

**Advances in Multiconfiguration
Pair Density Functional Theory
and Applications to Excited
State, Singlet-Triplet Gaps and
Magnetism**

A THESIS SUBMITTED TO THE FACULTY OF THE
GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA

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IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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NOVEMBER, 2020

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This thesis is dedicated to
my parents, Rajesh and Savita Sharma
for their endless love, support and encouragement

Acknowledgements

First and foremost I would like to thank my advisor, Professor Laura Gagliardi for her guidance and unwavering support throughout my doctoral research. She provided me the freedom to explore new areas of chemistry and be creative in my research. I thank Prof. Gagliardi for introducing me to an exciting field of theoretical chemistry and helping me at each step to become a better scientist. I thank her to give me the opportunity to present my work domestically and internationally, as well as to meet many individuals in the field who have influenced my research.

I would like to thank Professor Don Truhlar for guidance on various projects. I thank him for always challenging me to look at the problems from many angles and to try to explain all aspects of science, which has helped mold me into a better researcher and problem solver. I would also like to thank Professor Connie Lu and Dr. Bianca Ramirez for discussions and guidance on multiple bimetallic projects.

I would like to thank Dr. Varinia Bernales, Dr. Stefan Knecht, Dr. Dale Pahls and Dr. Andrew Sand for helping me with various projects; I have learned a lot from them. Dr. Andrew Sand has helped me understand Molcas code and various other scientific concepts. I thank Dr. Stefan Knecht for very patiently helping me with the DMRG code and answering my many questions. I thank Dr. Varinia Bernales for helping me with various projects and multiple helpful scientific discussions. I thank Dr. Dale Pahls for helping me with the bimetallic project and introducing me to chemcraft.

I would like to thank my committee members, Professor Ilja Siepmann and Professor Turan Birol for graciously agreeing to be in my committee.

I would like to thank all the Gagliardi group members I had the opportunity to work with for having a large impact on my work. I would specially like to thank Debmalaya and Hung for multiple scientific and nonscientific discussions throughout my five years here; they have been a big part of my graduate life.

Lastly, I would like to thank my family and friends for their love and support. My parents have encouraged me throughout my graduate school, this would not have been possible without their support and motivation. I would like to thank Preet Mahalaya for his boundless patience, love and support.

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1. Introduction

Computational chemistry methods based on quantum mechanics play a fundamental role in explaining and predicting the properties of atoms and molecules such as excitation energies, electronic spectra, magnetism, characterization of chemical bonds, catalysis etc. It is therefore important to be able to correctly describe the interactions between electrons, also known as electron correlation, whose description is a major challenge for modern electronic structure methods. The correct description of electron correlation has been a major challenge in the development of these methods.¹⁻⁸ In electronic structure theory, the term “electron correlation” is often defined as the electronic many-body effect not covered in Hartree-Fock theory.^{9,10} The electron correlation effects become more prominent in strongly correlated systems such as excited states and multimetallic complexes involving metal-metal interactions. Qualitatively, electron correlation can be divided into two categories: static and dynamical correlation.¹¹

Static correlation arises when multiple configurations are required to correctly represent a state. This often happens when nearly degenerate states are present in a system. These systems are often called “multireference” or “strongly correlated” systems.¹¹⁻¹³ The multireference self consistent field (MCSCF) method is often used to incorporate the static correlation effects, where important configurations can be included in the description of a state of a molecule.¹⁴⁻¹⁶ The complete active space self consistent field (CASSCF) is a generalized subset of MCSCF theory where a user selects the most important electrons and orbitals as an active space and considers all possible electron configurations within the active space.¹⁵ All the doubly occupied orbitals not included in the active space are called inactive orbitals while the unoccupied orbitals are called virtual orbitals.

On the other hand, dynamical correlation refers to instantaneous electron-electron repulsion effects, mainly between electrons of opposite spins.¹¹ This type

of dynamical electron correlation can be recovered (to a good extent) through perturbative,¹⁷ coupled cluster^{18–20} or density functional methods.^{21,22} To include both static and dynamical correlation effects, several methods have been proposed, including CASPT2,²³ MRCI²⁴ and multireference CCSD.²⁵ Although these methods give accurate results, they are often limited by the size of the system due to computational cost.

Density functional theory (DFT),^{21,22} which is one of the most popular and computationally efficient methods to recover dynamical correlation, gives good structural and energetics predictions for single reference systems.^{26–28} In Kohn-Sham DFT, a single Slater determinant is used to calculate spin-densities of a representative system. The representative system models non-interacting electrons, in such a way that its density is the same as that of the interacting electrons. The spin-orbitals of this fictitious model are used to calculate the kinetic energy. A functional of the spin densities is used to represent the correction to the kinetic energy and the exchange and correlation energy. DFT is exact, for even a multireference system if the exact functional could be used in conjugation with a single-reference density; however, the existing approximate functionals are not found to work well for multireference systems.²⁹ The electronic structure methods are reviewed in section 1.1.

A recent computational method called multiconfiguration pair-density functional theory (MC-PDFT),³⁰ developed by Gagliardi and Truhlar groups, can be used to accurately account for electron correlation effects in multireference systems. The advantage of MC-PDFT is that it can accurately describe molecular systems and chemical reactions requiring less computational time and memory than other multireference methods, like, for example, multireference perturbation theory (CASPT2).³¹

One of the major applications of MC-PDFT is to study excited states and photochemical properties of molecular systems. Electronic excitations have wide range of applications extending from the vision of the eyes³² to the design of mod-

ern LED television sets,³³ biological sensors,³⁴ solar cells^{35,36} etc. Linear-response time-independent DFT (TD-KS-DFT)³⁷ is the popular method to study excited states. Although single-reference methods such as TD-KS-DFT can calculate valence excitations reasonably well, charge-transfer and Rydberg excited states are often poorly described.³⁸⁻⁴⁴ On the other hand, multireference methods such as CASPT2 are more successful in calculating excited states but are often limited by their computational cost. MC-PDFT is a good alternative as it gives results on par with CASPT2, if not better at lower computational cost. Charge-transfer excited of MnO_4^- and valence and Rydberg-like excited states of benzene are studied in Chapter 2 and Chapter 3, respectively.

One of the limitations of traditional CAS-based MC-PDFT is the size of the active-space that can be calculated. For example, molecular systems such as large polyenes and polyacenes containing more than 8 conjugated π bonds cannot be studied using CAS-PDFT. The minimal active-space for polyenes and polyacenes consists of all the conjugated π orbitals and their corresponding π^* orbitals in the active space. The polyacenes have interesting electronic properties and are used as biodegradable and low-cost electronic materials. Polyenes, on the other hand, form the building blocks for complicated biological systems such as retinal which is important for the vision of the eye, and various antibiotics such as amphotericin B, and nystatin. This limitation is solved by combining MC-PDFT with density matrix renormalization group (DMRG) wave function which was then successfully used to study singlet-triplet gaps in polyenes and polyacenes. (Chapter 4)

Another example of strong correlating systems is bimetallic species containing two interacting metal centers. Applications of these systems include homogeneous and heterogeneous catalysis, single-molecule magnets, multiferroics and more.⁴⁵⁻⁶⁰ One of the principle advantages of using bimetallic systems is the easy accessibility to fine tune changes in these complexes, for example, by changing one of the metals and simultaneously study the effects of the changes. Metal-metal bonded complexes are widely used as precatalysts, but the nature of the bond during the

actual catalytic cycle has not yet been identified in most cases.^{53,60–62} In magnetism, the interaction between the metals gives rise to different magnetic properties.^{63–67} The tris-hydroxobridged chromium dimer, known as Kremer’s dimer, contains two antiferromagnetically coupled chromium(III) metal ions and provides a classic example of a magnetic molecular system that poses a challenge for computational quantum chemistry.(Chapter 5) In this chapter, DMRG self-consistent field (SCF) wave functions are combined with PDFPT to predict the correct spin-state ordering, energy spacing, and magnetic coupling constant. The unpaired electron density is used to analyze the contribution of the superexchange mechanism. This methodology offers promise for revolutionary rational design of molecular magnets.

There are only a limited examples of metal-metal bonds reported in the literature thus far and even fewer for actinides-transition metal complexes.^{68–71} One such example is metalloligands $\text{U}(\text{}^i\text{Pr}_2\text{PCH}_2\text{NAr})_3\text{tacn}$ (1) and $\text{U}(\text{}^i\text{Pr}_2\text{PCH}_2\text{NPh})_3$ (2) proposed by the Lu group at the University of Minnesota. Actinides have not been greatly studied in regards to their bonding properties, and so the nature of a uranium multiply bonded directly to a transition metal has intrigued us. Moreover, a better understanding of these uranium complexes can also help in the safe handling and disposal of nuclear waste.⁷¹ (Chapter 6)

Although MC-PDFT (along with DMRG-PDFT) have been successful in calculating excited states and magnetic couplings for molecules, it still has some challenges. One such challenge is the active-space dependence of the MC-PDFT energies. In case of an ideal multi-reference quantum chemical method, the absolute energy of an atom or a molecule would converge to the full-CI limit upon increasing the active space; this is where MC-PDFT fails. It is therefore important to study the factors and variables affecting the convergence of MC-PDFT energies. (Chapter 7) This study paves the way for development of a new and better PDFPT functional in the future.

1.1 Theoretical Background

1.1.1 Wave functions and Operators

Wave functions and operators are the fundamental concepts of quantum mechanics. A wave function is a continuous, single-valued and square integrable function that contains all the information about a state. An operator consists of a mathematical operation that can be carried out on a function. In quantum mechanics, linear, Hermitian operators act on the wave function and correspond to physical observable quantities. For example, in the non-relativistic time-independent Schrödinger equation,^{8,72,73} the Hamiltonian operator (H) acts on a state described by a wave function (Ψ) and gives the energy (E) of the corresponding state as shown in the equation 1.1:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (1.1)$$

The Hamiltonian operator for a molecular system, is described by the position vectors of nuclei (R) and electrons (r_i). A diagram of the molecular coordinates is shown in Figure ??.

In atomic units, the Hamiltonian operator is written as

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.2)$$

where, Z_A , Z_B are atomic numbers of nuclei A and B, respectively, M_A is the ratio of the mass of nucleus A to the mass of an electron. In equation 1.2, the first two terms correspond to kinetic energy of electrons and nuclei, the third, fourth and fifth terms correspond to nucleus-electron attraction, electron-electron repulsion and nucleus-nucleus repulsion, respectively.

In order to simplify the calculations, Max Born and J. Robert Oppenheimer made an assumption that the motion of nuclei and electrons can be decoupled.⁷⁴ The Born-Oppenheimer approximation is motivated by the fact that nuclei are

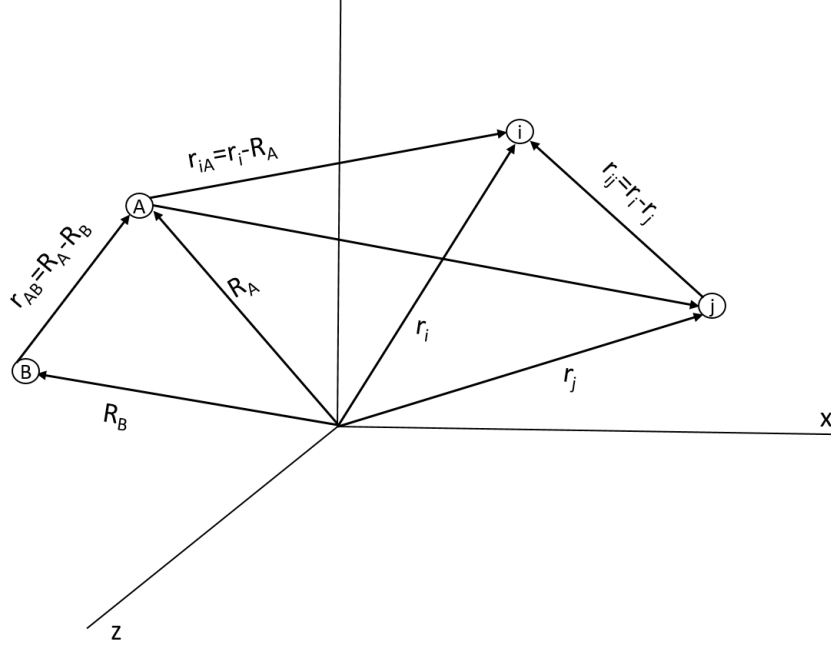


Figure 1.1: A molecular coordinate system. r_i, r_j correspond to two position vectors of electrons and R_A, R_B are position vectors for nuclei.⁸

much heavier than an electrons; thus, they move slowly. As a consequence of this approximation, the kinetic energy part in the equation 1.2 can be neglected and the nucleus-nucleus repulsion term becomes a constant. The resulting approximate Hamiltonian, called the electronic Hamiltonian, is given by

$$\hat{H}_{elec} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} \quad (1.3)$$

The electronic wave function depends on three spatial coordinates of the electrons (r) and the spin coordinate (ω). These coordinates can be combined and written as

$$\mathbf{x} = \{\mathbf{r}, \omega\}. \quad (1.4)$$

The product of spatial orbital and spin function (α or β) is known as spin orbital; i.e., $\chi(\mathbf{r}) = \Phi(\mathbf{r})\alpha$.

The Schrodinger equation can be solved exactly for one electron systems.⁷⁵ However, once we start adding electrons, it becomes more difficult to solve due

to interaction between electrons. In order to simplify the calculations, Hartree theory⁸ assumes that electrons do not interact with each other and the wave function is expressible as a product of the one-particle functions:

$$\Psi_{HP} = \chi(\mathbf{r}_1)\chi(\mathbf{r}_2)\cdots\chi(\mathbf{r}_N) \quad (1.5)$$

The wave function shown in equation 1.5 is known as Hartree Product. Although Hartree product is very convenient, it fails to describe the antisymmetry of the wave function for fermions. A wave function for fermions should be antisymmetric with respect to exchange of any space-spin coordinates.^{8,10,75}

The antisymmetric wave function for N electrons system can be written as

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad (1.6)$$

The determinant form shown above is called a Slater determinant.⁷⁶ The factor of $\frac{1}{\sqrt{N!}}$ is the normalization factor and $\chi(\mathbf{x}_i)$ are spin orbitals. For convenience, the Slater determinant can be written as $|\chi_i, \chi_j, \cdots, \chi_n\rangle$, or simply $|i, j, \cdots, n\rangle$. It should be noted that the normalization factor is not written explicitly but it is still there.

1.1.2 Restricted Hartree-Fock

In this section, the Hartree-Fock theory will be discussed. Hartree-Fock^{77,78}(HF) method is one of the earliest attempts to solve electronic Hamiltonian. It is an important milestone in the history of electronic structure theory as it incorporated the antisymmetry of the wave function.¹¹ The method uses single-determinant wave function (equation 1.6) and the energy is obtained by solving $\langle\Psi|H_{elec}|\Psi\rangle$. The approximate molecular orbitals are formed by LCAO.^{8,8} The HF wave func-

tion is obtained in a variational manner, i.e. the wave function that minimizes the energy is the best wave function for the given molecular system. The HF wave function is an eigenfunction of the Fock^{77,78} operator:

$$\hat{f}(\mathbf{x}_i)\chi_i(\mathbf{x}_i) = \epsilon_i\chi_i(\mathbf{x}_i), \quad (1.7)$$

where $f(\mathbf{x}_i)$ is the *Fock* operator, χ_i are spin orbitals and ϵ_i are orbital energies. The Fock operator is given by:

$$\hat{f}(\mathbf{x}_i) = \hat{h}(\mathbf{x}_i) + v^{HF}(\mathbf{x}_i) \quad (1.8)$$

$$= \hat{h}(\mathbf{x}_i) + \sum_j \hat{J}_j(\mathbf{x}_i) - \hat{K}_j(\mathbf{x}_i), \quad (1.9)$$

where, the one electron integral $\hat{h}$, corresponds to kinetic energy and electron-nuclear attraction:

$$\hat{h}(\mathbf{x}_i)\chi_i(\mathbf{x}_i) = \left[\int d\mathbf{x}_1 \chi_1^*(\mathbf{x}_1) \left[-\frac{1}{2}\Delta_i^2 + \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right] \chi_1(\mathbf{x}_1) \right] \chi_i(\mathbf{x}_i) \quad (1.10)$$

v^{HF} in equation 1.8 is Hartree-Fock potential, which can be split into coulomb and exchange terms. The coulomb repulsion between an electron and an average electron cloud is:

$$\hat{J}_j(\mathbf{x}_i)\chi_i(\mathbf{x}_i) = \left[\int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) \frac{1}{r_{ij}} \chi_j(\mathbf{x}_2) \right] \chi_i(\mathbf{x}_i) \quad (1.11)$$

The last term in equation 1.8 is exchange term, K_j , arising due to antisymmetry of the wave function. The exchange term is:

$$\hat{K}_j(\mathbf{x}_i)\chi_i(\mathbf{x}_i) = \left[\int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) \frac{1}{r_{ij}} \chi_i(\mathbf{x}_2) \right] \chi_j(\mathbf{x}_i) \quad (1.12)$$

The two-electron part in Hartree-Fock theory is the instantaneous electron-electron repulsion is replaced with an average cloud.⁸

1.1.3 Including Electron Correlation

In this section, the methods for including electron correlation will be discussed. In Hartree-Fock theory, the probability of finding two electrons on top of each other is zero but the movement of electrons with different spins is independent of each other.^{2,3} This implies that some electron correlation is missing in Hartree-Fock theory.¹⁰ The lack of electron correlation is arising from (1) the approximation that each electron is moving in a static electric field generated by all the other electrons, (2) single configuration wave function.¹¹ The first type of missing electron-correlation is called dynamical correlation and the later is called static correlation. It should be noted that the distinction in the two types of electron correlation is not rigid.

To include dynamical correlation, methods like perturbation theory¹⁷ and couple-cluster theory¹⁸ are used. In case of systems with degenerate or nearly degenerate configurations, it is inadequate to describe the ground state of the system using a single determinant wave function.¹⁴ Such systems are dominated by static correlation. In order to include static electron correlation, full configuration interaction and other multi-configuration methods^{14,16} like CASSCF,¹⁵ CASPT2,²³ MC-PDFT³⁰ should be used. The methods like Full CI,⁷⁹ CASPT2 and MC-PDFT includes both dynamical and static correlation. These methods will be discussed in detail in the following sections.

1.1.4 Full Configuration Interaction

Full configuration interaction (CI) is a highly correlated post HF method to solve non relativistic time independent Schrodinger equation.²⁴ In CI, an N electron wave function is written as a linear combinations of all the possible configurations.^{??} All the determinants are obtained from excitations and substitutions

from Hartree-Fock reference wave function (Ψ_0)

$$|\Phi\rangle = C_0 |\Psi_0\rangle + \sum_{ra} C_a^r |\Psi_a^r\rangle + \sum_{a<b, r<s} C_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{r<s<t, a<b<c} C_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \dots \quad (1.13)$$

Where, a,b,c are occupied spin orbitals in the Hartree-Fock reference determinant while r,s,t are virtual spin orbitals in the reference. $|\Psi_a^r\rangle$ means spin orbital a is replaced by spin orbital r in the reference. Each determinant consists of N occupied spin orbitals; the set of these N orbitals is called a configuration. In equation 1.13, terms C_0 , C_a^r , etc. are CI coefficients which are variationally optimized to minimize the energy.

The CI method gives exact solution of the time-independent Schrodinger equation for complete basis set. The correlation energy is defined as the difference between the true energy and the Hartree-Fock energy in a complete basis.

$$E_{\text{corr}} = \epsilon_{\text{exact}} - E_{HF}^{\infty} \quad (1.14)$$

A complete basis is practically impossible. However, the "exact" energy can be computed for a given basis set. The correlation energy¹⁰ for a given basis set is given by

$$E_{\text{corr}}^{\text{basis}} = \epsilon_{\text{exact}}^{\text{basis}} - E_{HF}^{\text{basis}} \quad (1.15)$$

Although the full CI method gives the most accurate energy approximation for a given basis set, it is not practically feasible to do CI calculations for larger systems. For most practical purposes, CI wave function is truncated after single (CIS)^{75,80} or double excitations (CISD).^{80,81}

1.1.5 Multiconfigurational Self-Consistent-Field

In the case of systems having degenerate states or near degenerate states, more than one configuration is required to accurately describe the system. Since full CI is not practical for larger systems, MCSCF methods are needed which includes

multiple configurations selected by the user.^{14,82} The MCSCF wave function is:

$$\Psi_{MCSCF} = \sum_I C_I |I\rangle, \quad (1.16)$$

where, $|I\rangle$ are Slater determinants or CSFs⁷⁵ selected by user. Here, CSFs are linear combination of Slater determinants and are eigenstates of the linear momentum operator, $\hat{L}_Z$, the spin projection operator, $\hat{S}_Z$ and the spin operator, $\hat{S}^2$. C_I are the coefficient that determine the weight of each configuration. The MCSCF energy expression in second quantization⁷⁵ is:

$$E = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} d_{pqrs} + V_{N-N}, \quad (1.17)$$

where, h_{pq} is the one electron integral, corresponding to kinetic energy and electron-nuclear attraction,

$$h_{pq} = \int \phi_p^*(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{\mathbf{r}_{1A}} \right) \phi_q(\mathbf{r}_1) d\mathbf{r}_1, \quad (1.18)$$

g_{pqrs} is the electron-electron integral,

$$g_{pqrs} = \int \int \phi_p^*(\mathbf{r}_1) \phi_q^*(\mathbf{r}_2) \left(\frac{1}{\mathbf{r}_{12}} \right) \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (1.19)$$

D_{pq} is the one-body reduced density matrix:

$$D_{pq} = \sum_{I,J} C_I C_J \langle I | a_p^\dagger a_q | J \rangle, \quad (1.20)$$

and d_{pqrs} is the two-body reduced density matrix is:

$$d_{pqrs} = \sum_{I,J} C_I C_J \langle I | a_p^\dagger a_r^\dagger a_s a_q | J \rangle \quad (1.21)$$

In equations, 1.20 and 1.21, $a_p^\dagger$ and a_p correspond to creation and annihilation operators. The MCSCF energy is minimized with respect to the orbitals and CI

coefficients.⁸² The final optimized orbitals $\mathbf{C}$ can be written as a unitary transformation $\mathbf{U}$ of the original orbitals $\mathbf{C}_0$.

1.1.6 Complete Active Space Self-Consistent Field

Complete active space self-consistent field (CASSCF) is the most popular MCSCF method where a set of electrons and orbitals are selected as an *active space*.^{15,83} The active space generally includes all the near degenerate orbitals which are expected to take part in a reaction or interaction.¹⁵ The set of all the other occupied spin orbitals not included in the active space are called *inactive orbitals*. A full CI is carried out within the active space while keeping the inactive and virtual orbitals constant in all the configurations. The Figure ?? shows the pictorial representation of different CASSCF orbitals.

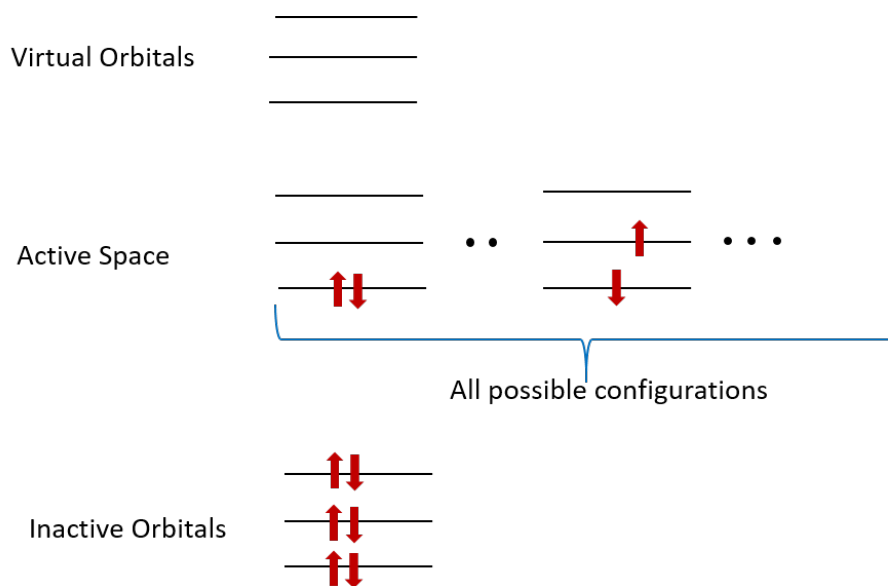


Figure 1.2: Description of different orbitals in CASSCF. Full CI is carried out in active space while keeping inactive and virtual orbitals constant.

The CASSCF energy can be written in terms of active and inactive orbitals

as given by:

$$E = 2 \sum_i h_{ii} + \sum_{ij} (2g_{iijj} - g_{ijij}) + \sum_{vw} h_{vw} D_{vw} + \sum_{ivw} (2g_{iivw} - g_{iviw}) D_{vw} + \frac{1}{2} \sum_{vwxy} g_{vwxy} d_{vwxy} + V_{N-N} \quad (1.22)$$

where indices i,j denote inactive orbitals while v,w,x and y denote active orbitals. The definitions of different terms are as previously described in equations 1.18-1.21.

RASSCF method^{83,84} is an extension of CASSCF method, where active space is further divided into subspaces (RAS1, RAS2 and RAS3). RAS1 contains doubly occupied orbitals with a specified number of holes permitted. All possible distribution of electrons are allowed in RAS2 while RAS3 can contain only a limited number of electrons. GASSCF⁸⁵ and SplitCAS⁸⁶ methods allow further expansion of the active space.

1.1.7 Perturbation Theory

Moller-Plesset Perturbation theory of second order (MP2)¹⁷ is a post-HF method used to add electron correlation effects. In perturbation theory, the Hamiltonian $\hat{H}$ is written as the sum of a reference Hamiltonian $\hat{H}_0$ and added perturbation $\hat{H}'$:

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad (1.23)$$

The perturbation operator $\hat{V}$ can be written as:

$$\hat{H}' = \hat{H} - \hat{H}_0 \quad (1.24)$$

$$= \hat{H} - \hat{F} - \langle \Phi_0 | \hat{H} - \hat{F} | \Phi_0 \rangle \quad (1.25)$$

where $\hat{H}$ is the Hamiltonian and Φ_0 is the lowest eigenstate of the Fock operator $\hat{F}$. Since Φ_0 is an eigenstate of $\hat{F}$, the first order correction to the energy is zero:

$$\langle \Phi_0 | \hat{H}' | \Phi_0 \rangle = 0 \quad (1.26)$$

Therefore, at least second order perturbation correction is required. The MP2 energy is:

$$E_{MP2} = \left[\langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle + \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle \right] + \sum_{i>0} \frac{|\langle \Phi_i | \hat{H}' | \Phi_0 \rangle|^2}{\langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle - \langle \Phi_i | \hat{H}_0 | \Phi_i \rangle} \quad (1.27)$$

$$= E_{HF} + E_{corr,MP2} \quad (1.28)$$

where, E_{HF} is the HF energy and $E_{corr,MP2}$ is the correction to the E_{HF} . The MP2 method recovers dynamical correlation to some extent; however, it is not able to recover the static correlation as it contains single reference HF wave function.

1.1.8 The Multiconfigurational Second-Order Perturbation Method

Multi-reference SCF methods are effective in describing near degeneracy correlation effects. However, further improvement in MCSCF methods are needed to correctly describe the dynamical electron correlation.⁸⁷ Multireference perturbation methods can recover the (dynamical) electron correlation. In CASPT2 method, CASSCF wave function is used as the reference wave function $|0\rangle$.²³ The configurational space is divided into four different subspaces. The first subspace V_0 is spanned by zeroth-order wave function $|0\rangle$ while the subspace spanned by orthogonal complement to $|0\rangle$ is called V_k subspace. The third subspace, V_{SD} is spanned by states generated from single and double excitation from V_0 subspace and not included in the first two subspaces. The last subspace, $V_{TQ\dots}$ contains all the higher excitation not included in other subspaces.²³ The Hamiltonian for

CASPT2 is:

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_k \hat{F} \hat{P}_k + \hat{P}_{SD} \hat{F} \hat{P}_{SD} + \hat{P}_{TQ...} \hat{F} \hat{P}_{TQ...} \quad (1.29)$$

where $\hat{F}$ is a one particle operator and P_0 , P_k , P_{SD} and $P_{TQ...}$ are projector ($|0\rangle \langle 0|$) into V_0 , V_k , V_{SD} and $V_{TQ...}$ subspaces respectively.

1.1.9 Density Functional Theory

So far we have discussed various wave function methods. In this section, density functional approach to solving Schrodinger equation will be introduced.²¹ The electron density is the central quantity in density functional theory (DFT):

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad (1.30)$$

where ρ is the electron density, which is equal to the probability of finding an electron in space dr_1 ($\mathbf{x} \equiv (\mathbf{r}, \mathbf{s})$; r is the spatial coordinate and s is the spin coordinate). The first Hohenberg-Kohn theorem⁸⁸ states that there is a one-to-one mapping between electron density, the potential v and the ground-state wave function Ψ_0 . This implies that the electron density can determine all the ground-state properties of a many electron system.⁸⁹ The energy in terms of the density is

$$E(\rho) = T(\rho) + E_{eN}(\rho) + E_{ee}(\rho), \quad (1.31)$$

where T, E_{eN} and E_{ee} are kinetic energy, electron-nuclear energy and electron-electron interaction energy, respectively. The exact expression for electron-nuclear potential energy is known in DFT:

$$E_{eN}(\rho) = \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}. \quad (1.32)$$

T and E_{ee} are also functions of electron density ρ . The explicit form of these two energy components are not known, and calculating these terms is a major

challenge in DFT. For E_{ee} , there are two parts: classical coulomb interaction and non-classical *exchange* interaction. However, the form for the classical coulomb interaction part of the E_{ee} can be extracted:

$$E_{ee}(\rho) = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_x(\rho) \quad (1.33)$$

$$= J(\rho) + E_x(\rho), \quad (1.34)$$

where first term is the classical coulomb interaction and E_x is the non-classical exchange part of E_{ee} . Let us assume functional $F_{HK}(\rho)$ contains the kinetic energy and electron-electron interactions:

$$E(\rho) = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F_{HK}(\rho) \quad (1.35)$$

According to second Hohenberg-Kohn theorem,^{88,90} the exact ground state electron density would minimize the energy.

$$E_0 \leq E(\tilde{\rho}) = T(\tilde{\rho}) + E_{eN}(\tilde{\rho}) + E_{ee}(\tilde{\rho}), \text{ or,} \quad (1.36)$$

$$\leq \int \tilde{v}(\mathbf{r})\tilde{\rho}(\mathbf{r})d\mathbf{r} + F_{HK}(\tilde{\rho}), \quad (1.37)$$

where $\tilde{\rho}$ is the approximate guess for the density of the system. In other words, the exact ground-state density should minimize F_{HK} . The major challenge of the DFT is to determine the exact expression for F_{HK}

In Kohn-Sham (KS) theory, a fictitious system of non-interacting particles(electrons) is considered such that the density is same as that of interacting electrons. Effective potential is determined from the this density of interacting electron system. Kinetic energy in KS theory is determined from the wave function for non-interacting electrons.

$$T_S(\rho) = \sum_i^N \langle \Psi_i | \hat{T} | \Psi_i \rangle ; \quad \rho_S(\mathbf{r}) = \sum_i^N |\Psi_i(\mathbf{r})|^2 = \rho(\mathbf{r}) \quad (1.38)$$

where Ψ_i are orbitals of non-interacting system. The subscript S denotes single electron equations. It should be noted that the kinetic energy T_S is not equal to the exact kinetic energy. In order to account for the correction in kinetic energy and exchange-correlation effects, a functional, E_{xc} is used.

$$E(\rho) = \int v_S(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + T_S(\rho) + J(\rho) + E_{xc}(\rho) \quad (1.39)$$

where the *exchange – correlation* energy is defined as:

$$E_{xc}(\rho) = (T(\rho) - T_S(\rho)) + (E_{ee}(\rho) - J(\rho)). \quad (1.40)$$

There is no exact expression known for E_{ex} and therefore, different approximations are used. A few such approximations are highlighted in the following section.

1.1.9.1 Approximate Density Functional: LDA and GGA

The local density approximation (LDA) model⁹¹ is one of the initial successful models upon which other approximate exchange-correlation functionals are built. This method use the uniform electron gas model²² where electrons move in a positively charged external potential such that overall system is neutral. In LDA method, E_{ex} can be written as:

$$E_{xc}^{LDA}(\rho) = \int \rho(\mathbf{r})\epsilon_{xc}(\rho(\mathbf{r}))d\mathbf{r} \quad (1.41)$$

where, ϵ_{xc} is the exchange-correlation energy per particle in electron-gas model. The electron density $\rho(\mathbf{r})$ is actually the probability of finding an electron at a position $\mathbf{r}$ in the space. So, multiplying ϵ_{xc} with ρ basically implies that this energy per particle is being weighted by the probability of finding electron in the $d\mathbf{r}$. ϵ_{xc} can be further divided into exchange and correlation energy contributions.

$$\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho). \quad (1.42)$$

The expression for exchange part, ϵ_{xc} was approximately derived for electron gas model:^{91,92}

$$\epsilon_x(\rho) = -\frac{3}{4} \left(\frac{3\rho}{\pi} \right)^{\frac{1}{3}}. \quad (1.43)$$

The correlation part of the energy functional is more complicated and depends on the physical ground state wave function of the electron gas. It is generally derived from accurate Monte Carlo simulation.⁹³ LDA gives reasonably good results for ionization energies of atoms and dissociation energies of molecules. However, it fails when electron-correlation effects becomes dominating, for example in case of heavy fermions.^{91,94}

In order to design a better density functional, information about density alone is not enough. Gradients of density with respect to $\mathbf{r}$ are required to account for inhomogeneous character of electron density. In exchange-correlation energy functional, both $\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$ are used as shown in equation 1.44

$$E_{xc}^{GGA}(\rho_\alpha, \rho_\beta) = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) d\mathbf{r} \quad (1.44)$$

Generalized gradient approximation (GGA) functionals are found to improve on the atomization energies given by LDA by a factor of 3-5.⁹⁵ Meta-GGA functional^{91,96} use $\nabla^2\rho$ in addition to gradients and density. Another class of functional are known as hybrid functional²⁹ where E_{xc} is a combination of HF exchange and density functional (GGA or meta-GGA).

1.1.10 Multiconfiguration Pair-Density Functional Theory

To describe the multireference systems, KS-DFT is not a preferred choice. In KS-DFT spin densities are derived from a single Slater determinant which is not sufficient to correctly model these strongly correlated systems. Methods such as CASPT2 and MRCI²⁴ are generally used to recover both the static and dynamic correlations.¹¹ However, these wave function based methods are not practical for

large systems. Many attempts have been made to combine multireference WFT and DFT methods together to describe such systems.^{97–116} One of such successful theory is MC-PDFT where a CASSCF wave function is used to calculate the kinetic energy, electron nuclear attraction and the Coulomb classical electron-electron repulsion contributions to the total energy. The remaining *exchange – correlation* energy comes from the on-top density functional. The MC-PDFT energy can be written as

$$E = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} D_{pq} D_{rs} + E_{ot}[\rho, \Pi] \quad (1.45)$$

where the first term contains kinetic energy and electron-nuclear interaction while second term is coulomb repulsion. The last term is on-top energy term which depends on the electron density ρ and on-top pair density, Π . All the other terms are as described in equations 1.18-1.21. The on-top pair density can be written as:

$$\Pi(\mathbf{r}) = \binom{N}{2} \int |\Psi(x_1, x_2, \dots, x_N)|^2 ds_1 ds_2 \dots ds_N d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N |_{r_1=r_2=r} \quad (1.46)$$

The physical interpretation of the on-top pair density is the probability of finding two electrons on top of each other. Due to the Pauli exclusion principle, the probability of finding two electrons of same spins on top of each other is zero. This implies only electrons with opposite spin can be found at the same position in space.

1.1.10.1 Pair-Density Functionals

In practical KS spin density theory, E_{xc} is approximated in LDA, GGA, meta GGA and hybrid functionals. In these functionals the total density(ρ) and spin-

magnetization density (m) are defined as

$$\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r}) \quad (1.47)$$

and

$$m(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r}) \quad (1.48)$$

where ρ_α and ρ_β are densities of majority-spin electrons and minority-spin electrons respectively.

One of the major shortcomings of having approximate functionals is the “symmetry dilemma” where the Slater determinant with the correct symmetry gives incorrect energies while “broken symmetry” determinants give correct energies.^{117–119} In order to bypass the problem of symmetry dilemma, m is defined in terms of ratio of the on-top pair density and the total density¹¹⁷

$$m(\mathbf{r}) = \rho(\mathbf{r})[1 - R(\mathbf{r})]^{1/2} \quad (1.49)$$

where

$$R(\mathbf{r}) = \frac{4\Pi}{\rho(\mathbf{r})^2}. \quad (1.50)$$

In case of single reference wave functions, R is always unity. However, in case on multireference wave functions, R can be less than or greater than 1.

In MC-PDFT, “translated” GGA functionals³⁰ are used, where E_{xc} of previously defined functionals are translated as

$$E_{\text{ot}}^{GGA}(\rho(\mathbf{r}), \Pi(\mathbf{r})) = E_{\text{xc}}(\rho_{\alpha}^t(\mathbf{r}), \rho_{\beta}^t(\mathbf{r}), \rho_{\alpha}^{t'}(\mathbf{r}), \rho_{\beta}^{t'}(\mathbf{r})), \quad (1.51)$$

In the above equation, $\rho_{\alpha}^t(\mathbf{r})$ and $\rho_{\beta}^t(\mathbf{r})$ are translated alpha and beta densities while $\rho_{\alpha}^{t'}(\mathbf{r})$ and $\rho_{\beta}^{t'}(\mathbf{r})$ are the translated gradients of alpha and beta densities, respectively. The translation of alpha and beta densities are defined as:

$$\rho_{\alpha}^t(\mathbf{r}) = \begin{cases} \frac{\rho}{2} \left(1 + \sqrt{1 - \frac{4\Pi}{\rho^2}} \right), & \text{when } \frac{4\Pi}{\rho^2} \leq 1 \\ \frac{\rho}{2}, & \text{when } \frac{4\Pi}{\rho^2} > 1 \end{cases} \quad (1.52)$$

and

$$\rho_{\beta}^t(\mathbf{r}) = \begin{cases} \frac{\rho}{2} \left(1 - \sqrt{1 - \frac{4\Pi}{\rho^2}} \right), & \text{when } \frac{4\Pi}{\rho^2} \leq 1 \\ \frac{\rho}{2}, & \text{when } \frac{4\Pi}{\rho^2} > 1 \end{cases} \quad (1.53)$$

A similar translation is used for the gradients of alpha and beta densities. These translated densities are then used to calculate spin-magnetization

$$m(\rho, \Pi) = \rho_{\alpha}^t(\mathbf{r}) - \rho_{\beta}^t(\mathbf{r}). \quad (1.54)$$

Overall, these translated functionals are found to give reasonably good results for multireference systems.

Another “fully-translated” functional¹²⁰ has been developed where gradients of the on-top density and the total one-particle density are used in addition to the on-top density and the total density. In addition, the fully-translated functionals are designed to have continuous first and second derivatives to facilitate the future incorporation of the on-top density functional into the SCF procedure. The fully

translated GGA functionals are defined as:

$$E_{ot}[\rho(\mathbf{r}), \Pi(\mathbf{r})] = E_{xc} \left(\rho(\mathbf{r}), \left\{ \begin{array}{ll} \rho(\mathbf{r})\chi_t(R) & \text{when } R < R_0 \\ \rho(\mathbf{r})\chi_{ft}(R), & \text{when } R_0 \leq R \leq R_1 \\ 0 & \text{when } R > R_1 \end{array} \right\}, \right. \\ \left. \rho'(\mathbf{r}), \left\{ \begin{array}{ll} \rho'(\mathbf{r})\chi_t(R) + \rho(\mathbf{r})\chi'_t(R) & \text{when } R < R_0 \\ \rho'(\mathbf{r})\chi_{ft}(R) + \rho(\mathbf{r})\chi'_{ft}(R), & \text{when } R_0 \leq R \leq R_1 \\ 0 & \text{when } R > R_1 \end{array} \right\} \right) \quad (1.55)$$

where χ_t , χ_{ft} , χ'_t and χ'_{ft} are defined as

$$\chi_t(R) = (1 - R)^{\frac{1}{2}} \quad (1.56)$$

$$\chi_{ft}(R) = A(R - R_1)^5 + B(R - R_1)^4 + C(R - R_1)^3 \quad (1.57)$$

$$\chi'_t(R) = -\frac{1}{2}R'(1 - R)^{-\frac{1}{2}} \quad (1.58)$$

$$\chi'_{ft}(R) = R'[5(R - R_1)^4 + 4(R - R_1)^3 + 3(R - R_1)^2] \quad (1.59)$$

where R and R_1 are unitless parameters, and A, B and C are determined such that the E_{ot} is continuous with respect to continuous first and second derivatives. The normal translation and *full* translation has been applied to the existing PBE functional, and the resulting functionals are called tPBE and ftPBE, respectively.

2. Electronic Spectrum of MnO_4^-

Reproduced in part from:

Multiconfiguration pair-density functional theory investigation of the electronic spectrum of MnO_4^- , Prachi Sharma, Donald G Truhlar and Laura Gagliardi, *Journal of Chemical Physics*, **2018**, 48, 124305.

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2.1 Introduction

Permanganate ion (MnO_4^-) is one of the most studied inorganic chemical systems. Due to its oxidizing property, permanganate ion has found numerous uses in both chemistry laboratories and everyday life. It is employed as an oxidant in organic chemistry laboratories for synthesis of various compounds, including alcohols and carboxylic acids.^{121,122} In industry, permanganate is extensively used in water treatment and waste control to monitor taste, odors, color and biological growth.¹²³ In addition, permanganate is used in the treatment of several skin conditions.^{124,125}

The permanganate ion has a tetrahedral geometry, with T_d point group symmetry. Its characteristic pink color was historically described as due to intense ligand-to-metal charge transfer transitions. The electronic structure of permanganate and its spectrum have been the subject of several experimental and theoretical studies. The first experimental visible-UV spectra of MnO_4^- was reported by Teltow in two papers in 1938 and 1939.^{126,127} In 1952, Wolfsberg and Helmholtz made the first attempt to decipher its electronic structure and characterize the low-lying bands using molecular orbital theory.¹²⁸ Interestingly, their calculations predicted the t_2 virtual orbital to be lower in energy than the e orbital, leading to the assignment of first two excitations as $1t_1 \rightarrow 3t_2$ and $2t_2 \rightarrow 3t_2$. Later, in 1958, Ballhausen and Liehr suggested that the $2e$ is the lowest unoccupied orbital, in

accordance with the crystal field theory.¹²⁹ The electron spin resonance studies by Carrington, Schonland, and co-workers supported Ballhausen and Liehr’s results, showing the presence of an unpaired electron in an e-type orbital.^{130,131}

The first well-resolved spectrum was reported by Holt and Ballhausen in 1967 in measurements at liquid hydrogen and helium temperatures; they reported four distinct bands.¹³² Subsequently, Dahl and Ballhausen assigned the first two bands to $1t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$.¹³² Since then, various electronic structure methods have been employed to study the electronic spectrum of permanganate, including Hartree–Fock,^{133?, 134} configuration interaction with both single and double excitations (CISD),^{135,136} symmetry-adapted-cluster configuration interaction (SAC-CI),¹³⁷ equation-of-motion coupled cluster (EOM-CCSD) schemes,^{138–140} self-consistent restricted active space and complete active space (RASSCF and CASSCF) methods with second-order perturbation theory (PT2),^{141–143} second (CC2) and third order (CC3) coupled cluster response theory,¹⁴⁰ and range-separated complete active space short-range density functional theory (CAS-srDFT).¹⁴³ Furthermore, various studies were performed using time-dependent Kohn-Sham density functional theory (TD-KS-DFT), which was found to overestimate the excitation energies.^{140,144–148} Some improvements were obtained by using the orbital-relaxed self-consistent and constricted variational DFT (RSCF-CVDFT) by Ziegler and co-workers.¹⁴⁹ All the recent calculations agree on the

assignment of the first band (HOMO $\rightarrow$ LUMO, $1t_1 \rightarrow 2e$), however, the assignments of the second and third bands are more controversial.^{144,150} A detailed study of the vibronic structure of the absorption spectrum and the effects of Jahn-Teller distortion was performed by Neugebauer et al.¹⁵⁰ in 2005. Ziegler and co-workers later expanded on the understanding of the vibronic features of permanganate by using the Frank-Condon approximation to simulate the salient features of the experimental spectrum.¹⁴⁴ In general, single-reference and multireference methods result in different assignments of the second and third bands. Most single-reference methods, such as Hartree-Fock, CISD, TD-KS-DFT, CC2, and CC3, have had limited success in predicting these excitation energies, while multireference methods have performed better. The success of multireference methods suggests that static correlation cannot be ignored.^{137,140,142,143,151}

MnO_4^- has 32 valence electrons, 8 of which are nonbonding 2s orbitals on O atoms while the remaining 24, consisting of O 2p and Mn 3d and 4s orbitals, participate into the Mn–O bonding. It is therefore important to use an active space containing all 24 of these electrons. These 24 electrons are in 12 orbitals shown in Figure 2.1, labeled by their symmetry in the T_d point group. The excited states important for this study involve LUMO ($2e$) and LUMO+1 ($3t_2$) orbitals, and adding these to the active space brings it to 17 orbitals. Therefore, our active space has 24 electrons in 17 orbitals. This is the same size as the active space used in Pierloot for a CASPT2 treatment of per-

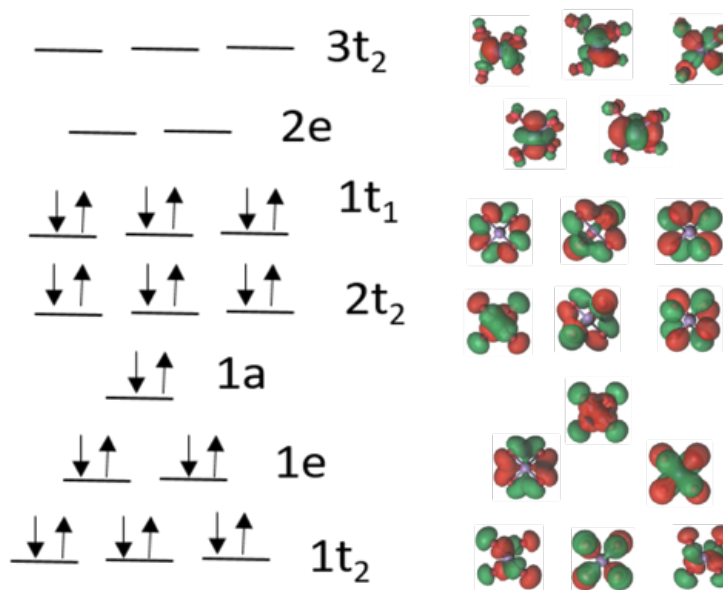


Figure 2.1: Qualitative MO diagram showing the natural orbitals resulting from the RASSCF calculation. The restricted active space of 24 electrons in 17 orbitals is shown. Only the dominating electronic configuration of the ground state is pictorially described on the left panel.

manganate spectra¹⁴¹ and by Li and coworkers for a restricted active space second-order perturbation theory (RASPT2)¹⁵² study. Both of these previous PT2 calculations agreed well with experiment.^{141,142}

In this study, we calculated the spectrum of MnO_4^- ion using RASSCF,⁸⁴ RASPT2^{152,153} and MC-PDFT.^{30,154} We also analyzed the multiconfigurational natures of the excited states.

2.2 Computational Methods

For RASSCF/RASPT2 and MC-PDFT calculations, an active space of 24 electrons in 17 orbitals was used. Twelve doubly occupied orbitals were assigned to the RAS1 subspace, no orbitals were in RAS2, and five virtual orbitals were placed in the RAS3 subspace, with up to four holes allowed in RAS1 and up to four particles in RAS3. Note

that MC-PDFT calculations based on a RASSCF reference may also be called RAS-PDFT. For the calculation of vertical excitation energies, we used the optimized CCSD(T) ground-state geometry from ref.,¹⁴² in which the Mn-O distance is 1.6029 Å.²⁴ The C_2 point group symmetry was used for RASSCF/ RASPT2 and MC-PDFT calculations. The cc-pVTZ basis set^{155,156} was used. A state-averaged RASSCF calculation averaged over 24 states (12 each in irreps A and B) was performed to generate the reference wave function for the subsequent MC-PDFT and RASPT2 calculations. MC-PDFT calculations were performed using the tPBE on-top functional.³⁰ For the RASPT2 calculations, we used the default IPEA shift of 0.25 a.u. and an imaginary shift of 0.1 a.u. to avoid possible intruder states.¹⁵⁷ The two-electron integral evaluation was simplified by employing the Cholesky decomposition technique.¹⁵⁸ All the calculations were performed using the Molcas 8.2 software package.¹⁵⁹ Oscillator strengths are calculated by combining RASSCF transition dipoles with RASSCF, RASPT2, or MC-PDFT excitation energies.

2.3 Results and Discussion

2.3.1 Orbitals of MnO_4^-

The low-energy electronic excitations involve the valence 3d and 4s orbitals of Mn and the 2p orbitals of O.⁴³ The three $1t_2$ orbitals are a combination of Mn $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ and O orbitals trans-

forming as t_2 , while the two $1e$ orbitals are a combination of Mn $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals with O $2p$ orbitals transforming as e orbitals. The $2e$ and $3t_2$ unoccupied orbitals are the corresponding anti-bonding orbitals of $1e$ and $1t_2$, respectively. The $1a$ orbital (Figure 2.1) is a combination of the Mn $4s$ and $3p$ orbitals and O $2p$ orbitals. The HOMO ($1t_1$) and HOMO-1 ($2t_2$) are mostly on oxygen with little contribution from the metal atom. It is interesting to note that Hartree-Fock calculations^{160,161} KS-DFT calculations and previous¹⁶⁰ MCSCF calculations yield delocalized orbitals. These delocalized orbitals show that it is oversimplified to simply describe the transitions as ligand-to-metal charge transfer.

2.3.2 Vertical Excitation Energies

We investigated the lowest ten states of MnO_4^- . Among these, only the excitations to ${}^1T_2$ states are allowed by symmetry and observed experimentally. Before we discuss the results in detail, we consider which experimental results one should use for comparison. Table 2.1 lists various experimental values for the first three bands. The experiment using the host crystal is based on measurements of KMnO_4 dissolved in a sample of KClO_4 at liquid hydrogen and helium temperatures, and it is frequently used as the reference for electronic structure studies.¹³² Recent studies of the solvation effects predicted a small blue shift of the first and third bands with respect to the gas phase, with these shifts more pronounced in crystals.^{143,162} In a

recent experiment by Houmøller et al. in vacuum, a red shift of 0.15 eV with respect to a water solution was observed in the first band.¹⁶² A smaller shift was observed for the other bands. These results were further confirmed by the CAS-srDFT study of Olsen et al.¹⁴³ In the following we will use the vacuum results as the reference.

Table 2.1: Vertical excitation energies (eV) of MnO_4^-

State	Vacuum	Aqueous	Crystal
1^1T_2	2.09/2.17	2.27/2.33	2.3/2.4
2^1T_2	3.55	-	3.6
3^1T_2	3.94	4.00	4.1

The vertical excitation energies calculated using RASSCF, RASPT2, and MC-PDFT are reported in Table 2.2 along with literature data.

Table 2.2: Vertical excitation energies (eV) for MnO_4^- ^a

State	Excitation ^b	RASSCF	RASPT2	MC-PDFT (tPBE)	CASPT2 ¹⁴¹	RASPT2* ¹⁴²	TD-KS- DFT (SAOP) ¹⁴²	RSCF- CV-DFT (B3LYP) ³¹	SAC- CI19	CR- EOM- CCSD24	Exp. ¹⁶²
X^1A_1		0	0	0	0	0	0	0	0	0	
1^1T_1	$1t_1 \rightarrow 2e$	2.06	2.16	1.89		1.93	2.65	1.65	2.18	2	
1^1T_2	$1t_1 \rightarrow 2e$	2.48	2.54	2.22	2.28	2.33	3.06	2.45	2.57	2.5	2.17
2^1T_1	$2t_2 \rightarrow 2e$	3.33	3.48	3.13		3.39	3.9	3.18	3.33	3.49	
2^1T_2	$2t_2 \rightarrow 2e$, $1t_1 \rightarrow 3t_2$, $1t_1 \rightarrow 2e$ ($2e^-$)	3.55	3.7	3.29	3.46	3.53	4.11	3.63	3.58	3.83	3.55
1^1E	$1t_1 \rightarrow 3t_2$, $1a_1 \rightarrow 2e$	3.8	3.94	3.62		3.9	4.48	3.73	3.41	3.8	
2^1E	$1a_1 \rightarrow 2e$	3.85	4.03	3.73		4.23	4.71	3.92	3.54	3.97	
3^1T_1	$1t_1 \rightarrow 3t_2$	3.95	4.14	3.7		3.93	4.97	3.81	4.12	4.1	
1^1A_2	$1t_1 \rightarrow 3t_2$	3.9	4.1	3.65		3.89	4.29	4.21	4.46	4.13	
3^1T_2	$1t_1 \rightarrow 3t_2$, $2t_2 \rightarrow 2e$	4.08	4.38	3.9	3.9	4.2	4.42	3.85	3.72	4.03	3.94
RMSD		0.2	0.34	0.15	0.09	0.18	0.67	0.18	0.26	0.26	
MUE		0.15	0.32	0.12	0.08	0.15	0.64	0.15	0.22	0.23	

^aThe first RASPT2 column is our calculation, while the RASPT2* column corresponds to the excitation energies listed in ref.¹⁴² RMSD is root-mean-square deviation from experiment; MUE is mean unsigned error relative to experiment.

^bFor states with mixed composition, the contributions are listed in order of decreasing coefficient.

Table 2.3: Main configuration weights

State	%	degeneracy	Configuration
X^1A_1	16.6	1	closed shell
	9.8	2	$1e \rightarrow 2e$
	6.5	2	$1t_2 \rightarrow 3t_2$
	6.4	2	$1t_2 \rightarrow 3t_2$
1^1T_1	32	1	$1t_1 \rightarrow 2e$
	14.6	1	$1t_1 1e \rightarrow 2e 2e$
	5.7	2	$1t_1 1t_2 \rightarrow 2e 3t_2$
1^1T_2	26.5	1	$1t_1 \rightarrow 2e$
	9.8	1	$1t_1 1e \rightarrow 2e^2$
	5.8	2	$1t_1 1t_2 \rightarrow 2e 3t_2$
2^1T_1	27	1	$2t_2 \rightarrow 2e$
	10.6	1	$2t_2 1e \rightarrow 2e^2$
	6.3	2	$2t_2 \rightarrow 2e, 1t_2 \rightarrow 3t_2$
2^1T_2	18.7	1	$2t_2 \rightarrow 2e$
	6.5	1	$2t_2 1e \rightarrow 2e^2$
	6	1	$1t_1^2 \rightarrow 2e^2$
	4.1	2	$2t_2 1t_2 \rightarrow 2e 3t_2$
	3.2	2	$1t_1 \rightarrow 3t_2$
1^1E	7.8	1	$1a_1 \rightarrow 2e$
	7.1	3	$1t_1 \rightarrow 3t_2$
2^1E	21.4	1	$1a_1 \rightarrow 2e$

Table 2.3 continued from previous page

	6.6	1	$1a_1e \rightarrow 2e^2$
	5.8	2	$1a_1t_2 \rightarrow 2e3t_2$
	4.5	1	$1a_1t_2 \rightarrow 2e3t_2$
1^1A_2	12.4	1	$1t_1 \rightarrow 3t_2$
	12.4	1	$1t_1 \rightarrow 3t_2$
	4.3	1	$1t_11e \rightarrow 3t_22e$
	4	1	$1t_11e \rightarrow 3t_22e$
3^1T_1	19.2	1	$1t_1 \rightarrow 3t_2$
	3.9	1	$1t_1 \rightarrow 3t_2$
	6.6	1	$1t_11e \rightarrow 3t_22e$
	6.1	1	$1t_11e \rightarrow 3t_22e$
3^1T_2	9.1	2	$1t_1 \rightarrow 3t_2$
	3.4	1	$2t_2 \rightarrow 2e$

Table 2.2 shows that RASSCF energies agree well with the experimental values with an MUE of 0.15 eV. The two RASPT2 columns of Table ?? correspond respectively to our results with the cc-pVTZ basis set and to the RASPT2 calculations by Li and co-workers, who used a customized basis set based on Stuttgart relativistic energy-consistent pseudopotential, ECP10MDF for Mn and aug-cc-pVDZ for O.24 Our RASPT2 calculation has an MUE of 0.32 eV, but the RASPT2 of Li et al. has a smaller error, which must be attributed basis set, symmetry, or a different RAS subspace division

(their paper does not specify the subspaces that they used).¹⁴² The MC-PDFT excitation energies are in excellent agreement with experiment, with an MUE of 0.12 eV. The biggest deviation in MC-PDFT energies is for the 2^1T_2 band. The MUEs are calculated over only the three experimentally available values so these MUEs should not be over-interpreted, but the good agreement with experiment provides some confidence that we can interpret the spectrum. The main configuration weights of the states are in Table 2.3. For most cases, these configurations agree with those found in ref.¹⁴² The configuration weights of the three bright states (which are the 1^1T_2 states) are of special interest because there has been considerable controversy⁴⁶ over which is lower, the $2t_2 \rightarrow 2e$ excitation or the $1t_1 \rightarrow 3t_2$. The first part of the answer from Table 2.3 is that none of the states is dominated by a single configuration; they are highly multiconfiguration with the dominant configurations contributing only 26.5%, 18.7%, and 19.2% for 1^1T_2 , 2^1T_2 , and 3^1T_2 , respectively, and contributing 9.1 to 32.0% for other excited states. With this observation of highly multiconfigurational character as a cautionary note against overinterpretation of the components, we do note though that the first band (1^1T_2) is $1t_1 \rightarrow 2e$, which agrees with literature.^{141,143,160} For the second band, we observed $2t_2 \rightarrow 2e$ as the main excitation, with smaller contributions from the $1t_1 \rightarrow 3t_2$ and $1t_1 \rightarrow 2e$ ($2e^-$) excitations while the third band comprising mainly of $2t_2 \rightarrow 2e$ excitation with some contributions from $1t_1 \rightarrow 3t_2$. Our results agree well those

reported by Jose et al. where they observed $1t_1 \rightarrow 3t_2$ excitation to be higher in energy than $2t_2 \rightarrow 2e$.¹⁴³ Table 2.4 shows the oscillator

Table 2.4: Calculated energies (eV) and oscillator strengths derived from dipole transition lengths^a

State	RASSCF		RASPT2		MC-PDFT		Exp. ¹⁶²
	ΔE	f	ΔE	f	ΔE	f	ΔE
1^1T_2	2.48	0.005	2.54	0.005	2.22	0.0044	2.17
2^1T_2	3.55	0.0015	3.7	0.0016	3.29	0.0015	3.55
3^1T_2	4.08	0.0071	4.38	0.0076	3.9	0.0073	3.94

^aThe oscillator strengths for all the other transitions are less than 0.00001.

strengths for the three dipole-allowed transitions corresponding to excitations from the $^1A_1$ ground state to the $^1T_2$ excited states.

2.3.3 Configurational Constitution of the States

Methods with multiconfigurational reference states have generally been found to predict more accurate excitation energies of the permanganate ion than do most single-reference methods. This characteristic is sometimes called strong correlation, high multireference character, or high static correlation, and it is expected to be encountered often in transition metal complexes due to near-degeneracy effects. It is thus useful to quantify the multiconfigurational nature of the various states. Here, we do this by using the M diagnostic⁴⁸ and the weight of the dominant configuration, as reported in Table 2.5.

All the M values are 0.15 or larger, and the weight of the dominant configuration is usually lower than 30%; these two ways of characterizing strong correlation agree that the multireference characters of all states are large. States 1^1E , 1^1A_2 , and 3^1T_2 are espe-

Table 2.5: The M diagnostic values and the weights of dominant configurations for each of the states^a

State (Td)	State (C ₂)	M value	Weight (%)
X ¹ A ₁	A	0.15	16
1 ¹ T ₁	A	0.24	32
	B	0.5	23
	B	0.5	23
	B	0.5	23
1 ¹ T ₂	A	0.41	26
	B	0.69	21
	B	0.69	21
2 ¹ T ₁	A	0.31	27
	B	0.4	21
	B	0.4	21
2 ¹ T ₂	A	0.6	19
	B	0.85	11
	B	0.85	11
1 ¹ E	A	1	14
	A	0.98	8
2 ¹ E	A	0.46	21
	A	0.3	28
3 ¹ T ₁	A	0.57	19
	B	0.64	16
	B	0.64	16
1 ¹ A ₂	A	1	12
3 ¹ T ₂	A	1	9
	B	0.82	14
	B	0.82	14

^aThe 1¹T₁ and 1¹T₂ states are triply degenerate, and 1¹E states are doubly degenerate, so there are three rows for each of these states.

cially highly multiconfigurational. The high static correlation may be one of the major reasons why most TD-KS-DFT and other single-reference electronic structure methods fail to predict quantitatively accurate MnO₄⁻ excitation energies.¹⁴⁰ The MC-PDFT energies obtained using the tPBE functional are also compared with KS-DFT results obtained with the PBE functional, as previously reported in literature (Table 2.6).¹⁴⁹ The tPBE excitation energies from MC-PDFT calculations are considerably better than the PBE ones from KS-DFT calculations.

Table 2.6: Comparison of MC-PDFT/tPBE with electronic structure results obtained with the PBE exchange-correlation functional

State	TD-KS-DFT PBE/TZ2P ¹⁴⁹	RSCF-CV-DFT PBE/TZ2P ¹⁴⁹	MC-PDFT tPBE/cc-pVTZ	Exp. ¹⁶²
1^1T_2	2.87	2.65	2.22	2.09/2.17
2^1T_2	3.94	3.87	3.29	3.55
3^1T_2	4.78	4.52	3.9	3.94
RMSD	0.46	0.33	0.15	
MUE	0.64	0.46	0.12	

2.4 Concluding Remarks

In 2011, Ziegler¹⁶¹ reviewed the history of theoretical work on permanganate ion from the 1950s to the present. He said “the notion of permanganate being an easy system is completely wrong. In fact, permanganate is one of the most difficult electronic systems to describe.” The present study, by elucidating the strong configuration mixing in the bright excited states, helps us to better understand the reasons for this difficulty. Both the ground state and the excited states are strongly correlated. We employed two multireference methods based on RASSCF wave functions, namely RASPT2 and MC-PDFT. The MC-PDFT excitation energies based on a RASSCF reference state agree well with the experimental values; they perform at least as well as RASPT2, but at a significantly lower computational cost. This good performance on this prototype tetroxo complex with is encouragin for the future application of MC-PDFT to complex inorganic spectra. The present calculations are more affordable (and therefore more readily extendable to larger systems)

than CASPT2 in two ways. First, for a given active space, PDFT requires less computer time and less storage than PT2; in particular it requires negligible computer time or storage beyond what is needed for the SCF step. For example, the cost of the post-SCF step is comparable to a single SCF cycle, whereas convergence of the SCF step itself requires about 40 cycles. Second, a CASSCF calculation in the C_2 symmetry used here involves 4.41 million CSFs (9.58 million determinants), whereas we obtained good results based on an SCF reference calculation with restrictions (RASSCF) that reduced the number of CSFs to 0.11 million CSFs (0.20 million determinants). The MC-PDFT results presented here are based on the tPBE on-top functional, and we compared the results to those calculated earlier by TD-KS-DFT with the parent PBE exchange-correlation functional. This comparison shows that MC-PDFT/ tPBE offers a considerable improvement over the corresponding KS-DFT method. MC-PDFT is thus a promising method for excited states of challenging strongly correlated systems with highly multiconfigurational ligand-to-metal charge transfer states.

3. Valence $\pi\pi^*$ Excitations in Benzene

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Valence $\pi\pi^*$ excitations in benzene studied by multiconfiguration pair-density functional theory, Prachi Sharma, Varinia Bernales, Donald G Truhlar and Laura Gagliardi, *Journal of Physical Chemistry Letters*, **2019**, 10, 75–81.

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3.1 Introduction

Benzene is one of the most studied molecules in chemistry. It is a building block in petrochemical industry and the precursor to several chemicals of more complex nature such as cumene and ethylbenzene. Although the chemical formula of benzene was long known, its electronic structure was a mystery for a long time. The first study was provided by Hückel in 1931 where he used a simple linear combination of p_z atomic orbitals to determine the energies of the π orbitals in conjugated systems.¹⁶³ The theory of conjugated systems was further developed by Goeppert-Mayer and Sklar where they used antisymmetrized products of molecular orbitals to calculate the excited states of benzene.¹⁶⁴ Pariser, Parr, and Pople devised what is now known as the Pariser-Parr-Pople Hamiltonian based on zero differential overlap which predicts the optical spectra of conjugated systems surprisingly well.^{165–167} The electronic spectrum of benzene is often regarded as a test bed for computational methods. Various multiconfigurational methods such as configuration interaction (CI),¹⁶⁸ configuration interaction by iterative selected perturbations (CIPSI),¹⁶⁹ complete active space self-consistent field (CASSCF),^{170–172} CASSCF contracted CI (CASSCF-CCI),¹⁷⁰ complete active space perturbation theory of second order (CASPT2),^{172?–175} multireference configuration interaction (MRCI),¹⁷⁶ and symmetry adapted cluster CI (SAC-CI)¹⁷⁷ have been used to cal-

culate excitation energies of benzene. Furthermore, numerous single reference methods such as Hartree-Fock,^{178,179} coupled cluster (CC) methods including CC2,^{175,180} CCSD,^{175,180} CC3,^{175,180} and coupled cluster with perturbative triples correction CCDR(3),¹⁸⁰ and time-dependent density functional theory (TDDFT) approaches^{181–191} have been used to study benzene. Benzene has D_{6h} spatial symmetry with a $^1A_{1g}$ ground state, and the four lowest valence singlet $\pi \rightarrow \pi^*$ excited states (in energetic order) are 1^1B_{2u} , 1^1B_{1u} , 1^1E_{1u} , and 2^1E_{2g} ; there are also about ten singlet Rydberg states and many triplet states in the energy range of these four singlet valence states.^{170,192} The states of benzene may be classified as ionic and covalent where the most important Rumer diagrams in a valence bond representation are the Kekule and Dewar structures for covalent states and are ionic structures for ionic states.^{193,193–196} The 1^1A_{1g} , 1^1B_{2u} , and 2^1E_{2g} states are covalent states while the 1^1B_{1u} and 1^1E_{1u} states are ionic states. The ionic and covalent nature of the electronic states of benzene was studied in detail by Nakayama and coworkers using the complete active space valence bond (CASVB) approach,¹⁹⁶ and it has been pointed out that the correlation effects are dissimilar in the two kinds of states, requiring a well-balanced method to treat them consistently.^{192,196} In this article, we propose a new way to analyze the ionic and covalent natures of the states in terms of individual components of the total electronic energy, and we compare two kinds of post-CASSCF method, namely perturbation the-

ory and pair-density functional theory, to see how well they can provide this kind of balanced treatment. We calculated excitation energies of the four lowest valence singlet $\pi \rightarrow \pi^*$ excited states of benzene and the four corresponding triplet states using CASSCF,¹⁵ CASPT2,^{23,197} and multiconfiguration pair-density functional theory (MC-PDFT)^{30,154} (with the latter two methods being post-CASSCF calculations) for four choices of active spaces.

3.2 Computational Details

The ground-state geometry optimized with the B3LYP exchange–correlation functional^{198–200} and the 6-31G(d,p) basis set²⁰¹ was used for multi-configurational calculations. State-averaged CASSCF and RASSCF calculations averaged over seven singlet states or over six triplet states were performed to generate the reference wave functions for the subsequent MC-PDFT and CASPT2/RASPT2 calculations. Whereas CASPT2 and RASPT2 add the external correlation energy (i.e., the correlation energy beyond that contained in the active-space SCF calculation) by perturbation theory, MC-PDFT calculates the energy from the MCSCF kinetic energy, density (ρ), and on-top density (Π) by using an on-top functional, which is analogous to exchange–correlation functional in KS-DFT. Currently used on-top functionals are translations of existing KS-DFT functionals and are functionals of ρ and Π . In this study, we used two on-top functionals trans-

lated from the PBE46 exchange-correlation functional by different translation schemes: translated-PBE (tPBE)³⁰ and fully translated PBE (ftPBE).¹²⁰ One can, if desired, tabulate the separate contributions of the translated exchange and correlation parts of the KS-DFT functional, but we do not do this in the present study. A triple zeta basis set, maug-cc-pVTZ,²⁰² is used for CASSCF, CASPT2, and MC-PDFT calculations with different choices of active spaces. For the CASPT2 calculations, we used the default IPEA shift, which is an empirical ionization-potential-electron-affinity correction applied to the zero-order Hamiltonian; the default value is of 0.25 a.u. We also applied an imaginary shift of 0.2 a.u. to avoid possible intruder states.[?] The two-electron integral evaluation was simplified by employing the Cholesky decomposition technique.¹⁵⁸ All the calculations were performed using the Molcas 8.2 software package.¹⁵⁹ The active spaces used are: CAS(6,6): 6π electrons in three π and three π^* orbitals. CAS(6,12): 6π electrons in three π , three π^* , and six π -like Rydberg orbitals. CAS(6,24): 6π electrons in three π , three π^* , and 18 π -like Rydberg orbitals. RAS(18,2,2;6,6,6) [which will be labeled simply as RAS(18,18)]: 12 doubly occupied C–C σ orbitals in RAS1; 6π electrons in three π and three π^* orbitals in RAS2, and 6 empty σ^* orbitals in RAS3. Up to two holes are allowed in RAS1 and up to two particles are allowed in RAS3.

3.3 Results and Discussion

To study the valence $\pi\pi^*$ excitations in benzene, an active space consisting of π and π^* orbitals is the natural choice. However, as previously pointed out by Roos et al., the correct description of the wave function for the 1^1B_{1u} , 1^1B_{1u} , 1^1B_{2u} , and 2^1E_{2g} ionic states requires the inclusion of Rydberg orbitals.^{171,172} In Table 3.1, we report the CASSCF, CASPT2, and MC-PDFT excitation energies obtained with the (6,6) active space that does not include the Rydberg orbitals. We see that CASSCF overestimates the excitation energies for all ionic states by more than 1 eV, and MC-PDFT (with either the tPBE on-top functional or the ftPBE on-top functional) gives only marginally better results, which is not surprising since it is based on the density and on-top density of the CASSCF wave function. CASPT2, however, includes the first-order perturbation of the wave function by excitation into external orbitals, some of which have Rydberg character, and this is apparently the reason for the improved results.

3.3.1 Expanding the Active Space to Include Rydberg Character

To include Rydberg and other orbitals in the CASSCF wave function and density, we considered three cases of more expanded active spaces: CAS(6,12), CAS(6,24), and RAS(18,18). The excitation en-

Table 3.1: CASSCF, CASPT2, and MC-PDFT excitation energies (eV) for benzene with the (6,6) active space.

State	CASSCF	CASPT2	tPBE	ftPBE	Exp.
1^1B_{2u}	4.86	5.03	5.24	5.13	4.90 ^a
1^1B_{1u}	7.87	6.23	5.01	5.01	6.20 ^a
1^1E_{1u}	9.28	6.98	5.48	5.48	6.94 ^b
2^1E_{2g}	8.12	8.17	8.4	8.31	7.8±0.2 ^c
1^3B_{1u}	3.81	4.19	4.48	4.36	3.94 ^d
1^3E_{1u}	4.86	4.86	4.84	4.82	4.76 ^d
1^3B_{2u}	7.09	5.58	4.5	4.54	5.60 ^d
1^3E_{2g}	7.21	7.41	7.71	7.61	7.49±0.25 ^e
MUD ^f	0.74	0.09	0.64	0.59	

^aRef.;²⁰³ Absorption spectrum from a seeded He jet.

^b Ref.;²⁰⁴ Laser flash experiment done in cyclohexane solution.

^c Ref.²⁰⁵ The 2^1E_{2g} close in energy to a 1^1E_{2g} Rydberg state, and it is sometimes labeled 1^1E_{2g} .

^d Ref.;²⁰⁶ Experiment done in solvent and corrected by solvent shift.

^e See Ref.¹⁷² for details and references therein.

^f Mean unsigned deviation from experiment

ergies for these larger active spaces are reported in Table 3.2, where MC-PDT shows significant improvement compared to CAS(6,6). In particular, for the 1^1B_{1u} and 1^3B_{2u} states, MC-PDFT (the tPBE and ftPBE columns in Tables 3.1 and 3.2) predicts a correct ordering of states when Rydberg orbitals are included. Furthermore, while MC-PDFT using the RAS(18,18) density predicts the correct energy trend, RASSCF excitation energies are worse than the CAS(6,12) and CAS(6,24) excitation energies. This suggests that the RAS(18,18) active space might generate different wave functions compared to CAS(6,12) and CAS(6,24). This can be checked by visualizing the orbitals, as is done in Figure 3.1. The figure shows that the CAS(6,12) and CAS(6,24) active spaces include Rydberg orbitals with π -symmetry, but the RAS(18,18) active space instead

includes σ^* orbitals. This demonstrates that one does not necessarily obtain better results simply by increasing the size of the active space; rather it is necessary to ensure that it includes the orbitals needed for a balanced treatment. For example, by comparing calculations based on CASSCF with a (6,12) active space to calculations based on CASSCF with a (6,24) active space, it can be concluded that further addition of π -type Rydberg orbitals improves both CASSCF and MC-PDFT results, thus showing the importance of π -type Rydberg orbitals for the balanced treatment of benzene.

Table 3.2: CASSCF, CASPT2 and MC-PDFT excitation energies (eV) with CAS(6,12), CAS(6,24) and RAS(18,2,2;6,6,6) active spaces.

State	CASSCF	CASPT2	tPBE	ftPBE	Exp.
CAS(6,12)					
1^1B_{2u}	4.96	4.95	5.15	5.02	4.9
1^1B_{1u}	7.25	6.41	5.56	5.63	6.2
1^1E_{1u}	8.48	7.1	6.01	6.05	6.94
2^1E_{2g}	8.15	8.08	8.26	8.15	7.8 ± 0.2
1^3B_{1u}	3.94	4.12	4.45	4.31	3.94
1^3E_{1u}	4.83	4.79	4.81	4.78	4.76
1^3B_{2u}	6.52	5.74	4.95	5.02	5.6
1^3E_{2g}	7.31	7.32	7.63	7.51	7.49 ± 0.25
MUD	0.47	0.11	0.41	0.34	
CAS(6,24)					

Table 3.2 continued from previous page

State	CASSCF	CASPT2	tPBE	ftPBE	Exp.
1^1B_{2u}	5.06	4.95	5.13	5.03	4.9
1^1B_{1u}	7.05	6.41	5.72	5.8	6.2
1^1E_{1u}	8.34	7.1	6.13	6.16	6.94
2^1E_{2g}	8.18	8.08	8.23	8.12	7.8 ± 0.2
1^3B_{1u}	4.06	4.12	4.41	4.29	3.94
1^3E_{1u}	4.87	4.79	4.81	4.76	4.76
1^3B_{2u}	6.33	5.8	5.12	5.18	5.6
1^3E_{2g}	7.37	7.34	7.57	7.45	7.49 ± 0.25
MUD	0.44	0.11	0.34	0.28	
RAS(18,18)					
State	RASSCF	RASPT2	tPBE	ftPBE	Exp.
1^1B_{2u}	5.25	5.03	5.05	4.94	4.9
1^1B_{1u}	7.6	6.23	5.71	5.74	6.2
1^1E_{1u}	8.84	7.1	6.08	6.12	6.94
2^1E_{2g}	8.73	7.98	8.19	8.11	7.8 ± 0.2
1^3B_{1u}	4.21	4.11	4.32	4.18	3.94
1^3E_{1u}	5.17	4.75	4.75	4.72	4.76
1^3B_{2u}	6.88	5.67	5.08	5.17	5.6
1^3E_{2g}	7.85	7.21	7.54	7.43	7.49 ± 0.25
MUD	0.81	0.07	0.33	0.29	

Further confirmation of the interpretation of the above trends in

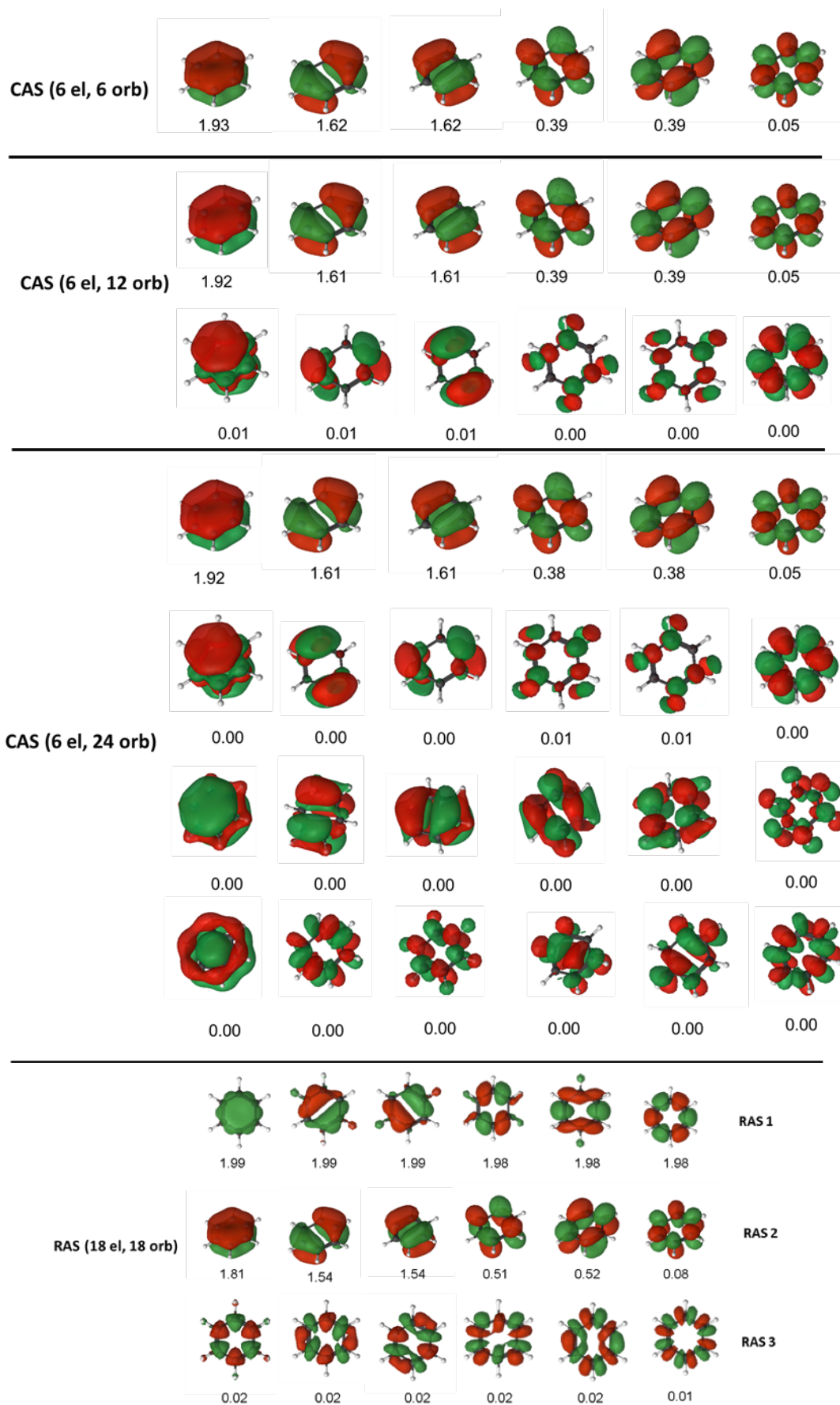


Figure 3.1: State-average orbitals in CAS(6,6), CAS(6,12), CAS(6,24) and RAS(18,18) along with state-average occupation numbers.

terms of Rydberg character is provided by the second moments in Table 3.3. The calculations were set up with the molecule in the xy plane, and the second column of Table 3.3 reports $\langle z^2 \rangle$, which is the second moment of the electron density distribution perpendicular to this plane. This value would be expected to be larger when excitation is made to an expanded π^* orbital. With the CAS(6,6) and RAS(18,18) active spaces that do not include Rydberg orbitals, all five $\langle z^2 \rangle$ are about the same size, but for CAS(6,12) and CAS(6,24) we observe larger $\langle z^2 \rangle$ values for the $^1B_{1u}$ and $^1E_{1u}$ states as anticipated above. This confirms that only the CAS(6,12) and CAS(6,24) active spaces give physically correct descriptions of the diffuse ionic states.

3.3.2 Decomposition of the MC-PDFT Energy

Here we propose and apply a new method to analyze the ionic and covalent character of the states in terms of the components of the total electronic energy. To further understand the differences in the characters of the wave functions for the various states, we decomposed the total MC-PDFT energies into components as per eq. 3.1:²⁰⁷

$$E^{MC-PDFT} = V_{NN} + \langle \Psi^{MC} | \hat{T} | \Psi^{MC} \rangle + V_{ne} + V_C + E_{ot} \quad (3.1)$$

$$E^{MC-PDFT} = V_{NN} + \langle \Psi^{MC} | \hat{T} | \Psi^{MC} \rangle + V_{ne} + V_C + E_{ex} + E_{corr} \quad (3.2)$$

The first term on the right-hand side of eq. 3.1 corresponds to the nuclear-nuclear interaction, the second, the third, and the fourth terms correspond respectively to the kinetic energy of the reference CASSCF system, the nuclear-electronic attraction, and the classical Coulomb interaction of the electronic charge cloud with itself. The last term corresponds to the on-top energy contribution, which can be decomposed into exchange and correlation contributions, as is done in eq 3.2. The V_{NN} term has no effect on vertical excitation energies, and the contributions of the other terms on the MCPDFT vertical $S_0 \rightarrow S_n$ vertical excitation energies (calculated by subtracting the ground-state energy contributions from the excited-state ones) are reported in columns 3–7 of Table 3.3; the sum of these contributions is in the last column. For CAS(6,12) and CAS(6,24), we observe a big change in nuclear-electronic and classical interelectronic Coulomb energies with respect to the ground state for the $^1B_{1u}$ and $^1E_{1u}$ states, while such a change is not observed in the case of CAS(6,6) and RAS(18,18) active spaces. This is consistent with expectations since the ionic states ($^1B_{1u}$ and $^1E_{1u}$) should show decrease in the nuclear-electron attraction (i.e., increase in its magnitude since it is negative) with respect to the ground state due to the larger separation of Rydberg charge density from the nuclei. The decrease in the classical Coulomb electron-electron repulsion is also consistent with a more diffuse electronic charge distribution. Furthermore, a more diffuse charge distribution is also consistent with

Table 3.3: Second moments (in atomic units) and energy decomposition (energies in eV) of the excitation energies of benzene for different active spaces.

State	$\langle z^2 \rangle$	KE	N-e	Coulomb	on-top energy		MC-PDFT
					exchange	correlation	
CAS(6,6)							
1^1A_{1g}	30.128	-	-	-	-	-	-
1^1B_{2u}	30.145	8.93	3.34	-6.44	-0.76	0.17	5.24
1^1B_{1u}	30.212	5.84	5.14	-6.77	0.92	-0.12	5.01
1^1E_{1u}	30.197	7.15	5.14	-7.31	0.56	-0.06	5.48
2^1E_{2g}	30.049	15.64	2.11	-7.96	-1.68	0.3	8.4
CAS(6,12)							
1^1A_{1g}	30.115	-	-	-	-	-	-
1^1B_{2u}	30.218	10.57	-0.28	-4.4	-0.9	0.16	5.15
1^1B_{1u}	32.1	-3.61	45.79	-39.52	2.81	0.09	5.56
1^1E_{1u}	32.142	-1.37	43.41	-38.52	2.32	0.16	6.01
2^1E_{2g}	30.123	17.9	-3.49	-4.52	-1.91	0.28	8.26
CAS(6,24)							
1^1A_{1g}	30.153	-	-	-	-	-	-
1^1B_{2u}	30.298	10.12	1.72	-6.17	-0.68	0.14	5.13
1^1B_{1u}	31.77	-2.91	38.58	-32.48	2.46	0.07	5.72
1^1E_{1u}	31.941	-0.93	39.23	-34.47	2.16	0.14	6.13
2^1E_{2g}	30.176	16.48	0.13	-7.09	-1.53	0.24	8.23
RAS(18,18)							
1^1A_{1g}	29.789	-	-	-	-	-	-
1^1B_{2u}	29.593	11.03	-4.5	-0.43	-1.2	0.15	5.05
1^1B_{1u}	29.668	8.93	-2.41	-1.38	0.74	-0.17	5.71
1^1E_{1u}	29.643	10.79	-4.1	-0.73	0.19	-0.09	6.07
2^1E_{2g}	29.443	18.41	-8.31	-0.04	-2.12	0.25	8.19

a decrease in the kinetic energy (with respect to the ground state). These trends appear in the CAS(6,12) and CAS(6,24) cases, but they are not detected in the CAS(6,6) and RAS(18,18) cases (Table 3.3). This evidence for the difference between tight covalent states and diffuse ionic states is more direct than the previous arguments involving re-expansion of the wave functions in terms of Rumer diagrams.

3.3.3 Scaling the Components of the On-Top Functional

We have focused so far on how the accuracy of the MC-PDFT predictions depends on the active space, but it also clearly depends on the quality of the on-top density functional. So far we have used on-top functionals obtained by simple translations^{30,120} of Kohn-Sham generalized gradient approximations based on local exchange and correlation. In Kohn-Sham DFT the accuracy of the predictions of excitation energies of Rydberg states can be improved by increasing the amount of local exchange,^{208–210} and it was found in two studies that simply scaling the exchange energy by a factor c_{ex} equal to 1.25 and scaling the correlation energy by a factor c_{corr} equal to 0.50. The two functionals optimized with these values were denoted HLE16²⁰⁹ and HLE17.²¹⁰ Although the excited states under consideration here are valence states, they do have considerable Rydberg character. Therefore, using a high portion of local exchange could improve the MC-PDFT excitation energies for benzene. Here, we explored scaling the exchange and correlation in existing on-top functionals (tPBE and ftPBE) by replacing eq. 3.2 with

$$E^{MC-PDFT} = V_{NN} + \langle \Psi^{MC} | \hat{T} | \Psi^{MC} \rangle + V_{ne} + V_C + c_{ex} E_{ex} + c_{corr} E_{corr} \quad (3.3)$$

Since the first two excited states (1^1B_{2u} and 1^1B_{1u}) contain both covalent and ionic states, we considered these states for testing the

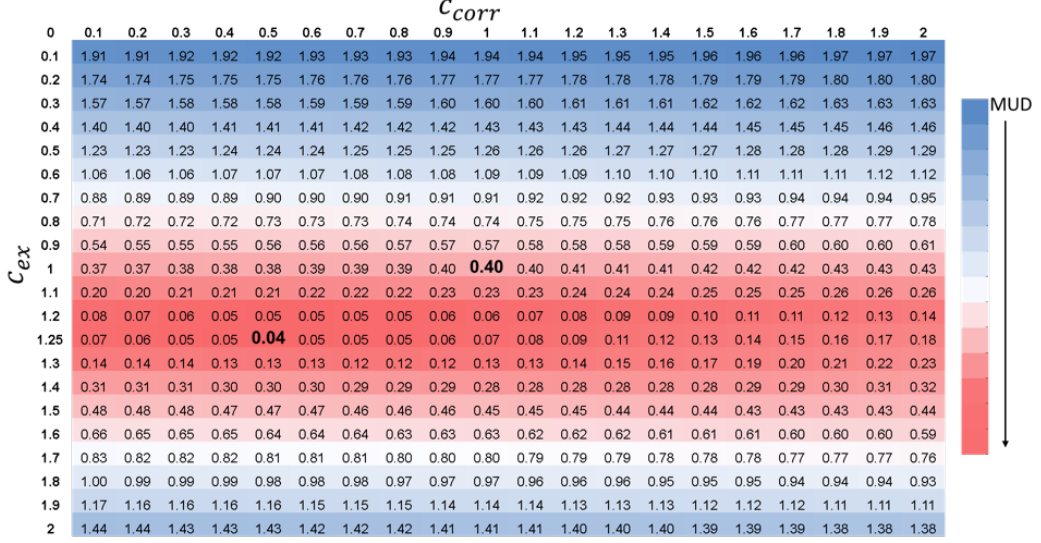


Figure 3.2: Mean unsigned deviation (MUD) for the first two excitation energies (S1 and S2) for CAS(6,12) and CAS(6,24) cases. MUD for standard tPBE functional (c_{ex} and $c_{corr}=1$) and the smallest MUD are shown in bold.

effect of changing c_{ex} and c_{corr} . Furthermore, since only the (6,12) and (6,24) active spaces give physically correct descriptions of the diffuse ionic states, we performed the exploration only for these two active spaces. In Figure 3.2, we report the mean unsigned deviations averaged over the first two excitation energies for CAS(6,12) and CAS(6,24) as functions of c_{ex} and c_{corr} (each value is an average of four errors, corresponding to the two active spaces and the two excitation energies). It is observed that a value of c_{ex} slightly higher than 1 improves the accuracy of the excitation energies for the first two states of benzene. Remarkably, but encouragingly, values of $c_{ex}=1.25$ and $c_{corr}=0.5$ give the lowest mean unsigned deviation in this test.

Next, we calculated all eight singlet and triplet excitation energies of table 3.2 with $c_{ex}=1.25$ and $c_{corr}=0.5$ in tPBE and ftPBE

Table 3.4: MC-PDFT excitation energies (in eV) for CAS(6,24) and CAS(6,12) active spaces.

State	(6,24)		(6,12)			(6,6)		Exp.
	tPBE-HLE	ftPBE-HLE	tPBE-HLE	ftPBE-HLE	CASPT2 ^a	CASPT2 ^b	CC3(%T) ^c	
1^1B_{2u}	4.9	4.76	4.85	4.69	4.84	5.03	5.07	4.90d
1^1B_{1u}	6.3	6.4	6.22	6.29	6.3	6.23	6.68	6.20d
1^1E_{1u}	6.59	6.63	6.51	6.55	7.03	6.98	7.45	6.94e
2^1E_{2g}	7.73	7.6	7.64	7.51	7.9	8.17	8.43	7.8±0.2f
1^3B_{1u}	4.05	3.9	4.02	3.85	3.89	4.19	4.12	3.94g
1^3E_{1u}	4.62	4.57	4.58	4.54	4.49	4.86	4.9	4.76g
1^3B_{2u}	5.48	5.56	5.38	5.47	5.49	5.58	6.04	5.60g
1^3E_{2g}	6.98	6.83	6.91	6.76	7.12	7.41	7.49	7.49±0.25h
MUD	0.14	0.17	0.17	0.21	0.1	0.09	0.29	

^a Calculated using an experimental hexagonal geometry with C–C bond length at 1.395 and C–H at 1.085 at D_{2h} symmetry at the SA-CASSCF/CASPT2 level using a (6,12) active space. See ref.¹⁷² for details ^b CASPT2 calculations done in the current study with (6,6) active space. ^c Calculated using MP2/6-31G* optimized geometries at D_{2h} symmetry at the coupled cluster level. %T is the weight of the single excitations in the coupled cluster calculations. See ref.¹⁷⁵ for details. ^d Ref.;²⁰³ Absorption spectrum from a seeded He jet. ^e Ref.;²⁰⁴ Laser flash experiment done in cyclohexane solution. ^f Ref.²⁰⁵ ^g Ref.;²⁰⁶ Experiment done in solvent and corrected by solvent shift. ^h See Ref.¹⁷² for details and references therein.

on-top functionals. The results are in Table 3.4 where we use the notations tPBE-HLE and ftPBE-HLE for the functionals with scaled components. This simple scaling of the exchange and correlation coefficients improves all the excitation energies of benzene to a large extent. For example, in the case of the (6,24) active space we observe a mean unsigned deviation (MUD) from experiment of only 0.14 eV and 0.17 eV with tPBE-HLE and ftPBE-HLE, which may be compared to compared to 0.34 eV and 0.28 eV for the original tPBE and ftPBE functionals, respectively.

3.4 Concluding Remarks

We employed the CASSCF, CASPT2, and MC-PDFT methods to calculate the valence excited states of benzene with four active spaces, namely CAS(6,6), CAS(6,12), CAS(6,24) and RAS(18,18). While CASPT2 is less sensitive to the initial active-space choice, for MC-PDFT the CAS(6,6) and RAS(18,18) active spaces do not provide a qualitatively correct description of the electronic states of benzene, and we explained this by showing that the presence of π -type Rydberg orbitals in the active space is crucial to obtain the correct excitation energies. The lower active-space dependence of CASPT2 compared to MC-PDFT for the present application is apparently due to the explicit inclusion in the first-order perturbed wave function of external orbitals important for calculating the correlation energy. We decomposed the total MC-PDFT energy into its components to highlight the difference in the covalent and ionic states. For ionic states, we observed a large increase in the nuclear-electron attraction energy with respect to the ground state, while the Coulomb energy decreases. This is not observed for the covalent states. We also explored scaling the local exchange and correlation in the tPBE and ftPBE functionals as a way to improve the MC-PDFT excitation energies. A larger amount of local exchange than in the original PBE scheme improves the excitation energies of benzene.

4. Density Matrix Renormalization Group Pair-Density Functional Theory (DMRG-PDFT)

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Density matrix renormalization group pair-density functional theory (DMRG-PDFT): singlet–triplet gaps in polyacenes and polyacetylenes, Prachi Sharma, Varinia Bernales, Stefan Knecht, Donald G Truhlar and Laura Gagliardi, *Chemical Science*, **2019**, 10, 1716-1723.

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4.1 Introduction

The density matrix renormalization group (DMRG)^{211–214} is a powerful method to treat static correlation. Here we present an inexpensive way to add additional dynamic correlation energy to a DMRG wave function using pair-density functional theory (PDFT). We applied this new approach, called DMRG-PDFT, to study singlet-triplet gaps in polyacenes and polyacetylenes that require active spaces larger than the feasibility limit of the conventional complete active-space self-consistent field (CASSCF) method. Polyacenes (also called acenes) are strongly correlated molecular systems, the ground states of which have polyradical character.²¹⁵ The acenes are a series of compounds consisting of fused benzene rings; in the present article we only consider the case where they are arranged in a linear fashion as shown in Fig. 4.1. Polyacenes are especially interesting because their electronic properties make them useful for biodegradable and low-cost electronics.^{216–219} The smaller ones, such as naphthalene and anthracene, are used industrially to make various dyes, while larger acenes, like tetracene and pentacene along with their derivatives, are used as organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs).^{220–229} Recently, tetracene and pentacene have been found to undergo singlet-fission where a high-energy singlet exciton converts to two low-energy triplet excitons, thereby increasing the efficiency of solar cells by up to 40%.^{230?–235}

Polyenes are another example of strongly correlated systems that contains alternating single and double bonds; in the present article we will consider polyacetylenes as examples of this class of compounds. They are often used as model systems to understand the electronic properties of more complicated biological systems such as carotenoids, retinal, and various antibiotics such as amphotericin B, nystatin etc.^{236,237} Polyacetylenes also show high electrical conductivity, which further increases on doping with p-type dopants such as Br_2 , I_2 , Cl_2 , and AsF_5 .^{238–242}

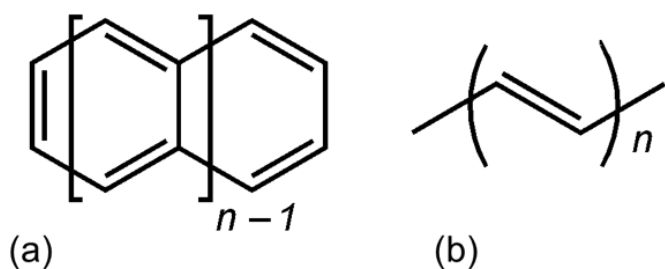


Figure 4.1: (a) n-acenes, (b) n-polyacetylene

The density matrix renormalization group (DMRG)^{211–214} algorithm is a replacement of the FCI solver in the CASSCF or CASCI methods.^{243,244} (CASCI is like CASSCF, but the orbitals are not self-consistently optimized for a given configuration list. In the present work we use self-consistently optimized orbitals.) The major advantage of DMRG comes from its polynomial scaling with respect to the size of the active space; this allows practical computation of numerically exact solutions for active spaces three to four times larger than standard CASSCF.²⁴⁵ Although multiconfigurational methods such

as CASSCF or DMRG can be effectively applied to capture static correlation, and they in principle reduce the difficulty in choosing which orbitals to include in the active space (because they allow more orbitals to be included), they are not efficient at capturing all the correlation energy because of the slow convergence of external correlation with respect to the number of orbitals and configurations included. A number of approaches have been advanced to make it more efficient to treat the dynamical correlation not included in an MCSCF-type calculation. For example, approaches that have been combined with DMRG include internally contracted multireference CI (MRCI),^{246,247} multireference perturbation theory (MRPT),²⁴⁸⁻²⁵⁹ and wave function theory–short range density functional theory (WFT-srDFT)..²⁶⁰ In the present study we introduce the use of multiconfiguration pair-density functional theory (MC-PDFT)^{30,154} to include dynamic electron correlation beyond that captured within a DMRG wave function; this two-step procedure will be called DMRG-PDFT. The major advantage of DMRG-PDFT is that it treats both static and dynamic electron-correlation and gives accurate results at significantly lower memory and computational costs than multireference perturbation treatments and MRCI approaches. Therefore, it can attain high accuracy that would be too expensive to be practical with other methods.

4.2 Theory

The matrix product state (MPS) is a key theoretical concept in the DMRG algorithm used here. In this section, we review the MPS and the DMRG algorithm.

4.2.1 Matrix product states (MPS) and density matrix renormalization group (DMRG)

Because DMRG (in a quantum-chemical context) is well described in the literature,^{211–214,250,261–269} we summarize only enough details as are necessary to specify the present applications. The non-relativistic electronic Hamiltonian may be written in second quantization as²⁷⁰

$$\hat{H} = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} e_{pqrs} + h_{\text{nuc}} \quad (4.1)$$

where p , q , r , and s denote molecular orbitals, and h_{pq} and g_{pqrs} are one- and two-electron integrals, respectively, E_{pq} is the singlet excitation operator, and e_{pqrs} is the two-electron excitation operator. The excitation operators can be written in terms of creation and annihilation operators as

$$E_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}, \quad (4.2)$$

and

$$e_{pqrs} = \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{p\sigma}^\dagger a_{r\tau} a_{s\tau} a_{q\sigma}, \quad (4.3)$$

where Greek letters label the spin functions associated with the molecular orbitals p , q , r , and s . The electronic energy for eigenstate $|\Psi\rangle$ is expressed as

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} d_{pqrs} + V_{NN} \quad (4.4)$$

where V_{NN} is the nuclear-nuclear repulsion energy; D_{pq} and d_{pqrs} are the elements of one-electron and two-electron reduced density matrices (RDMs), respectively. Each spatial orbital l (also referred to as a site in DMRG terminology) is associated with four possible occupations:

$$n_l = \{ |vac\rangle, | \uparrow \rangle, | \downarrow \rangle, | \uparrow \downarrow \rangle \} \quad (4.5)$$

The eigenstate $|\Psi\rangle$ of the Hamiltonian 4.1 can be written in an occupation number basis as

$$|\Psi\rangle = \sum_{n_l} C^{n_1 n_2, \dots, n_L} |n_1 n_2 \dots n_L\rangle, \quad (4.6)$$

where $|n_1 n_2 \dots n_L\rangle$ is an occupation-number vector, which is a particular way of writing a Slater determinant; L is the number of orbitals; and $C^{n_1 n_2 \dots n_L}$ is a configuration interaction (CI) coefficient, which may be considered to be a tensor of order L with $4L$ elements. The CI coefficients $C^{n_1 n_2 \dots n_L}$ can also be written as the product of L matrices A^{n_l} , labeled $l = 1, 2, \dots, L$, each having $\min(4^l, 4^{L+1-l})$

elements.

$$|\Psi\rangle = \sum_{n_l} A^{n_1} A^{n_2} \dots A^{n_L} |n_1 n_2 \dots n_L\rangle, \quad (4.7)$$

The size of the matrices A^{n_l} increases exponentially towards the middle of the product, then decreases again.²⁴⁴ Equation 4.7 is called a matrix product state (MPS). Note, that the first and the last matrices in equation 4.7 are in practice 1×4 -dimensional row and 4×1 -dimensional column vectors, respectively, such that the final contraction of the matrices A^{n_l} yields a scalar CI coefficient $C^{n_1 n_2 \dots n_L}$. If no truncation is made in the matrix products, the MPS is equivalent to full configuration interaction (FCI). For practical work, one retains at most M terms in each of the matrix multiplication steps; this approximation is called compression, and M is called the bond dimension. Compression is the main approximation of DMRG as compared to FCI. The compressed MPS is then variationally optimized to give an upper bound to the ground-state energy. Thus, DMRG may be considered to be a way to calculate an approximate wave function that gives an upper bound to the FCI energy. We note though that we (and others) apply FCI only within the active space, so what we obtain is an upper bound to the CASSCF energy, which in turn is an upper bound to the FCI energy, which is an upper bound to the complete configuration interaction (CCI) energy, which is exact. (CCI is FCI with a complete basis set). As we have just explained, if one did not truncate the bond dimension in DMRG, the

resulting wave function would correspond to FCI among the active orbitals, i.e., to CASSCF. In this context, DMRG may be considered to offer a possibility to calculate an approximate CASSCF wave function in a controlled manner such that it gives a variational upper bound to the CASSCF energy. However, its efficiency allows one to use many more active orbitals than in conventional CASSCF. The approximate solution to the large-active space CASSCF problem will typically have a lower (and hence more accurate) energy than the uncompressed solution to the small-active-space CASSCF problem. To correct the DMRG energy for dynamic correlation, we use pair-density functional theory.

4.3 Implementation

The DMRG-PDFT implementation is based on an interface between the existing MC-PDFT code in the OpenMolcas 8.3 software package^{159,271} and the DMRG code in the QC-MAQUIS program.^{261,264?} The MC-PDFT energy can be written in terms of inactive and active orbitals as

$$\begin{aligned}
E^{MC-PDFT} = & 2 \sum_i h_{ii} + \sum_{ij} (2g_{iijj} - g_{ijij}) + \sum_{uv} h_{uv} D_{uv} \\
& + \sum_{iuv} (2g_{iiuv} - g_{iviu}) + \frac{1}{2} \sum_{uvxy} g_{uvxy} d_{uvxy} + E_{ot}(\rho, \Pi) + V_{NN},
\end{aligned}
\tag{4.8}$$

where i and j are inactive and u, v, x and y are active molecular orbital indices, and ρ and Π are the density and the on-top density. To calculate the energy according to equation 4.8, we need the one-electron and two-electron RDMs, from which we calculate the density and the on-top pair-density. The one and two-electron RDMs are obtained from the DMRG wave function, while the density and on-top pair density are calculated according to:

$$\rho = \sum_{ij} D_{ii} \phi_i(r) \phi_i(r) + \sum_{uv} D_{uv} \phi_u(r) \phi_v(r) \quad (4.9)$$

$$\begin{aligned} \Pi = & \sum_{ij} D_{ii} D_{jj} \phi_i(r) \phi_j(r) \phi_i(r) \phi_j(r) + \sum_{iuv} D_{ii} D_{uv} \phi_i(r) \phi_i(r) \phi_u(r) \phi_v(r) \\ & + \sum_{uv} d_{uvxy} \phi_u(r) \phi_v(r) \phi_x(r) \phi_y(r) \end{aligned} \quad (4.10)$$

where again i and j are inactive and u, v, x and y are active molecular orbital indices.

4.4 Computational Methods

The vertical singlet–triplet gaps for polyacetylenes and polyacenes were computed using DMRG-PDFT. Geometries are very important for adiabatic S-T gaps. The geometries of the polyacenes for both the singlet (1^1A_g) and triplet (1^3B_{3u}) states were taken from ref.²⁷² We optimized the geometry of polyacetylenes at the same level of theory as the polyacenes, using the Kohn-Sham density functional

theory with the B3LYP exchange–correlation functional^{273,274} and the 6-31G(d, p) basis set. The optimized structures were then used to perform DMRG calculations followed by DMRG-PDFT calculations. All DMRG-PDFT calculations were performed with the tPBE on-top density functional.²⁷⁵ The 6-31+G(d,p) basis set was used for all DMRG-PDFT calculations. The active space is denoted as usual as (n, m) where n is the number of active electrons, and m is the number of active orbitals. The active spaces used here correspond to all the π electrons distributed in all the valence π orbitals; thus $n = m$. For all polyacene calculations, we constrained the wave functions to D_{2h} symmetry, where the ground state has symmetry ^1A_g , and the lowest triplet state has symmetry $^3B_{3u}$. For the polyacetylene calculations, C_{2h} symmetry was imposed. The ground state has symmetry ^1A_g , and the lowest triplet state has symmetry ^3B_u . The convergence with respect to the bond dimension M was tested from 100 to 2000 for naphthalene and anthracene, and M was set to 500 for higher acenes. The convergence for polyacetylenes was studied from $M = 4$ to $M = 1000$. The DMRG calculations were performed with QCMAQUIS.^{261,264,276? ,277}

4.5 Results and Discussion

4.5.1 Singlet–Triplet Gap in Polyacenes

The results for vertical and adiabatic singlet-triplet (S-T) gaps of naphthalene are reported in Table 4.1 as functions of bond dimension M . Convergence is reached at $M = 200$ with a value for the DMRG vertical excitation energy of 3.05 eV. The DMRG-PDFT vertical excitation energy is 3.35 eV, with a small deviation from other high-level calculations, in particular a deviation of 1.5% from CCSD(T)²⁷⁸ and a deviation of 2.3% from DMRG-ec-MRCISD+Q92; in contrast plain DMRG without adding external correlation by PDFT has 7.4% and 11.1% deviations, respectively. The DMRG-PDFT adiabatic excitation energy is 2.91 eV, which is within the range of values (2.65–3.06 eV) calculated by various methods in refs.^{219,236,279–282} These results are encouraging because DMRG-PDFT is applicable to much larger systems than other methods of comparable accuracy.

In Table 4.2, vertical and adiabatic singlet-triplet (S-T) gaps for different bond dimensions are reported for anthracene. We see convergence at $M = 1000$, and we observe a significant improvement in both vertical and adiabatic singlet–triplet gaps when the MC-PDFT method is used to add external correlation energy to the DMRG wave function. The S-T gap predicted by DMRG decreases

Table 4.1: Dissociation energy (De in eV) of H₂ for various active spaces (tPBE/cc-pVTZ).^a

M	DMRG		DMRG-PDFT		GAS-PDFT		Experiment	
	Vert.	Ad.	Vert.	Ad.	Vert.	Ad.	Vert.	Ad.
					3.36	3.06	3.43,b	3.30c
100	3.08	2.67	3.31	2.89			2.78,	2.79
200	3.05	2.66	3.35	2.91				
500	3.05	2.66	3.35	2.91				
1000	3.05	2.66	3.35	2.91				

^aGeneralized active-space pair density functional theory with tPBE functional and 6-31G+(d,p) basis set from ref.²⁷² ^bDMRG-externally correlated multireference CI, DMRG-ec-MRCISD+Q at geometries optimized by UB3LYP/6-31G(d); see ref²⁸³ for details. ^cRestricted CCSD(T) with pV ∞ Z basis set at geometries optimized by B3LYP/cc-PVTZ; see ref²⁷⁸ for details. ^d Vibrationally corrected experimented values; see ref²⁸¹ and²⁸² for experimental details. Δ ZPE = -0.14 eV calculated by B3LYP/6-31G(d,p).

Table 4.2: Dissociation energy (De in eV) of H₂ for various active spaces (tPBE/cc-pVTZ).^a

M	DMRG		DMRG-PDFT		GAS-PDFT		Experiment	
	Vert.	Ad.	Vert.	Ad.	Vert.	Ad.	Vert.	Ad.
					2.22	1.97	2.47,b	2.46c
100	2.46	2.05	2.28	2.00			1.95-	1.97
200	2.42	2.03	2.26	1.97				
500	2.34	1.97	2.33	2.00				
1000	2.31	1.96	2.36	2.02				
2000	2.30	1.95	2.38	2.04				

^aGeneralized active-space pair density functional theory with tPBE functional and 6-31G+(d,p) basis set from ref.²⁷² ^bDMRG-externally correlated multireference CI, DMRG-ec-MRCISD+Q at geometries optimized by UB3LYP/6-31G(d); see ref²⁸³ for details. ^cRestricted CCSD(T) with pV ∞ Z basis set at geometries optimized by B3LYP/cc-PVTZ; see ref²⁷⁸ for details. ^d Vibrationally corrected experimented values; see ref²⁸¹ and²⁸² for experimental details. Δ ZPE = -0.10 eV calculated by B3LYP/6-31G(d,p).

when the bond dimension is increased, but the DMRG-PDFT gap increases along the same sequence of M values. A key result is that the DMRG-PDFT results show less dependence on M than do the plain DMRG results; in fact DMRG-PDFT gives results close to the nest previously available values^{278,279,281,283,284} even for an M value as small as $M = 100$.

Table 4.3: Adiabatic singlet–triplet gaps ($E_{\text{triplet}} - E_{\text{singlet}}$, in eV) for polyacenes.

	DMRG ^a	DMRG-PDFT ^a	GAS-PDFT ^b	pp-RPA ^c	DMRG-CASPT2 ^d	DMRG-CASPT2 ^e	CCSD(T) ^f	DMRG-ec-MRCISD+Q ^g	ACI-DSRG-MRPT2 ^h	ZPE ⁱ	exp.
Naphthalene (10, 10)	2.66	2.91	3.06	2.87	-	-	2.85	2.71	2.70	-0.14	2.64j, 2.65k
Anthracene (14, 14)	1.97	2.00	1.97	1.98	1.73	1.69	2.09	1.81	1.87	-0.10	1.85j, 1.87l
Tetracene (18, 18)	1.54	1.37	1.46	1.39	1.29	1.18	1.45	1.23	1.23	-0.08	1.28j
Pentacene (22, 22)	1.24	0.98	1.10	0.98	0.86	0.82	1.10	0.92	0.78	-0.06	0.86 ± 0.03m
Hexacene (26, 26)	0.93	0.73	0.85	0.66	0.58	0.62	0.77	0.67	0.49	-0.06	0.54 ± 0.05n
Heptacene (30, 30)	0.67	0.62	0.72	0.39	-	-	0.58	0.48	0.33	-0.05	-
MUD o	0.17	0.06	0.04	0.04	0.08	0.13	0.17	0.07	0.09		

^a $M = 500$. ^bGeneralized active-space pair density functional theory with the tPBE functional and the 6-31+G(d,p) basis set; for details see ref. ²⁷²

^c particle-particle random phase approximation (pp-RPA) with the B3LYP functional at geometries optimized by UB3LYP/6-31G*. See ref. ²¹⁹

for details. ^dDMRG-CASPT2 at geometries optimized by CASPT2-D/cc-pVTZ(-f); see ref. ²⁸⁵ for details. ^eDMRG-CASPT2 at geometries optimized by CAM-B3LYP/6-31G*; see ref. ²⁸⁵ for details. ^fRestricted CCSD(T) (FPA-5Z3) at geometries optimized by B3LYP/cc-pVTZ with added ZPE correction; see ref. ²⁷⁸ for details. ^gDMRG-ec-MRCISD+Q on geometry optimized by UB3LYP/6-31G(d); see ref. ²⁸³ for details.

^hAdaptive CI with density a density-fitted implementation of second-order perturbative multiconfiguration driven similarity renormalization group (ACI-DSRG-MRPT2) calculations; see ref. ²⁸⁶ ⁱZero-point energy correction; calculated by B3LYP/6-31G(d,p). ^jsee ref. ²⁸¹ ^kref. ²⁸² ^lref. ²⁸⁷

^mref. ²⁸⁸ ⁿref. ²⁸⁰ ^oMean unsigned deviation with respect to vibrationally corrected experimental S-T gap

Table 4.4: Vertical singlet–triplet gaps ($E_{\text{triplet}} - E_{\text{singlet}}$, in eV) for polyacenes.

	DMRG ^a	DMRG-PDFT ^a	GAS-PDFT ^b	CCSD(T) ^c	DMRG-MRCISD+Q ^d
Naphthalene	3.05	3.35	3.36	3.30	3.43
(10, 10)					
Anthracene	2.34	2.33	2.22	2.46	2.47
(14, 14)					
Tetracene	1.88	1.58	1.69	1.75	1.81
(18, 18)					
Pentacene	1.56	1.13	1.29	1.36	1.36
(22, 22)					
Hexacene	1.19	0.79	0.99	0.99	0.98
(26, 26)					
Heptacene	0.81	0.61	0.75	0.78	0.67
(30, 30)					

^aM=500.^bGAS-PDFT with 6-31+G(d,p) basis set; for details see ref.²⁷²^cRestricted CCSD(T) with pV ∞ Z basis set at geometries optimized by B3LYP/cc-PVTZ; see ref²⁷⁸ for details.^dDMRG-ec-MRCISD+Q on geometry optimized by UB3LYP/6-31G(d); see ref.²⁸³ for details.

Table 4.5: Vertical singlet–triplet gaps ($E_{\text{triplet}} - E_{\text{singlet}}$, in eV) for polyacenes.

	DMRG	DMRG-PDFT ^a	GAS-PDFT ^b	CCSD(T) ^c	DMRG-MRCISD+Q ^d
Naphthalene (10, 10)	3.05	3.35	3.36	3.30	3.43
Anthracene (14, 14)	2.34	2.33	2.22	2.46	2.47
Tetracene (18, 18)	1.88	1.58	1.69	1.75	1.81
Pentacene (22, 22)	1.56	1.13	1.29	1.36	1.36
Hexacene (26, 26)	1.19	0.79	0.99	0.99	0.98
Heptacene (30, 30)	0.81	0.61	0.75	0.78	0.67

^aaM=500. ^bGAS-PDFT with 6-31+G(d,p) basis set; for details see ref.²⁷² ^c Restricted CCSD(T) with pV ∞ Z basis set at geometries optimized by B3LYP/cc-PVTZ; see ref²⁷⁸ for details. ^dDMRG-ec-MRCISD+Q on geometry optimized by UB3LYP/6-31G(d); see ref.²⁸³ for details.

The adiabatic S-T gaps for various systems, from naphthalene to heptacene, obtained with $M = 500$ are compared to literature values in Table 4.3. We observe that DMRG-PDFT gives very good agreement with the vibrationally corrected experimental S-T gaps for adiabatic singlet–triplet gaps with a mean unsigned deviation (MUD) of only 0.06 eV while DMRG without external correlation gives an MUD of 0.17 eV. While DMRG-CASPT2 and ACI-DSRG-MRPT2 underestimate the S-T gap with respect to the experiment, CCSD(T) tends to overestimate. The generalized active-space-pair density functional theory (GAS-PDFT) gives excellent agreement with the experimental results. In GAS102 based methods, the active space is further divided into smaller subspaces and only certain excitations are allowed within them, thereby making these methods more affordable. One difficulty with these approaches, though, is to choose the appropriate subspaces and appropriate restrictions on the kinds of included electron excitations because such choices are not systematic and often require subjective chemical intuition and specialized expertise. The vertical S-T gaps are reported in Table C.4. In absence of dynamic correlation, DMRG overestimates the S-T gap for acenes larger than naphthalene. The adiabatic and vertical S-T gaps for DMRG and DMRG-PDFT are compared with experimental values for larger polyacenes in Fig. 4.2, showing reasonable agreement for both DMRG and DMRG-PDFT adiabatic S-T gaps.

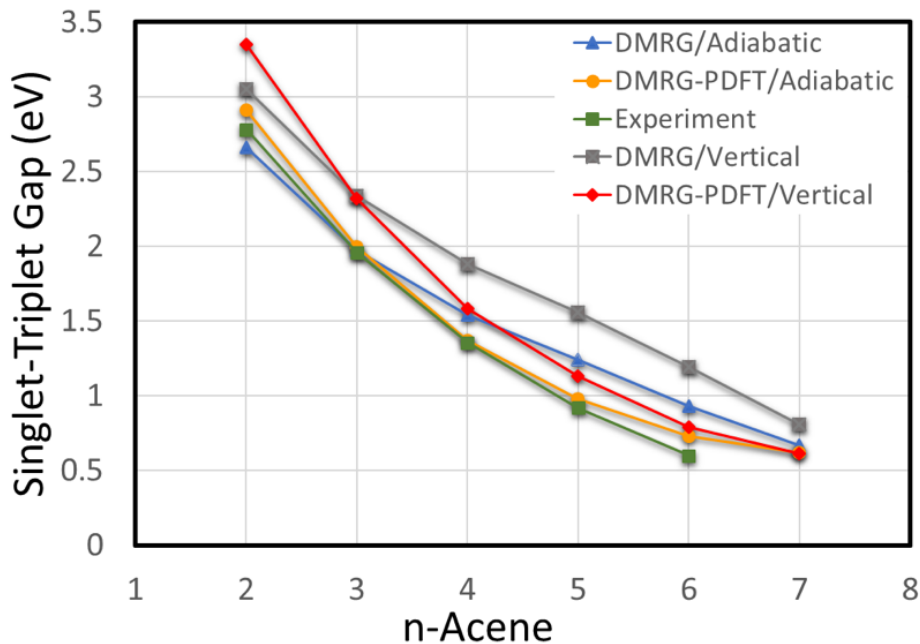


Figure 4.2: Adiabatic and vertical singlet–triplet gaps for polyacenes. Experimental values are vibrationally corrected.

4.5.2 Singlet–triplet Gap in Polyacetylenes

Singlet–triplet energies for polyacetylenes as calculated by DMRG and DMRG-PDFT are reported in Table C.4. For smaller polyacetylenes (ethylene to octatetraene), DMRG-PDFT results agree well with the experimental values with an MUD of 0.18 eV. Our DMRG-PDFT results agree with CASPT2 results within 0.2 eV, which is encouraging because DMRG-PDFT is applicable to much larger systems than conventional CASPT2 or DMRG-PT2. Note that we used a small bond dimension of 50 for all the acetylene singlet–triplet gaps presented in Table.[?] For acetylenes smaller than hexatriene, the DMRG results converge to the CASSCF values, which is not surprising because we found that ethylene and butadiene calculations need M values of only 4 and 16 to reproduce the CASSCF

results. However, as could be expected, the deviation between the DMRG and CASSCF values increases for larger acetylenes when we use a fixed value of M .

Table 4.6: Vertical singlet–triplet gap (E_{triplet} – E_{singlet}, in eV) for polyacetylenes

number of monomers	Active space	DMRG	DMRG-PDFT	CASSCF	CASPT2	Literature values	Exp. ^a
1	(2,2)	4.34	4.67	4.34	4.54	4.63 ^b	4.3-4.6
2	(4,4)	3.37	3.46	3.37	3.38	3.45 ^b , 3.20 ^d	3.22
3	(6,6)	2.80	2.79	2.80	2.73	2.80 ^b , 2.40 ^d	2.61
4	(8,8)	2.43	2.37	2.43	2.33	2.42 ^c , 2.10 ^d	2.10
5	(10,10)	2.29	1.99	2.19	2.07	2.20 ^c , 1.89 ^d	
6	(12,12)	2.20	1.79	2.01	1.88	2.00 ^c	
7	(14,14)	2.17	1.59	1.88	1.75	1.90 ^c	
8	(16,16)	2.20	1.52				
9	(18,18)	1.03	0.07				
MUD ^e		0.20	0.18	0.20	0.16		

^a Experimental band maxima for ethylene,²⁸⁹⁻²⁹² butadiene,²⁹³ and hexatriene.²⁹⁴

^b CCSD(T)/ cc-pVTZ result from ref.²⁹⁵ ^c UCCSD result from ref.²⁹⁶ ^d Multireference Møller-Plesset study corrected for basis-set and active-space effects, from ref.²⁹⁷ ^e Mean unsigned deviation from experiment

We plotted the convergence of singlet–triplet gaps in DMRG and DMRG-PDFT with respect to conventional CASSCF and MC-PDFT in Fig. 4.3. DMRG-PDFT converges faster with respect to M and shows less dependence on M than does DMRG. In Fig. 4.4, we show the average time required for DMRG and DMRG-PDFT with $M = 50$ as compared to the time for CASPT2 calculations for polyacetylenes (the times are averaged over singlet and triplet). All the calculations were performed on a single processor with a maximum memory of 62 gigabytes. The DMRG-PDFT calculations take considerably less time than the corresponding CASPT2 calculations for higher polyacetylenes (five or more monomers). For example, for seven monomers, CASPT2 takes fifteen times longer than DMRG-

PDFT.

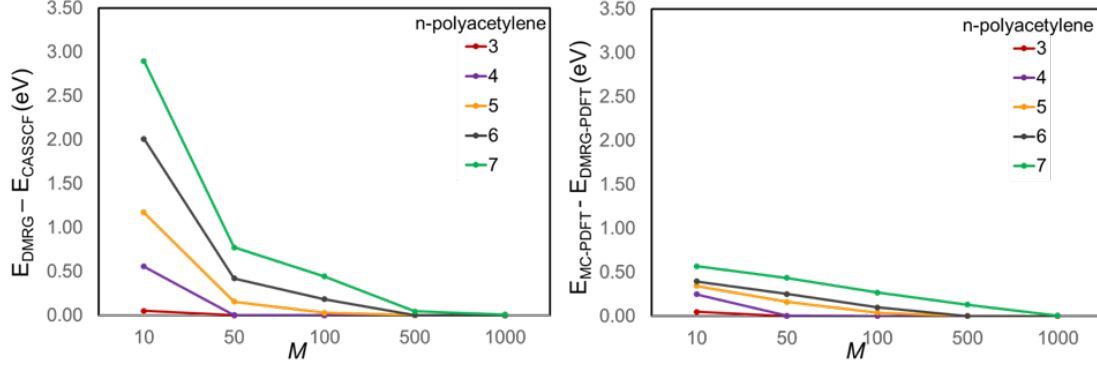


Figure 4.3: Convergence of (a) DMRG and (b) DMRG-PDFT with respect to conventional CASSCF and MC-PDFT, respectively. The ordinate is the mean of the difference between (a) conventional CASSCF and DMRG energies and (b) conventional MC-PDFT and DMRG-PDFT energies for singlet and triplet states.

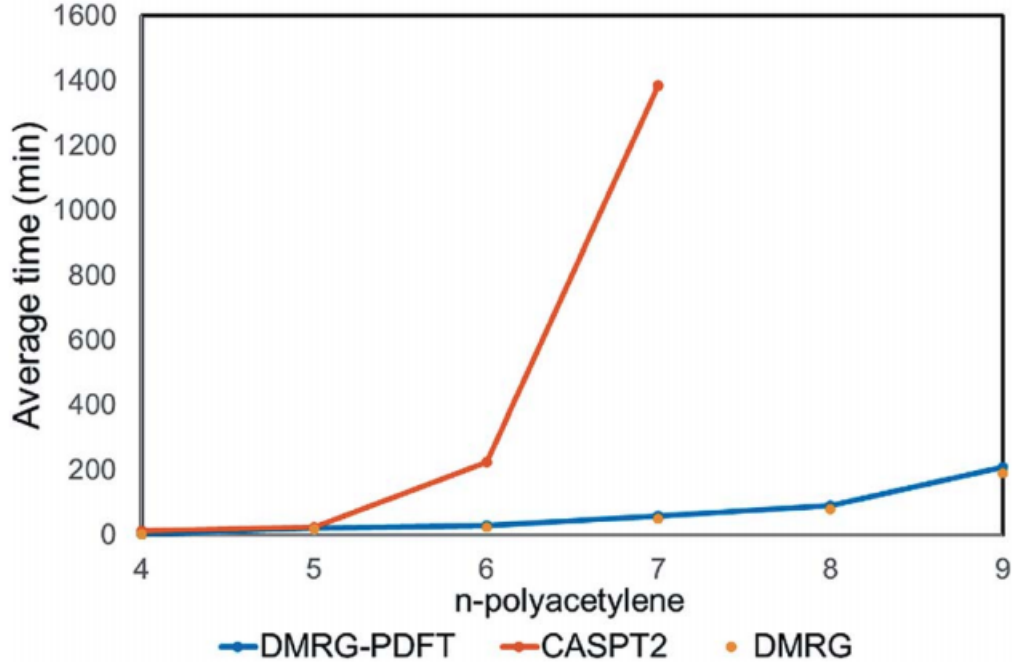


Figure 4.4: Average compute time (averaged over singlet and triplet) required for DMRG, DMRG-PDFT, and CASPT2 calculations on polyacetylenes with a single processor. The DMRG and DMRG-PDFT data are indistinguishable in the plot.

4.6 Conclusions

We have presented a new method, DMRG-PDFT, that combines the advantages of the DMRG and MC-PDFT approaches. We used

the resulting new method to calculate singlet–triplet gaps in polyacenes and polyacetylenes. The energy gaps calculated using DMRG were found to be close to the reference data, and we found that the DMRG-PDFT calculations are in most of the cases even more accurate than their bare DMRG counterparts. For polyacenes, singlet–triplet energies match reasonably well with the literature including experimental as well as various high-level calculations such as CCSD(T), DMRG-CASPT2, and DMRG-ec-MRCISD+Q values. For polyacetylene systems, we compared DMRG and DMRG-PDFT values with $M = 50$ to standard CASSCF and CAS-PDFT, and we found that DMRG-PDFT shows less dependence on the bond dimension than DMRG. Using the on-top density functional to add external correlation energy to DMRG wave functions is shown to be a promising approach to study large systems at an affordable cost.

5. Magnetic Coupling in a Tris-hydroxo-bridged Chromium Dimer

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Magnetic Coupling in a Tris-hydroxo-bridged Chromium Dimer Occurs Through Ligand Mediated Superexchange in Conjunction with Through-Space Coupling, 2020, 142, 16644–16650, Prachi Sharma, Donald G Truhlar and Laura Gagliardi, *Journal of the American Chemical Society*. Copyright 2020 American Chemical Society.

5.1 Introduction

Molecular magnets have applications and potential applications in information storage, quantum computation, and molecular electronics via materials combining magnetooptical, electrooptical, and/or novel switching capabilities.^{298–300} Compounds containing several magnetic centers have been extensively studied because of the many possible ways in which the spin carriers can magnetically interact.⁴ The magnetic coupling arises when the spin at one nucleus polarizes the electrons orbiting around that nucleus, and these electrons spin polarize neighboring magnetic nuclei. In the case of a dinuclear magnet with two open-shell transition metals, the magnetic properties are often characterized based on the scalar magnetic coupling constant (J) between the two interacting nuclei.^{301,302} A prototype experimentally and computationally studied system is tris-hydroxo-bridged Cr(III)-Cr(III) system (Kremer’s dimer)³⁰³ which consists of two antiferromagnetically coupled Cr(III) metal centers with d^3 - d^3 electron configuration. See Figure 5.1. Kremer’s dimer poses two major challenges for quantum chemistry methods: (1) the determination of the correct spin ordering and magnetic coupling; (2) understanding the magnetic coupling mechanism through which the two spin centers interact. In this paper we show that a quantum chemical method introduced in 2019, namely pair-density functional theory based on a large density matrix renormalization group wave function can cap-

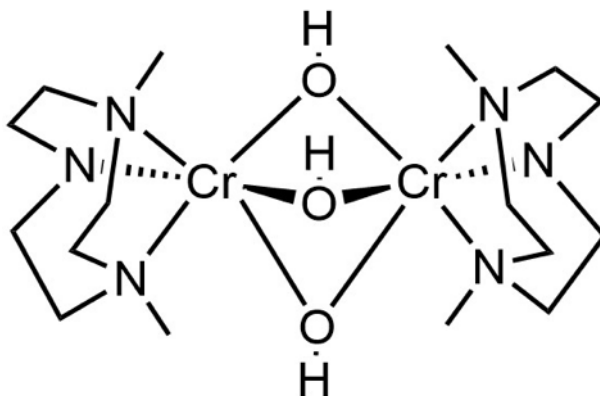


Figure 5.1: $[L_2Cr(III)_2(\mu-OH)_3]^{3+}$ [L = N,N',N''-trimethyl-1,4,7-triazacyclononane].

ture all the electron correlation effects for this system and for the first time properly describe these two phenomena.

The magnetic coupling constant is given by the difference between the high spin (HS) and low spin (LS) energies divided by the difference between the $\langle \hat{S}^2 \rangle$ (expectation value of the $\hat{S}^2$ spin operator) values of the HS and LS states:³⁰⁴

$$J = -\frac{E_{HS} - E_{LS}}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{LS}} \quad (5.1)$$

According to experimental studies, the ground state has singlet spin symmetry, and the order of spin-state energies given by density functional theory, DFT, is $E(S = 0) < E(S = 3) < E(S = 1) < E(S = 2)$ where S is the total spin quantum number.³⁰⁵ The reported experimental value of J is -66 cm^{-1} ,³⁰⁶ where the negative sign indicated antiferromagnetic coupling. Kohn-Sham density functional theory (KS theory) has been the major theoretical method used so far to model molecular magnets, and the first application of KS

theory to this problem failed the first challenge by incorrectly predicting the spin-state ordering and overestimating the energies of intermediate spin states by thousands of wavenumbers.³⁰⁵ However, Pantazis³⁰⁷ showed that those poor results were due to not recognizing the broken spin-symmetry of the variationally optimum KS states (which are not eigenfunctions of the $\hat{S}^2$ spin operator) and even more to using incorrect configurations in the intermediate spin states. Employing KS theory with proper configurations and approximate spin projection,³⁰⁴ he obtained qualitatively correct results with KS theory.³⁰⁷ Pantzasis³⁰⁷ also pointed out that a more physical representation of the low-spin states requires a multireference treatment based on a method such as complete-active-space self-consistent field^{15,83,308} (CASSCF) theory or the density matrix renormalization group^{211–214} (DMRG). He found that CASSCF with a small active space consisting of the 3d orbitals of the two Cr metals (6 active electrons in 10 active orbitals, i.e., (6e,10o)) gives the correct spin ordering, but with $J = -17 \text{ cm}^{-1}$, a factor of 3.9 too small. Adding post-SCF correlation by n-electron valence state perturbation theory (NEVPT2)^{20–23} $J = -32 \text{ cm}^{-1}$, value, still a factor of 2.1 too small.¹¹ An expansion in the active space to (24e,19o) and (30e,22o) in the DMRG-SCF approximation gave $J = -24 \text{ cm}^{-1}$, value, a factor of 2.8 too small. We conclude that correlation energy converges too slowly with active space size to obtain the correct results with an active space method. Since adding post-SCF cor-

relation to the small active space gives a poor result, we conclude that one must add post-SCF correlation to a large-active-space SCF calculation, which is usually unaffordable by conventional methods; a similar conclusion may be drawn from earlier work by Roemelt et al.³⁰⁹ The second challenge pertains the understanding of the mechanism by which the two chromium ions interact. Two coupling mechanisms are typically considered: (a) direct coupling of two magnetic centers interacting through space and (b) the superexchange mechanism where the interaction between the two magnetic centers is mediated by one or more diamagnetic bridging ligands.³¹⁰⁻³¹⁴ The direct mechanism may take place through bonding or, in some multiply bridged dimers, without bonding if the bridging ligands bring the metal centers in close proximity. An initial study of the Kremer’s dimer predicted the interaction to occur only through superexchange,³⁰³ while later Niemann et al. studied the trend in Cr-Cr bond lengths and J coupling values which led them to conclude that a direct Cr-Cr interaction occurs, with a complete absence of superexchange.³⁰⁶ In another study, McDouall and coworkers used the CASSCF method with an active space comprising of all the 3d orbitals and described the mechanism as direct coupling through space.³⁰⁵ Pantazis concluded that the interaction takes place through a strong direct mechanism and relatively weaker superexchange.³⁰⁷ To resolve this it is important to use important to use a large active space including the hydroxo ligand orbitals as well as to

consider the unpaired density on the bridging ligands. It should be noted that post MCSCF methods such as strongly correlated (SC) NEVPT2 and strongly internally correlated (SIC) NEVPT2 have been reported in the literature¹¹ for a small active space containing 3d orbitals however, but no post-MCSCF study has been reported for an active space containing the hydroxo ligand orbitals, although Roemelt et al. considered a post-SCF treatment of a bis- μ -oxo/ μ -acetato Mn(III,IV) dimer with a (19,16) active space including oxo 2p orbitals.³⁰⁹ In this study, we present spin-gaps and magnetic coupling constant obtained by combining^{315,316} CASSCF, DMRG-SCF and restricted active space SCF (RASSCF) with multiconfiguration pair-density functional theory^{30,154} (MC-PDFT), which calculates the energy from a multiconfiguration wave function and an on-top density functional. Moreover, to address the second challenge concerning the mechanism of magnetic interaction we put forward the use of unpaired electron density obtained from pure spin MC-PDFT functionals.

5.2 Computational Details

In this study we calculated four spin states of $[\text{L}_2\text{Cr(III)}_2(\mu\text{-OH})_3]^{3+}$ [$\text{L} = \text{N}, \text{N}', \text{N}''$ -trimethyl-1,4,7-triazacyclononane] (Figure 5.1) by building an MC-PDFT calculation on top of, in turn, CASSCF, restricted active space SCF³¹⁷ (RASSCF), and DMRG-SCF; these calculations

are denoted respectively as CAS-PDFT, RAS-PDFT, and DMRG-PDFT. (Two sets of DMRG calculations will be distinguished as DMRG1 and DMRG2.) We used the geometry from ref³⁰⁷ where crystallographic structural data are used for all the atoms except the hydrogen atoms, whose positions are optimized by KS theory using the TPSS-D3BJ35,^{318,319} functional. The CASSCF, RASSCF and MC-PDFT calculations were performed using the OpenMolcas software package.³²⁰ DMRG calculations were performed using the QC-Maquis interface with OpenMolcas.^{261,264,276?,277} The computational cost arising from the two-electron integrals was greatly reduced by employing Cholesky decomposition.¹⁵⁸ An ultrafine grid was used for MC-PDFT calculations. The def2-TZVP³²¹ basis set and the translated PBE (tPBE) functional were used for all calculations. We used the following active spaces in the various calculations: CASSCF: We used (6e,10o) using 3d orbitals of the two Cr atoms. RASSCF: We used (30e, 22o) divided into two subspaces. RAS1 contains two Cr 3s, six Cr 3p, and four ligand 2p orbitals, and this subspace is doubly occupied except for up to two holes. RAS2 consists of ten 3d orbitals with all possible occupancies. The orbitals are shown in Figure 5.2. DMRG1-SCF: We used (30e, 22o) with CASSCF orbitals for the initial guess and a DMRG bond dimension (M) of 1000. DMRG2-SCF: We used (30e, 22o) with RASSCF orbitals for the initial guess and $M = 1000$.

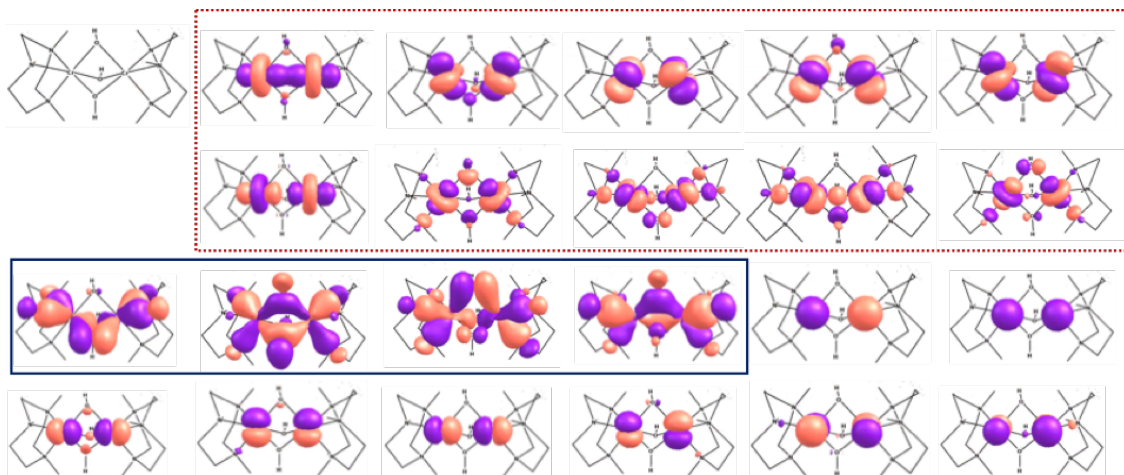


Figure 5.2: Natural orbitals in the RASSCF active-space. The orbitals in the dashed red rectangle are in RAS2 and are 3d orbitals of the two chromium centers. All the other orbitals belong to RAS1. The orbitals in the black solid rectangle are ligand-metal bonding orbitals and contain contributions from the metal 3p and 3d orbitals along with the 2p orbitals of oxygen atoms of the bridging hydroxyl ligands.

5.3 Results and Discussion

The spin ladders for CASSCF and CAS-PDFT calculations are compared with literature values in Figure 5.3. The first spin ladder corresponds to the CASSCF reported in ref³⁰⁷ while the second CASSCF corresponds to the current study. Note that the CASSCF energies reported in this study (blue lines in Figure 5.2) are slightly different from those in ref³⁰⁷ due to different starting orbitals (ref³⁰⁷ used localized KS orbitals). Although CASSCF gives the correct spin ordering, it underestimates J by factors of 3.5–3.9. The figure also contains the SC-NEVPT2 and FIC-NEVPT2 post-SCF results reported in ref.³⁰⁷ Of the five methods in the figure, CAS-PDFT gives J closest to the experimental value, although it is still a factor of 1.7 too small. This is because the CASSCF active-space used here

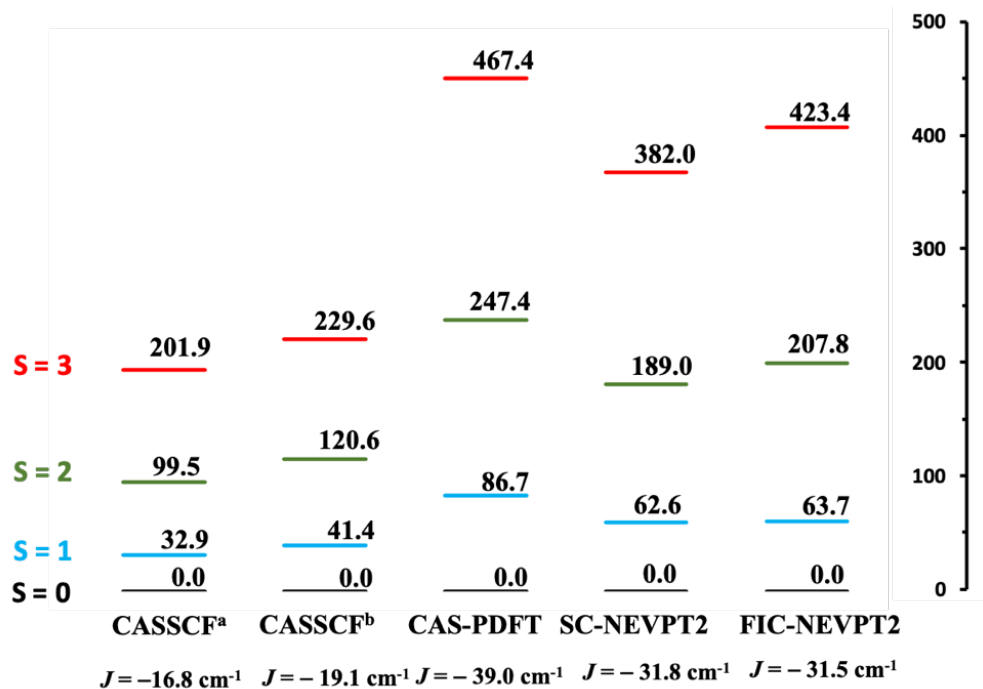


Figure 5.3: Spin ladder (in cm^{-1}) for CASSCF, CAS-PDFT, SC-NEVPT2 and FIC-NEVPT2 methods. An active space consisting of six electrons in ten 3d orbitals was used in all these calculations. The CASSCF^a and both NEVPT2 results are from ref 11. The CASSCF^b results are from the present study.

includes the only the 3d orbitals, which are not sufficient to describe the ligand-mediated superexchange mechanism, and also perhaps because the smaller active space does not represent the correlation energy as well as the larger active space does.

The comparison to NEVPT2 in Figure 5.3 is noteworthy from the point of view of computational cost. The cost of an entire MC-PDFT calculation scales the same as the underlying MCSCF method, and MC-PDFT can be used in conjunction with CASSCF, RASSCF, or DMRG-SCF with a nominal computational cost (1% of computational time was taken by the PDFT module), while other methods such as NEVPT2 add considerably to the computational time and memory cost. Figure 5.3 shows that MC-PDFT and NEVPT2 give

Table 5.1: Relative energies of spin states and coupling constant (J) in cm^{-1} .

Method	M	Energy relative to S = 0			J
		S = 1	S = 2	S = 3	
KS-PBE				1613 ^b	-128 ^c
RASSCF		62	181	343	-29
DMRG1-SCF	500	98	489	267	-22
	1000	68	313	295	-25
DMRG2-SCF	1000	145	66	-16	-
DMRG3-SCF ^a	1000	48	143	287	-24
RAS-PDFT		144	424	766	-64
DMRG1-PDFT	500	84	353	642	-54
	1000	134	482	664	-55
DMRG2-PDFT	1000	150	465	812	-68
Experiment		140 ^b	408 ^b	784 ^b	-66 ^a
^a Ref ³⁰⁶ ^b Ref ³⁰⁵ ^c Ref ³⁰⁷					

comparable-quality results despite this difference in cost, and the affordability of PDFT approach allows us to advance economically to larger active spaces. Results for the larger (30e,22o) active space presented in Table 5.1; this active space contains ligand-metal orbitals that are important for ligand-mediated superexchange. As explained above, DMRG1 and DMRG2 differ in the initial guess orbitals, and it is worthwhile to present both results as a warning because DMRG calculations can in principle show significant dependence on the starting orbitals and orbital ordering unless they are fully converged with respect to M . DMRG3 is taken from ref 11 where orbitals were obtained through “localization of quasi-restricted DFT orbitals using the Pipek–Mezey44 localization algorithm” and orbitals containing ligand-metal overlap were not present.

Comparing Table 5.1 to Figure 5.3 shows that the RASSCF method predicts the spin-state splitting energies and magnetic coupling constant in better agreement with experiment than CASSCF. DMRG1-SCF underestimates the $S = 3$ state for both $M = 500$ and $M = 1000$, and DMRG-SCF2, which started from RASSCF optimized orbitals, results in an incorrect spin state ordering. This could be because DMRG-SCF is far from convergence at $M = 1000$ and the ordering may change with high bond dimensions. DMRG-PDFT has been observed to converge faster with respect to bond dimension than the parent DMRG.³⁰ It is very interesting that Table 5.1 shows that all four PDFT calculations predict the correct spin ordering even when used on top of DMRG-SCF with incorrect spin ordering, i.e., it eliminates the effect of the initial guess orbitals to a large extent. In addition to the correct spin ordering, PDFT gives more consistent spin-gap values than SCF. It is very encouraging that all four PDFT calculations give small errors (2–18% with an average of 10%) in J . Superexchange is a mechanism that favors antiferromagnetic coupling (more negative J) of weakly coupled metal centers due to mixing in configurations in which mediating ligands that are nominally diamagnetic have some paramagnetism. In superexchange, a virtual electron transfer from the ligand ion into the d shell of the magnetic ion, therefore, creating unpaired electron density at the ligand center.^{314,322–324} Often the discussion of superexchange has been based on indirect inference, e.g., if the nature of the

ligands, their geometrical arrangement, or the type of treatment of the ligands has an effect on the magnetic constants, it is an indication of superexchange. A more direct measure of superexchange is therefore to consider the presence of unpaired electrons on the diamagnetic ligands. The density (D) of unpaired electrons⁴⁸ should be distinguished from the magnetization density m , typically written as $\rho_\alpha - \rho_\beta$, where ρ_σ is the density of electrons with spin component $\sigma = \alpha$ or β . For example, in any pure singlet, m is zero everywhere in space, whereas D is usually nonzero [and in a so called open-shell singlet (also called a hyper open-shell singlet), m can even be $O(1)$]. In MC-PDFT we can compute unpaired densities from the on-top pair density. In the past³² we have labeled these as translated spin densities (ρ_α^t and ρ_β^t) to make a connection with spin-polarized Kohn-Sham density functional theory, but since MC-PDFT is based on pure spin functions, it is technically more appropriate to interpret

$$D(r) \equiv \rho_\alpha^t - \rho_\beta^t \quad (5.2)$$

as the unpaired density at position r . In the present work we take advantage of the ability of density matrix renormalization group (DMRG) and RASSCF to apply MC-PDFT to large and complex systems to compute unpaired electron densities on the mediating ligands of the tris-hydroxo-bridged chromium dimer compound to compute $D(r)$ and thereby to obtain – for the first time – direct evidence

of the presence of superexchange. Figure 5.4 shows two-dimensional contour plots of $D(r)$ in three planes through the origin, as calculated by CAS-PDFT and DMRG-PDFT. We used DMRG2-PDFT unpaired densities in Figure 5.4; however, a similar result is obtained by DMRG1-PDFT and RAS-PDFT (Figures E.10 and E.11). The key indication of superexchange is unpaired electron density on the bridging hydroxo ligands. The left panel in part a of Fig. 5.4 shows no unpaired density on the bridging ligands in the CAS-PDFT calculation, which yielded $J = -39 \text{ cm}^{-1}$, and hence at least 39 cm^{-1} of the magnetic coupling comes from through-space interaction without superexchange. However, the right panel of part a shows significant unpaired density in the DMRG2-PDFT calculation, which yielded $J = -68 \text{ cm}^{-1}$, and this indicates that a noticeable part of the additional 29 cm^{-1} of magnetic coupling comes from superexchange. (Although the Figure 5.4 shows the unpaired electron density for the $S = 0$ state, a similar trend is observed for the other states.) Parts b and c of Fig. 5.4 show unpaired electron density in the XZ and XY planes containing the Cr atoms, and this unpaired density does not change appreciably between the CAS-PDFT and DMRG-PDFT calculations. The question remains of whether the more negative J in the RAS case as compared to the CAS case (the change of J from -39 cm^{-1} with the CAS active space to -64 cm^{-1} with the RAS active space) might be due to the addition of the Cr 3 and 3p orbitals as active orbitals rather than the ligand 2p orbitals. Ideally we would

check this by using an intermediate-size active space where we only add the ligand orbitals and not the Cr 3s and 3p orbitals; however, this is not easy to converge. Therefore we checked this by an indirect route. In particular, we performed a calculation in which we deleted the three hydroxide bridging ligands of the chromium dimer, and we studied the effect adding the Cr 3s and 3p orbitals in this case where the complication of bridging ligand orbitals does not arise because there are no bridging ligands. (A similar approach was followed by Boyn et al.³²⁵ in their study of the magnetic coupling mechanism in a cobalt quinoid dimer complex.) The results are summarized in Table E.4. We found that, in the absence of the hydroxide ligands, an increase in the active space by adding Cr 3s and 3p orbitals actually makes J less negative, not more negative. This is consistent with our interpretation that more negative J obtained when we change from the CAS active space to the RAS active space in Kremer’s dimer (i.e., in the species containing the bridging ligands) involves superexchange.

5.4 Summary and Conclusions

To summarize, the findings of this study are: An active space with only the Cr d orbitals is not enough for the complete physical representation of the magnetic coupling in Kremer’s dimer, although MC-PDFT substantially improves over the CASSCF spin gaps and

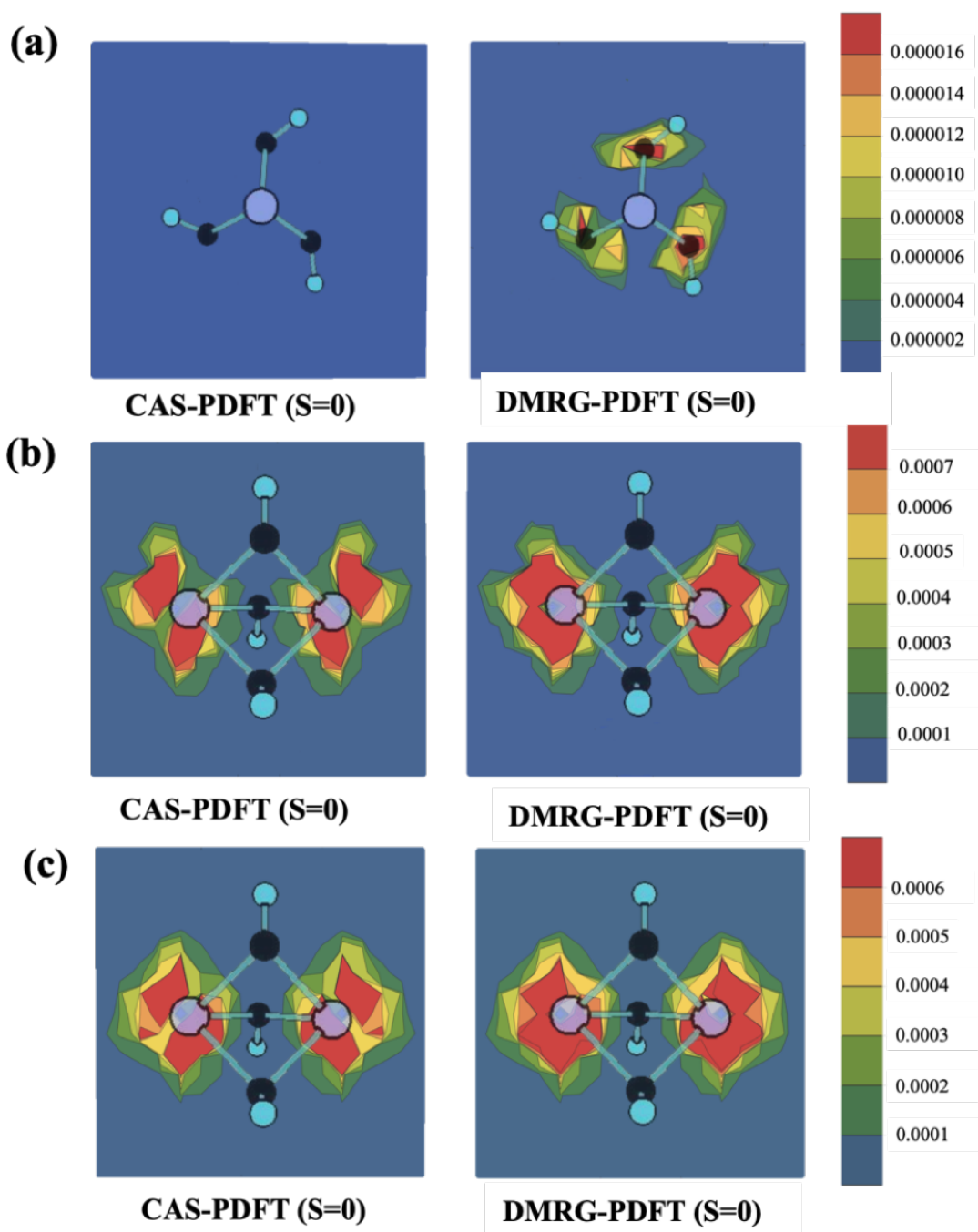


Figure 5.4: Unpaired density for CAS-PDFT (left) and DMRG-PDFT (right) for Kremer's complex in (a) the YZ-plane, (b) the XZ-plane, and (c) the XY-plane. The colors purple, black, and blue corresponds to chromium, oxygen and hydrogen atoms, respectively.

magnetic coupling even with such a small active space. A large active space containing chromium valence electrons and ligand orbitals is important for the correct description of the magnetic coupling mechanism and spin gaps. The DMRG-PDFT unpaired electron density plots suggest that a significant magnetic coupling occurs through ligand-mediated superexchange in conjunction with through-space coupling. A post SCF-PDFT calculation built on either RASSCF or DMRG-SCF wave functions corrects the spin gap and spin-state ordering in RASSCF and DMRG-SCF. It is shown that DMRG-PDFT gives good results even for a small bond-dimension and even when DMRG-SCF gives incorrect spin ordering. This is especially encouraging because the polynomial cost scaling of DMRG should allow calculations on even larger and more complex systems. DMRG-SCF and RASSCF are both approximations to CASSCF and are used when a full CASSCF is practically unaffordable. In RASSCF, the number of configurations is reduced by dividing the active-space into subspaces and only allowing a certain number of holes and excitations within the subspaces. In DMRG, the wave function is recast in terms of matrix product states and their number is truncated; the size of the active space then depends on the bond dimension, M . DMRG converges slowly with respect to M , and sometimes a large M is required (depending on the active-space size) to approach full CI within the active-space. Although DMRG-SCF has not converged with respect to M and is sensitive to the choice of initial

orbitals, DMRG-PDFT is observed to have a very little dependence on these parameters. Furthermore, DMRG-PDFT and RAS-PDFT gives similar unpaired density plots. We conclude that a large active space as well as a post-SCF correlation calculation are needed for a correct physical description of magnetic coupling in Kremer’s dimer, and we show that the PDFT approach works well with both RAS and DMRG approximations. This is very encouraging from a physical interpretation point of view because these two kinds of approximation to CASSCF are quite different so their agreement provides evidence that they both represent what would be obtained in a CASSCF calculation with these large numbers of active electrons and active orbitals. Furthermore, it is very encouraging from a practical point of view because one or another of these methods may be more feasible for other large problems. RAS-PDFT and DMRG-PDFT predict magnetic coupling in excellent agreement with the experimentally reported value and are very promising for studying magnetic coupling in metal complexes.

6. Multiple Bonds in Uranium-Transition Metal Complexes

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Multiple Bonds in Uranium–Transition Metal Complexes,
Prachi Sharma, Dale R Pahls, Bianca L Ramirez, Connie C Lu and
Laura Gagliardi, *Inorganic chemistry*, **2019**, 58, 10139-10147.

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6.1 Introduction

Metal-metal bonding is a fundamental concept in chemistry that affects the properties of the systems of interest and is instrumental to understanding structure and reactivity, metal-surface chemistry, and metal-based catalysis.^{46–60} Compared to transition metals, the nature of metal-metal bonds involving f-block metals, especially the actinide series, has been less explored.^{48,49,51,326,327} The 5f orbitals of the actinides, such as uranium, have suitable spatial extension to participate in bonding that makes the d-f heterobimetallic bond an interesting target to improve our understanding of the interplay of the d and f orbitals. Reviewing both theoretical and experimental data in the literature, very few examples have been reported for bonding between an actinide, such as uranium and a transition metal to date. The first attempt to synthesize a uranium-transition metal (U-TM) compound was made by Stone in 1971.³²⁸ He reported the synthesis of a uranium-manganese complex with carbonyl ligands; however, the complex, being highly air sensitive, decomposed before it could be analyzed. In 1987, Sternal and Marks³²⁹ reported the successful synthesis of uranium-ruthenium and uranium-iron complexes, though the x-ray diffraction was not reported for these complexes. Although U-TM complexes are promising, the research in the field had been dormant for more than a decade. Later in 2000, Ephritikhine and coworkers³³⁰ reported the successful synthesis and

characterization of urana[1]ferrocenophane compounds with Fe-U-Fe bonds where the average U-Fe bond length lies between 3.12-3.65 Å, which is shorter than the covalent U-Fe distance of 3.28 Å.³³¹ Since then, several bimetallic U-TM complexes have been reported in the literature including experimental³³²⁻³⁴⁴ as well as predominantly theoretical studies.³⁴⁵⁻³⁴⁹ The bonding interactions in these previously reported U-TM compounds are predominantly dative;^{335-337,339,342-344} however, minor σ and π contributions were also predicted in some complexes by computational calculations.^{332-334,341} Bimetallic complexes generally contain numerous low-lying states, and therefore it is important to use a multireference method to accurately predict the nature of chemical bonding.³²⁹ Multireference methods such as complete active-space self-consistent field method (CASSCF)^{14,15,83} have been employed to explore the bonding of f-block metals, particularly in uranium chemistry.^{345,347,349-355} Multireference calculations have predicted the existence of high bond orders in the uranium-uranium bond of U₂.^{353,355} Furthermore, multiple computational studies have explored uranium-ligand bonding,^{350,351,356-358} and uranium-transition metal chemistry.³⁴⁵⁻³⁴⁹ In this paper, we explore the chemical bonding between a first row transition metal and a uranium atom in TMU[(ⁱPr₂PCH₂NAr)₃tacn] (UTM-1) and TMU(ⁱPr₂PCH₂NPh)₃ (UTM-2) species where TM=Cr, Mn, Fe, Co, Ni. UTM-1 and UTM-2 are comprised of nonadentate (ⁱPr₂PCH₂NHAr)₃tacn and bidendate ⁱPr₂PCH₂NPh ligands,

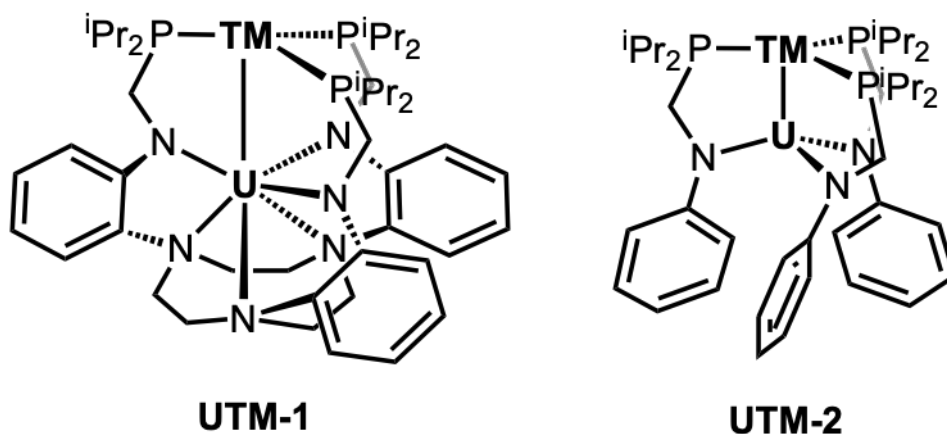


Figure 6.1: Schematic representation of (left) $\text{TMU}[(^i\text{Pr}_2\text{PCH}_2\text{NAr})_3\text{tacn}]$ (UTM-1) and (right) $\text{TMU}(^i\text{Pr}_2\text{PCH}_2\text{NPh})_3$ (UTM-2), where $\text{TM} = \text{Cr, Mn, Fe, Co, Ni}$.

respectively; both containing hard amido and soft phosphine groups. We focus on first row transition metals because the 5f-3d interactions are less explored compared to f-block and second row transition metals and because of the unique electronic structures and greater spin-flexibility of first row transition metals, these interactions might have unique features. The structures of the potential U-TM complexes are shown in Figure 6.1. The complexes hypothesized here are inspired by previous work by Ramirez et al.³⁵⁹ in which the same ligands were employed to make 4f-3d Lu-Ni bimetallic species. In this study, we employ DFT and multireference methods to predict the stability and nature of the bonding in these novel complexes.

6.2 Computational Details

The structures of UTM-1 and UTM-2 ($\text{TM} = \text{Cr, Mn, Fe, Co and Ni}$) complexes were optimized with the PBE13 functional with D3 dispersion correction,³⁶⁰ using the unrestricted formalism, UPBE-D3.

UPBE-D3 gave satisfactory results for related bimetallic systems featuring the same ligand.³⁵⁹ The def2-TZVP basis set³²¹ was used for the transition metals, N and P, while the Stuttgart/Dresden pseudopotential³⁶¹ was used for uranium. All the other atoms (C and H) were treated using the def2-SVP basis set. All the DFT calculations were performed with the Gaussian 09 software.³⁶² Single point calculations were performed at the PBE-D3 optimized geometries using the complete active space, CASSCF method,¹⁵ to gain insight into the electronic structure of the UTM-2 complexes. The ANO-RCC-vtzp basis set³⁶³ was employed for U and TM, while a double zeta quality ANO-RCC-vdzp basis set was used for N and P atoms. A minimal basis set of ANO-RCC type was used for C and H. Douglas–Kroll–Hess Hamiltonian was used to include scalar relativistic effects.^{364,365} The active space employed in the CASSCF calculations consists of the valence 5f and 6d orbitals of U and the 3d and 4s orbitals of TM. Larger active-spaces were also explored, however there were no changes in the final results (see Appendix). The electronic excitation energies were calculated at multistate complete active space second order perturbation theory (MS-CASPT2) level of theory.^{197,366} We used the default ionization- potential-electron-affinity (IPEA) shift of 0.25 a.u., which is an empirical correction applied to the zero-order Hamiltonian.¹⁵⁷ We also applied an imaginary shift of 0.2 a.u. to avoid possible intruder states. The Molcas 8.0 software package²² was used for the CASSCF calculations.¹⁵⁹

The effective bond order (EBO) was calculated using the formula 1e

$$EBO = \frac{\sum_i (B_i - AB_i)}{2} \quad (6.1)$$

where, B_i and AB_i are the occupation numbers of bonding and antibonding natural orbital in an orbital pair, respectively, and the sum runs over all the orbital pairs.

6.3 Results

Unrestricted DFT (UPBE-D3) calculations were performed for UTM-1 and UTM-2 (TM=Cr, Mn, Fe, Co, Ni) complexes for various possible spin states. Table 6.1 summarizes the results for different spin states for the UTM-1 complexes. The most stable spin state results are highlighted. DFT optimized geometries show that the shortest U-TM bond occurs between U and Mn atoms. The most stable spin states for UCr-1, UMn-1, UFe-1, UCo-1 and UNi-1 complexes as determined from UPBE-D3 calculations are the doublet, singlet, doublet, triplet and quartet state, respectively. The formal shortness ratio (FSR) is defined as the ratio of metal-metal bond distance to the sum of their single-bond metallic radii.³⁶⁷⁻³⁶⁹ A FSR value of 1 suggests the presence of single bond, while a smaller value indicates multiple bonds. According to their FSR values, UCr-1, UMn-1, UFe-1 and UCo-1 complexes should have multiple bonds between the two metals, while the UNi-1 complex shows a weaker interaction. The

DFT results along with CASSCF and CASPT2 relative energies for UTM-2 are summarized in Table 6.2. The U-TM bond distance does not change significantly between UTM-1 and UTM-2. CASSCF and CASPT2 relative energies follows the trend as DFT for all UTM-2 complexes but UCr-2. In UCr-2, CASSCF predicts sextet to be the ground spin state with 0.4 kcal/mol lower in energy than the doublet, however, after applying perturbative correction to the CASSCF energies (i.e. CASPT2), the doublet spin state appears as the ground state. The Mayer bond order for UTM-1 and UTM-2 at the ground spin state are reported in Table 6.3. For UCr and UMn complexes, Mayer bond order is same for the two ligands, however, UTM-2 favors shorter bond lengths for UFe, UCo and UNi which is in line with the trend seen in LuNi complexes with the two ligands.³⁵⁹ To understand the nature of uranium and first-row transition metals, UTM-2 were further studied with multiconfigurational methods as they are smaller calculations and thus require fewer computational resources such as time and memory.

6.3.1 UCr Complex

In 2013, Infante and co-workers proposed a six-fold bonding for a theoretical CrU diatomic molecule with EBO of 5.3.³⁴⁹ However, this diatomic molecule could be experimentally synthesized only in extreme conditions. In this paper, we investigate the nature of bonding in synthetically motivated UCr[(ⁱPr₂PCH₂NHAr)₃tacn] (UCr-1) and

Table 6.1: Geometrical Parameters, including Bond Lengths (Å) and Angles (deg) for UTM-1 obtained from DFT calculations. Bond lengths in Angstroms (Å). The most stable spin states are highlighted.

UTM	UCr				UMn			UFe			UCo			UNi	
Spin (2S+1)	2	4	6	8	1	3	5	2	4	6	1	3	5	2	4
Cal. S ²	0.75	3.75	8.75	15.75	0.00	2.00	6.00	0.75	3.75	8.75	0.02	2.00	6.00	0.77	3.75
U-TM	1.99	2.07	2.28	3.00	1.94	2.03	2.17	2.02	2.20	2.75	2.25	2.26	2.63	2.68	2.72
Avg TM-P	2.40	2.39	2.38	2.37	2.35	2.32	2.34	2.28	2.27	2.24	2.22	2.22	2.22	2.20	2.21
Avg U-N _{facn}	2.80	2.78	2.78	2.73	2.79	2.80	2.79	2.80	2.81	2.75	2.80	2.80	2.78	2.76	2.76
Avg U-N _{amide}	2.41	2.45	2.44	2.41	2.40	2.44	2.45	2.42	2.43	2.41	2.40	2.40	2.41	2.38	2.40
E ^{DFT} (kcal/mol)	0.0	11.6	27.6	41.6	0.0	13.3	37.1	0.0	20.1	47.2	7.5	0.0	28.8	10.2	0.0
FSR ^a	0.68	0.71	0.78	1.03	0.67	0.70	0.84	0.71	0.77	0.96	0.80	0.80	0.94	0.96	0.97

^aFSR: Formal shortness ratio; it is the ratio between calculated bond length and the sum of covalent radii of the two metals.

Table 6.2: Geometrical Parameters, including Bond Lengths (Å) and Angles (deg) for UTM-2 obtained from DFT calculations. Bond lengths in Angstroms (Å). The most stable spin states are highlighted. Relative energies with respect to the most stable spin-state are calculated at DFT, CASSCF and CASPT2 levels of theory.

UTM	UCr				UMn			UFe			UCo			UNi	
Spin (2S+1)	2	4	6	8	1	3	5	2	4	6	1	3	5	2	4
Cal. S ²	0.75	3.75	8.75	15.75	1.00	2.00	6.00	0.75	3.75	8.75	0.03	2.00	6.00	0.79	3.75
U-TM	1.99	2.07	2.29	2.75	1.94	2.03	2.20	2.02	2.21	2.62	2.23	2.25	2.47	2.64	2.62
Avg TM-P	2.39	2.41	2.39	2.36	2.35	2.33	2.35	2.30	2.28	2.27	2.24	2.23	2.24	2.21	2.24
Avg U-N _{amide}	2.38	2.38	2.37	2.41	2.36	2.37	2.37	2.35	2.36	2.32	2.33	2.34	2.34	2.30	2.33
E ^{DFT} (kcal/mol)	0.0	13.0	26.9	41.9	0.0	19.6	45.3	0.0	19.6	45.3	6.8	0.0	28.0	4.7	0.0
E ^{CASSCF} (kcal/mol)	0.0	5.2	-0.4	14.2	0.0	15.2	21.4	0.0	6.9	38.8	21.3	0.0	57.7	10.7	0.0
E ^{CASPT2} (kcal/mol)	0.0	22.7	29.1	47.6	0.0	38.5	73.1	0.0	26.5	83.8	14.4	0.0	64.3	22.3	0.0
FSR ^a	0.68	0.71	0.78	0.94	0.67	0.70	0.76	0.70	0.77	0.91	0.80	0.80	0.88	0.94	0.94

^aFSR: Formal shortness ratio; it is the ratio between calculated bond length and the sum of covalent radii of the two metals.

Table 6.3: Mayer bond order (BO) calculated at DFT level for ground spin state for UTM-1

	UCr	UMn	UFe	UCo	UNi
Mayer BO UTM-1	3.3	3.6	2.8	1.5	0.5
Mayer BO UTM-2	3.3	3.6	2.9	1.6	0.7

UCr(*i*Pr₂PCH₂NHAr)₃ (UCr-2) complexes. Since the bond-distance between Cr and U and other geometric parameters are similar between the UCr-1 and UCr-2 complexes, we further investigated UCr-2 complex using multiconfigurational methods. Figure 6.2 shows a comparison between the previously reported electronic structure of the diatomic molecule CrU,³⁴⁹ and the complex UCr-2 proposed in this study. The electronic structure of CrU contains $(1\sigma)^2(1\sigma)^2(1\pi)^4(1\delta)^4$. The second sigma bond in CrU has contribution from 7s and 6d of U. Since the U atom is formally U³⁺ in UCr-2 while it is U⁰ in CrU, we do not observe a second sigma (2σ) bond in UCr-2. The occupation numbers for CASSCF orbitals for UCr-2 are reported in Figure 6.2. A comparison between the MO diagrams of CrU diatomic molecule reported in ref.³⁴⁹ and UCr-2 complexes.

6.3.2 UMn-2 Complex

Inspection of the CASSCF wave function shows that UMn-2 is highly multiconfigurational, with a 70% dominant configurational $((\sigma)^2(\pi)^4(\delta)^4)$ weight and 7% weight for the configuration- $((\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2)$. A formal quintuple bond between uranium and manganese with an EBO of 4.3 is predicted. Such a high bond order between uranium and manganese is unprecedented. Figure 6.3 shows the UMn-2 bonding and antibonding orbitals present in the active space. The atomic orbitals on Mn and U along with the resulting bonding orbitals are shown in Figure 6.4. The UMn-2 σ and δ bonding molecular orbitals

Table 6.4: Detailed CASSCF Orbital Analysis of UTM-2 Species^a

Complex	Orbital	%TM	%U	total electrons	EBO	Percent of main configuration
UCr-2	σ	48.5 (4s:3.9; 3d:92.4)	51.5 (5f:88.2; 7p:4.1)	1.78	3.3	80%
	π	63.2 (3d:99.9)	36.8 (6d: 60.9; 5f: 39.1)	1.91		
	π	66.5 (3d: 99.9)	33.6 (6d: 65.5; 5f:34.5)	1.91		
	δ	52.2 (3d: 96.9; 4s: 2.9)	47.8 (5f: 99.9)	1.67		
UMn-2	σ	60.2 (3d:97.2; 4p: 2.8)	39.8 (5f: 96.0; 6d:4.0)	1.85	4.3	69%
	π	69.7 (3d: 99.9)	30.3 (6d: 60.4; 5f: 34.9)	1.91		
	π	68.7 (3d: 99.9)	31.3 (6d:57.8; 5f:38.1)	1.91		
	δ	75.7 (3d: 96.3; 4p: 3.7)	24.3 (5f:95.8; 6d:4.2)	1.81		
	δ	71.3 (3d:96.3; 4s:3.7)	28.7 (6d:4.8; 5f:95.1)	1.77		
UFe-2	σ	65.3 (3d: 99.9)	34.7 (6d:9.2; 5f:90.7)	1.82	2.7	78%
	π	77.7 (3d:98.3; 4p:1.7)	22.3 (6d:59.2; 5f:34.5)	1.91		
	π	75.4 (3d: 99.9)	24.6 (6d:58.9; 5f:34.9)	1.91		
	3d(Fe)-5f/6d(U)	95.7 (3d:95.8; 4p:4.1)	4.3 (6d:32.5; 5f:67.4)	1.92		
	3d(Fe)-5f/6d(U)	97.2 (3d:95.9; 4p:3.9)	2.8 (6d:46.4; 5f:53.5)	1.93		
UCo-2	3d/4p(Co)-6d(U)	88.2 (3d:98.3; 4p:1.6)	10.3 (6d:99.9)	1.93	1.9	86%
	3d/4p(Co)-5f/6d(U)	88.3 (3d:97.9; 4p:2.0)	10 (6d:85.0; 5f:1.5)	1.93		
	3d(Co)-5f/6d(U)	91.8 (3d:95.4; 4p:3.7)	8.2 (7s:20.7; 6d:79.3)	1.94		
	3d(Co)-5f/6d(U)	95.9 (3d:97.7; 4p:2.3)	4.2 (7s:33.3; 6d:66.7)	1.94		
UNi-2	3d/4s/4p(Ni)-5f/6d(U)	34.5 (3d:31.6; 4p:37.1; 4s:28.4)	57.7 (7s:41.8; 6d:38.8; 5f:13.5)	1.01	0.5	91%
	3d/4s(Ni)-7s/6d(U)	88.6 (3d:97.4; 4s:2.6)	11.4 (6d:66.7; 7s:33.3)	1.95		

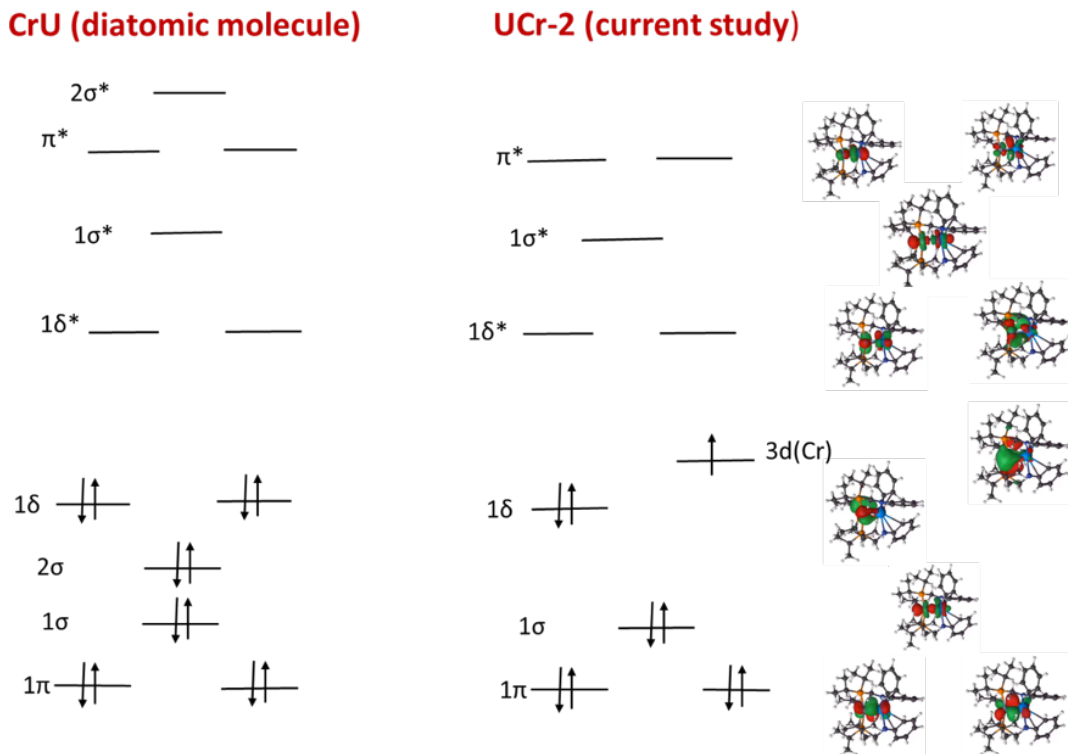


Figure 6.2: A comparison between the MO diagrams of CrU diatomic molecule reported in ref.³⁴⁹ and UCr-2 complexes.

contain minor contributions (5%) from uranium 6d atomic orbitals. The δ -type orbital contains major contributions from the U $5f_{z^3}$ and the Mn $3d_{z^2}$ orbitals while the two δ orbitals are mainly composed of the U $5f_{z(x^2-y^2)}$ and $5f_{xyz}$ and Mn $3d_{x^2-y^2}$ and $3d_{xy}$. The two π -orbitals also have major contributions from U 6d orbitals in addition to U $5f_{yz^2}$ and Mn $3d_{yz}$ and U $5f_{xz^2}$ and Mn $3d_{xz}$.

To study the electronic spectra of UMn-2 complex, MS-CASPT2 was employed. The major configurations for all the low-lying excited states consist of $\delta \rightarrow \delta^*$ transitions (Table 6.5). The MS-CASPT2 data show the first excited state to be a triplet state (T1). The infrared-spectra were calculated at the UPBE-D3 level (SI). The U-Mn stretching is predicted at 474 cm^{-1} which is comparable to the

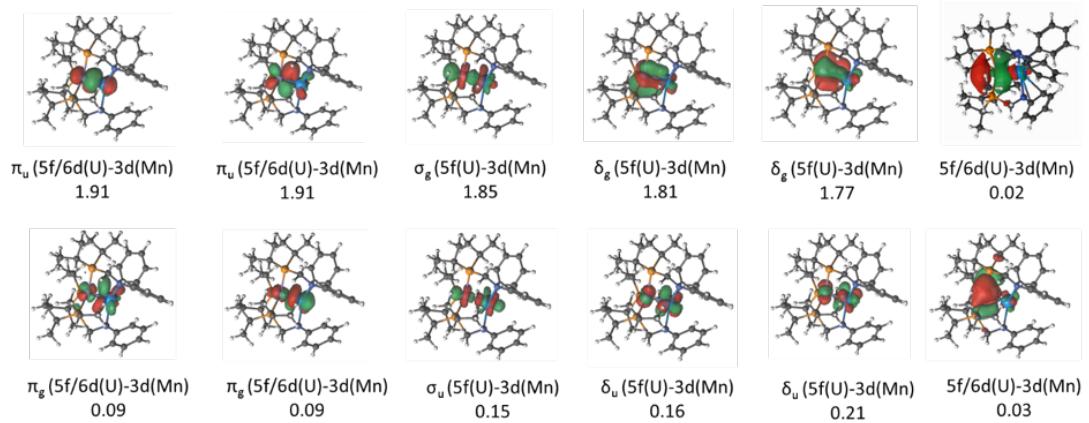


Figure 6.3: UMn-2 orbitals predicted by CASSCF (10, 12) for the singlet state along with the occupation number of the orbitals.

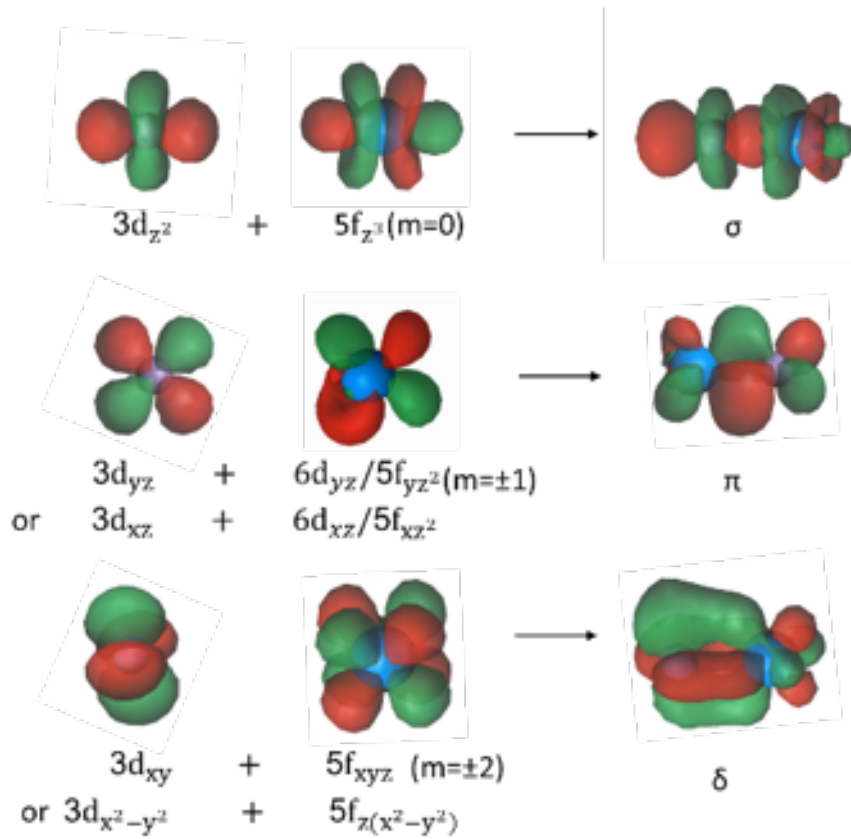


Figure 6.4: Combinations of the metal 3d, 5f and 6d atomic orbitals that participate in metal-metal bonding in UMn-2 complex.

Table 6.5: MS-CASPT2 excitation energies from S_0 in eV and nm for the lowest singlet and triplet states and their electronic configurations for UMn-2.

State	E (eV)	E (nm)	Configuration
S_0	0.0	0	45.2% $(\sigma)^2(\pi)^4(\delta)^4(\delta^*)^0$ 33.0% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_1	1.48	837	79.7% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_2	1.65	750	71.1% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_3	1.74	712	79.4% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
S_2	1.76	705	80.6% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
T_4	1.82	682	75.9% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
S_3	1.84	673	79.4% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$
S_4	1.98	626	79.6% $(\sigma)^2(\pi)^4(\delta)^3(\delta^*)^1$

IR-frequency reported for dichromium (434 cm^{-1}); 24 P-Mn-P stretch are observed at 277 cm^{-1} and 269 cm^{-1} respectively.

6.3.3 UFe-2 Complex

The UFe-2 complex shows a formal triple bond between U and Fe, with an effective bond order of 2.7. The three bonding orbitals are shown in Figure 6.5. A comparison of UFe-2 molecular orbital (MO) diagram shows that the Fe $3d_{z^2}$, $3d_{xz}$ and $3d_{yz}$ orbitals overlap with U $5f_{z^3}$, $5f_{xz^2}$ and $5f_{yz^2}$. One would expect a higher bond order for UFe-2 based on the electronic configuration of Fe, however, $3d_{x^2-y^2}$ and $3d_{xy}$ are localized on the Fe center and, thus, do not participate in bonding. We compare the frontier molecular orbitals of UFe-2 and UMn-2 complexes in Figure 6.6. The unpaired electron of UFe-2 is localized on the uranium $5f_{x(x^2-3y^2)}$ orbital.

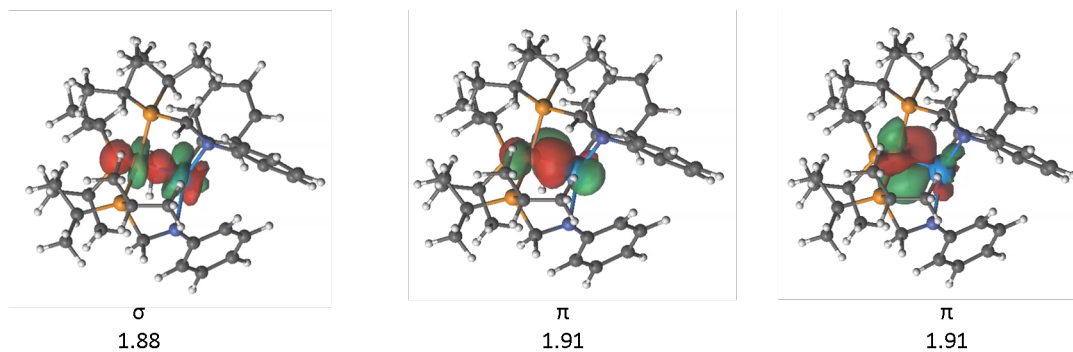


Figure 6.5: Bonding orbitals in UFe-2 complex. The occupation numbers of the orbitals are shown in the brackets.

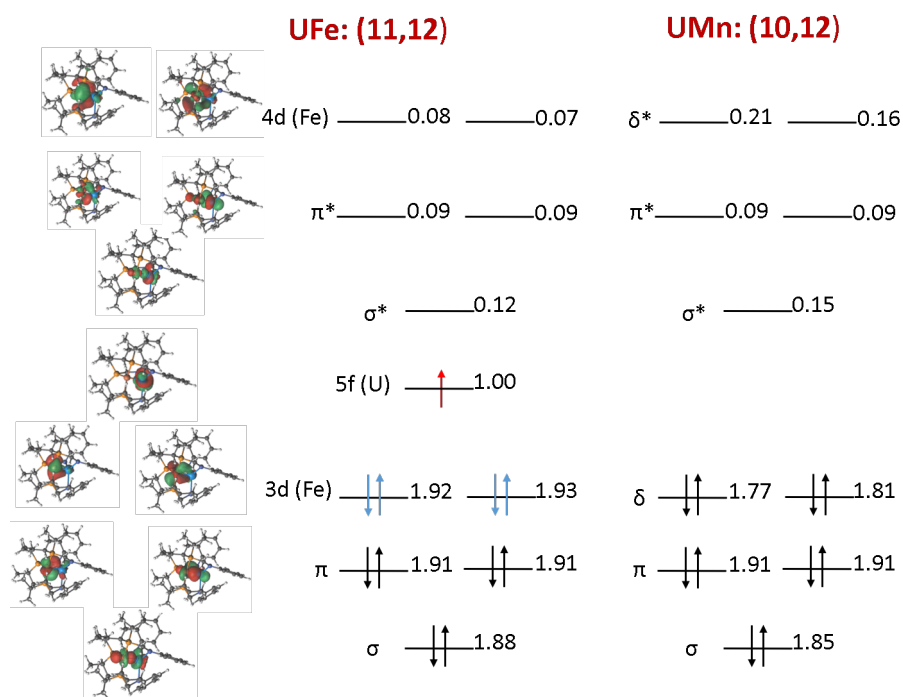


Figure 6.6: A comparison between the MO diagrams of UFe-2 and UMn-2 complexes. The blue and red colors represent electrons localized on Fe and U, respectively

6.3.4 UCo-2 and UNi-2 complexes

The interaction between the uranium and cobalt atoms in UCo-2 is different from those of UMn-2 and UFe-2. It is more dative in nature, directed from the occupied Co 3d orbitals towards the U 6d orbitals while the U 5f orbitals do not participate in the bonding. Since, the most stable spin state of the UCo-2 complex is the triplet state, the two unoccupied electrons are localized on U 5f orbitals. Although there are four orbitals with nonzero contributions from the uranium atom (Figure 6.7), only two orbitals show an effective overlap between U and Co as the contribution of uranium atom is more than 10% (Table 6.4). In contrast, in the UNi-2 complex with a quintet spin ground state, we observe the presence of half-a-bond (Figure 6.8) and a singly occupied orbital containing significant contributions from the U $5f_{z^3}$ and Ni $3d_{z^2}$ orbitals. Interestingly, the trends for bond order and bond-length observed for UTM-2 are similar to observations made in the previously reported family of complexes $\text{TMCr}(\text{N}(\text{o}-(\text{NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4)_3)$ (TM=Mn, Fe, Co, Ni).⁴⁷

6.3.5 Natural Bond Orbital Analysis

The density functional natural bond orbital (NBO) analysis studies predict quadruple bonds in UCr-2 while a five-fold bonding in UMn-2 (Table 6.6). In case of UCr-2, DFT NBO calculation also predicts the presence of half-a-delta-bond in addition to the four bonding MOs

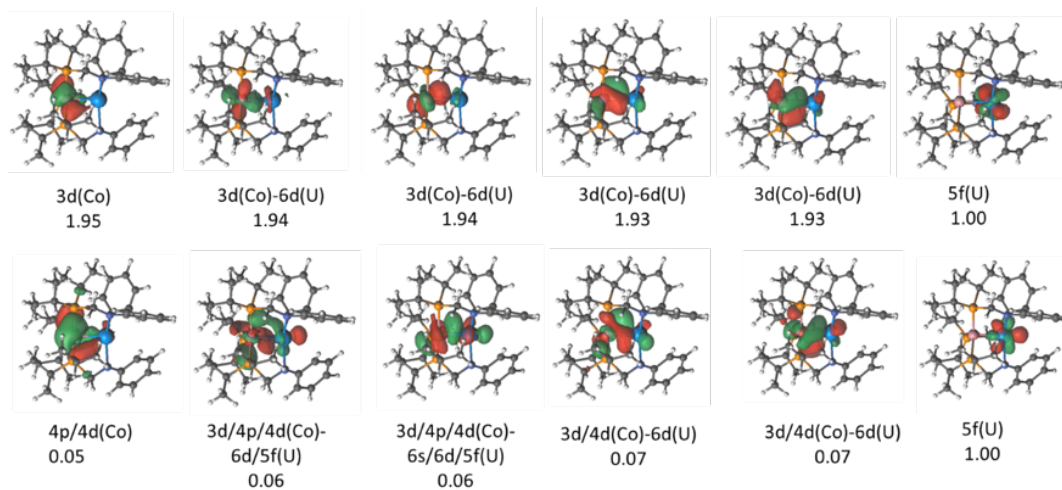


Figure 6.7: UCo-2 orbitals predicted by CASSCF (13, 12) for the triplet state along with their occupation numbers.

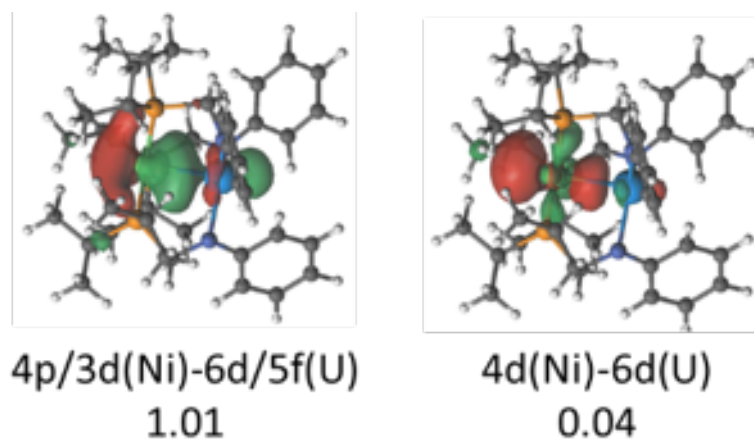


Figure 6.8: Bonding and antibonding orbitals in UNi-2 complexes along with their occupation numbers.

predicted by CASSCF studies. For UMn-2 complex, CASSCF and NBO agrees well where both methods predict presence of a quintuple bond between U and Mn. Strangely, for UFe-2 molecule, only alpha spin orbitals show the presence of molecular bonds between U and Fe, while no bonding MOs are found among beta spin orbitals. It should be noted that these bimetallic complexes are highly multireference and DFT NBO calculations are not always reliable.

6.3.6 Charge and Spin Density Analysis

The Mulliken³⁷⁰ and LoProp³⁷¹ charge densities are shown in Table 6.7. While the CASSCF LoProp charge density on U remains almost constant along the series, for TM it increases from Cr to Mn and then decreases again for Fe and does not change significantly thereafter. DFT and CASSCF Mulliken charge densities present different trends for U and TM. The spin densities obtained from unrestricted DFT calculations show that the unpaired electron is located on Cr in UCr-2, while it is located on U rather than on TM in UFe-2, UCo-2 and UNi-2, while for UCr-2 (Table 6.8). These results are in agreement with the picture that emerges from the CASSCF MOs analysis (Figure 6.2, Figure 6.6 and Figure 6.8).

6.3.7 Binding Energies

We also calculated the binding energies by subdividing UTM-1 and UTM-2 into the following fragments: UTM-1 is divided up into

Table 6.6: Detailed DFT Natural Bond Orbital Analysis of UTM-2 Species

Complex	Orbital	%TM	%U	total electrons
UCr-2	σ (alpha)	63 (3d: 84.4; 4p: 13.4)	37 (6d:7.8; 5f:90.2)	0.89
	π (alpha)	65.3 (3d: 91.3; 4p: 8.7)	34.7 (5f:58.3; 6d:40.3)	0.89
	π (alpha)	66 (3d:82.4; 4p:17.6)	34 (6d:34.6; 5f:63.6)	0.9
	δ (alpha)	63.8 (3d: 79.6; 4p: 20.4)	36.23 (6d; 6.6; 5f: 92.8)	0.88
	δ (alpha)	68.8 (3d:85.4; 4p: 13.9)	31.2 (5f:90.0; 6d:9.4)	0.87
	σ (beta)	59.6 (3d: 82.9; 4p: 15.1)	40.4 (6d:7.7; 5f:90.5)	0.89
	π (beta)	64.5 (3d: 91.3; 4p: 8.7)	35.5 (5f:60.9; 6d:37.9)	0.92
	π (beta)	63 (3d:81.3; 4p:18.6)	37 (6d:35.0; 5f:63.4)	0.9
	δ (beta)	61.9 (3d: 86.5; 4p: 12.9)	38.1 (6d; 8.0; 5f: 91.6)	0.87
	σ	66.6 (3d: 87.8; 4p: 9.04)	33.4 (6d:8.9; 5f:89.9)	1.77
	π	71.8 (3d: 79.1; 4p: 20.9)	21.2 (6d; 67.7; 5f: 30.8)	1.78
	π	70.5 (3d:73.9; 4p: 26.1)	29.5 (5f:65.7; 6d:33.0)	1.74
UMn-2	δ	70.2 (3d: 85.4; 4p: 14.6)	29.8 (5f:93.1; 6d:6.3)	1.78
	δ	70.7 (3d:85.8; 4p:14.52)	29.8 (6d:8.0; 5f:91.5)	1.77
	σ (alpha)	73.6 (3d: 89.2; 4p: 10.2)	26.4 (6d:16.2; 5f:82.6)	0.9
	δ (alpha)	76.2 (3d: 79.5; 4p: 16.3)	23.8 (6d; 16.8; 5f: 80.3)	0.87
	δ (alpha)	80.4 (3d: 97.5)	19.6 (6d:12.5; 5f: 86.3)	0.92

Table 6.7: Mulliken and LoProp charges for U and TM in UTM-2 complexes for the most stable spin states.

UCr-2 (S=2)	U		Cr	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.333	2.247	-0.476	-0.235
DFT	0.458	N/A	-0.276	N/A
UMn-2 (S=0)	U		Mn	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.329	2.16	-0.692	-0.069
DFT	0.471	N/A	0.056	N/A
UFe-2 (S=2)	U		Fe	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.355	2.291	-0.516	-0.154
DFT	0.64	N/A	-0.161	N/A
UCo-2 (S=3)	U		Co	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.148	2.345	0.107	-0.171
DFT	0.799	N/A	-0.339	N/A
UNi-2 (S=4)	U		Ni	
	Mulliken	LoProp	Mulliken	LoProp
CASSCF	3.037	2.136	-0.259	-0.166
DFT	0.678	N/A	-0.206	N/A

Table 6.8: Spin Densities for U and TM in UTM-2 complexes for the most stable spin states.

UCr-2		UMn-2		UFe-2		UCo-2		UNi-2	
U	Cr	U	Mn	U	Fe	U	Co	U	Ni
0.266	0.62	0	0	1.368	-0.337	2.226	-0.157	3.003	-0.06

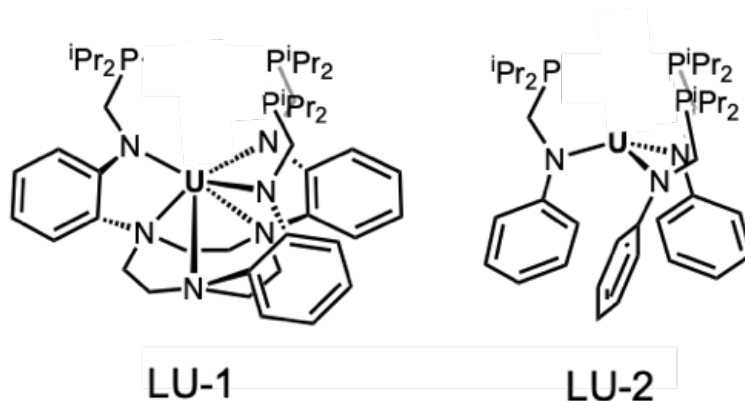


Figure 6.9: Schematic representation of (left) $[(i\text{Pr}_2\text{PCH}_2\text{NAr})_3\text{U}]$ (LU-1), and (right) $(i\text{Pr}_2\text{PCH}_2\text{NPh})_3\text{U}$ (LU-2).

Table 6.9: Binding energies (kcal/mol) for UTM-1 and UTM-2.

	UCr	UMn	UFe	UCo	UNi
UTM-1	-84.7	-111.6	-136.5	-135.6	-123.9
UTM-2	-78.5	-105.4	-130.2	-129.5	-116.2

$$\text{LU} = \text{U}[(i\text{Pr}_2\text{PCH}_2\text{N})\text{C}_6\text{H}_5]_3$$

$(i\text{Pr}_2\text{PCH}_2\text{NAr})_3\text{U}$ (which we name LU-1 and TM, and UTM-2 is divided up into $(i\text{Pr}_2\text{PCH}_2\text{NPh})_3\text{U}$ (which we name LU-2) and TM (Figure 6.9). They were calculated at the DFT level for the most stable spin state of each species (Table 6.9). The optimized LU-1 and LU-2 species have a quartet ground state. The binding energies do not follow the same trend as the bond-orders since these are not diatomic molecules and the ligand also plays a role. The binding energies increases from UCr-1 to UFe-1 then decreases from UFe-1 to UNi-1; a similar trend is observed for the UTM-2 complexes. Although, the U-TM bond lengths are shorter in UTM-2 than in UTM-1, the binding energies are higher for UTM-1 suggesting that TM is bound more strongly to the phosphine ligands in UTM-1 than in UTM-2.

6.4 Conclusions

In summary, we presented a study of the bonding of uranium with the first-row transition metals Cr, Mn, Fe, Co, and Ni, in the UTM[(*i*Pr₂PCH₂NAr)₃tacn] (UTM-1) and UTM-(*i*Pr₂PCH₂NAr)₃ (UTM-2) species. Higher bond orders have yet to be obtained (or predicted) between a transition metal and uranium, and our predictions point to which specific metal–metal pairing will ultimately lead to these higher order TM-U bonds. A systematic study of the uranium-first-row transition metal interaction demonstrates the wide tunability of bond orders across the period, ranging from formally quintuple to single by replacing the transition metal in UTM-2. The periodic trend shows an increase in bond order from Cr to Mn and then a decrease across the period. We predict for the first time 5-fold bonding between U and Mn in the synthetically inspired complexes: UMn-2. The electronic spectra of UMn-2 complex shows low-lying $\delta \rightarrow \delta^*$ singlet and triplet transitions. We observed the presence of dative bonds in UCo-2, which are directed from the 3d orbitals of Co to the unoccupied 6d orbital of uranium, while UNi contains a half bond between U and Ni. Our study will help the future design of novel uranium–transition metal compounds with multiple bonds.

7. Challenges in MC-PDFT: Active Space Dependence

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Active Space Dependence in Multiconfiguration Pair-Density Functional Theory, Prachi Sharma, Donald G Truhlar and Laura Gagliardi, *Journal of Chemical Theory and Computation*, **2018**, 14, 660–669.

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7.1 Introduction

A variety of approaches have been proposed that combine CASSCF and DFT methods to treat strongly correlated systems.^{97,99? –116} However, most of them have two unsatisfactory properties: (1) double counting of electron correlation, as CASSCF contains some dynamic correlation which is counted again in standard exchange-correlation functionals, and (2) the fact that if one represents the density by a multiconfigurational wave function with the correct spin and spatial symmetries, conventional density functionals sometimes yield very inaccurate energies. Multiconfiguration pair-density functional theory⁶⁵⁻⁷⁵ (MC-PDFT) overcomes these two problems. The first problem, double counting, is eliminated by computing the total energy as the sum of the kinetic energy and the classical electrostatic energy of an MCSCF reference wave function plus an energy contribution from an on-top energy functional, which is analogous to the exchange-correlation functional in KS-DFT. The on-top energy density is approximated as a functional of the density (ρ) and the on-top pair density (Π). The on-top density functional implicitly includes electron exchange, electron–electron correlation, and the difference between the exact kinetic energy and that computed from the reference MCSCF wave function. Since no electron correlation term is included twice (e.g., the MCSCF correlation energy is never used), there is no electron correlation double counting. The second

problem has been solved so far by introducing on-top energy functionals that are simple translations of KS-DFT functionals, called translated functionals³⁰ and fully translated functionals.¹²⁰ They depend on the on-top pair density and the total density in contrast to exchange-correlation functionals that depend on the α and β spin densities.

In this study, we explore MC-PDFT electron correlation as a function of active space for the H_2 and N_2 systems. We note that for H_2 , an active space of (2,2) (which denotes, in the usual convention, two active electrons in two active orbitals) is already large enough to include the dominant near-degeneracy correlation in the dissociating bond, and in N_2 , an active space of (6,6) is large enough for this purpose. But we look at much larger active spaces (which we would not use in practical MC-PDFT calculations) to learn about how the results change as the active space is enlarged. First we consider H_2 . Sections 7.3 to 7.7 consider the decomposition of the MC-PDFT energy into its various contributions, the virial theorem, the dependence of the on-top energy and the kinetic energy on the choice of active space, the dependence of the MC-PDFT energy on the density (ρ) and the on-top density (Π), the on-top energy as a function of the on-top ratio and its spatial distribution, and the basis set dependence of the on-top ratio. Section 7.8 extends the discussion to N_2 . Section 7.9 presents concluding remarks, including a summary of key points.

7.2 Computational Methods

To understand how the on-top energy functional changes with the active space, multireference calculations were performed on the H₂ and N₂ molecules, using the cc-pVTZ^{155,156} basis set for several active spaces. Basis set effects were also investigated by repeating the calculations with the quadruple zeta basis set, cc-pVQZ. The experimental equilibrium bond lengths (1.4 a₀ for H₂ and 2.08 a₀ for N₂) were used in all cases except for the discussion of the dissociation energies and virial theorem.⁷⁸⁻⁸⁰ Since the virial theorem is only valid at the equilibrium geometry, the bond distance was optimized at the CASSCF level for various active spaces, to study how closely the virial theorem is satisfied. The translated PBE functional (tPBE)^{30,372} was used for MC-PDFT calculations. All the calculations were performed using the Molcas 8.1 software package.¹⁵⁹

7.3 Energy Decomposition in MC-PDFT and the Virial Theorem

If one uses translated functionals, the MC-PDFT energy can be written as:

$$E^{\text{MC-PDFT}} = V_{\text{NN}} + \langle \Psi^{\text{MC}} | T | \Psi^{\text{MC}} \rangle + V_{\text{ne}}(\rho(\mathbf{r})) + V_{\text{C}}(\rho(\mathbf{r})) + E_{\text{ot}}(\rho(\mathbf{r}), |\nabla\rho|, \Pi(\mathbf{r})) \quad (7.1)$$

The first term of equation 7.1 corresponds to the nuclear-nuclear interaction, the second, the third, and the fourth terms correspond

respectively to the kinetic energy of the reference system, the nuclear-electron attraction, and the classical Coulomb interaction of the electronic charge cloud with itself. The last term corresponds to the on-top energy contribution, which is a functional of the density (ρ), its gradient ($\nabla\rho$) and the on-top pair density (Π). If one used fully translated functionals, then E_{ot} would also depend on the gradient of the on-top pair density ($\nabla\Pi$), but in this article we only use a translated functional, namely the tPBE functional.³⁰ The translated GGA functionals are a simple translation of the KS-DFT GGA exchange-correlation functional, given by eq. 1.51 and eq. 1.52. The exchange-correlation energy in KS-DFT includes the difference between the kinetic energy of the non-interacting system and of the interacting system:

$$E_{\text{xc}} = (T - T_S) + V_{\text{nonclassical}} = T_C^{\text{KS}} + V_{\text{nonclassical}}, \quad (7.2)$$

where T is the kinetic energy of the interacting system, T_S is the kinetic energy of the non-interacting system described by a Slater determinant, T_C^{KS} is the difference between the two quantities; and $V_{\text{nonclassical}}$ is the difference between the full quantum mechanical electrostatic energy and the classical electrostatic energy, consists of the exchange and other nonclassical electrostatic energy terms (which may be called the correlation part). In MC-PDFT the kinetic energy is derived from the interacting CASSCF wave function,

therefore, in analogy to equation 7.2 , if the MCSCF calculation were to give the exact density, the resulting on-top energy would be given by:

$$E_{\text{ot}} = (T - \langle \Psi^{\text{MC}} | T | \Psi^{\text{MC}} \rangle) + V_{\text{nonclassical}} = T_C^{\text{MC}} + V_{\text{nonclassical}}, \quad (7.3)$$

(If the density is not exact, there should also be a correction to the electron-nuclear attraction.) The difference, T_C^{MC} , in kinetic energy between the real system and the reference system described by the CASSCF wave function changes with the active space, as does $V_{\text{nonclassical}}$. Therefore, even though MC-PDFT does not explicitly divide E_{ot} into the two contributions to equation 7.3, it is important to understand to what extent E_{ot} given by the approximate on-top functionals that have been used (for example, the tPBE³⁰ functional that is used here) varies with the choice of active space. The formalism summarized above (eq. 7.1 to eq.7.3) E_{ot}) does not have an established connection to the exact density functional theory.³⁷³ Rather it is a formalism that combines an explicitly multiconfigurational reference wave function with a new kind of density functional to treat multireference systems.

In Table ?? the nature of the 28 orbitals involved in these active spaces is reported. This active space corresponds to a full-CI expansion for cc-pVTZ basis set. In Table 7.2 the MC-PDFT, CASSCF, and CASPT2 total energies are reported for five active spaces, and

the MC-PDFT energy is decomposed into the various contributions specified by eq. 7.1. Table 7.2 shows that upon increasing the active space (the number of configuration state functions also increases), at the equilibrium geometry, the kinetic energy $\langle \Psi^{\text{MC}} | T | \Psi^{\text{MC}} \rangle$ would increase in accordance with the virial theorem.⁶⁴⁻⁶⁶ Therefore the kinetic energy difference, T_C^{MC} , would decrease and, therefore, if there were no change in $V_{\text{nonclassical}}$, the on-top energy would also decrease (i.e., increase in magnitude since it is negative). Table 7.2 shows that $\langle \Psi^{\text{MC}} | T | \Psi^{\text{MC}} \rangle$ does increase and E_{ot} does decrease upon enlarging the active space. However, the change in the on-top energy depends also on other components of the energy, in particular, for fixed internuclear distance, the nuclear-electron attraction energy (V_{ne}) and the classical electron-electron Coulomb energy (V_{C}). Table 7.3 shows that both of these components change significantly in proceeding from the (2,2) active space to the (2,6) active space. Encouragingly, as a consequence of all these changes, $E^{\text{MC-PDFT}}$ changes less than E^{CASSCF} . Nevertheless, as expected, the MC-PDFT total energy converges more slowly upon increasing the active space than does the CASPT2 total energy. The kinetic, nuclear-electron attraction, and classical electron-electron Coulomb repulsion energies converge much faster than the on-top energy with respect to the active space. Table 7.2 shows that the slow convergence of the on-top energy (and not the convergence of the kinetic MCSCF kinetic energy) is responsible for the slow convergence of the MC-PDFT

energy. Tables 7.2 and 7.3 show that MC-PDFT performs well for smaller active spaces, for example, in proceeding from the (2,2) active space to the (2,4) one, $E^{\text{MC-PDFT}}$ changes less than V_{ne} , V_{C} , or E_{ot} . Furthermore, the increase in $\langle \Psi^{\text{MC}} | T | \Psi^{\text{MC}} \rangle$ when the active space is increased from (2,2) to (2,6) is more than compensated by the decrease of E_{ot} . However, the MC-PDFT energy is not stable with respect to increasing the active space to sizes much larger than needed to account for near-degeneracy correlation. This leads to the recommendation that, at least with the presently available on-top density functionals, MC-PDFT should be employed with a small active space, large enough to account for near-degeneracy correlation, but not so large as to include significantly more dynamic correlation.

Table 7.1: Orbitals Used in the Various Active Spaces^{a,b}

1	$1\sigma_{\text{g}}$	2	$1\sigma_{\text{u}}$	3	$2\sigma_{\text{g}}$
4	$2\sigma_{\text{u}}$	5	$1\pi_{\text{ux}}$	6	$1\pi_{\text{uy}}$
7	$3\sigma_{\text{g}}$	8	$1\pi_{\text{gx}}$	9	$1\pi_{\text{gy}}$
10	$3\sigma_{\text{u}}$	11	$4\sigma_{\text{g}}$	12	$4\sigma_{\text{u}}$
13	$5\sigma_{\text{g}}$	14	$2\pi_{\text{ux}}$	15	$2\pi_{\text{uy}}$
16	$2\pi_{\text{gx}}$	17	$2\pi_{\text{gy}}$	18	$5\sigma_{\text{u}}$
19	$6\sigma_{\text{g}} (\text{dz}^2)$	20	$3\pi_{\text{ux}} (\text{dxz})$	21	$3\pi_{\text{uy}} (\text{dyz})$
22	$1\delta_{\text{gd}_{\text{xy}}}$	23	$1\delta_{\text{gd}_x}^2 - y^2$	24	$6\sigma_{\text{u}} (\text{dz}^2)$
28	$1\delta_{\text{ud}_x}^2 - y^2$				

^aAll 28 reported here correspond to the full-CI expansion for the cc-pVTZ basis set. ^bActive space (2,4) involves orbitals 1–4; active space (2,6) involves orbitals 1–6, etc.

Consistent with the trends already seen in Table 7.2, Table 7.4 shows that the H_2 dissociation energy agrees well with the exper-

Table 7.2: Energy decomposition (eV) for H_2 at its experimental equilibrium geometry ($1.4 a_0$). MC-PDFT calculations were performed using the tPBE functional with the cc-pVTZ basis set.

Active Space	KE	$E_{\text{on-top}}$	$E_{\text{MC-PDFT}}$	E_{CASSCF}	E_{CASPT2}	E_{new}	E_{new}^{xc}
(2,1)	30.59	-98.80	48.75	-18.81	-18.81	-30.83	-31.69
(2,2)	31.65	-99.47	36.04	-19.52	-31.84	-31.33	-31.79
(2,4)	31.71	-99.29	35.91	-19.74	-31.96	-31.54	-31.83
(2,6)	31.87	-99.26	35.97	-20.13	-32.09	-31.82	-31.89
(2,10)	31.90	-99.30	35.99	-20.24	-32.19	-31.86	-31.90
(2,28)	31.90	-99.28	35.99	-20.40	-32.34	-31.90	-31.90

^a(2,1) is the same as Hartree–Fock.

Table 7.3: Differences in energies (eV) for H_2 at its experimental equilibrium geometry ($1.4 a_0$). MC-PDFT calculations were performed using the tPBE functional with cc-pVTZ.

Active Space	ΔKE	ΔE_{ne}	ΔE_{C}	ΔE_{ot}	$\Delta E_{\text{MC-PDFT}}$	ΔE_{CASSCF}	ΔE_{CASPT2}
(2,4) - (2,2)	0.06	0.18	-0.14	-0.22	-0.12	-0.21	-0.05
(2,6) - (2,4)	0.16	0.03	0.07	-0.39	-0.13	-0.28	-0.06
(2,10) - (2,6)	0.03	-0.03	0.02	-0.11	-0.10	-0.04	0.00
(2,28) - (2,10)	0.00	0.01	0.00	-0.16	-0.16	-0.04	0.00

imental value (4.75 eV)³⁷⁴ for the smaller active spaces, (2,2) and (2,4), but it is unstable to making the active space much larger than is needed to account for near-degeneracy correlation.

Table 7.4: Dissociation energy (De in eV) of H_2 for various active spaces (tPBE/cc-pVTZ).^a

Active Space	$E_{\text{MC-PDFT}}$	E_{CASSCF}	E_{CASPT2}
(2,2)	4.68	4.13	4.59
(2,4)	4.79	4.34	4.63
(2,6)	4.93	4.66	4.69
(2,10)	5.02	4.66	4.70
(2,28)	5.18	4.70	4.70

^acalculated using the experimental equilibrium geometry ($1.4 a_0$). The accurate value of the dissociation energy is 4.75 eV .

7.4 Dependence of the Density and On-Top Pair Density on the Active Space

In an attempt to understand the trends in Tables 7.2 and 7.3, we examined the active space dependence of the electronic density and on-top pair density. Figure 7.1 shows the on-top pair density, $\Pi(\mathbf{r})$, for various active spaces, namely (2,1), which is the Hartree-Fock case, and (2,2), (2,4), and (2,28). In most regions of space, the probability of finding two electrons on top of each other decreases with an increase in the active-space.⁸⁴ We find that the on-top densities change more between the (2,2) and (2,4) active spaces than between the (2,4) and (2,28) ones. However, the difference in MC-PDFT energies is larger between the (2,4) and (2,28) than between (2,2) and (2,4) (see Table 7.3). Figure 7.1(top) shows the change of the on-top densities only along the bond axis; but Figure 7.1 (bottom) shows that the trend of a smaller change between the (2,2) and (2,4) active spaces than between the (2,4) and (2,28) ones is true more generally. Therefore we can conclude that the large difference in the MC-PDFT energies of H_2 when proceeding beyond the level of correlation needed to treat the near-degeneracy correlation is due mainly to variables other than the on-top densities.

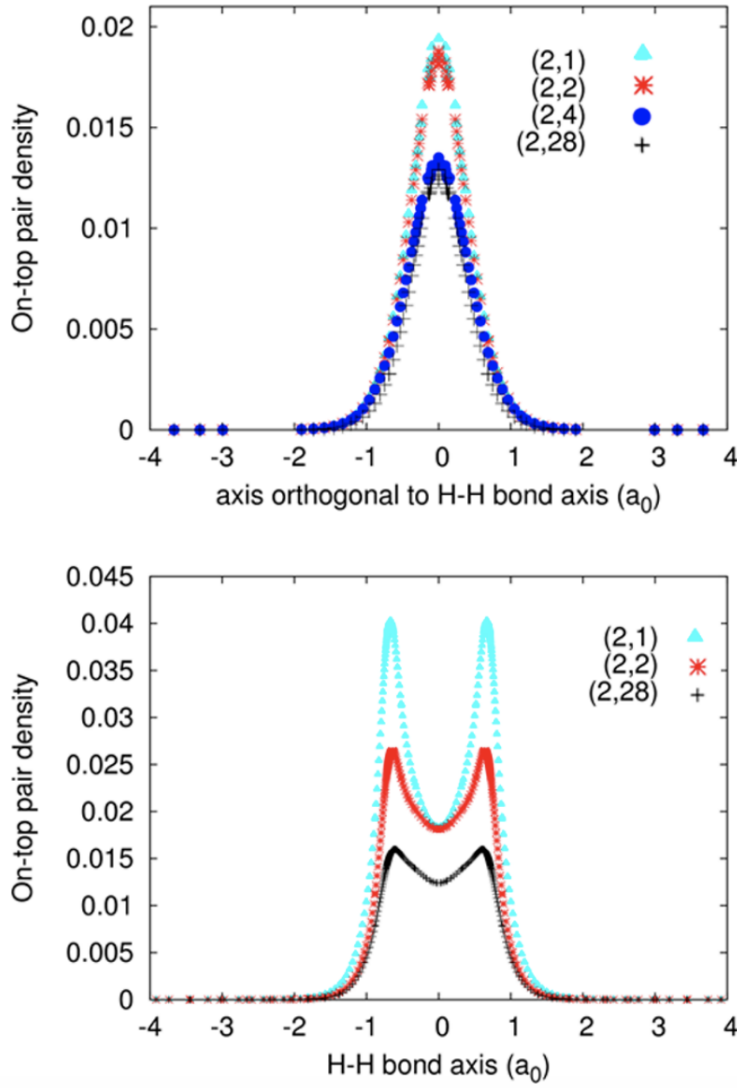


Figure 7.1: (a) On-top pair densities along (top) the bond axis, and (bottom) the axis orthogonal to the H-H bond axis for active spaces (2,1), (2,2), (2,4), and (2,28). The two H atoms are positioned at -0.7 and $0.7 a_0$ respectively. Distances in plots are given in atomic units (a_0) where $1 a_0 = 1 \text{ bohr} = 0.5292 \text{ \AA}$. The units for coordinates are electrons per cubic bohr.

A similar analysis was performed for the electronic density. Figure 7.2 shows the electron density for (2,1), (2,2), and (2,28) active spaces. The plot for (2,4) density is not shown in Figure 7.2(top) as it lies between (2,2) and (2,28) and is not visually distinguishable at the given scale, and in fact the difference between (2,2) and (2,28) is barely visible. The differences between the Hartree-Fock electron

density (CAS (2,1)) and the various multireference densities are plotted in Figure 7.2(bottom). The density increases in the middle of the bond when the active space increases from (2,2) to (2,4) and it decreases at the nuclei when the active space increases to (2,28). It cannot be concluded from Figure 7.2 whether the change in the density is the reason behind the slow convergence of the MC-PDFT energy.

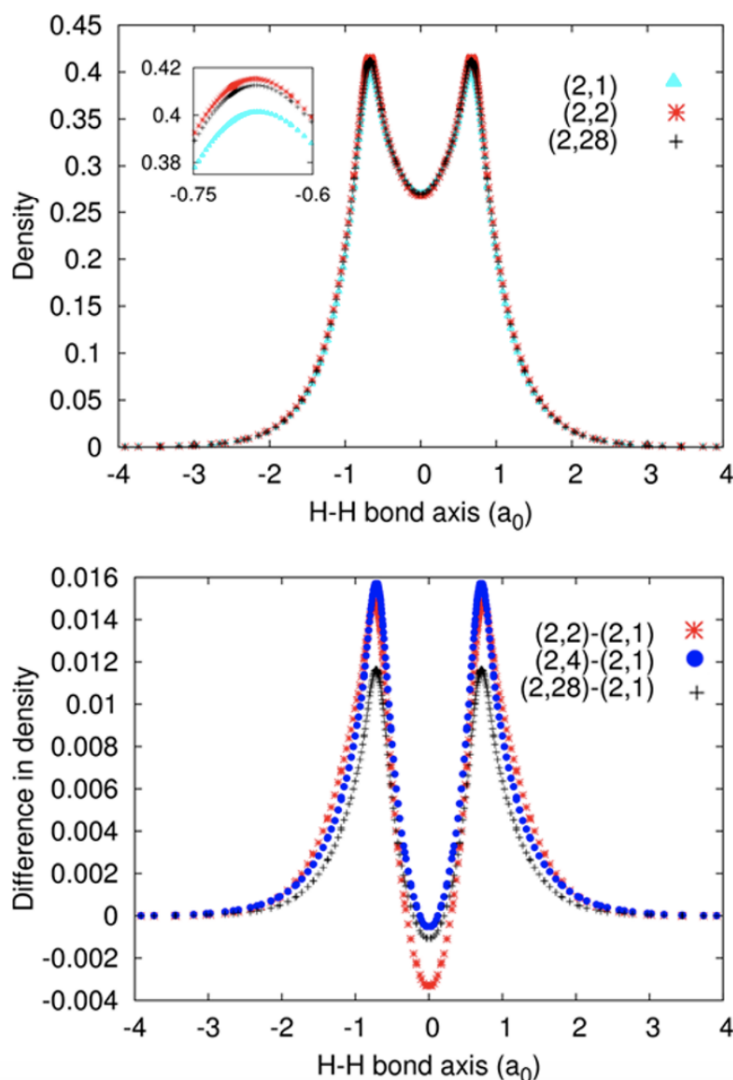


Figure 7.2: (top) The electron densities for active spaces: (2,1), (2,2) and (2,28) for H_2 molecule and (bottom) the difference in electron density from the (2,1) density. The two H atoms are at -0.7 and $0.7 a_0$, respectively, and the plot is along the bond axis.

7.5 Dependence of MC-PDFT Functionals on the Density

The translated on-top functional E_{ot} depends on the density, the density gradient, and the on-top ratio defined as:

$$R = (4\Pi(\mathbf{r}))/[\rho(\mathbf{r})]^2 \quad (7.4)$$

To check the density dependence of the on-top functional, we defined a test functional ($E_{\text{ot}}^{\text{test}}$) that depends only on the density and its gradient but not on the on-top pair density; in this test functional, the on-top ratio R is set equal to 1 for all values of ρ and Π . The resultant test energy, which replaces eq. 7.1, can be written as:

$$E^{\text{test}} = V_{\text{NN}} + \langle \Psi^{\text{MC}} | T | \Psi^{\text{MC}} \rangle + V_{\text{ne}}(\rho(\mathbf{r})) + V_{\text{C}}(\rho(\mathbf{r})) + E_{\text{xc}}^{\text{test}}(\rho(\mathbf{r}), |\nabla\rho|, \Pi(\mathbf{r})) \quad (7.5)$$

The results of using the test functional are compared with those obtained with the actual on-top functional in Table 7.5. The table shows that E^{test} converges faster with respect to increasing the active space than does the MC-PDFT energy, which suggests that the slow convergence of MC-PDFT energies with respect to the active space is not related to the electron density changes.

Table 7.5: Differences in energies (in eV) for H₂ at equilibrium geometry (1.4 a₀).

ΔE_{ot}	$\Delta E_{\text{MC-PDFT}}$	ΔE_{CASSCF}	ΔE_{CASPT2}	
(2,4) - (2,2)	-0.22	0.06	-0.12	0.16
(2,6) - (2,4)	-0.39	-0.02	-0.13	0.24
(2,10) - (2,6)	-0.11	-0.01	-0.10	0.01
(2,28) - (2,10)	-0.16	0.00	-0.16	0.01

^a The first column shows the two active spaces for which the difference in energies are listed. MC-PDFT calculations were performed using the tPBE functional. The cc-pVTZ basis set was used.

7.6 On-top ratio (R) as a Function of Active Space and How It Changes the On-top Energy

Since, the on-top functional is a functional of the on-top ratio,³⁰ we examined the dependence of the MC-PDFT energy on the on-top ratio. Although neither the electron density nor the on-top pair density converge slowly with the active space, the on-top ratio is a nonlinear function of the density and it can change more rapidly than the density. The changes in the on-top ratio with respect to different active spaces along the H-H axis and along the orthogonal axis are shown in Figure 7.3. The on-top ratio values do not differ significantly along the H-H bond axis for active spaces larger than (2,2), although there is a large difference in on-top ratio between the (2,10) and (2,28) active spaces in the tail region (Figure 7.3(top)). However, the tail region does not generally contribute significantly to the total energy. However, the on-top ratio changes significantly along the axis orthogonal to the H-H bond (Figure 7.3) even in re-

gions that contribute appreciably to the energy. For example, while the on-top ratio plots for active spaces (2,4) and (2,6) overlap along the bonding axis, they are different along the axis orthogonal to H-H bond. The differences in energies between these two active spaces might be due to the difference in the on-top ratio along the orthogonal axis between the active spaces. Additionally, to understand which regions in space contribute to the difference in the MC-PDFT energies with change in the active space, it is important to examine the spatial distribution of the on-top energy. The on-top energy density is plotted in Figure 7.4, where, the on-top energy is distributed into contributions from boxes of volume ΔV equal to $(0.4)^3$ bohr³:

$$E_{\text{ot}} = 0.064a_0^3 \sum_i [\Delta E_{\text{ot}}/\Delta V]_i \quad (7.6)$$

where the sum is over boxes. The first contour plot in Figure 7.4 shows a section of the on-top energy density $[\Delta E_{\text{ot}}/\Delta V]_i$ in a plane containing the two nuclei. The blue and the green regions encompassing the two hydrogen atoms contribute the most to the total on-top energy. To explore the active space dependence of the on-top energy, the difference in the on-top energy density between the (2,4) and (2,2) active spaces and between the (2,6) and (2,4) active spaces are investigated in other two plots of Figure 7.4. By comparing on-top ratio change plots (Figure 7.3) with the on-top energy plots (Figure 7.4 middle and bottom), it can be observed

that the difference in the on-top energy density distribution between different active spaces follows the same trend as the ratio. The on-top ratios for (2,2) and (2,4) differ near the center of the bond and in the tail region (Figure 7.3). Also, near the region between $-2 a_0$ and $-1 a_0$, the on-top ratio plots nearly coincide for the two active spaces. The on-top energy density plot is observed to show a similar trend as the ratio. It should be noted that although there is a large difference in the on-top ratios for the two active spaces in the tail region, the on-top energy is comparatively small in that region (orange region in the middle plot in Figure 7.4). Similarly, for the (2,4) and (2,6) active spaces, the on-top ratio values differ along the axis orthogonal to the H-H bond. A similar trend is observed in the on-top energy contour plot with the two blue regions having the highest difference in the on-top energy density (Figure 7.4 (bottom))

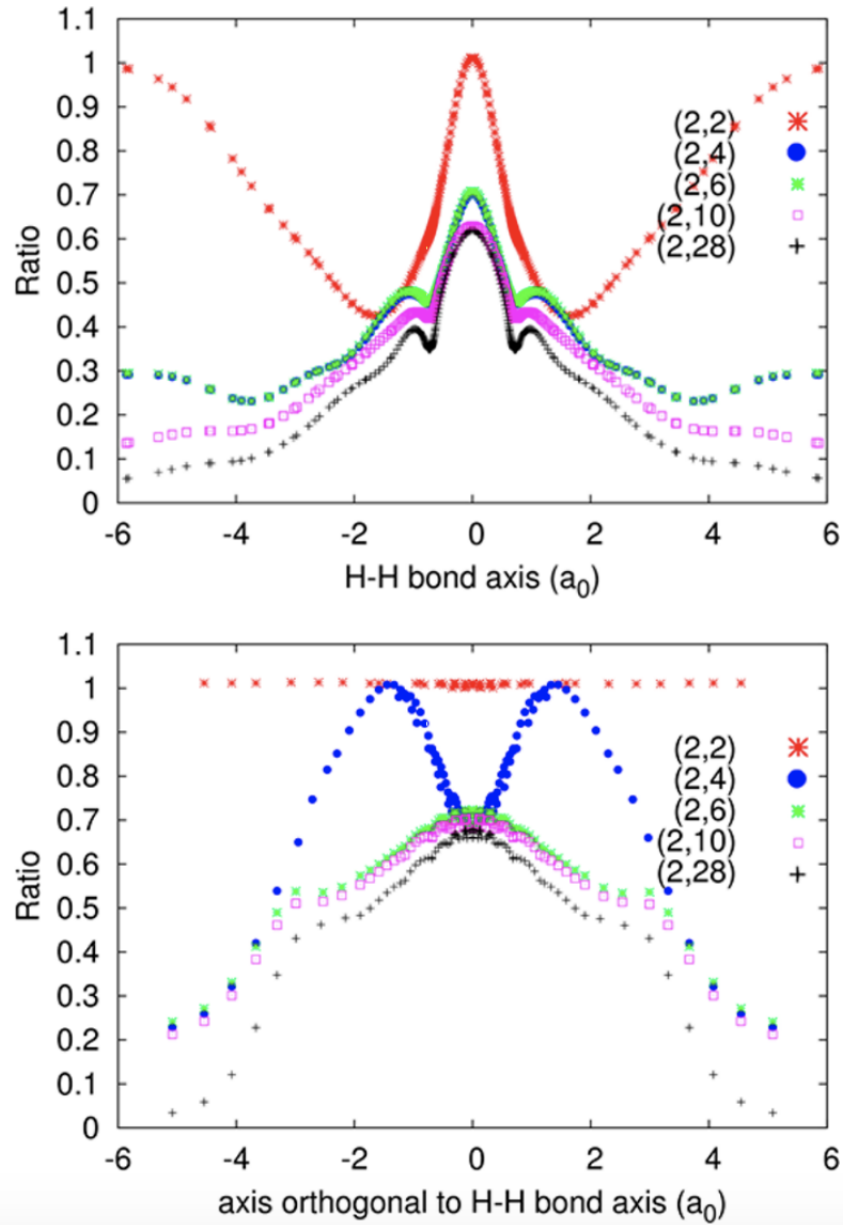


Figure 7.3: (top)The figure shows the change in the on-top ratio along the H-H bond axis while figure (bottom) shows the on-top ratio with respect to change in the coordinate axis orthogonal to the H-H bond axis. The H atoms are placed at $-0.7 a_0$ and $0.7 a_0$.

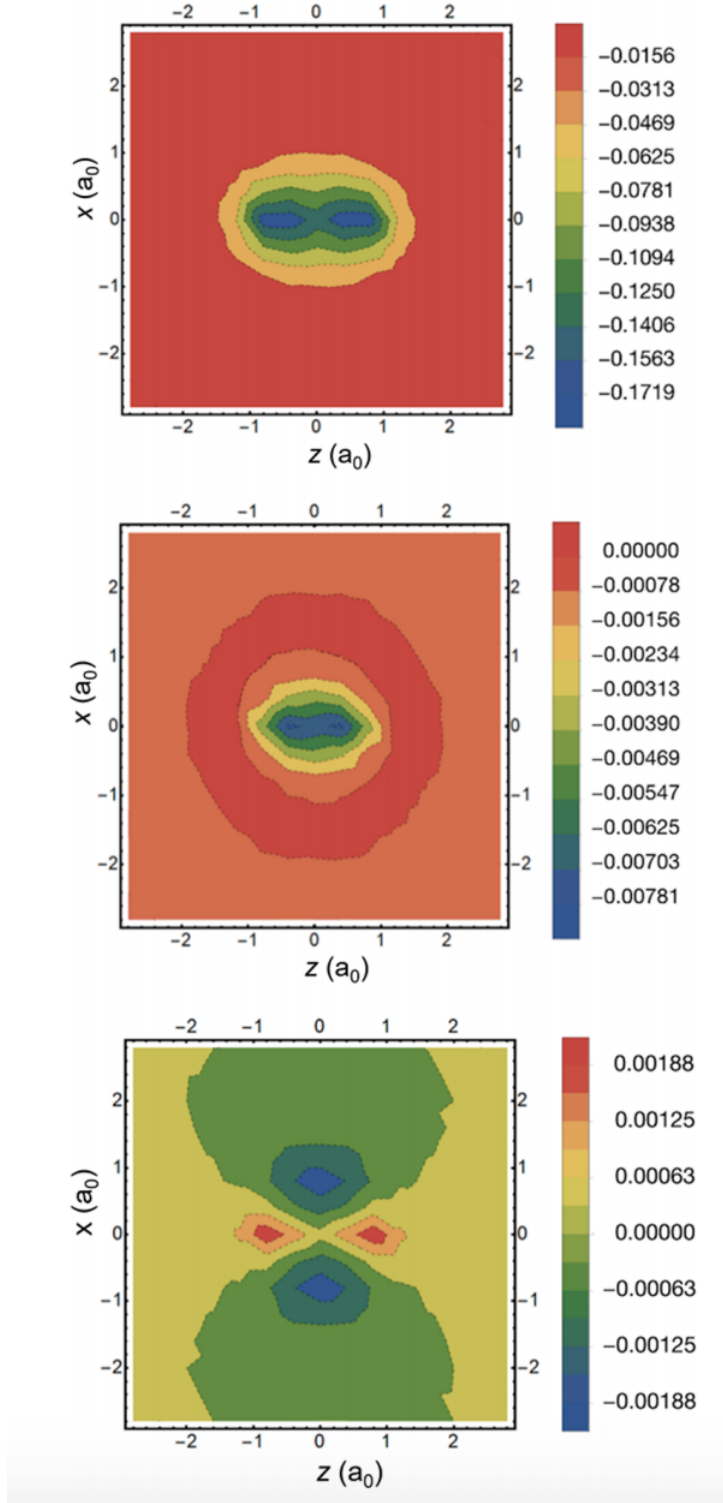


Figure 7.4: Spatial distribution of on-top energy density for (top) H_2 (2,2), (middle) difference in on-top energy density between the (2,4) and (2,2) active space, and (bottom) difference in on-top energy density between the (2,6) and (2,4) active space. The H atoms are placed $-0.7 a_0$ and $0.7 a_0$, respectively on the z axis.

7.7 Basis Set Dependence of On-Top Ratio

To understand the convergence and kinetic energy dependence of the on-top energy, the satisfaction of the virial theorem for the various CASSCF wave functions is investigated. The virial ratio, i.e., the ratio of the CASSCF total energy to the kinetic energy should be -1 if the virial theorem is satisfied. The basis set dependence of the virial ratio for the H_2 molecule is reported in Table 7.7. By going from a triple-zeta basis set to a quadruple-zeta basis set the fulfillment of the virial theorem improves by one order of magnitude. In contrast to the basis set dependence, when the basis set is unchanged, there is no systematic improvement of the fulfillment of the virial theorem by increasing the active space. The basis set dependence of the on-top ratio was also investigated; the on-top ratios for various active spaces obtained with the cc-pVQZ basis set are shown in Figure 7.5. The results converge at the tail region for larger active spaces, (2,10) and (2,28). However, there is still a considerable difference in the on-top ratios along the axis perpendicular to the bond axis. This suggests that increasing the basis set would not necessarily result in the convergence of the on-top energy in MC-PDFT.

Table 7.6: Kinetic energy (eV), CASSCF energy (eV), and CASSCF virial ratio for various active spaces and two basis sets for H₂.^a

	Active Spaces	$\langle \Psi^{\text{MC}} T \Psi^{\text{MC}} \rangle$	E_{CASSCF}	$E_{\text{CASSCF}} / \langle \Psi^{\text{MC}} T \Psi^{\text{MC}} \rangle$
cc-pVTZ	(2,2)	31.26	-31.34	-1.0024
	(2,4)	31.48	-31.54	-1.0022
	(2,6)	31.77	-31.82	-1.0017
	(2,10)	31.79	-31.86	-1.0022
	(2,28)	31.90	-31.90	-1.0001
cc-pVQZ	(2,2)	31.34	-31.35	-1.0005
	(2,4)	31.68	-31.69	-1.0005
	(2,6)	31.83	-31.85	-1.0006
	(2,10)	31.85	-31.89	-1.0012
	(2,28)	31.92	-31.93	-1.0004

^aIn comparing this table to Table 7.2, note that geometries re optimized by CASSCF here, whereas in Table 7.2 they are for the experimental geometry.

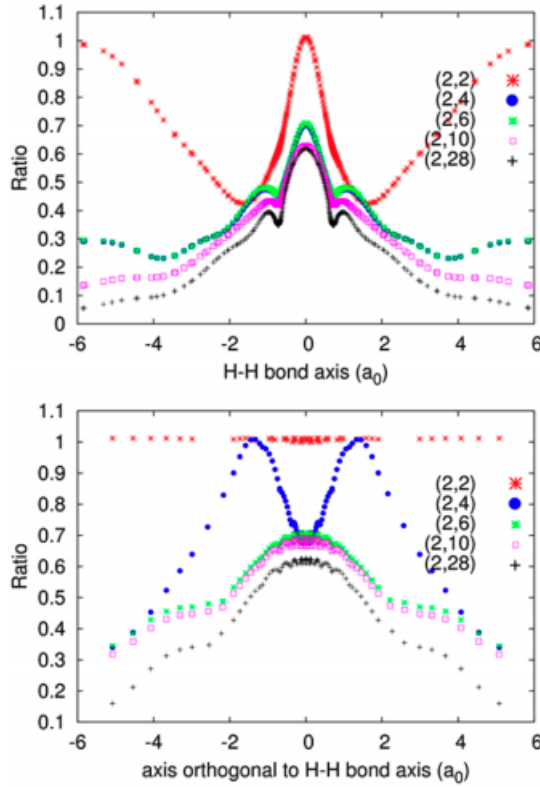


Figure 7.5: (top) The figure shows the on-top ratio along the H-H bond axis while the figure (bottom) shows the on-top ratio with respect to the coordinate axis orthogonal to the H-H bond axis. The tPBE/cc-pVQZ level of theory was used. The H atoms are placed at $-0.7 a_0$ and $0.7 a_0$, respectively.

7.8 Electron Correlation in N₂

To examine what happens when we go beyond two-electron systems, we next explored the active space dependence of the N₂ molecule. The orbitals used to define the various active space are identified in Table 7.8 and the energy contributions for N₂ at its equilibrium geometry are reported in Table ???. The kinetic energy increases with the active space, while the on-top energy decreases (eq.), as in case of H₂. As the active space increases, the sum of nuclear attraction and classical Coulomb repulsion decreases as expected according to the virial theorem. Since MC-PDFT is not a variational method, the total MC-PDFT energies do not necessarily decrease with an increase in the active space. The differences in energies (eV) for N₂ at the experimental equilibrium geometry are reported in Table 7.9. MC-PDFT shows less active-space dependence than CASSCF, and the dependence is similar to that for CASPT2. The decrease in the on-top energy complements the change in the kinetic, nuclear-electron attraction, and classical electron-electron Coulomb repulsion energies.

The on-top energy density distributions are also analyzed for N₂ where each volume element (ΔV) is $(0.6)^3$ bohr₃. The on-top energy density distribution (Figure 7.6(top)) for N₂ with the (6,6) active space shows that the region around the nuclei gives the largest contribution to the total energy, followed by the region between the

Table 7.7: The orbitals involved in the active spaces for N_2 . Active space(6,6) involves orbitals 1–6, active space (10,8) involves orbitals 1–8, and active space (10,10) involves orbitals 1–10

1	$3\sigma_g(2p)$	2	$1\pi_{ux}(2p)$	3	$1\pi_{uy}(2p)$
4	$1\pi_{gx}(2p)$	5	$1\pi_{gy}(2p)$	6	$3\sigma_u(2p)$
7	$2\sigma_g(2s)$	8	$2\sigma_u(2s)$	9	$4\sigma_g(3s)$
10	$4\sigma_u(3s)$				

Table 7.8: Energy decomposition (eV) for N_2 at the experimental equilibrium geometry (2.08 a0). MC-PDFT calculations were performed using the tPBE functional with the cc-pVTZ basis set.

Active Space	KE	$E_{\text{on-top}}$	$E_{\text{MC-PDFT}}$	E_{CASSCF}	E_{CASPT2}	E_{new}	E_{new}^{xc}
(6,6)	2969.92	-8259.93	2042.50	-371.16	-2977.23	-2969.29	-2975.51
(10,8)	2970.55	-8260.82	2042.98	-371.41	-2977.26	-2969.63	-2975.60
(10,10)	2971.54	-8260.06	2041.70	-371.78	-2977.17	-2970.60	-2975.71

nuclei. The region showed in the first figure in Figure 7.6 contributes 99.99% to the total on-top energy. The middle plot in Figure 6 shows the difference between (10,10) and (6,6) on-top energies per unit volume. The violet region in the Figure 7.6(middle) located around $[-2, -1]$ and $[2, 1]$ (z, x coordinates) contributes largely towards the difference in the on-top energy between the (10,10) and (6,6) active spaces. This region corresponds to the sudden decrease in the on-top ratio for the (10,10) active space around $-2 a_0$ and $2 a_0$ on the z axis in Figure 7.7. The tail regions (beyond $3 a_0$ or $-3 a_0$ in case of N_2) do not contribute significantly towards the energy. These results agree with the H2 case where the on-top energy follows the similar trend as the on-top ratio except at the tail regions, which do not contribute significantly to the energy. Table 7.10 shows that the virial theorem is satisfactorily fulfilled.

Table 7.9: Differences in energies (eV) for N_2 at the experimental equilibrium geometry ($2.08 a_0$). The first column shows the two active spaces for which the difference in energies are listed. MC-PDFT calculations were performed using the tpBE functional with the cc-pVTZ basis set.

Active Space	ΔKE	ΔE_{ne}	ΔE_C	ΔE_{ot}	$\Delta E_{MC-PDFT}$	ΔE_{CASSCF}	ΔE_{CASPT2}
(10,8) - (6,6)	0.63	-0.89	0.49	-0.25	-0.03	-0.34	-0.09
(10,10) - (10,8)	0.99	0.76	-1.29	-0.37	0.10	-0.97	-0.10

Table 7.10: Test for the fulfillment of the virial theorem for various active spaces and two basis sets for N_2 . Energies are in eV.

	Active Spaces	$\langle \Psi^{MC} T \Psi^{MC} \rangle$	E_{CASSCF}	$E_{CASSCF} / \langle \Psi^{MC} T \Psi^{MC} \rangle$
cc-pVTZ	(6,6)	2969.33	-2969.29	-0.99999
	(10,8)	2969.65	-2969.63	-0.99999
	(10,10)	2971.13	-2970.60	-0.99982
cc-pVQZ	(6,6)	2969.29	-2969.50	-1.00007
	(10,8)	2969.88	-2969.84	-0.99999
	(10,10)	2970.97	-2969.84	-0.99995

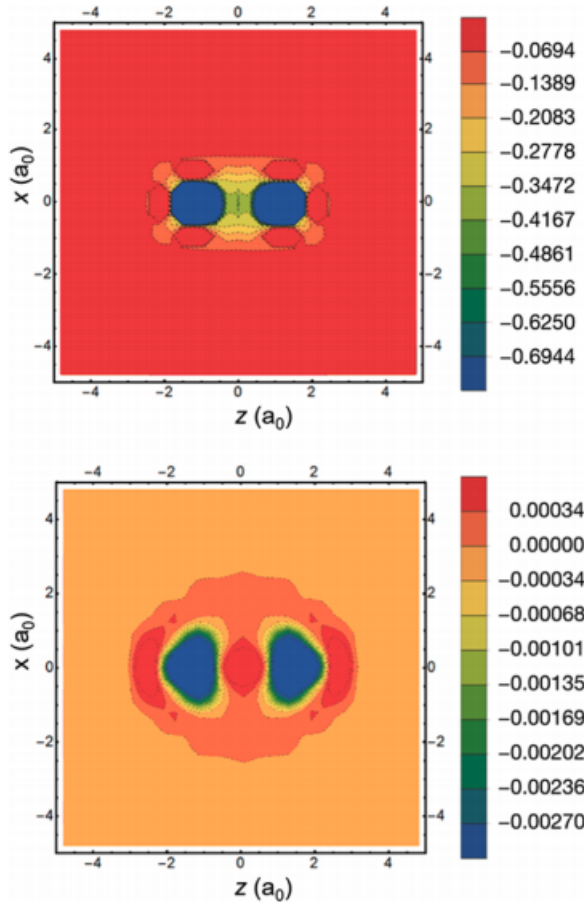


Figure 7.6: Spatial distribution of on-top energy density for (top) N_2 (6,6), (bottom) difference in the on-top energy density between (10,10) and (6,6) active spaces. The N atoms are placed $\pm 1.04 a_0$ all figures should be correctly sized to fit into a and $1.04 a_0$, respectively on the z axis.

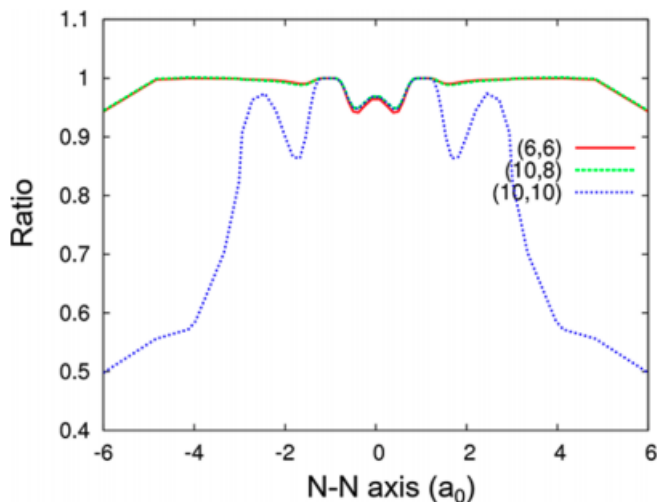


Figure 7.7: The figure shows the on-top ratio along the N-N bond axis for various active space choices. The N atoms are placed at $-1.04 a_0$ and $1.04 a_0$, respectively.

7.9 Concluding Remarks

We defined the on-top energy as the sum of two contributions: (i) the difference between the exact electron kinetic energy and the electron kinetic energy of the partially correlated MCSCF system and (ii) the electron exchange and correlation effects on the electronic potential energy. We broke the total MC-PDFT energy down into components and investigated the dependence of the components on the active space choice for the H_2 and N_2 molecules. Upon increasing the active space, the kinetic energy increases and CASSCF energy decreases, but for practical active spaces the MC-PDFT total energy is less dependent on the active space than is either of these other quantities. In the case of H_2 , the MC-PDFT energy has not converged even upon expanding the active space to (2,10) and (2,28), which are studied to understand fundamental issues, and not because this kind of active

space would be used in practice; we find in this fundamental test that the slow convergence of the MC-PDFT energy is due to the slow convergence of the on-top energy. The electron density, the on-top pair density, and the on-top ratio were also investigated as functions of active space. While the on-top pair density and the total density converge well with increase of the active space, their ratio (which is called the on-top ratio) converges more slowly, and it is found to have a spatial distribution similar to that of the on-top energy. We also explored the fulfillment/non-fulfillment of the virial theorem for different active spaces and basis sets. We find that the deviations from fulfillment of the virial theorem by the CASSCF wave functions due to the finite (incomplete) size of the one-electron basis sets are large enough that the virial theorem constraints do not provide a useful way to understand the active-space dependence of the MC-PDFT energy in practical calculations. For the N_2 case, we examined only more reasonable choices of the active space, and we found a smooth convergence (with respect to increasing the active space) of the MC-PDFT total energy and the other quantities. In the N_2 case, the virial theorem is also better fulfilled than in the H_2 case. This result is promising since N_2 is a many-electron system, and the active spaces that we investigated are more realistic than in the H_2 case and more representative of complex systems than one may investigate in the future with this method. We anticipate that the detailed analysis of components of the energy that was examined

in this work will be useful in the future for designing improved on-top energy functionals for physically motivated active spaces.

A. Appendix 1

Table A.1: Vertical excitation energies in eV for MnO_4^- . The first and the second columns corresponds to the excited state symmetries for T_d and C_2 point group symmetries, respectively.

T_d	C_2	RASSCF	RASPT2	MC-PDFT
X^1A_1	A	0	0	0
1^1T_1	A	2.08	2.14	1.92
	B	2.05	2.18	1.88
	B	2.05	2.18	1.88
1^1T_2	A	2.5	2.5	2.24
	B	2.47	2.57	2.21
	B	2.47	2.57	2.21
2^1T_1	A	3.33	3.45	3.15
	B	3.32	3.5	3.12
	B	3.32	3.5	3.12
2^1T_2	A	3.56	3.66	3.3
	B	3.54	3.71	3.29
	B	3.54	3.71	3.29

1^1E	A	3.78	3.9	3.6
	A	3.82	3.98	3.64
2^1E	A	3.85	4.02	3.72
	A	3.85	4.03	3.74
1^1A_2	A	3.9	4.1	3.65
3^1T_1	A	3.96	4.14	3.71
	B	3.94	4.15	3.69
	B	3.94	4.15	3.69
3^1T_2	A	4.05	4.33	3.89
	B	4.09	4.4	3.9
	B	4.09	4.4	3.9

Table A.2: Absolute energies in a.u. for first 12 states in irrep A and irrep B for MnO_4^- in C_2 symmetry.

RASSCF	RASPT2	MC-PDFT
Irrep: A		
-1449.455	-1450.871	-1451.496
-1449.366	-1450.779	-1451.414
-1449.347	-1450.764	-1451.4

-1449.311	-1450.723	-1451.361
-1449.302	-1450.714	-1451.354
-1449.292	-1450.698	-1451.341
-1449.291	-1450.697	-1451.34
-1449.289	-1450.7	-1451.336
-1449.289	-1450.703	-1451.336
-1449.287	-1450.695	-1451.339
-1449.285	-1450.693	-1451.336
-1449.281	-1450.685	-1451.329

Irrep: B

-1449.367	-1450.777	-1451.415
-1449.367	-1450.777	-1451.415
-1449.349	-1450.761	-1451.401
-1449.349	-1450.761	-1451.401
-1449.312	-1450.72	-1451.362
-1449.312	-1450.72	-1451.362
-1449.302	-1450.711	-1451.355
-1449.302	-1450.711	-1451.355
-1449.285	-1450.693	-1451.338
-1449.285	-1450.693	-1451.338
-1449.279	-1450.682	-1451.328
-1449.279	-1450.682	-1451.328

B. Appendix 2

Table B.1: Absolute energies (in Hartrees) for CASSCF, tPBE, ftPBE, and CASPT2

Active-space	Spin	Root	CASSCF	tPBE	ftPBE	CASPT2
CAS (6, 6)	1	1	-230.844726	-231.951695	-232.048984	-231.726096
CAS (6, 6)	1	2	-230.66599	-231.759057	-231.860323	-231.541384
CAS (6, 6)	1	3	-230.555368	-231.767442	-231.864796	-231.497206
CAS (6, 6)	1	4	-230.546193	-231.643029	-231.743625	-231.425279
CAS (6, 6)	1	5	-230.546193	-231.643137	-231.743873	-231.426201
CAS (6, 6)	1	6	-230.503865	-231.750394	-231.847632	-231.469495
CAS (6, 6)	1	7	-230.503865	-231.749995	-231.847514	-231.469744
CAS (6, 6)	3	1	-230.704731	-231.786898	-231.8887	-231.57212
CAS (6, 6)	3	2	-230.666282	-231.773744	-231.871922	-231.547441
CAS (6, 6)	3	3	-230.666282	-231.773744	-231.871926	-231.547699
CAS (6, 6)	3	4	-230.584162	-231.786432	-231.88231	-231.520863
CAS (6, 6)	3	5	-230.579595	-231.668215	-231.769231	-231.453743
CAS (6, 6)	3	6	-230.579594	-231.668215	-231.769245	-231.453755
CAS (6, 12)	1	1	-230.864751	-231.952341	-232.04938	-231.723687
CAS (6, 12)	1	2	-230.682619	-231.763122	-231.864808	-231.54162
CAS (6, 12)	1	3	-230.598318	-231.748049	-231.842492	-231.488037
CAS (6, 12)	1	4	-230.565389	-231.648772	-231.74997	-231.426697
CAS (6, 12)	1	5	-230.565389	-231.648807	-231.750075	-231.426933
CAS (6, 12)	1	6	-230.553026	-231.73138	-231.827152	-231.463009
CAS (6, 12)	1	7	-230.553025	-231.731349	-231.827144	-231.4627
CAS (6, 12)	3	1	-230.719957	-231.788979	-231.891164	-231.572236
CAS (6, 12)	3	2	-230.687208	-231.775413	-231.873855	-231.547618
CAS (6, 12)	3	3	-230.687206	-231.775413	-231.873854	-231.547651
CAS (6, 12)	3	4	-230.625311	-231.770502	-231.864769	-231.512655

CAS (6, 12)	3	5	-230.596279	-231.671843	-231.773536	-231.454561
CAS (6, 12)	3	6	-230.596278	-231.671842	-231.773538	-231.454561
CAS (6, 24)	1	1	-230.886856	-231.952135	-232.049611	-231.723687
CAS (6, 24)	1	2	-230.700823	-231.763446	-231.864866	-231.54162
CAS (6, 24)	1	3	-230.627719	-231.741937	-231.836342	-231.488037
CAS (6, 24)	1	4	-230.586235	-231.649645	-231.751033	-231.426697
CAS (6, 24)	1	5	-230.586233	-231.649646	-231.751033	-231.426933
CAS (6, 24)	1	6	-230.580555	-231.72702	-231.823292	-231.463009
CAS (6, 24)	1	7	-230.58054	-231.727024	-231.823293	-231.4627
CAS (6, 24)	3	1	-230.737743	-231.790007	-231.891929	-231.572226
CAS (6, 24)	3	2	-230.707749	-231.775449	-231.874629	-231.547629
CAS (6, 24)	3	3	-230.707748	-231.775448	-231.874628	-231.547658
CAS (6, 24)	3	4	-230.654291	-231.763988	-231.859136	-231.510526
CAS (6, 24)	3	5	-230.616634	-231.67385	-231.775813	-231.454007
CAS (6, 24)	3	6	-230.616632	-231.673849	-231.775813	-231.454007
RAS (18, 18)	1	1	-230.997611	-231.931368	-232.024873	-231.727865
RAS (18, 18)	1	2	-230.804679	-231.745727	-231.843401	-231.545972
RAS (18, 18)	1	3	-230.718343	-231.721659	-231.813804	-231.492876
RAS (18, 18)	1	4	-230.676616	-231.630331	-231.726795	-231.434465
RAS (18, 18)	1	5	-230.676614	-231.63039	-231.726954	-231.434524
RAS (18, 18)	1	6	-230.67289	-231.708198	-231.800082	-231.466726
RAS (18, 18)	1	7	-230.67289	-231.708031	-231.79998	-231.467027
RAS (18, 18)	3	1	-230.842732	-231.772646	-231.871379	-231.576858
RAS (18, 18)	3	2	-230.807663	-231.756878	-231.851329	-231.553218
RAS (18, 18)	3	3	-230.807663	-231.756879	-231.851332	-231.553246
RAS (18, 18)	3	4	-230.744893	-231.744676	-231.834878	-231.519605
RAS (18, 18)	3	5	-230.708949	-231.654401	-231.751722	-231.462896
RAS (18, 18)	3	6	-230.708948	-231.6544	-231.75173	-231.462964

Table B.2: Electronic part of second moment for benzene with different active spaces (in atomic units)

CAS (6,6)

State	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\langle r^2 \rangle$
$1^1 A_{1g}$	215.088	215.088	30.128	400.049
$1^1 B_{2u}$	216.043	216.043	30.145	462.23
$1^1 B_{1u}$	215.88	215.88	30.212	461.973
$1^1 E_{1u}$	215.686	216.262	30.197	462.145
$2^1 E_{2g}$	216.914	216.221	30.049	463.185

CAS (6,12)

State	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\langle r^2 \rangle$
$1^1 A_{1g}$	214.839	214.839	30.115	459.793
$1^1 B_{2u}$	216.036	216.036	30.218	462.289
$1^1 B_{1u}$	217.483	217.483	32.1	467.066
$1^1 E_{1u}$	218.213	217.03	32.142	467.384
$2^1 E_{2g}$	216.781	216.308	30.123	463.212

CAS (6,24)

State	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\langle r^2 \rangle$
$1^1 A_{1g}$	214.891	214.891	30.153	459.935
$1^1 B_{2u}$	216.187	216.186	30.298	462.671
$1^1 B_{1u}$	216.933	216.933	31.77	465.635
$1^1 E_{1u}$	217.355	217.278	31.941	466.574
$2^1 E_{2g}$	216.682	216.683	30.176	463.541

RAS (18,18)

Table B.3: XYZ coordinates of benzene (in Angstroms)

H	0.0000	-2.4826	0.0000
H	2.1500	1.2413	0.0000
H	2.1500	-1.2413	0.0000
H	0.0000	2.4826	0.0000
H	-2.1500	1.2413	0.0000
H	-2.1500	-1.2413	0.0000
C	0.0000	1.3963	0.0000
C	1.2092	0.6981	0.0000
C	1.2092	-0.6981	0.0000
C	0.0000	-1.3963	0.0000
C	-1.2092	0.6981	0.0000
C	-1.2092	-0.6981	0.0000

State	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\langle r^2 \rangle$
1^1A_{1g}	215.164	215.164	29.789	460.118
1^1B_{2u}	215.818	215.818	29.593	461.23
1^1B_{1u}	215.729	215.729	29.668	461.126
1^1E_{1u}	215.497	216.009	29.643	461.149
2^1E_{2g}	216.409	216.079	29.443	461.931

Table B.4: XYZ coordinates of benzene (in Angstroms)

H	0.0000	-2.4826	0.0000
H	2.1500	1.2413	0.0000
H	2.1500	-1.2413	0.0000
H	0.0000	2.4826	0.0000
H	-2.1500	1.2413	0.0000
H	-2.1500	-1.2413	0.0000
C	0.0000	1.3963	0.0000
C	1.2092	0.6981	0.0000
C	1.2092	-0.6981	0.0000
C	0.0000	-1.3963	0.0000
C	-1.2092	0.6981	0.0000
C	-1.2092	-0.6981	0.0000

C. Appendix 3

Table C.1: Absolute energies for DMRG and DMRG-PDFT in Hartrees for vertical S-T gaps for polyacenes.

n-acene	Spin state	Active -space	M	DMRG	DMRG-PDFT
2-acene	Triplet	(10, 10)	100	-383.387011	-385.19205
2-acene	Triplet	(10, 10)	200	-383.388475	-385.189633
2-acene	Triplet	(10, 10)	300	-383.388489	-385.189603
2-acene	Triplet	(10, 10)	500	-383.388489	-385.189603
2-acene	Triplet	(10, 10)	1000	-383.388489	-385.189603
2-acene	Singlet	(10, 10)	100	-383.50016	-385.313681
2-acene	Singlet	(10, 10)	200	-383.500679	-385.312667
2-acene	Singlet	(10, 10)	300	-383.500691	-385.312633
2-acene	Singlet	(10, 10)	500	-383.500691	-385.312633
2-acene	Singlet	(10, 10)	1000	-383.500691	-385.312633
2-acene	Singlet	(10, 20)	100	-383.51745	-385.317672
2-acene	Triplet	(10, 20)	100	-383.399425	-385.200343
2-acene	Singlet	(10, 20)	500	-383.525466	-385.312135
2-acene	Triplet	(10, 20)	500	-383.410957	-385.191529
2-acene	Singlet	(10, 20*)	500	-383.51799	-385.31306
2-acene	Triplet	(10, 20*)	500	-383.403857	-385.190442
3-acene	Triplet	(14, 14)	100	-536.1009	-538.6542
3-acene	Triplet	(14, 14)	200	-536.1092	-538.6479
3-acene	Triplet	(14, 14)	300	-536.1128	-538.6442
3-acene	Triplet	(14, 14)	500	-536.1159	-538.6404
3-acene	Triplet	(14, 14)	1000	-536.1176	-538.6373
3-acene	Triplet	(14, 14)	2000	-536.118	-538.6362
3-acene	Singlet	(14, 14)	100	-536.1912	-538.7379
3-acene	Singlet	(14, 14)	200	-536.1981	-538.7309

3-acene	Singlet	(14, 14)	300	-536.2003	-538.7282
3-acene	Singlet	(14, 14)	500	-536.2017	-538.7259
3-acene	Singlet	(14, 14)	1000	-536.2025	-538.7242
3-acene	Singlet	(14, 14)	2000	-536.2027	-538.7238
4-acene	Triplet	(18,18)	500	-688.825271	-692.086857
4-acene	Singlet	(18,18)	500	-688.894332	-692.144985
5-acene	Triplet	(22, 22)	500	-841.5323	-845.532
5-acene	Singlet	(22, 22)	500	-841.5778	-845.5679
6-acene	Triplet	(26, 26)	500	-994.209879	-998.964357
6-acene	Singlet	(26, 26)	500	-994.253558	-998.993342
7-acene	Triplet	(30, 30)	500	-1146.893043	-1152.39919
7-acene	Singlet	(30, 30)	500	-1146.922746	-1152.421666

Table C.3: Absolute energies for DMRG and DMRG-PDFT in Hartrees for vertical S-T gaps for n-polyacetylenes

n	M	DMRG		tPBE	
		S	T	S	T
2	10	-231.909738	-231.806787	-233.034404	-232.931874
	20	-231.909738	-231.806787	-233.034404	-232.931874
	50	-231.909738	-231.806787	-233.034404	-232.931874
	100	-231.909738	-231.806787	-233.034404	-232.931874
	500	-231.909738	-231.806787	-233.034404	-232.931874
	1000	-231.909738	-231.806787	-233.034404	-232.931874
3	10	-231.909738	-231.806787	-233.0361	-232.933787
	20	-231.911517	-231.808628	-233.034404	-232.931874
	50	-231.911517	-231.808628	-233.034404	-232.931874
	100	-231.911517	-231.808628	-233.034404	-232.931874
	500	-231.911517	-231.808575	-233.034404	-232.931874
	1000	-231.911517	-231.808575	-233.034404	-232.931874
4	10	-308.818458	-308.716125	-310.33134	-310.244237
	20	-308.827789	-308.735682	-310.327045	-310.241257

	50	-308.832396	-308.74292	-310.322311	-310.235252
	100	-308.832488	-308.743005	-310.322142	-310.235121
	500	-308.832488	-308.743005	-310.322142	-310.235121
	1000	-308.832488	-308.743005	-310.322142	-310.235121
5	10	-385.717914	-385.622614	-387.621768	-387.547175
	20	-385.740515	-385.648237	-387.620513	-387.548729
	50	-385.749642	-385.665635	-387.614405	-387.541102
	100	-385.753077	-385.671447	-387.610764	-387.535877
	500	-385.753473	-385.673106	-387.610083	-387.533515
	1000	-385.753473	-385.673106	-387.610083	-387.533515
6	10	-462.62076	-462.506609	-464.913481	-464.855461
	20	-462.650284	-462.551896	-464.91649	-464.850096
	50	-462.662533	-462.581531	-464.90904	-464.84382
	100	-462.670096	-462.591472	-464.903034	-464.838521
	500	-462.674399	-462.600396	-464.898159	-464.8294
	1000	-462.674421	-462.600578	-464.898103	-464.829012
7	10	-539.499629	-539.409086	-542.210914	-542.154255

Table C.6: Atomic coordinates for n-polyacetylenes (H₂C=CH₂)_n, optimized by B3LYP/6-31G(d,p). XYZ Cartesian coordinates are in Angstroms.

n=1				
C	-0.662958	0	0.00000	
C	0.662958	0	0.00000	
H	-1.256559	-0.924026	0.00000	
H	1.256559	-0.924026	0.00000	
H	-1.256559	0.924026	0.00000	
H	1.256559	0.924026	0.00000	
n=2				
C	1.855098	0.114866	0.00000	
C	-1.855098	-0.114866	0.00000	
C	0.643269	-0.423208	0.00000	

C	-0.643269	0.423208	0.00000
H	2.022642	1.200276	0.00000
H	-2.022642	-1.200276	0.00000
H	2.772605	-0.488763	0.00000
H	-2.772605	0.488763	0.00000
H	0.475726	-1.508617	0.00000
H	-0.475726	1.508617	0.00000

n=3

C	-3.075055	0.167498	0.00000
C	3.075055	-0.167498	0.00000
C	-1.867388	-0.418911	0.00000
C	1.867388	0.418911	0.00000
H	-3.180907	1.24926	0.00000
H	3.180907	-1.24926	0.00000
H	-3.991128	-0.413469	0.00000
H	3.991128	0.413469	0.00000
H	-1.805249	-1.50708	0.00000
H	1.805249	1.50708	0.00000
C	-0.606997	0.297372	0.00000
C	0.606997	-0.297372	0.00000
H	-0.661631	1.386399	0.00000
H	0.661631	-1.386399	0.00000

n=4

C	-4.308669	0.197146	0.00000
C	4.308669	-0.197146	0.00000
C	-3.110874	-0.411353	0.00000
C	3.110874	0.411353	0.00000
H	-4.394907	1.280613	0.00000
H	4.394907	-1.280613	0.00000
H	-5.23494	-0.367304	0.00000

H	5.23494	0.367304	0.00000
H	-3.069439	-1.500574	0.00000
H	3.069439	1.500574	0.00000
C	-1.839087	0.279751	0.00000
C	1.839087	-0.279751	0.00000
C	-0.634371	-0.341144	0.00000
C	0.634371	0.341144	0.00000
H	-1.871161	1.369551	0.00000
H	1.871161	-1.369551	0.00000
H	-0.607249	-1.431263	0.00000
H	0.607249	1.431263	0.00000
n=5			
C	-5.544122	0.214299	0.00000
C	5.544122	-0.214299	0.00000
C	-4.350171	-0.402736	0.00000
C	4.350171	0.402736	0.00000
H	-5.622764	1.298325	0.00000
H	5.622764	-1.298325	0.00000
H	-6.474236	-0.343751	0.00000
H	6.474236	0.343751	0.00000
H	-4.31685	-1.492261	0.00000
H	4.31685	1.492261	0.00000
C	-3.074155	0.278469	0.00000
C	3.074155	-0.278469	0.00000
C	-1.872943	-0.352359	0.00000
C	1.872943	0.352359	0.00000
H	-3.097453	1.368452	0.00000
H	3.097453	-1.368452	0.00000
H	-1.855664	-1.442745	0.00000
H	1.855664	1.442745	0.00000

C	-0.600949	0.317418	0.00000
C	0.600949	-0.317418	0.00000
H	-0.616498	1.407635	0.00000
H	0.616498	-1.407635	0.00000
n=6			
C	-6.780165	0.224843	0.00000
C	6.780165	-0.224843	0.00000
C	-5.587871	-0.395931	0.00000
C	5.587871	0.395931	0.00000
H	-6.855486	1.309093	0.00000
H	6.855486	-1.309093	0.00000
H	-7.711938	-0.330412	0.00000
H	7.711938	0.330412	0.00000
H	-5.558134	-1.485572	0.00000
H	5.558134	1.485572	0.00000
C	-4.310074	0.280869	0.00000
C	4.310074	-0.280869	0.00000
C	-3.110354	-0.354381	0.00000
C	3.110354	0.354381	0.00000
H	-4.32947	1.37091	0.00000
H	4.32947	-1.37091	0.00000
H	-3.09748	-1.444853	0.00000
H	3.09748	1.444853	0.00000
C	-1.837018	0.309854	0.00000
C	1.837018	-0.309854	0.00000
C	-0.636207	-0.330789	0.00000
C	0.636207	0.330789	0.00000
H	-1.847524	1.400093	0.00000
H	1.847524	-1.400093	0.00000
H	-0.626779	-1.421145	0.00000

H	0.626779	1.421145	0.00000
n=7			
C	-8.016413	0.231484	0.00000
C	8.016413	-0.231484	0.00000
C	-6.824842	-0.390985	0.00000
C	6.824842	0.390985	0.00000
H	-8.090236	1.315832	0.00000
H	8.090236	-1.315832	0.00000
H	-8.94893	-0.322511	0.00000
H	8.94893	0.322511	0.00000
H	-6.796748	-1.480677	0.00000
H	6.796748	1.480677	0.00000
C	-5.546279	0.283772	0.00000
C	5.546279	-0.283772	0.00000
C	-4.34719	-0.353545	0.00000
C	4.34719	0.353545	0.00000
H	-5.563863	1.373834	0.00000
H	5.563863	-1.373834	0.00000
H	-4.336393	-1.444053	0.00000
H	4.336393	1.444053	0.00000
C	-3.073314	0.308052	0.00000
C	3.073314	-0.308052	0.00000
C	-1.872942	-0.335356	0.00000
C	1.872942	0.335356	0.00000
H	-3.081425	1.398294	0.00000
H	3.081425	-1.398294	0.00000
H	-1.866428	-1.425761	0.00000
H	1.866428	1.425761	0.00000
C	-0.600391	0.322405	0.00000
C	0.600391	-0.322405	0.00000

H	-0.606257	1.412748	0.00000
H	0.606257	-1.412748	0.00000
n=8			
H	4.316637	-1.39863	0.00000
H	-4.316637	1.39863	0.00000
H	3.104331	1.426781	0.00000
H	-3.104331	-1.426781	0.00000
H	1.841023	-1.409856	0.00000
H	-1.841023	1.409856	0.00000
H	0.632466	1.417725	0.00000
H	-0.632466	-1.417725	0.00000
H	9.325912	-1.320043	0.00000
H	-9.325912	1.320043	0.00000
H	10.185553	0.317808	0.00000
H	-10.185553	-0.317808	0.00000
H	8.034061	1.477254	0.00000
H	-8.034061	-1.477254	0.00000
H	6.799346	-1.376374	0.00000
H	-6.799346	1.376374	0.00000
H	5.573884	1.442478	0.00000
H	-5.573884	-1.442478	0.00000
C	9.252725	-0.235656	0.00000
C	-9.252725	0.235656	0.00000
C	4.309669	-0.30839	0.00000
C	-4.309669	0.30839	0.00000
C	3.109422	0.336355	0.00000
C	-3.109422	-0.336355	0.00000
C	1.836908	-0.319522	0.00000
C	-1.836908	0.319522	0.00000
C	0.636059	0.327343	0.00000

C	-0.636059	-0.327343	0.00000
C	8.061436	0.38754	0.00000
C	-8.061436	-0.38754	0.00000
C	6.782578	-0.286305	0.00000
C	-6.782578	0.286305	0.00000
C	5.583715	0.351954	0.00000
C	-5.583715	-0.351954	0.00000

Table C.7: Atomic coordinates for n-polyacetylenes (H₂C=CH₂)_n, optimized by B3LYP/6-31G(d,p). XYZ Cartesian coordinates are in Angstroms.

n=1			
C	-0.662958	0	0.00000
C	0.662958	0	0.00000
H	-1.256559	-0.924026	0.00000
H	1.256559	-0.924026	0.00000
H	-1.256559	0.924026	0.00000
H	1.256559	0.924026	0.00000
n=2			
C	1.855098	0.114866	0.00000
C	-1.855098	-0.114866	0.00000
C	0.643269	-0.423208	0.00000
C	-0.643269	0.423208	0.00000
H	2.022642	1.200276	0.00000
H	-2.022642	-1.200276	0.00000
H	2.772605	-0.488763	0.00000
H	-2.772605	0.488763	0.00000
H	0.475726	-1.508617	0.00000
H	-0.475726	1.508617	0.00000
n=3			
C	-3.075055	0.167498	0.00000
C	3.075055	-0.167498	0.00000

C	-1.867388	-0.418911	0.00000
C	1.867388	0.418911	0.00000
H	-3.180907	1.24926	0.00000
H	3.180907	-1.24926	0.00000
H	-3.991128	-0.413469	0.00000
H	3.991128	0.413469	0.00000
H	-1.805249	-1.50708	0.00000
H	1.805249	1.50708	0.00000
C	-0.606997	0.297372	0.00000
C	0.606997	-0.297372	0.00000
H	-0.661631	1.386399	0.00000
H	0.661631	-1.386399	0.00000
n=4			
C	-4.308669	0.197146	0.00000
C	4.308669	-0.197146	0.00000
C	-3.110874	-0.411353	0.00000
C	3.110874	0.411353	0.00000
H	-4.394907	1.280613	0.00000
H	4.394907	-1.280613	0.00000
H	-5.23494	-0.367304	0.00000
H	5.23494	0.367304	0.00000
H	-3.069439	-1.500574	0.00000
H	3.069439	1.500574	0.00000
C	-1.839087	0.279751	0.00000
C	1.839087	-0.279751	0.00000
C	-0.634371	-0.341144	0.00000
C	0.634371	0.341144	0.00000
H	-1.871161	1.369551	0.00000
H	1.871161	-1.369551	0.00000
H	-0.607249	-1.431263	0.00000

H	0.607249	1.431263	0.00000
n=5			
C	-5.544122	0.214299	0.00000
C	5.544122	-0.214299	0.00000
C	-4.350171	-0.402736	0.00000
C	4.350171	0.402736	0.00000
H	-5.622764	1.298325	0.00000
H	5.622764	-1.298325	0.00000
H	-6.474236	-0.343751	0.00000
H	6.474236	0.343751	0.00000
H	-4.31685	-1.492261	0.00000
H	4.31685	1.492261	0.00000
C	-3.074155	0.278469	0.00000
C	3.074155	-0.278469	0.00000
C	-1.872943	-0.352359	0.00000
C	1.872943	0.352359	0.00000
H	-3.097453	1.368452	0.00000
H	3.097453	-1.368452	0.00000
H	-1.855664	-1.442745	0.00000
H	1.855664	1.442745	0.00000
C	-0.600949	0.317418	0.00000
C	0.600949	-0.317418	0.00000
H	-0.616498	1.407635	0.00000
H	0.616498	-1.407635	0.00000
n=6			
C	-6.780165	0.224843	0.00000
C	6.780165	-0.224843	0.00000
C	-5.587871	-0.395931	0.00000
C	5.587871	0.395931	0.00000
H	-6.855486	1.309093	0.00000

H	6.855486	-1.309093	0.00000
H	-7.711938	-0.330412	0.00000
H	7.711938	0.330412	0.00000
H	-5.558134	-1.485572	0.00000
H	5.558134	1.485572	0.00000
C	-4.310074	0.280869	0.00000
C	4.310074	-0.280869	0.00000
C	-3.110354	-0.354381	0.00000
C	3.110354	0.354381	0.00000
H	-4.32947	1.37091	0.00000
H	4.32947	-1.37091	0.00000
H	-3.09748	-1.444853	0.00000
H	3.09748	1.444853	0.00000
C	-1.837018	0.309854	0.00000
C	1.837018	-0.309854	0.00000
C	-0.636207	-0.330789	0.00000
C	0.636207	0.330789	0.00000
H	-1.847524	1.400093	0.00000
H	1.847524	-1.400093	0.00000
H	-0.626779	-1.421145	0.00000
H	0.626779	1.421145	0.00000
n=7			
C	-8.016413	0.231484	0.00000
C	8.016413	-0.231484	0.00000
C	-6.824842	-0.390985	0.00000
C	6.824842	0.390985	0.00000
H	-8.090236	1.315832	0.00000
H	8.090236	-1.315832	0.00000
H	-8.94893	-0.322511	0.00000
H	8.94893	0.322511	0.00000

H	-6.796748	-1.480677	0.00000
H	6.796748	1.480677	0.00000
C	-5.546279	0.283772	0.00000
C	5.546279	-0.283772	0.00000
C	-4.34719	-0.353545	0.00000
C	4.34719	0.353545	0.00000
H	-5.563863	1.373834	0.00000
H	5.563863	-1.373834	0.00000
H	-4.336393	-1.444053	0.00000
H	4.336393	1.444053	0.00000
C	-3.073314	0.308052	0.00000
C	3.073314	-0.308052	0.00000
C	-1.872942	-0.335356	0.00000
C	1.872942	0.335356	0.00000
H	-3.081425	1.398294	0.00000
H	3.081425	-1.398294	0.00000
H	-1.866428	-1.425761	0.00000
H	1.866428	1.425761	0.00000
C	-0.600391	0.322405	0.00000
C	0.600391	-0.322405	0.00000
H	-0.606257	1.412748	0.00000
H	0.606257	-1.412748	0.00000
n=8			
H	4.316637	-1.39863	0.00000
H	-4.316637	1.39863	0.00000
H	3.104331	1.426781	0.00000
H	-3.104331	-1.426781	0.00000
H	1.841023	-1.409856	0.00000
H	-1.841023	1.409856	0.00000
H	0.632466	1.417725	0.00000

H	-0.632466	-1.417725	0.00000
H	9.325912	-1.320043	0.00000
H	-9.325912	1.320043	0.00000
H	10.185553	0.317808	0.00000
H	-10.185553	-0.317808	0.00000
H	8.034061	1.477254	0.00000
H	-8.034061	-1.477254	0.00000
H	6.799346	-1.376374	0.00000
H	-6.799346	1.376374	0.00000
H	5.573884	1.442478	0.00000
H	-5.573884	-1.442478	0.00000
C	9.252725	-0.235656	0.00000
C	-9.252725	0.235656	0.00000
C	4.309669	-0.30839	0.00000
C	-4.309669	0.30839	0.00000
C	3.109422	0.336355	0.00000
C	-3.109422	-0.336355	0.00000
C	1.836908	-0.319522	0.00000
C	-1.836908	0.319522	0.00000
C	0.636059	0.327343	0.00000
C	-0.636059	-0.327343	0.00000
C	8.061436	0.38754	0.00000
C	-8.061436	-0.38754	0.00000
C	6.782578	-0.286305	0.00000
C	-6.782578	0.286305	0.00000
C	5.583715	0.351954	0.00000
C	-5.583715	-0.351954	0.00000

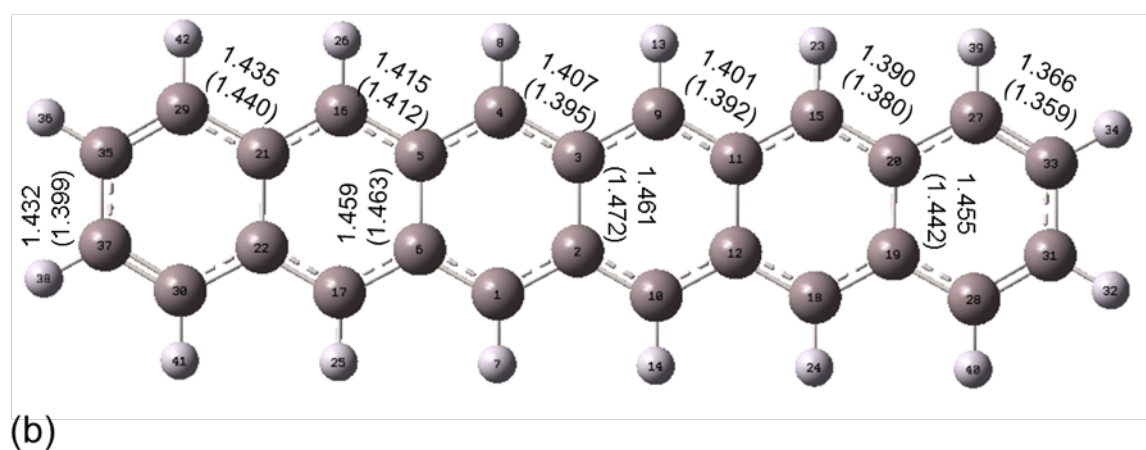
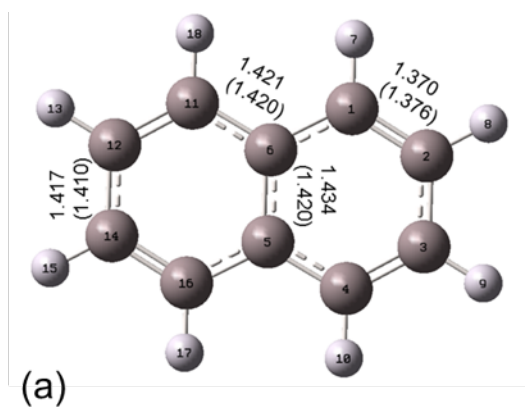


Figure C.1: Comparison between calculated and experimental geometries (B3LYP/6-31G(d,p)) of naphthalene and hexacene. The mean deviation in bond lengths are 0.007 and 0.011 Å, respectively

Table C.2: Absolute energies for DMRG and DMRG-PDFT in Hartrees for adiabatic S-T gaps for polyacenes

n-acene	Spin state	Active- space	M	DMRG	DMRG-PDFT
2-acene	Triplet	(10, 10)	100	-383.402018	-385.207464
2-acene	Triplet	(10, 10)	200	-383.403057	-385.205917
2-acene	Triplet	(10, 10)	300	-383.403065	-385.205895
2-acene	Triplet	(10, 10)	500	-383.403065	-385.205895
2-acene	Triplet	(10, 10)	1000	-383.403065	-385.205895
2-acene	Triplet	(10, 20)	100	-383.425105	-385.207451
2-acene	Triplet	(10, 20)	500	-383.425105	-385.207451
2-acene	Triplet	(10, 20*)	500	-383.418488	-385.206737
3-acene	Triplet	(14, 14)	100	-536.1159	-538.6642
3-acene	Triplet	(14, 14)	200	-536.1232	-538.6586
3-acene	Triplet	(14, 14)	300	-536.1266	-538.6554
3-acene	Triplet	(14, 14)	500	-536.1292	-538.6523
3-acene	Triplet	(14, 14)	1000	-536.1306	-538.6498
3-acene	Triplet	(14, 14)	2000	-536.131	-538.6489
4-acene	Triplet	(18,18)	500	-688.837735	-692.094622
5-acene	Triplet	(22, 22)	500	-841.5323	-845.532
6-acene	Triplet	(26, 26)	500	-994.219323	-998.966566
7-acene	Triplet	(30, 30)	500	-1146.898064	-1152.398852

Table C.4: Absolute energies for CASSCF, CASPT2, and MC-PDFT in Hartrees for vertical S-T gaps for n-polyacetylenes^a

n	Spin state	Active space	CASSCF	CASPT2	MC-PDFT
1	Singlet	(2,2)	-78.070184	-78.321268	-78.070184
1	Triplet	(2, 2)	-77.910609	-78.154313	-78.289453
2	Singlet	(4, 4)	-154.99066	-155.47975	-155.74711
2	Triplet	(4, 4)	-154.86664	-155.35556	-155.61985
3	Singlet	(6, 6)	-231.91152	-232.638264	-233.034404
3	Triplet	(6, 6)	-231.80863	-232.537893	-232.931874
4	Singlet	(8, 8)	-308.832488	-309.797215	-310.322141
4	Triplet	(8, 8)	-308.693791	-309.660058	-310.18245
5	Singlet	(10, 10)	-385.753473	-386.956445	-387.610082
5	Triplet	(10, 10)	-385.673106	-386.880315	-387.533515
6	Singlet	(12, 12)	-462.674421	-464.115744	-464.898098
6	Triplet	(12, 12)	-462.600578	-464.046516	-464.82901
7	Singlet	(14, 14)	-539.595331	-541.275123	-542.186155
7	Triplet	(14, 14)	-539.526334	-541.210963	-542.122632
8	Singlet	(16, 16)	-616.516208	-618.4345088	-619.474222
8	Triplet	(16, 16)	-616.450914	-618.3742628	-619.414971

^aHartree-Fock orbitals were used as the guess orbitals for all the calculations.

Sweeps 4, 5, and 6 were used for all the calculations except for 6-acene and 7-acene, and we found no change with respect to changing the number of sweeps.

We used 6 sweeps for 6-acene and 7-acene.

Table C.5: Vertical and adiabatic singlet-triplet gap ($E_{triplet} - E_{singlet}$), in eV) for naphthalene for (10, 10: $\pi\pi^*$) (or simply (10, 10), (10, 20 : $\pi\pi^*2\pi^*$), and (10, 20: $\pi\pi^*\sigma^*$) active spaces.

Active Space	M	DMRG		DMRG-PDFT		Reference values	
		Vert.	Ad.	Vert.	Ad.	Vert.	Ad.
						3.43, 3.30	2.78, 2.79
(10,10)	100	3.08	2.67	3.31	2.89		
(10, 20 : $\pi\pi^*2\pi^*$)	100	3.21	2.51	3.19	3		
(10, 10)	500	3.05	2.66	3.35	2.91		
(10, 20: $\pi\pi^*2\pi^*$)	500	3.12	2.73	3.28	2.85		
(10, 20: $\pi\pi^*\sigma^*$)	500	3.11	2.71	3.34	2.89		

D. Appendix 4

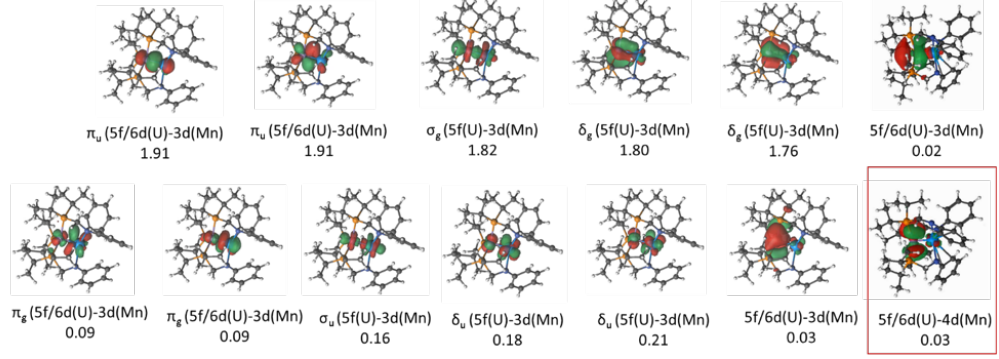


Figure D.1: UMn-2 orbitals predicted by CASSCF (10,13) for the singlet state along with the occupation number of the orbitals. The highlighted orbital is the extra orbital as compared to (10,12) active space. The occupation numbers do not change significantly on the expansion of active space from (10, 12) to (10, 13).

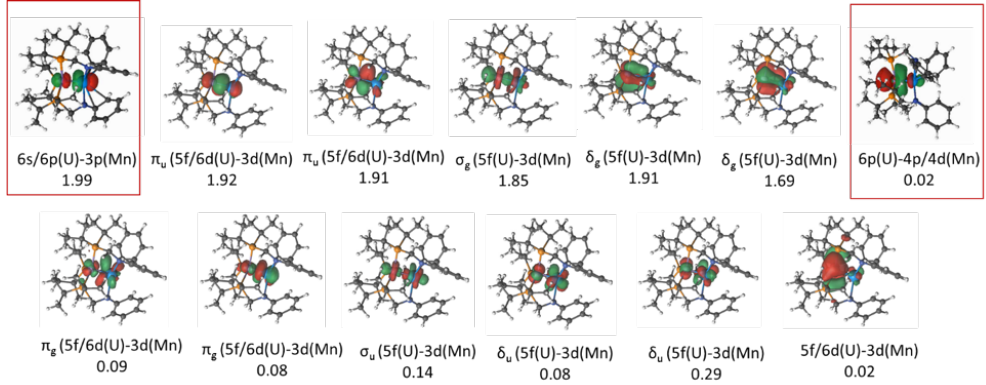


Figure D.2: UMn-2 orbitals predicted by CASSCF (12,13) for the singlet state along with the occupation number of the orbitals. The highlighted orbitals are different/extra orbital as compared to (10,12) active space. The highlighted orbitals consist of a doubly occupied orbital with contributions from core like 6s and 6p orbitals of U and 3p orbitals of Mn, and its correlating orbital.

Table D.1: Detailed CASSCF orbital analysis of UTM-2species.

Complex	Orbital	%TM	%U	total electrons	Electron TM	Electron U	EBO ^a	Mayer BO ^b
UCr-2	σ	48.5	51.5	1.78	0.86	0.92	3.3	3.3
	π	63.2	36.8	1.91	1.21	0.70		
	π	66.5	33.6	1.91	1.27	0.64		
	δ	52.2	47.8	1.67	0.87	0.80		
UMn-2	σ	60.2	39.8	1.85	1.11	0.74	4.3	3.6
	π	68.7	31.3	1.91	1.31	0.60		
	π	69.7	30.3	1.91	1.33	0.58		
	δ	75.7	24.3	1.81	1.42	0.43		
	δ	71.3	28.7	1.77	1.26	0.51		
UFe-2	σ	65.3	34.7	1.82	1.19	0.63	2.7	2.9
	π	77.7	22.3	1.91	1.48	0.43		
	π	75.4	24.6	1.91	1.44	0.47		
	3d(Fe)-5f/6d(U)	95.7	4.3	1.92	1.84	0.08		
	3d(Fe)-5f/6d(U)	97.2	2.8	1.93	1.88	0.05		
UCo-2	3d/4p(Co)-6d(U)	88.2	10.3	1.93	1.70	0.20	1.9	1.6
	3d/4p(Co)- 5f/6d(U)	88.3	10.0	1.93	1.70	0.19		
	3d(Co)-5f/6d(U)	91.8	8.2	1.94	1.78	0.16		
	3d(Co)-5f/6d(U)	95.9	4.2	1.94	1.86	0.08		
UNi-2	3d/4s/4p(Ni)- 5f/6d(U)	34.5	57.7	1.01	0.35	0.58	0.5	0.7
	3d/4s(Ni)- 7s/6d(U)	88.6	11.4	1.95	1.72	0.22		

^aOnly natural MO's with overlap percentage higher than 10% from either metal are considered as bonding MO's

^bCalculated at PBE-D3 level of theory

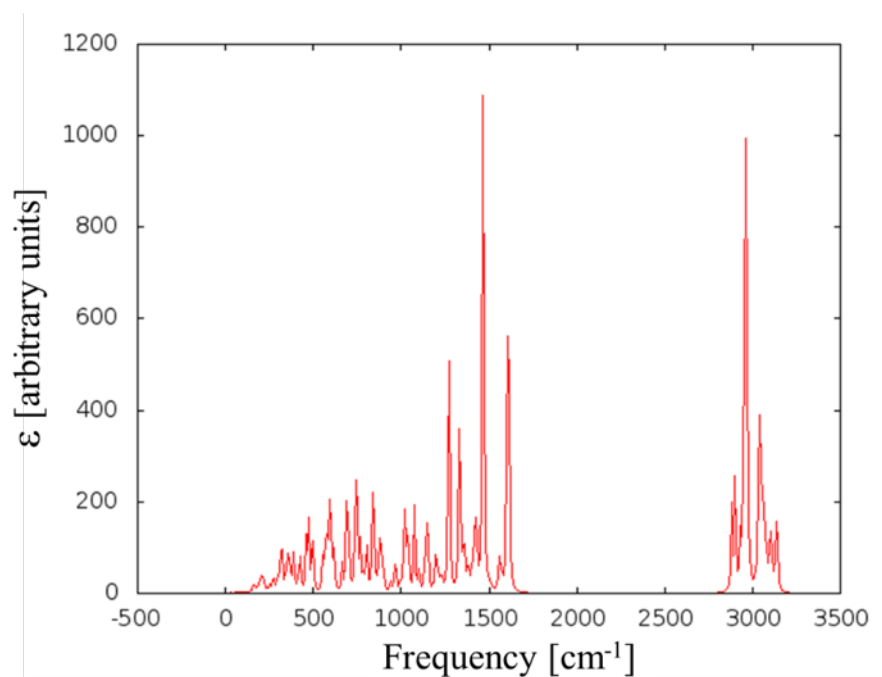


Figure D.3: Infrared spectra for UMn-2 complex calculated at DFT level of theory.

Table D.2: CASPT2/SO-RASSI excitation energies with respect to the ground state in eV for UMn-2.

State	E (eV)
1	0.00
2	1.31
3	1.32
4	1.39
5	1.52
6	1.52
7	1.53
8	1.60
9	1.77
10	1.90
11	1.91
12	1.94
13	2.05
14	2.07
15	2.12
16	2.21

SO-RASSI: Spin-orbit restricted active space state interaction

Table D.3: Absolute ground state CASSCF energies for UTM-2 complexes in atomic units.

UTM-2	Active -space	Spin	CASSCF
UCr-2	(9, 12)	2	-31700.300744
UMn-2	(10, 12)	1	-31808.005604
UFe-2	(11, 12)	2	-31922.069345
UCo-2	(12, 12)	3	-32042.676958
UNi-2	(13, 12)	4	-32169.689777

Table D.4: Absolute excited state CASSCF and MS-CASPT2 energies for UMn-2 complex in atomic units.

State	CASSCF	MS-CASPT2
S ₀	-31807.997814	-31812.214044
S ₁	-31807.952763	-31812.149387
S ₂	-31807.947309	-31812.146314
S ₃	-31807.944047	-31812.141250
T ₁	-31807.957504	-31812.159628
T ₂	-31807.951700	-31812.153265
T ₃	-31807.949063	-31812.150074
T ₄	-31807.945417	-31812.147258

E. Appendix 5

	1	2	3	4	5	6	7	8	9	10
Spin 0	1.015	1.015	0.983	0.983	1.087	0.911	0.002	0.002	0.000	0.002
Spin 1	1.012	1.012	0.986	0.986	1.072	0.926	0.002	0.002	0.000	0.002
Spin 2	1.006	1.006	0.991	0.991	1.043	0.955	0.002	0.002	0.000	0.002
Spin 3	1.000	1.000	0.998	0.998	1.000	0.998	0.002	0.002	0.000	0.002

Table E.1: Occupation numbers of CASSCF (6,10) natural orbitals

Spin 0	1	2	3	4	5	6	7	8	9	10	11
	1.020	1.020	0.986	0.986	1.109	0.898	0.013	0.014	0.013	0.014	1.996
	12	13	14	15	16	17	18	19	20	21	22
	1.996	1.996	1.996	1.999	1.999	1.991	1.991	1.991	1.991	1.991	1.991
Spin 1	1	2	3	4	5	6	7	8	9	10	11
	1.016	1.016	0.990	0.990	1.090	0.916	0.013	0.013	0.013	0.013	1.996
	12	13	14	15	16	17	18	19	20	21	22
	1.996	1.996	1.996	1.999	1.999	1.991	1.991	1.991	1.991	1.991	1.991
Spin 2	1	2	3	4	5	6	7	8	9	10	11
	1.010	1.010	0.996	0.996	1.055	0.951	0.013	0.013	0.013	0.013	1.996
	12	13	14	15	16	17	18	19	20	21	22
	1.996	1.996	1.996	1.999	1.999	1.991	1.991	1.991	1.991	1.991	1.991
Spin 3	1	2	3	4	5	6	7	8	9	10	11
	1.003	1.003	1.003	1.003	1.003	1.003	0.013	0.013	0.013	0.013	1.996
	12	13	14	15	16	17	18	19	20	21	22
	1.996	1.996	1.996	1.999	1.999	1.991	1.991	1.991	1.991	1.991	1.991

Table E.2: Occupation numbers of RASSCF (30,22) natural orbitals

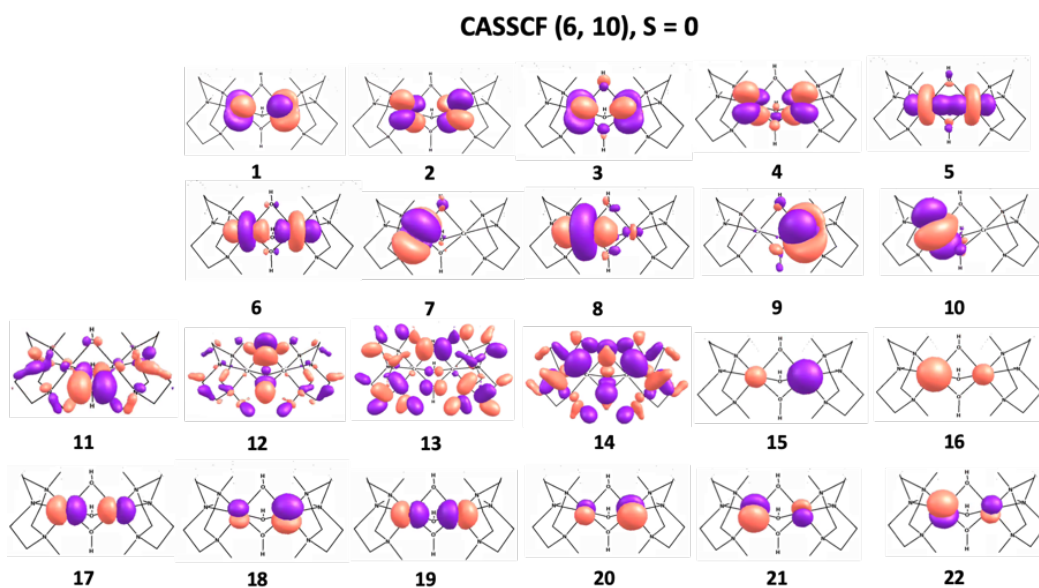


Figure E.1: Natural molecular orbitals obtained from CASSCF (6, 10), S=0 calculation. Orbitals 1-10 represents active space while 11-22 are inactive orbitals.

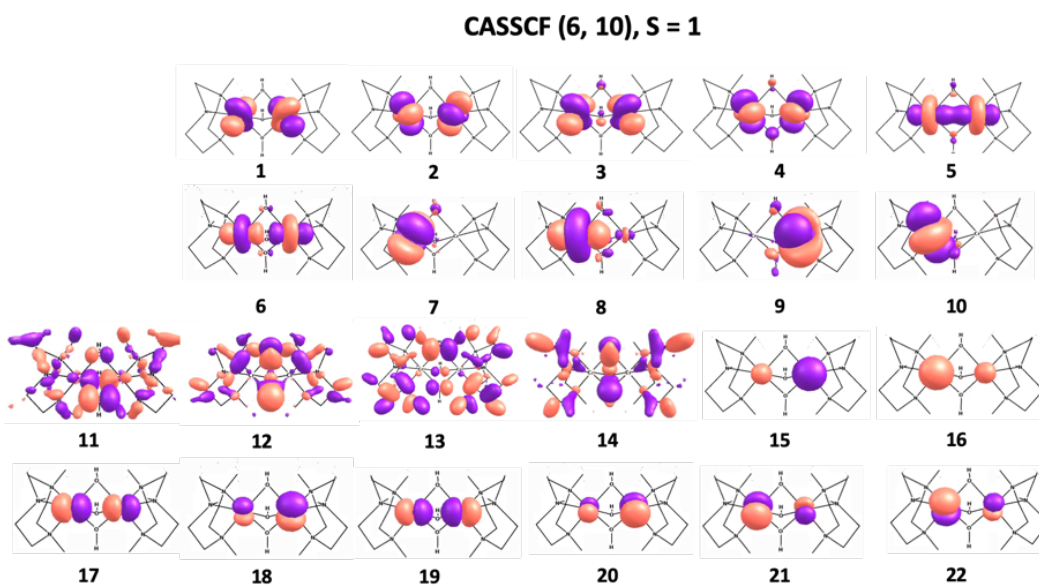


Figure E.2: Natural molecular orbitals obtained from CASSCF (6, 10), S=1 calculation. Orbitals 1-10 represents active space while 11-22 are inactive orbitals.

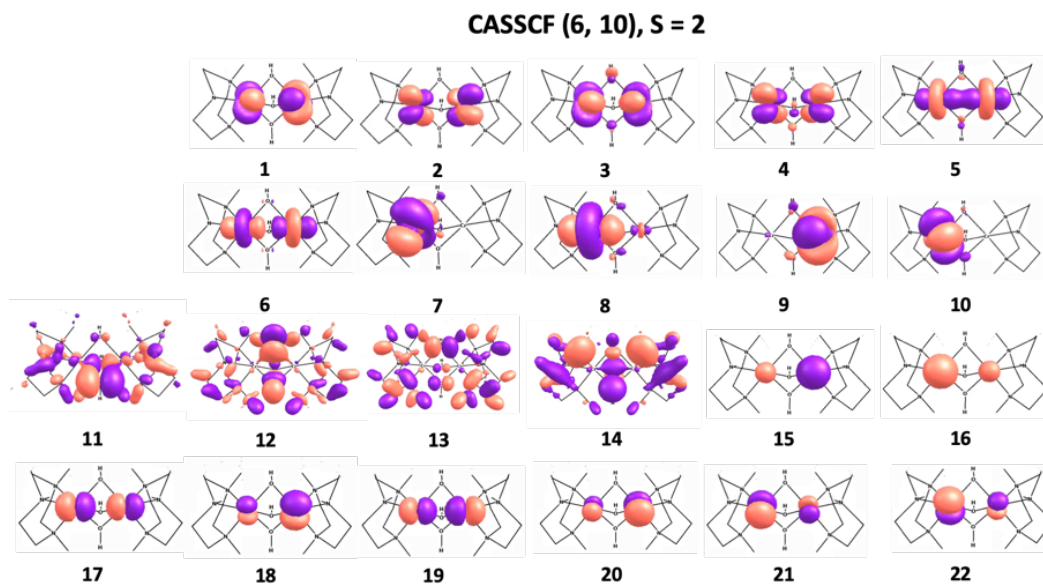


Figure E.3: Natural molecular orbitals obtained from CASSCF (6, 10), S=2 calculation. Orbitals 1-10 represents active space while 11-22 are inactive orbitals.

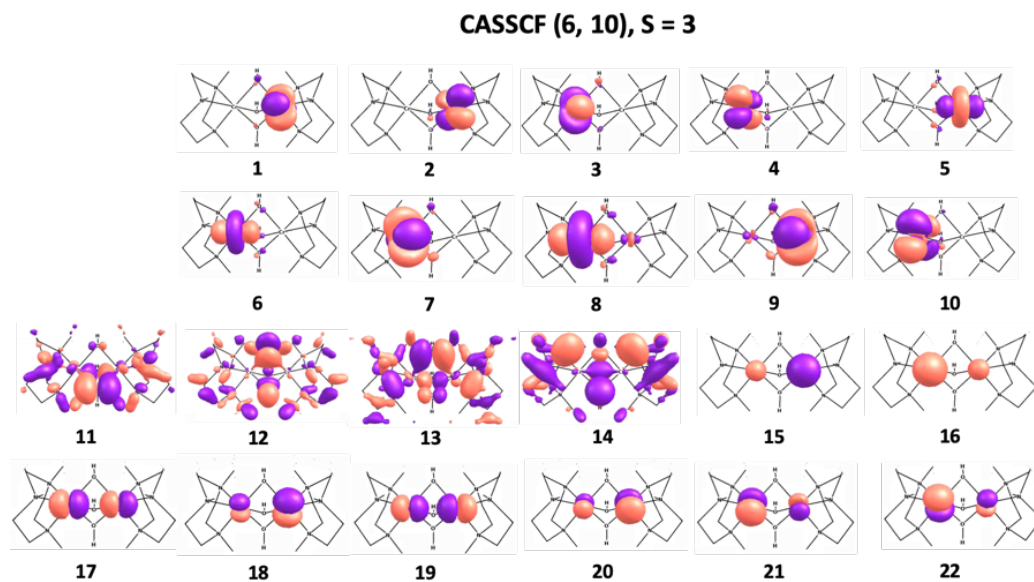


Figure E.4: Natural molecular orbitals obtained from CASSCF (6, 10), S=3 calculation. Orbitals 1-10 represents active space while 11-22 are inactive orbitals.

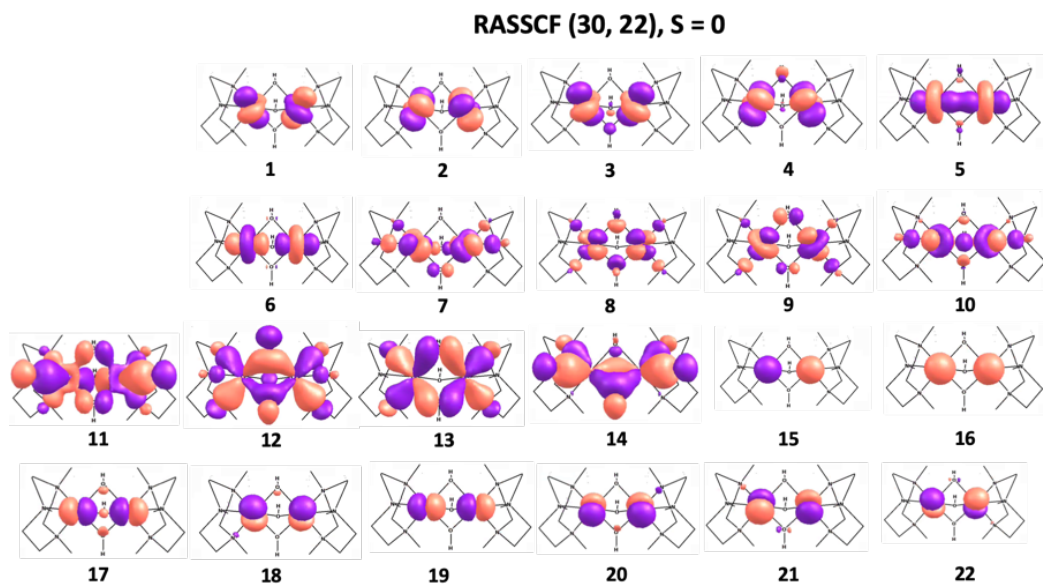


Figure E.5: Natural molecular orbitals obtained from RASSCF (30, 22), S=0 calculation.

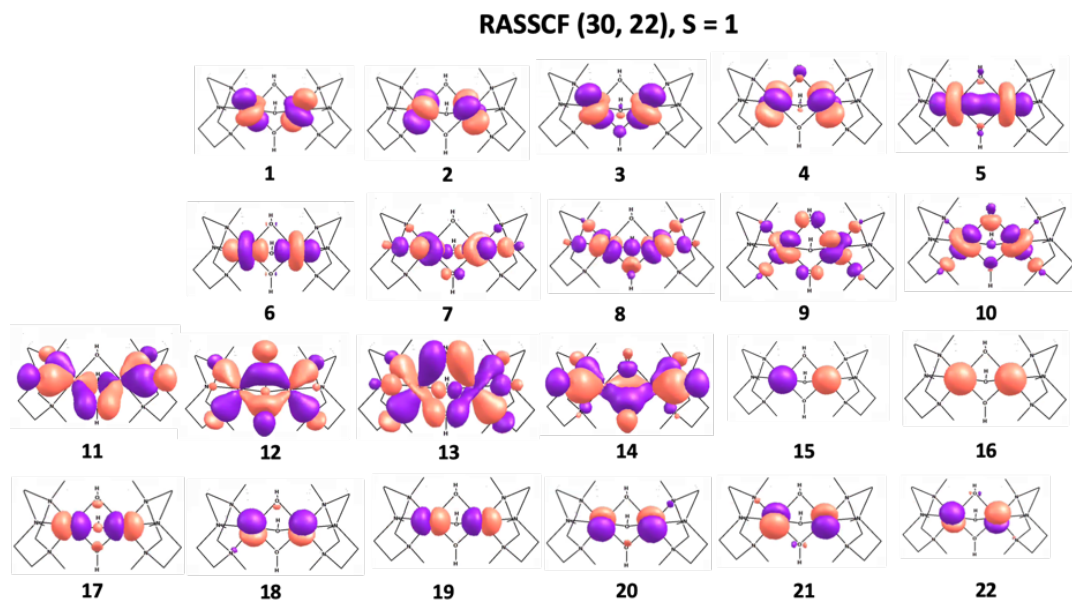


Figure E.6: Natural molecular orbitals obtained from RASSCF (30, 22), S=1 calculation.

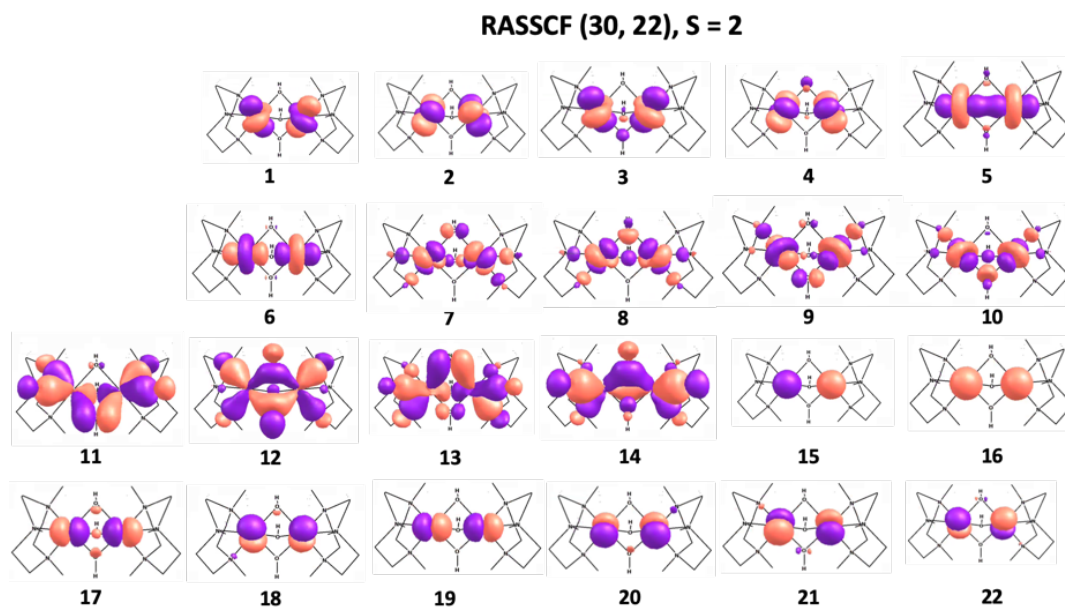


Figure E.7: Natural molecular orbitals obtained from RASSCF (30, 22), S=2 calculation.

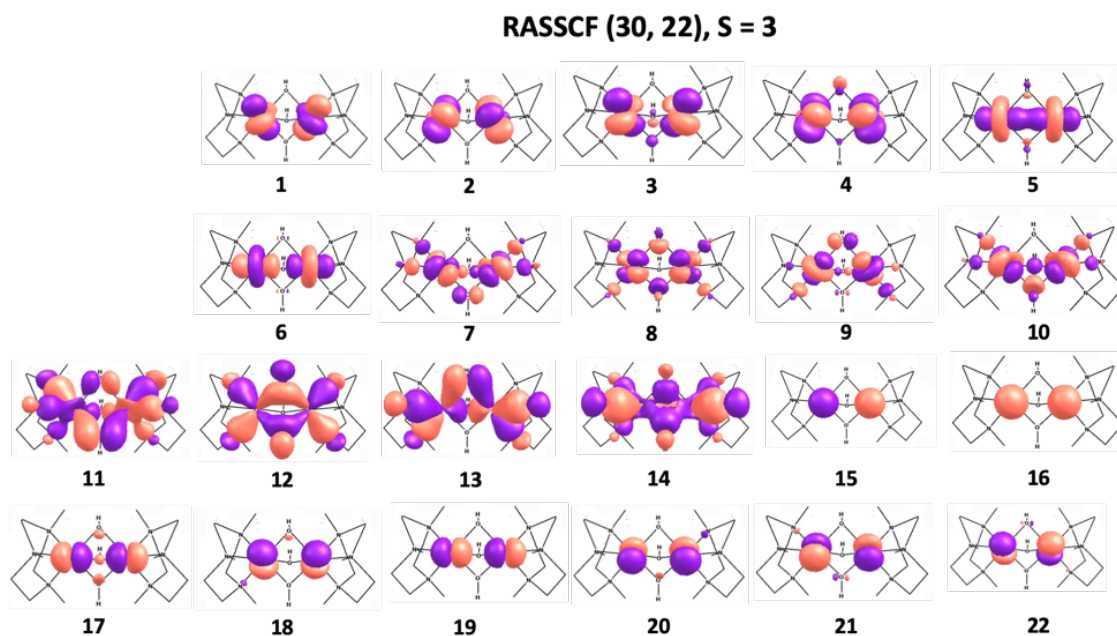


Figure E.8: Natural molecular orbitals obtained from RASSCF (30, 22), S=3 calculation.

Spin 0	1	2	3	4	5	6	7	8	9	10	11
	1.021	1.021	0.986	0.986	1.110	0.896	0.015	0.015	0.015	0.016	1.994
Spin 1	12	13	14	15	16	17	18	19	20	21	22
	1.995	1.994	1.995	1.999	1.999	1.990	1.990	1.991	1.991	1.991	1.991
Spin 2	1	2	3	4	5	6	7	8	9	10	11
	1.017	1.017	0.989	0.989	1.091	0.916	0.015	0.015	0.015	0.015	1.994
Spin 3	12	13	14	15	16	17	18	19	20	21	22
	1.995	1.994	1.995	1.999	1.999	1.990	1.990	1.991	1.991	1.991	1.991

Table E.3: Occupation numbers of DMRG-SCF (30,22) natural orbitals

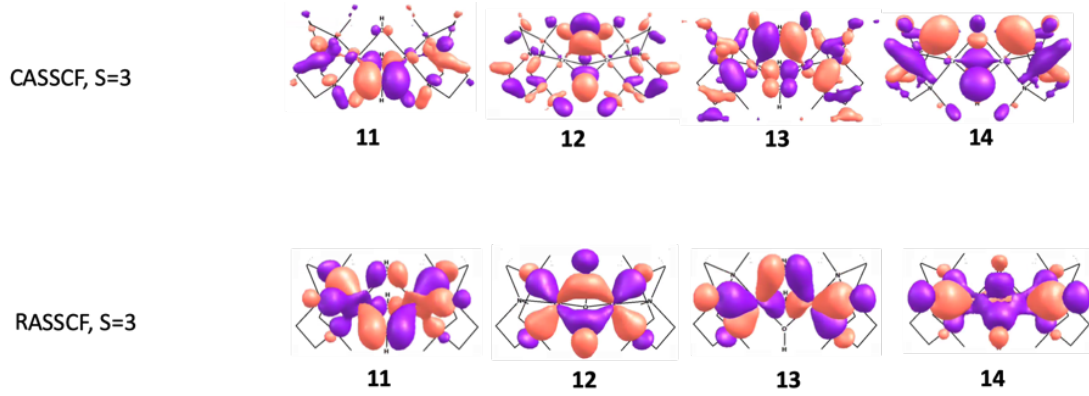


Figure E.9: Comparison between ligand orbitals in CASSCF vs RASSCF. Figures are plotted at isovalue = 0.04.

Method		Spin 0	Spin 1	Spin 2	Spin 3
	(<u>e.o</u>)				
CASSCF	(6,10)	-3345.601198	3345.601010	-3345.600649	-3345.600152
MC-PDFT	(6,10)	-3353.451373	-3353.450978	-3353.450246	-3353.449243
RASSCF	(30,22)	-3345.737324	-3345.737041	-3345.736499	-3345.735763
RASPT2	(30,22)	-3353.415529	-3353.414872	-3353.413598	-3353.412039
	<i>M</i>				
DMRG-SCF1	500	-3345.701312	-3345.700864	-3345.699083	-3345.700096
DMRG-PDFT1	500	-3353.437687	-3353.437304	-3353.436076	-3353.434762
DMRG-SCF1	1000	-3345.701592	-3345.701283	-3345.700166	-3345.700249
DMRG-PDFT1	1000	-3353.437545	-3353.437077	-3353.435491	-3353.43466
DMRG-SCF2	1000	-3345.741708	-3345.741045	-3345.741408	-3345.741779
DMRG-PDFT2	1000	-3353.413811	-3353.413126	-3353.411694	-3353.41011

Table E.4: Absolute MCSCF and MC-PDFT energies in hartree atomic units.

Method	Energy relative to $S = 0$			J
	$S = 1$	$S = 2$	$S = 3$	
CASSCF	251	754	1504	-125
CAS-PDFT	409	1254	2761	-230
RASSCF	357	1074	1990	-166
RAS-PDFT	402	1181	2258	-188

Table E.5: Relative energies of spin states and coupling constant (J) in cm-1 for the modified chromium dimer without the bridging hydroxide ligands. This table is based on a separate calculation where the three hydroxide ligands were deleted and the coupling constant was calculated for the modified molecule. We used CAS (6, 10) containing six electrons in ten chromium 3d orbitals and and RAS (22, 18) where 8 orbitals containing Cr 3s/3p were in RAS1 while the 3d orbitals were in RAS2. Two holes were allowed in RAS1. Both CAS and RAS spaces are analogous to active spaces used for Kremer’s dimer.

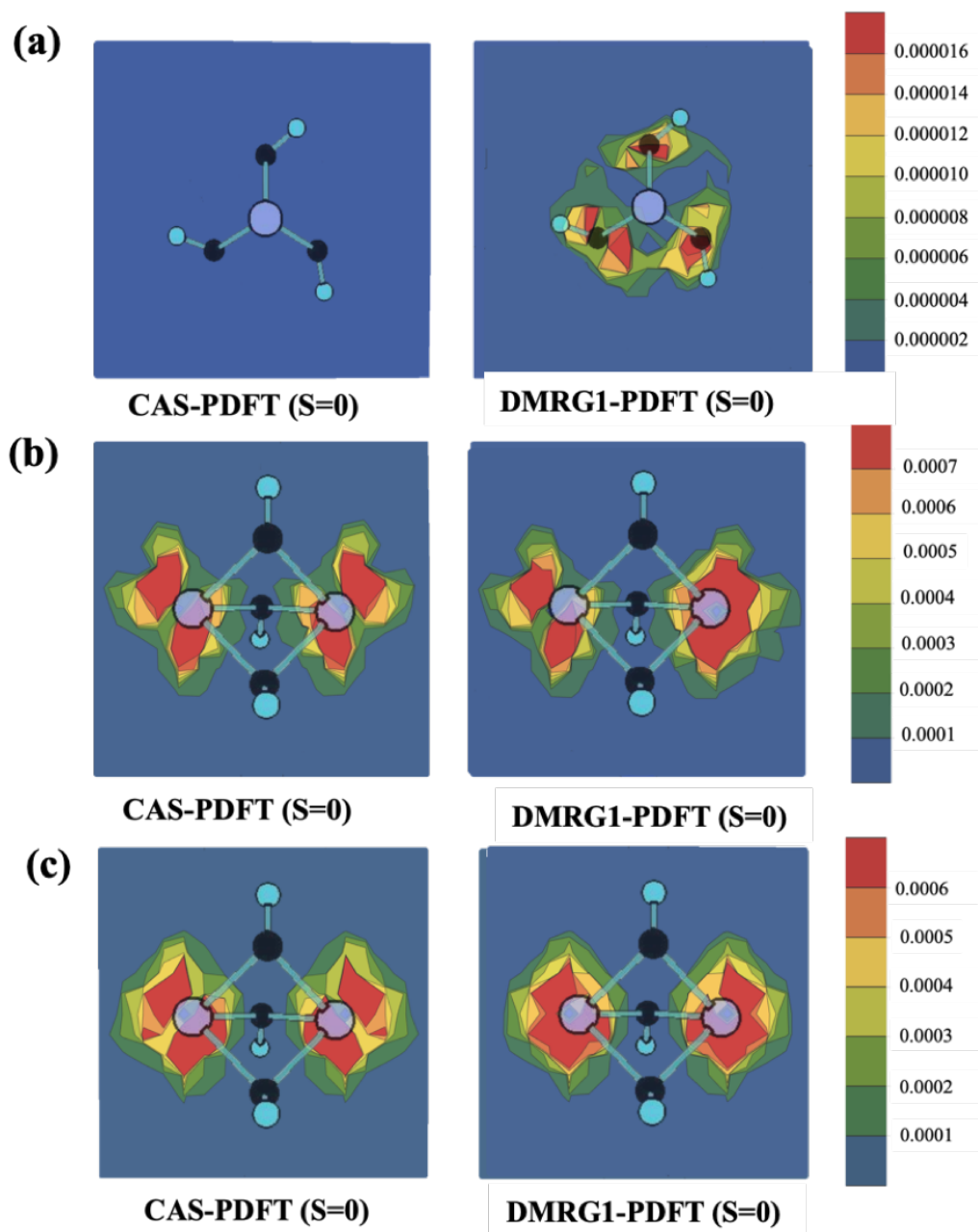


Figure E.10: Unpaired density for CAS-PDFT (left) and DMRG1-PDFT (right) for Kremer's complex in the (a) YZ-plane, (b) XZ-plane, and (c) XY-plane. The colors purple, black and blue corresponds to chromium, oxygen and hydrogen atoms, respectively.

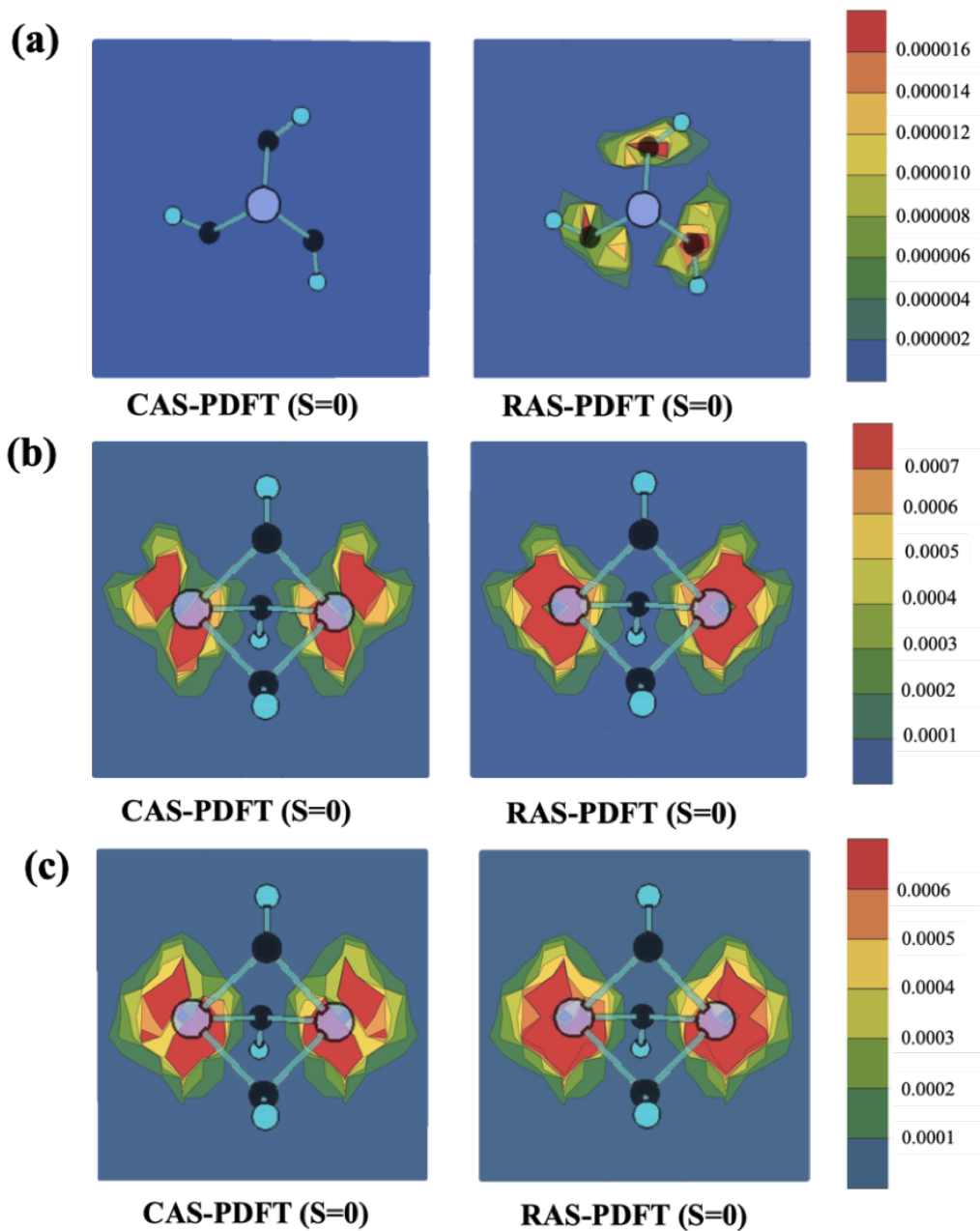


Figure E.11: Unpaired density for CAS-PDFT (left) and RAS-PDFT (right) for Kremer's complex in the (a) YZ-plane, (b) XZ-plane, and (c) XY-plane. The colors purple, black and blue corresponds to chromium, oxygen and hydrogen atoms, respectively.

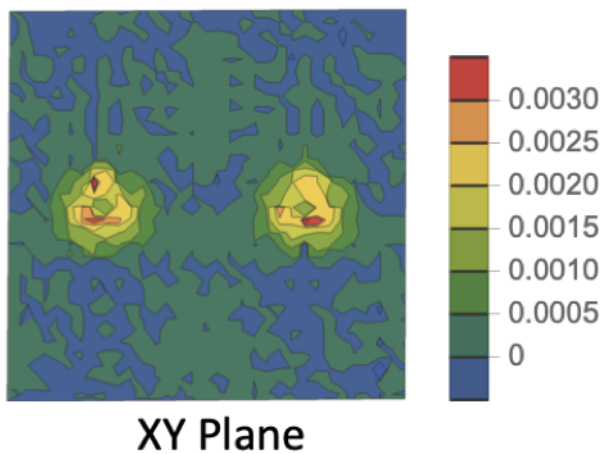
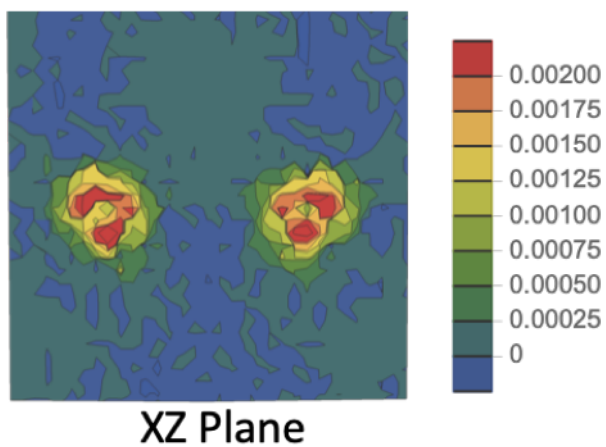
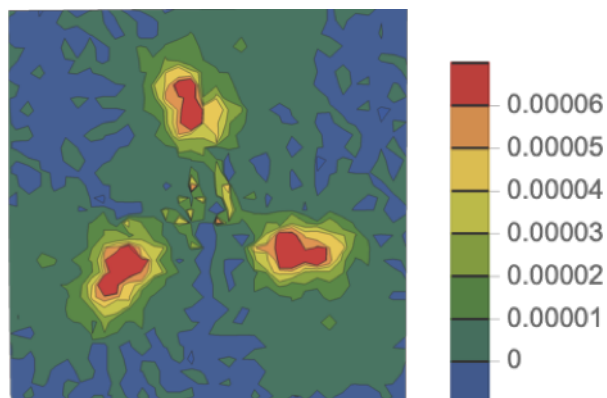


Figure E.12: Unpair electron density difference between $S=3$ (RAS-PDFT) and $S=0$ (RAS-PDFT). The positive values (green-red) shows $S=3$ has larger unpair density in that region while blue color depicts higher unapair density in $S=0$ state.

F. Appendix 6

Table F.1: Energy decomposition (in eV) for H₂ and N₂ molecules at equilibrium and dissociation geometries. MC-PDFT calculations were performed using the tPBE functionals with the cc-pVTZ basis set.

	Active spaces	$V_{nn}(\rho)$	$\langle \hat{T} \rangle$	$V_{ne}(\rho)$	$V_C(\rho)$	E_{ot}	$E^{MC-PDFT}$	E^{CASSCF}	E^{CASPT2}
H ₂ (at r_e)	(2,2)	19.07	31.26	-98.53	35.75	-19.4	-31.84	-31.34	-31.79
	(2,4)	19.23	31.48	-98.74	35.74	-19.67	-31.96	-31.54	-31.83
	(2,6)	19.36	31.77	-99.03	35.9	-20.1	-32.09	-31.82	-31.89
	(2,10)	19.35	31.79	-99.03	35.91	-20.2	-32.19	-31.86	-31.9
	(2,28)	19.46	31.9	-99.28	35.99	-20.4	-32.34	-31.9	-31.9
H ₂ (at $r=20a_0$)	(2,2)	1.36	27.2	-57.12	18.37	-14.65	-24.84	-27.2	-27.2
	(2,4)	1.36	27.2	-57.12	18.37	-14.65	-24.84	-27.2	-27.2
	(2,6)	1.36	27.2	-57.12	18.37	-14.65	-24.84	-27.2	-27.2
	(2,10)	1.36	27.2	-57.12	18.37	-14.65	-24.84	-27.2	-27.2
	(2,28)	1.36	27.2	-57.12	18.37	-14.65	-24.84	-27.2	-27.2
N ₂ (at r_e)	(6,6)	639.29	2969.33	-8255.18	-8255.18	2040.37	-371.04	-2977.23	-2969.29
	(10,8)	638.18	2969.65	-8253.62	-8254.32	2039.74	-371.58	-2977.11	-2970.44
	(10,10)	639.95	2971.13	-8256.77	-8253.63	2039.66	-371.83	-2977.01	-2970.81
N ₂ (at $r=20a_0$)	(6,6)	66.56	2960.46	-7118.19	1459.26	-366.09	-2967.45	-2960.46	-2966.15
	(10,8)	66.56	2960.46	-7118.19	1459.26	-366.09	-2967.45	-2960.46	-2966.2
	(10,10)	66.56	2961.06	-7118.56	1490.29	-366.71	-2967.36	-2961.07	-2966.21

Table F.2: Dissociation energies for H_2 for various choices of active space. Units in eV. The experimental dissociation energy is 4.75 eV.

Active Space	MC-PDFT	CASSCF	CASPT2
(2,2)	4.68	4.13	4.59
(2,4)	4.79	4.34	4.63
(2,6)	4.93	4.66	4.69
(2,10)	5.02	4.66	4.7
(2,28)	5.18	4.7	4.7

Table F.3: Dissociation energies for N_2 for various choices of active space. Units in eV. The experimental dissociation energy is 9.74 eV

Active Space	MC-PDFT	CASSCF	CASPT2
(6,6)	9.78	8.84	9.4
(10,8)	9.81	9.18	9.4
(10,10)	9.8	9.53	9.51

G. List of Acronyms

- ANO-RCC(-VTZP) = Atomic Natural Orbital and Relativistic Core Correlation (Valence Triple-Zeta with Polarization)
- BO = Born-Oppenheimer
- CASSCF = Complete Active Space Self-Consistent Field
- CASPT2 = Second-Order Complete Active Space Perturbation Theory
- CCSD = Couple Cluster Singles Doubles
- cc-(pVTZ/pVQZ) correlation-consistent (polarized with Valence Triple-Zeta/ Quadruple Zeta)
- (Full)CI = (Full) Configuration Interaction
- CSF = Configuration State Function
- def2-(TZVP) = Default -(Triple Zeta Valence Polarization)
- DMRG = Density Matrix Renormalization Group
- GGA = Generalized Gradient Approximation
- HF = Hartree-Fock
- KE = Kinetic Energy
- KS-DFT = Kohn-Sham Density Functional Theory
- LDA = Local Density Approximation
- MC = Multiconfigurational
- MC-PDFT = Multiconfiguration-Pair Density Field Theory
- MCSCF = Multiconfigurational Self-Consistent Field
- MO = Molecular Orbital

- MP2 = Second-Order Møller-Plesset Perturbation Theory
- MR = Multireference
- RASSCF = Restricted Active Space Self-Consistent Field
- RASSI = Restricted Active Space State Interaction
- RASPT2 = Second-Order Restricted Active Space Perturbation Theory
- SCF = Self-Consistent Field
- SD = Slater Determinant
- SR = Single-Reference
- TM = Transition Metal
- WF(T) = Wave Function (Theory)

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