutrum at, molestie non, nonummy vel, nisl. Ut lectus eros, malesuada sit amet, fermentum eu, sodales cursus, magna. Donec eu purus. Quisque vehicula, urna sed ultricies auctor, pede lorem egestas dui, et convallis elit erat sed nulla. Donec luctus. Curabitur et nunc. Aliquam dolor odio, commodo pretium, ultricies non, pharetra in, velit. Integer arcu est, nonummy in, fermentum faucibus, egestas vel, odio.

Sed commodo posuere pede. Mauris ut est. Ut quis purus. Sed ac odio. Sed vehicula hendrerit sem. Duis non odio. Morbi ut dui. Sed accumsan risus eget odio. In hac habitasse platea dictumst. Pellentesque non elit. Fusce sed justo eu urna porta tincidunt. Mauris felis odio, sollicitudin sed, volutpat a, ornare ac, erat. Morbi quis dolor. Donec pellentesque, erat ac sagittis semper, nunc dui lobortis purus, quis congue purus metus ultricies tellus. Proin et quam. Class aptent taciti sociosqu ad litora torquent per conubia nostra, per inceptos hymenaeos. Praesent sapien turpis, fermentum vel, eleifend faucibus, vehicula eu, lacus.

Bibliography

[1] T. B. Pedersen, B. Fernández, and H. Koch, J. Chem. Phys. **114**, 6983 (2001).

[2] M. Nooijen, K. R. Shamasundar, and D. Mukherjee, Mol. Phys. **103**, 2277 (2005).

[3] J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quantum Chem. **10**, 1 (1976).

[4] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).

[5] P. G. Szalay, M. Nooijen, and R. J. Bartlett, J. Chem. Phys. **103**, 281 (1995).

[6] H. P. Kelly and A. M. Sessler, Phys. Rev. **132**, 2091 (1963).

[7] H. P. Kelly, Phys. Rev. A **134**, 1450 (1964).

[8] W. Meyer, J. Chem. Phys. **58**, 1017 (1973).

[9] R. Ahlrichs, Comput. Phys. Commun. **17**, 31 (1979).

[10] S. Koch and W. Kutzelnigg, Theor. Chim. Acta **59**, 387 (1981).

[11] M. Gelus, R. Ahlrichs, V. Staemmler, and W. Kutzelnigg, Chem. Phys. Lett. **7**, 503 (1970).

[12] V. Staemmler and M. Jungen, Chem. Phys. Lett. **16**, 187 (1972).

[13] R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler, and W. Kutzelnigg, J. Chem. Phys. **62**, 1235 (1975).

[14] H. Kollmar and V. Staemmler, J. Am. Chem. Soc. **99**, 3583 (1977).

[15] J. Wasilewski, V. Staemmler, and S. Koch, Phys. Rev. A **38**, 1289 (1988).

[16] A. G. Taube and R. J. Bartlett, J. Chem. Phys. **130**, 144112 (2009).

[17] F. Coester, Nucl. Phys. **7**, 421 (1958).

[18] F. Coester and H. Kümmel, Nucl. Phys. **17**, 477 (1960).

[19] J. Čížek, J. Chem. Phys. **45**, 4256 (1966).

[20] R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. **14**, 561 (1978).

[21] T. D. Crawford and H. F. Schaefer, Rev. Comp. Chem. **14**, 33 (2000).

[22] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).

[23] I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics* (Cambridge University Press, Cambridge, UK, 2009).

[24] C. Kollmar and F. Neese, Mol. Phys. **108**, 2449 (2010).

[25] J. P. Daudey, J. L. Heully, and J. P. Malrieu, J. Chem. Phys. **99**, 1240 (1993).

[26] J. P. Malrieu, H. Zhang, and J. Ma, Chem. Phys. Lett. **493**, 179 (2010).

[27] M. Nooijen and R. J. Le Roy, J. Mol. Struct. **768**, 25 (2006).

[28] C. Kollmar and F. Neese, J. Chem. Phys. **135**, 84102 (2011).

[29] C. Kollmar and A. Heßelmann, Theor. Chem. Acc. **127**, 311 (2010).

[30] U. Bozkaya and C. D. Sherrill, J. Chem. Phys. **139**, 054104 (2013).

[31] E. SoydaÅ§ and U. Bozkaya, J. Comput. Chem. **35**, 1073 (2014).

[32] U. Bozkaya, J. Chem. Phys. **139**, 154105 (2013).

[33] F. Wennmohs and F. Neese, Chem. Phys. **343**, 217 (2008).

[34] F. Neese, F. Wennmohs, and A. Hansen, J. Chem. Phys. **130**, 114108 (2009).

[35] W. Kutzelnigg, J. Chem. Phys. **125**, 171101 (2006).

[36] D. A. Mazziotti, Phys. Rev. Lett. **101**, 253002 (2008).

[37] D. A. Mazziotti, Phys. Rev. A **81**, 62515 (2010).

[38] A. E. DePrince and D. A. Mazziotti, Mol. Phys. **110**, 1917 (2012).

[39] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **107**, 432 (1997).

[40] D. A. Mazziotti, Chem. Phys. Lett. **289**, 419 (1998).

[41] D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998).

[42] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **110**, 2800 (1999).

[43] L. Kong, Int. J. Quantum Chem. **111**, 3541 (2011).

[44] M. Hanauer and A. Köhn, Chem. Phys. **401**, 50 (2012).

[45] M. Nakata and K. Yasuda, Phys. Rev. A **80**, 42109 (2009).

[46] H. van Aggelen, B. Verstichel, P. Bultinck, D. Van Neck, P. W. Ayers, and D. L. Cooper, J. Chem. Phys. **132**, 114112 (2010).

[47] B. Verstichel, H. van Aggelen, D. Van Neck, P. W. Ayers, and P. Bultinck, J. Chem. Phys. **132**, 114113 (2010).

[48] J. M. Herbert and J. E. Harriman, Adv. Chem. Phys. **134**, 261 (2007).

[49] A. C. Simmonett, J. J. Wilke, H. F. Schaefer, and W. Kutzelnigg, J. Chem. Phys. **133**, 174122 (2010).

[50] A. Y. Sokolov, J. J. Wilke, A. C. Simmonett, and H. F. Schaefer, J. Chem. Phys. **137**, 054105 (2012).

[51] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **120**, 7350 (2004).

[52] A. Y. Sokolov, A. C. Simmonett, and H. F. Schaefer, J. Chem. Phys. **138**, 024107 (2013).

[53] A. Y. Sokolov and H. F. Schaefer, J. Chem. Phys. **139**, 204110 (2013).

[54] D. A. Mazziotti, ed., *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*, Advances in Chemical Physics, Vol. 134 (John Wiley & Sons, Inc., Hoboken, NJ, 2007).