Applications of Coupled Cluster Theory on Infrared Spectroscopy and the Development of Multireference Driven Similarity Renormalization Group

by

CHENYANG LI

(Under the Direction of Henry F. Schaefer III)

Abstract

Ab initio quantum chemistry has evolved into a matured field, with tools capable of providing reliable predictions of molecular properties. Notwithstanding the progress, much effort has been investigated in developing methodologies that address very challenging systems. Herein, three studies are presented, including both the application and development of electronic structure theory. First, a study on nonahydridorhenate dianion and molecular potassium and sodium rhenium hydride is reported using coupled cluster theory. Second, the potential energy surface of the methylene internal rotation is carefully investigated for n-propyl radical. The fundamental vibrational frequencies are predicted using second-order vibrational perturbation theory, and energy levels of the methylene torsional motion are also determined. Third, a multireference generalization of the driven similarity renormalization group is introduced. A perturbative analysis of the corresponding equations leads to an efficient and intruder-free multireference perturbation theory.

INDEX WORDS: *ab initio* quantum chemistry, electronic structure theory, coupled cluster theory, driven similarity renormalization group, many-body perturbation theory, vibrational perturbation theory, focal point analysis, nonahydridorhenate dianion, *n*-propyl radical

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DEDICATION

To my parents and friends

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Chapter 1

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Computational quantum chemistry has matured from a highly specialized field into a full-fledged, ubiquitous and indispensable tool that is capable of challenging experimental findings. Thermochemical energetics can now be predicted within chemical accuracy (< 1.0 kcal mol⁻¹) for most small molecules using the state-of-the-art electronic structure theory—a tremendous feat.¹ Despite the successes over the past several decades, electronic structure theories are still developing to provide more accurate results and more efficient implementations for challenging systems such as medium- to large-sized biomolecules,² transition-metal clusters,³ and electronic excited states.^{4,5} In this chapter, some of the most widely used theoretical methods are briefly overviewed, including single reference coupled cluster theory,⁶ focal point analysis,⁷ and second-order vibrational perturbation theory.⁸ Moreover, the recently proposed driven similarity renormalization group approach is also introduced.⁹

The central problem in quantum chemistry is to find accurate approximations for eigenfunctions and eigenvalues of the Schrödinger equation.^{10–12} The most general form of the Schrödinger equation is the time-dependent expression,

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t) = \hat{H}\Psi(\mathbf{x},t), \qquad (1.1)$$

where \hbar is the reduced Planck constant, \hat{H} is the Hamiltonian operator of the system, and $\Psi(\mathbf{x}, t)$ is the wave function that depends on the positions of particles (\mathbf{x}) and the time (t). For a time-independent Hamiltonian, the solution for Eq. (1.1) may be expressed as,

$$\Psi(\mathbf{x},t) = e^{-itH/\hbar}\psi(\mathbf{x}),\tag{1.2}$$

where $e^{-it\hat{H}/\hbar}$ is the time-evolution operator, and $\psi(\mathbf{x})$ obeys the time-independent Schrödinger

equation,

$$\hat{H}\psi(\mathbf{x}) = E\psi(\mathbf{x}). \tag{1.3}$$

In the above equation, E gives the energy of the system, and for an N-electron M-atom system the non-relativistic Hamiltonian with atomic unit is,

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \sum_{A=1}^{M} \frac{\nabla_{A}^{2}}{2M_{A}} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{r_{AB}}.$$
 (1.4)

In the above equation, r_{xy} corresponds to the distance between particles x and y; M_A is the mass ratio between nucleus A and an electron, and Z_A is the atomic number of nucleus A.

Unfortunately, there is no analytic solution for the time-independent Schrödinger equation except for hydrogenic atoms. A common simplification for Eq. (1.3) is to impose the Born-Oppenheimer (BO) approximation, which is based on the wide separation in classical time scales of electronic and nuclear motion due to the enormous mass difference between nuclei and electrons.^{11–13} Under the BO approximation, $\psi(\mathbf{x})$ is written as $\psi(\mathbf{x}) = \psi_{e}(\mathbf{r}; \mathbf{R})\psi_{nuc}(\mathbf{R})$, where \mathbf{R} is a set of nuclear coordinates and \mathbf{r} is a set of electronic coordinates. As a result, Eq. (1.3) can be solved in two steps: (1) for a fixed molecular geometry, determine the electronic Schrödinger equation for $\psi_{e}(\mathbf{r}; \mathbf{R})$, which is \mathbf{R} -dependent parametrically,

$$\left(-\sum_{i=1}^{N}\frac{\nabla_{i}^{2}}{2}-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_{A}}{r_{iA}}+\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}\right)\psi_{e}(\mathbf{r};\mathbf{R})=E_{e}(\mathbf{R})\psi_{e}(\mathbf{r};\mathbf{R}),$$
(1.5)

and (2) solve the nuclear Schrödinger equation on the potential established by electrons,

$$\left(-\sum_{A=1}^{M} \frac{\nabla_A^2}{2M_A} + E_{\text{total}}(\mathbf{R})\right) \psi_{\text{nuc}}(\mathbf{R}) = E_{\text{nuc}} \psi_{\text{nuc}}(\mathbf{R}),$$
(1.6)

where the total energy $[E_{\text{total}}(\mathbf{R})]$ is given by $E_{\text{total}}(\mathbf{R}) = E_{\text{e}}(\mathbf{R}) + \sum_{A=1}^{M} \sum_{B>A}^{M} (Z_A Z_B / r_{AB}).$

In *ab initio* electronic structure theory, the simplest wave function model is the Hartree-Fock (HF) model.^{12,14} The HF approximation employs a wave function consisting of a single configuration of spin orbitals [a single Slater determinant (SD) or a single configuration state function (CSF)]. For an *N*-electron system with a spin-orbital basis $\{\phi_p\}$ of dimension *L*, a single SD wave function is

$$\psi_{\rm SD}(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \cdots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix}$$
(1.7)

where \mathbf{x}_j is the composite coordinate of electron j, which contains both its spatial (\mathbf{r}_j) and spin (ω_j) coordinates. Those orbitals appearing in the HF wave function are called occupied orbitals and the rest L - N orbitals are unoccupied (virtual). The electronic energy is minimized with respect to the variations of the occupied spin orbitals. The resulting optimal orbitals are eigenfunctions of the Fock operator with orbital energies as eigenvalues,

$$f(i)\phi(\mathbf{x}_i) = \varepsilon\phi(\mathbf{x}_i),\tag{1.8}$$

$$f(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1} \frac{Z_A}{r_{iA}} + \sum_{k \neq j} [J_k(i) - K_k(i)], \qquad (1.9)$$

where J_k and K_k are Coulomb and exchange operators, respectively. Note that f(i) is a oneelectron operator, and the electron-electron interaction is expressed in an average way such that the *i*-th electron experiences the potential created by all other electrons. In practice, a finite set of spacial molecular orbitals $\{\chi_i(\mathbf{r})\}$ is used, and each $\chi_i(\mathbf{r})$ is usually expanded by a linear combination of Gaussian-type atomic basis functions. The introduction of a basis leads the HF equation [Eq. (1.8)] to the Roothaan equation,¹⁵ which can be solved iteratively. This iterative procedure is called the self-consistent field (SCF) procedure.

The Hartree-Fock approximation is a very successful model that has been widely applied to qualitative studies for molecular systems. Most of the total electronic energy can be recovered from the HF wave function. The missing electronic energy is known as electron correlation, and is due to neglecting the instantaneous interactions between electrons in the HF approximation.^{12,14} Since SDs are proper N-electron basis functions for expanding any N-electron wave function, a systematic approach to include electron correlations is expressing the wave function as a linear combination of SDs with different electronic configurations. There are two approaches to address the electron correlation problem: (1) when HF approximation provides a qualitative description of the wave function, correlations can be captured by including excited configurations based on the HF reference; (2) when the strong mixing of near-degenerate configurations occurs, a multiconfigurational wave function is required to yield a qualitative description of the system. One usually speaks of dynamic correlations for the first approach and static correlations for the second, ^{14,16,17} yet there is no strict distinction between the two. The dynamic correlation is efficiently recovered by configuration interaction (CI), perturbation theory, and coupled cluster theory, while the static correlation is generally included by an active space.

1.2 COUPLED CLUSTER THEORY

Coupled cluster (CC) theory provides an efficient way to recover dynamic correlations. CC is firstly introduced to quantum chemistry by Čížek in the late $1960s^{6,18}$ and together with Paldus in the early 1970s.^{19,20} During the past half century, CC has been well appreciated to yield highly reliable results with affordable computational cost. Indeed, coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)],²¹ perhaps the most popular method in the CC family, is always referred as the "gold standard" in the complete basis set limit.²² Nowadays, the CC hierarchy based on a HF reference has been established,^{23–25} and the research focus has moved on to the multireference generalization of CC theory.²⁶ Due to the devastating scaling of CC methods, approximating the original CC ansatz for larger systems is also an active area.²⁷ Here we review the single reference CC (SRCC) theory in brief.

The coupled cluster wave function is obtained by applying the exponential excitation operator on the HF wave function,

$$|\Psi_{\rm CC}\rangle = e^T |\Psi_{\rm HF}\rangle, \qquad (1.10)$$

where \hat{T} is the excitation operator and if truncated at certain level n,

$$\hat{T} = \sum_{k=1}^{n} \hat{T}_k.$$
(1.11)

In Eq. (1.11), the k-body component of \hat{T} is defined as

$$\hat{T}_k = \frac{1}{(k!)^2} \sum_{ij\cdots}^{\mathbf{O}} \sum_{ab\cdots}^{\mathbf{V}} t^{ab\cdots}_{ij\cdots} \hat{a}^{\dagger}_a \hat{a}^{\dagger}_b \cdots \hat{a}_j \hat{a}_i, \qquad (1.12)$$

where ij and ab correspond to occupied and virtual orbital indices (i.e. $i, j \in \mathbf{O}$ and $a, b \in \mathbf{V}$), respectively. The cluster amplitude $t_{ij\cdots}^{ab\cdots}$ is defined as $t_{ij\cdots}^{ab\cdots} = \langle \Psi_{ij\cdots}^{ab\cdots} | \hat{T}_k | \Psi_{\text{HF}} \rangle$, where $\Psi_{ij\cdots}^{ab\cdots}$ is a k-tuple excited determinant. The truncation level n of the excitation operator represents the hierarchy of CC theory. For example, n = 2 recovers the CC singles and doubles (CCSD) method; n = 3 reproduces the CC singles, doubles and triples (CCSDT) method, and n = N recaptures the full configuration interaction (FCI) in which electrons are arranged in all possible ways for a finite basis set.

To obtain the electronic energy, we insert Eq. (1.10) to the electronic Schrödinger equation

[Eq. (1.5)],

$$\hat{H} |\Psi_{\rm CC}\rangle = \hat{H} e^{\hat{T}} |\Psi_{\rm HF}\rangle = E e^{\hat{T}} |\Psi_{\rm HF}\rangle, \qquad (1.13)$$

and the energy is given by $E = \langle \Psi_{\rm HF} | \hat{H} (1 + \hat{T} + \hat{T}^2/2) | \Psi_{\rm HF} \rangle$ under the intermediate normalization condition.^{23–25} Alternatively, Eq. (1.13) can be written as,

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_{\rm HF}\rangle = \bar{H}|\Psi_{\rm HF}\rangle = E|\Psi_{\rm HF}\rangle, \qquad (1.14)$$

where the similarity transformed Hamiltonian \overline{H} is introduced and may be expanded using the Baker-Campbell-Hausdorff (BCH) formula,

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}], \hat{T}].$$
(1.15)

This BCH expansion naturally terminates at the term of quadruply nested commutator, and the reason can be found in Refs. 23–25. The electronic energy is therefore,

$$E = \langle \Psi_{\rm HF} | \bar{H} | \Psi_{\rm HF} \rangle, \qquad (1.16)$$

and cluster amplitudes are determined by left projecting the excited determinants,

$$0 = \langle \Psi_{ij\cdots}^{ab\cdots} | \bar{H} | \Psi_{\rm HF} \rangle \,. \tag{1.17}$$

Coupled cluster theory is closely related to many-body perturbation theory (MBPT).^{23–25} A perturbative analysis of the CCSD equations shows that CCSD is complete up to the third order of MBPT, but fails to include triple excitation contributions for completing the fourth-order MBPT (MBPT4). In order to recover the full MBPT4, the $E_T^{[4]}$ term is appended to the CCSD energy. The resulting theory is called CCSD[T].^{23,28} The popular CCSD(T) contains

an additional energy contribution $E_{ST}^{[5]}$ that appears at the fifth order and involves both single and triple excitations. This fifth-order term has made CCSD(T) the most successful method in the CC family, yet the reason for including this particular term is not straightforward. One interesting explanation originates from an unusual perturbative analysis, where CCSD energy is treated as the zeroth-order quantity.²⁹ This analysis shows that $E_T^{[4]}$ and $E_{ST}^{[5]}$ naturally arrive together in the third order, which provides a rationalization for the CCSD(T) theory.

1.3 DRIVEN SIMILARITY RENORMALIZATION GROUP

Besides the coupled cluster theory described above, renormalization group (RG) approach has become a new active area in *ab initio* quantum chemistry. The most famous RG theory is the density matrix renormalization group (DMRG),³⁰ which is introduced to quantum chemistry in the late 1990s.^{31,32} DMRG is able to efficiently recover static correlations, and DMRG performs extraordinarily well for noncritical one-dimensional systems. Another widely-used RG approach, yet less familiar to quantum chemists, is the similarity renormalization group (SRG) or flow-equation theory.^{33–35} SRG is developed based on continuous unitary transformations that suppress off-diagonal matrix elements of the Hamiltonian, leading towards a band-diagonal form. Solving the SRG equations requires integrations of the differential equations, which is not numerically robust. From this perspective, the driven similarity renormalization group (DSRG) approach is proposed recently.⁹ In this section, the singlereference SRG equations and the fundamental ideas of DSRG are overviewed. A detailed description of the DSRG and its multireference generalization are given in Chapter 4.

The SRG Hamiltonian $[\bar{H}(s)]$ is brought to a diagonal form via a continuous unitary transformation $[\hat{U}(s)]$ on the original bare Hamiltonian \hat{H} ,

$$\bar{H}(s) = \hat{U}(s)\hat{H}\hat{U}^{\dagger}(s), \qquad (1.18)$$

where s is called the flow parameter and can be related to an energy cutoff. The following boundary conditions are required, (1) $\bar{H}(0) = \hat{H}$, and (2) $\bar{H}(\infty)$ has a structure that the reference is fully decoupled with its excited configurations. The derivative of $\bar{H}(s)$ with respect to s is given by the generator $\eta(s)$ of the transformation $\hat{U}(s)$,

$$\frac{d\bar{H}(s)}{ds} = [\eta(s), \bar{H}(s)], \qquad (1.19)$$

and $\eta(s)$ is anti-Hermitian $\eta(s) = \frac{d\hat{U}(s)}{ds}\hat{U}^{\dagger}(s) = -\eta^{\dagger}(s)$. There are different ways to parametrize $\eta(s)$. The canonical form introduced by Wegner³⁵ is $\eta(s) = [\bar{H}^{d}(s), \bar{H}(s)]$, where $\bar{H}^{d}(s)$ is the diagonal part of the SRG Hamiltonian.

The perturbative analysis of the single-reference SRG leads to a similar second-order energy expression to the Møller-Plesset perturbation theory (MP2),

$$E^{(2)}(s) = \frac{1}{4} \sum_{ijab} \frac{|\langle ij||ab\rangle|^2}{\Delta^{ij}_{ab}} [1 - e^{-2s(\Delta^{ij}_{ab})^2}], \qquad (1.20)$$

where $\langle ij||ab \rangle$ is the antisymmetrized two-electron integral in physicists' notation, and Δ_{ab}^{ij} is the Møller-Plesset energy denominator expressed in terms of orbital energies $\Delta_{ab}^{ij} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$. The superiority for Eq. (1.20) over the original MP2 is that $E^{(2)}$ will not diverge even if Δ_{ab}^{ij} goes to zero for finite values of s. Also notice that for $|\Delta_{ab}^{ij}|$ greater than the energy cutoff $\Lambda = 1/\sqrt{2s}$, the second-order energy is barely changed compared to regular MP2 energy. Contrarily, $E^{(2)}(s)$ is approximately zero when $|\Delta_{ab}^{ij}| \ll \Lambda$. As a consequence, s can be used to separate different energy scales.

At this point, it is clear that SRG is numerical robust even at perturbative level, yet solving the set of differential equations will loose this robustness. Thus, we would like to formulate a theory that keeps the good and discards the bad of the SRG, which has been the fundamental motivation to develop the DSRG.⁹ In DSRG, the unitary operator $\hat{U}(s)$ is parameterized as the exponential of an anti-Hermitian operator $\hat{A}(s)$:

$$\hat{U}(s) = e^{\hat{A}(s)},$$
 (1.21)

where $\hat{A}(s)$ is truncated to particle rank n, i.e. $\hat{A}(s) = \sum_{k=1}^{n} \hat{A}_{k}(s)$, and its k-body component is related to the k-body excitation operator in Eq. (1.12) $\hat{A}_{k}(s) = \hat{T}_{k}(s) - \hat{T}_{k}^{\dagger}(s)$. Analogous to the SRG, we require that $\hat{U}(0) = 1$ which is trivially satisfied by $\hat{A}(0) = 0$, and $\hat{U}(\infty)$ fully decouples the reference from excited states.

DSRG postulates that the Hamiltonian is driven by an Hermitian source operator $\hat{R}(s)$. Specifically, the non-diagonal part of the transformed Hamiltonian $[\bar{H}(s)]_{\rm N}$,^{36,37} is equal to the source operator for all values of s:

$$[\bar{H}(s)]_{\rm N} = \bar{R}(s).$$
 (1.22)

Once the source operator is specified, the DSRG equation [Eq. (1.22)] implicitly defines the unitary transformation $\hat{U}(s)$. The electronic energy is obtained by taking the expectation value of the DSRG transformed Hamiltonian:

$$E(s) = \langle \Psi_{\rm HF} | \bar{H}(s) | \Psi_{\rm HF} \rangle.$$
(1.23)

Note that Eqs. (1.22) and (1.23) are evaluated at fixed values of the flow parameter and do not require numerical integration as in the case of the SRG.

1.4 FOCAL POINT ANALYSIS

Chemical accuracy (1.0 kcal mol^{-1}) has long been pursued in computational thermochemistry, which requires the usage of electron-correlation methods and large basis sets. The most widely used approach to achieve chemical accuracy is perhaps the Gaussian-n (Gn, n = 2, 3, 4) theory,³⁸ which yields a typical accuracy of 1 - 2 kcal mol⁻¹. However, a few kcal mol⁻¹ errors of the energetics will result in a huge difference for chemical kinetics, such as rate constants and branching ratios. Besides, some methods in the Gn family involve empirical parameters. Thus, a more accurate *ab initio* method is strongly needed, and focal point analysis (FPA) is such an approach that is able to yield subchemical accuracy (0.1 kcal mol⁻¹) by systematically extrapolating the electronic energy to the *ab initio* limit.^{7,39–43}

A core technique used in FPA is the basis set extrapolation. In FPA, a series of Dunning's correlation-consistent cc-pVXZ (or aug-cc-pVXZ or cc-pCVXZ) basis sets⁴⁴⁻⁴⁶ is employed for extrapolation, where X is the cardinal number—the maximum angular momentum function presents in the basis set. The correlation-consistent basis sets are designed according to the principal expansion^{14,17,47} which guarantees a smooth convergence to the complete basis set (CBS) limit when increasing the value of X. For hydrogen atom, Kutzelnigg has shown that one-electron even-tempered Gaussian basis sets converge according to $\sim e^{-a\sqrt{n}}$, where a is a parameter, and n is the dimension of the basis set.⁴⁸ FPA commonly utilizes an another extrapolating formula based on numerical observations, ^{49,50}

$$E_{\rm HF}(X) = E_{\rm HF}^{\infty} + Ae^{-BX}, \qquad (1.24)$$

where A, B, and $E_{\rm HF}^{\infty}$ are fitting parameters, and $E_{\rm HF}^{\infty}$ is the extrapolated CBS HF energy.

For two-electron convergence, the basis set incompleteness error decreases frustratingly slow because expanding the wave function using Slater determinants fails to satisfy the electron cusp condition.⁵¹ Consequently, the correlation energy $[E_{\text{corr}}(X) = E_{\text{method}}(X) - E_{\text{HF}}(X)]$ converges to the CBS limit according to^{52,53}

$$E_{\rm corr}(X) = E_{\rm corr}^{\infty} + CX^{-3}, \qquad (1.25)$$

where C and E_{corr}^{∞} are parameters to be determined, and the latter is the extrapolated correlation energy in the CBS limit. The electron correlation methods employed in FPA follow the hierarchy of MP2, CCSD, CCSD(T), CCSDT, CCSDT(Q), etc. For higher levels of theories, such as CCSDT and CCSDT(Q), it is generally unattainable to use large enough basis sets for extrapolations. In such cases, the additive argument is assumed. Namely, the energy difference is independent of basis set.

The focal point approach is computationally economical and flexible. FPA uses the geometry optimized at the highest possible level of theory throughout, and no re-optimization is performed. Observing the convergence step by step enables one to estimate the error bars and to target the source of error immediately. One may stop further computations whenever the desired accuracy is reached. Moreover, other extrapolation formulae may be employd in FPA.⁵⁴ In practice, additional corrections, such as diagonal Born-Oppenheimer correction⁵⁵ and first-order relativistic corrections, ⁵⁶ are appended to the final extrapolated energy to account approximations made in solving the electronic Schrödinger equation [Eq. (1.5)].¹ If enthalpies are of interest, the zero-point vibrational energy (ZPVE) should also be included. Pragmatic examples of FPA are given in Chapter 3.

1.5 Second-Order Vibrational Perturbation Theory

An infrared spectrum originates when a molecule absorbs infrared radiations that are in resonance with the transitions between vibrational levels. In order to obtain the vibrational levels theoretically, the nuclear Schrödinger equation is solved on a potential energy surface (PES) of dimension 3N - 6 (3N - 5) for an N-atom nonlinear (linear) molecule. The substantial degrees of freedom make the complete characterization of PES extremely difficult,⁵⁷ and thus simplifications are demanded. In the most common cases, the nuclear motion is considered to be restricted around the equilibrium position, and the potential energy can be

expanded around this equilibrium,

$$V = V_0 + \frac{1}{2} \sum_{ij} f^{ij} R_i R_j + \frac{1}{6} \sum_{ijk} f^{ijk} R_i R_j R_k + \frac{1}{24} \sum_{ijkl} f^{ijkl} R_i R_j R_k R_l + \dots$$
(1.26)

where R_i describes the displacement from its equilibrium, and $\{R_i\}$ forms a set of complete and nonredundant nuclear displacement coordinates.⁵⁷ In Eq. (1.26), f^{ij} , f^{ijk} , and f^{ijkl} correspond to quadratic, cubic and quartic force constants, respectively. The general form of a *n*-th order force constant is given by

$$f^{ij\cdots} = \underbrace{\frac{\partial^n V_0}{\partial R_i \partial R_j \cdots}}_{n}.$$
(1.27)

Usually, a set of normal coordinates is used to decouple the classical vibrational motions, and each vibrational mode is treated as a harmonic oscillator, i.e. V is truncated after the quadratic term in Eq. (1.26). This harmonic approximation always overestimates the fundamental transition, and empirical scaling factors are introduced to reproduce experimental values.⁵⁸ A more elegant way is to include anharmonic effect by considering higher-order force constants in the expansion as long as the harmonic model is an appropriate zerothorder approximation. This expansion naturally leads to the idea of perturbation theory. In second-order vibrational perturbation theory (VPT2), the zeroth-order Hamiltonian is identical to the one under the harmonic approximation, and the cubic and quartic force constants as well as Coriolis effects and centrifugal distortions are treated as the perturbation.^{8,59,60}

The vibrational energy levels for asymmetric-top molecules are given by

$$G(v) = G_0 + \sum_{i} \omega_i \left(v_i + \frac{1}{2} \right) + \sum_{i \ge j} \chi_{ij} \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right) + \cdots, \qquad (1.28)$$

where higher-order terms are neglected. In the above equation, v_i is the vibrational quantum

number of the *i*-th mode, ω_i is the *i*-th harmonic frequency, χ_{ij} is the vibrational anharmonic constant, and G_0 is a scalar term independent with quantum numbers. The term G_0 in Eq. (1.28) is almost universally neglected, and it contains kinetic energy elements as well as contributions from cubic and quartic force constants.^{1,42} According to Eq. (1.28), the expression of ZPVE is given by:

$$G(0) = G_0 + \sum_{i} \frac{\omega_i}{2} + \sum_{i \ge j} \frac{\chi_{ij}}{4},$$
(1.29)

and the *i*-th fundamental transition (anharmonic frequency) is:

$$\nu_i = G(\nu_i = 1) - G(\nu_i = 0) = \omega_i + 2\chi_{ii} + \frac{1}{2} \sum_{i \neq j} \chi_{ij}.$$
(1.30)

The expressions of anharmonic constants for asymmetric-top molecules are

$$\chi_{ii} = \frac{1}{16} \phi_{iiii} - \sum_{j} \frac{\phi_{iij}^2 (8\omega_i^2 - 3\omega_j^2)}{16\omega_j (4\omega_i^2 - \omega_j^2)},\tag{1.31}$$

$$\chi_{ij} = \frac{1}{4} \phi_{iijj} - \sum_{k} \frac{\phi_{iik} \phi_{jjk}}{4\omega_k} - \sum_{k} \phi_{ijk}^2 \frac{\omega_k (\omega_i^2 + \omega_j^2 - \omega_k^2)}{2\Delta_{ijk}} + \sum_{\alpha} B_{\alpha} (\zeta_{ij}^{\alpha})^2 \left(\frac{\omega_i}{\omega_j} + \frac{\omega_j}{\omega_i}\right), \quad (1.32)$$

where $\Delta_{ijk} = (\omega_i + \omega_j + \omega_k)(-\omega_i + \omega_j + \omega_k)(\omega_i - \omega_j + \omega_k)(\omega_i + \omega_j - \omega_k)$, B_{α} is the equilibrium rotational constant, ζ_{ij}^{α} is the Coriolis zeta constant that couples normal coordinates Q_i and Q_j through the rotation about axis α , and $\phi_{ij\dots}$ is the force constant under dimensionless normal coordinates.^{57,60} Careful examinations on Fermi and Darling–Dennison resonances^{8,61} are required in VPT2 calculations. The resonance problems are routinely solved by setting up the effective Hamiltonian with deperturbed diagonal elements.^{8,62–64} Finally, we note that VPT2 equations for symmetric-top molecules have also been derived.⁵⁹

1.6 **PROSPECTUS**

We continue by presenting the first post-Hartree-Fock study on nonahydridorhenate dianion $[\text{ReH}_9]^{2-}$ in Chapter 2. The equilibrium geometries and vibrational frequencies of $[\text{ReH}_9]^{2-}$ and $M_2\text{ReH}_9$ (M = Na, K) sandwich complexes are investigated using coupled cluster methods with the new generation energy-consistent relativistic pseudopotentials and correlation-consistent basis sets. Second-order vibrational perturbation theory (VPT2) is used to address the anharmonic effect. The predicted geometries and vibrational frequencies of $[\text{ReH}_9]^{2-}$ generally agree with experiments, and including the counterions improves the predictions of vibrational frequencies in the Re–H stretching region.

In Chapter 3, we carefully studied the potential energy surface (PES) of the methylene hindered internal rotation for *n*-propyl radical. Four unique stationary points are characterized on the PES, and their relative energies are obtained by highly accurate focal point analysis. The energy levels of the methylene torsional motion are subsequently solved by the one-dimensional vibrational Schödinger equation using the numerically exact Cooley-Numerov approach. The band origins for eleven vibrational modes that are largely uncoupled with the methylene internal rotation are predicted by VPT2.

In Chapter 4, we proposed the multireference (MR) generalization of the driven similarity renormalization group (DSRG) approach. In order to gain some insight of the MR-DSRG theory, a perturbative analysis is performed at the second order. The resulting perturbation theory, termed DSRG-MRPT2, prevents the intruder-state problem, and yields results of similar accuracy to other MR perturbation theories. A recommended range of the flow parameter is also determined, which provides a benchmark for future computations.

Chapter 2

The Remarkable $[ReH_9]^{2-}$ Dianion: Molecular Structure and Vibrational Frequencies^{*}

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2.1 Abstract

The equilibrium geometries and vibrational frequencies of the extraordinary $[\text{ReH}_9]^{2^-}$ dianion (D_{3h} symmetry) are investigated using Hartree-Fock (HF) theory, coupled-cluster theory with single and double excitations (CCSD) and coupled-cluster theory with single, double and perturbative triple excitations [CCSD(T)]. The new generation of energy-consistent relativistic pseudopotentials and correlation consistent basis sets [Re: cc-pVXZ-PP and H: cc-pVXZ (X = D, T, Q)] are used. Anharmonicity was considered using second-order vibrational perturbation theory. The predicted geometries and vibrational frequencies generally agree with experimental findings. In order to stabilize the [ReH₉]²⁻ dianion, the M_2 ReH₉ (M = Na, K) sandwich complexes (D_{3h} symmetry) are studied at the CCSD(T)/VTZ (VTZ = Re: cc-pVTZ-PP; H, Na, K: cc-pVTZ) level of theory. Compared to the [ReH₉]²⁻ dianion, the predicted vibrational frequencies involving Re-H stretching modes are improved, indicating the importance of considering counterions in electronically dense systems. The natural bond orbital analysis shows that H only bonds with the center Re, and the 5*d* orbitals of Re and 1*s* orbitals of H are major factors for the covalent Re-H bonding.

2.2 INTRODUCTION

Nonahydridorhenate dianion, $[\text{ReH}_9]^{2-}$, represents the first example of a nine-coordinate soluble homoleptic transition metal hydride. Its structure is the well-known faced-tricapped trigonal prism. $[\text{ReH}_9]^{2-}$ is a remarkable dianion not only for the unusual coordination, but also for the serpentine path leading to its discovery. An excellent review by R. B. King⁶⁵ details the discovery of $[\text{ReH}_9]^{2-}$. Only a brief overview is provided here.

Rhenium was discovered in the mid 1920s and named after the river Rhine.^{66–68} Its existence was predicted by Dmitri Mendeleev who placed rhenium together with manganese and halogens in his original periodic table, because elements were organized according to the number of valence electrons.⁶⁹ In 1937, to pursue the lower valence state of rhenium, Lundell and Knowles utilized amalgamated zinc to reduce an acidified perrhenate (ReO_4^-) solution.⁷⁰ Potentiometric titration of the resulting solution indicated the presence of a rhenium anion (Re^-), which was designated "rhenide". The name is analogous to halide, since the lowest valency of rhenium "followed" the halogen subgroup in Group VII of the periodic table described previously. In 1947, Pauling suggested a structure of "rhenide" in which Re(-I)might bond with four water molecules to form a square planar geometry, since Re(-I) is isoelectronic with Pt(II).⁷¹ The first solid "rhenide", KRe-4H₂O, was isolated by Kleinberg and co-workers using potassium metal as the reducing agent in aqueous ethylenediamine solution.^{72,73} Shortly thereafter, Ginsberg and co-workers revealed that the solid "rhenide" is actually a soluble potassium rhenium hydride.^{74–76} They also eliminated the possibility of the existence for "rhenide" by analyzing the UV absorption spectrum.⁷⁷ Eventually, in 1964, almost thirty years after the discovery of "rhenide", potassium rhenium hydride was structurally characterized as K₂ReH₉ ($P\bar{6}2m$ space group) from X-ray crystallography and neutron diffraction studies.^{78,79}

Inspired by the discovery of K_2ReH_9 , other types of cations have been used to extend the $[ReH_9]^{2-}$ family, including Na₂ReH₉, NaKReH₉, $((C_2H_5)_4N)_2ReH_9$, BaReH₉.^{80,81} For elements of Group VII, K_2TcH_9 is the only known technetium compound incorporating similar nine coordinate $[TcH_9]^{2-}$ units.⁸² No analogous manganese compound has yet been reported, while theoretical studies have suggested its viability.^{83,84} Among the above mentioned compounds, BaReH₉ has the highest (4.5:1) hydrogen to metal ratio. Unfortunately, because of the high atomic weight of the metal atoms, the hydrogen content is only 2.7 wt%, too small for use as a hydrogen storage material.⁸⁵

Much experimental work has been devoted to understanding the internal vibrations of the $[\text{ReH}_9]^{2-}$ salts. Ginsberg and coworkers reported the solid-state IR spectra of $M_2\text{ReH}_9$ $[M_2 = \text{Na}_2, \text{NaK}, \text{K}_2, ((\text{C}_2\text{H}_5)_4\text{N})_2]$ where much fewer bands were observed than the number of D_{3h} symmetry allowed transitions.^{75,80} To augment the limited IR data, White and Wright measured inelastic neutron scattering (INS) spectra for K₂ReH₉ and Na₂ReH₉ at 90 K.⁸⁶ The INS spectroscopy, being unrestricted by selection rules, strongly overlapped with the IR spectra in the bending region. Shortly thereafter, Creighton and Sinclair measured the Raman spectrum of K₂ReH₉ both in an oriented single crystal at 90 K and in aqueous solution at 300 K.⁸⁷ Moreover, they obtained the first fairly complete vibrational spectrum of the [ReH₉]²⁻ dianion by combining the IR, INS and Raman spectra of K₂ReH₉. More recently, Parker *et al.* investigated the vibrational spectrum of BaReH₉ using IR, Raman and INS spectroscopies and observed fewer bands than expected.⁸⁸ This was interpreted as the result of accidental degeneracies between the "missing" and "observed" modes since all vibrations should be present in the INS spectrum.

Numerous theoretical researches have considered the structure and properties of the $[\text{ReH}_9]^{2-}$ dianion. In 1992, Shen and Partridge reported the first *ab initio* computations on the isolated $[\text{ReH}_9]^{2-}$ dianion using all-electron non-relativistic Hartree-Fock theory.⁸⁹ The predicted geometry and vibrational frequencies showed only adequate agreement with the above-described experimental work. Parker and co-workers studied the isolated dianion using density functional theory (DFT) and encountered analogous discrepancies between theory and experiment.⁸⁸ They also investigated the BaReH₉ unit cell with periodic DFT computations that broadly reproduced the experimental fundamental transitions and concluded that periodic computations were required to incorporate the long-range Coulomb interactions. Other plane-wave based DFT calculations aimed to understand the electronic structure,^{83,90} and to predict the structural changes under high pressure for BaReH₉, discussing its potential as a high-temperature superconductor.⁹¹

In the current research, we have employed state-of-the-art theoretical methods to optimize the molecular structure and to predict the vibrational frequencies of the isolated $[\text{ReH}_9]^{2-}$ dianion and the $M_2\text{ReH}_9$ (M = Na, K) sandwich complexes. Specifically, we report the first post-Hartree-Fock studies using coupled-cluster theory to consider electron correlation effects. Moreover, relativistic effects are included with the new energy-consistent pseudopotentials of Peterson and co-workers. We have also analyzed the natural bond orbitals to understand the electronic nature of these systems.

2.3 Computational Methods

The geometry optimization of the $[ReH_9]^{2-}$ dianion was initially carried out using Hartree-Fock (HF) theory, coupled-cluster theory with single and double excitations (CCSD)⁹² and CCSD with perturbative triple excitations $[CCSD(T)]^{21,93,94}$ under D_{3h} symmetry constraints. All D_{3h} structures were subsequently shown to be equilibrium geometries by vibrational analyses. The Dunning correlation consistent cc-pVXZ (X = D, T and Q) basis sets were employed for the H atoms⁴⁴ with the standard contractions, and Peterson's cc-pVXZ-PP (X = D, T and Q) basis sets were utilized for the Re atom with the new energy-consistent relativistic pseudopotentials.⁹⁵ Following the construction of the basis set, the outer-core Hartree-Fock molecular orbitals, mainly arising from the atomic Re $5s^25p^6$ orbitals, were frozen for the electron correlation methods. The notation VXZ (X = D, T, Q) is used to describe the above-mentioned mixed basis sets. Anharmonic vibrational frequencies for the isolated dianion were computed at the CCSD(T)/VTZ level of theory using second-order vibrational perturbation theory (VPT2).^{8,60} The requisite cubic and semi-diagonal quartic force constants were obtained from finite differences of the numerical second derivatives. Equilibrium geometries and harmonic vibrational frequencies were obtained using the MOL-PRO 2010.1 package.⁹⁶ Anharmonic frequencies were evaluated with CFOUR.⁹⁷

The single-reference character of the molecular wavefunctions is confirmed by analysing the coupled-cluster diagnostics $(T_1, {}^{98,99} D_1 {}^{100})$ and maximum amplitudes $(T_1 \max, T_2 \max)$, as reported in Table 2.1. Wilson and co-workers' recent study¹⁰¹ of 3*d* transition-metal containing molecules suggests that the diagnostic criteria are $T_1 < 0.05$ and $D_1 < 0.15$ for *d*block species using single-reference methods, in contrast to the original standards $T_1 < 0.02$ and $D_1 < 0.05$, developed for molecules containing first-row atoms.

Table 2.1: Coupled-cluster diagnostics and maximum amplitudes with respect to various methods and basis sets for the $[\text{ReH}_9]^{2-}$ dianion at the CCSD and CCSD(T) equilibrium geometries. As described in the text, the basis sets VXZ = Re: cc-pVXZ-PP and H: cc-pVXZ (X = D, T, Q).

		CCSD		$\operatorname{CCSD}(\mathrm{T})$			
	VDZ	VTZ	VQZ	VDZ	VTZ	VQZ	
T_1 Diagnostic	0.019	0.019	0.020	0.019	0.019	0.020	
D_1 Diagnostic	0.032	0.035	0.036	0.032	0.035	0.036	
$T_1 \max^{\mathrm{a}}$	0.029	0.029	0.029	0.029	0.029	0.028	
$T_2 \max^{\mathbf{a}}$	0.046	0.034	0.034	0.047	0.034	0.028	

^a Absolute value of the largest T_1 and T_2 amplitudes.

In order to balance the multiply-charged nature of the $[\text{ReH}_9]^{2-}$ dianion, two alkali metal counterions were deliberately placed along the C_3 axis of the $[\text{ReH}_9]^{2-}$ molecule to form $M_2\text{ReH}_9$ (M = Na, K) sandwich compounds (D_{3h} symmetry). The optimized geometries and harmonic frequencies were obtained at CCSD(T) level of theory with the cc-pVTZ-PP basis set for the Re atom and cc-pVTZ basis sets for other atoms. Specifically, the contractions for alkali metals are Na(16s10p2d1f/5s4p2d1f) and K(20s14p3d1f/6s5p3d1f).^{102,103} In accordance with the design of the basis sets, frozen-core approximations were applied for the coupled-cluster treatments. Computations for the $M_2\text{ReH}_9$ (M = Na, K) sandwich complexes were performed with CFOUR.⁹⁷

The natural population analysis (NPA)¹⁰⁴ and natural bond orbital (NBO)^{105,106} computations for the $[\text{ReH}_9]^{2-}$ dianion and $M_2\text{ReH}_9$ (M = Na, K) sandwich compounds were carried out at the CCSD level of theory. To take advantage of the NBO 5.0 package¹⁰⁷ interfaced with QCHEM 4.1,^{108,109} we switched to the Los Alamos effective core potential sets (LANL2DZ)¹¹⁰ for Re atom. The uncontracted LANL08(f) basis set¹¹¹ was applied for Re and the correlation consistent cc-pVTZ basis sets for other atoms. The frozen molecular orbitals are defined in the manner previously mentioned (4 orbitals for $[\text{ReH}_9]^{2-}$, 14 orbitals for Na_2ReH_9 and 22 orbitals for K_2ReH_9).

2.4 Results and Discussions

2.4.1 Geometric Structure

Assuming the known D_{3h} symmetry, the optimized structure of the $[\text{ReH}_9]^{2-}$ dianion has two symmetry independent hydrogens yielding a faced-tricapped trigonal prism (Figure 2.1). Six prism hydrogen atoms are located at the prism vertices and the other three cap hydrogen atoms reside along the center of the prism rectangular faces. Experiments have determined that the $[\text{ReH}_9]^{2-}$ dianion occupies two distinct Wyckoff positions in the crystal structure, namely the "a site" with D_{3h} symmetry and the "d site" with C_{3h} symmetry.^{79,112} Since Ginsberg and co-workers⁷⁹ averaged the Re–H bond lengths for the two different Re positions (a and d sites) and symmetry independent hydrogens (prism and cap hydrogens), they necessarily obtained identical bond distances (1.68 Å) for Re–H_{prism} and Re–H_{cap}. A more recent neutron diffraction experiment on the K₂ReH₉ crystal¹¹² yields 1.674 Å for Re–H_{cap} (r_1) and 1.696 Å for Re-H_{prism} (r_2), when only the average of two distinct sites is taken. The detailed structural parameters are reported in Table 2.2 together with the experimental data from the neutron diffraction measurements.

All *ab initio* methods present satisfactory agreement with experiment, considering that our theoretical predictions are in the gas phase. As the basis set size increases, no dramatic change of the geometry is observed. The disparity between the geometry obtained at the highest CCSD(T)/VQZ level of theory and the neutron diffraction structure of Bronger *et al.*¹¹² is only 0.008 and 0.022 Å for the Re–H_{cap} and Re–H_{prism} distances, respectively. Recently reported DFT computations also predict the geometry of the isolated dianion uding various functionals and basis sets.⁸⁸ Comparing to the experimental values,¹¹² the Re–H_{cap} and Re–H_{prism} bond lengths are overestimated by 0.015 – 0.026 Å and 0.022 – 0.039 Å, respectively.



Figure 2.1: The equilibrium geometry of the isolated $[\text{ReH}_9]^{2-}$ (D_{3h} symmetry) dianion at the CCSD(T) level of theory with cc-pVXZ-PP (X = D, T, Q) basis sets for the Re atom and the corresponding cc-pVXZ basis sets for H atoms, along with experimental findings. Note that another cap hydrogen atom is hidden in the back of the molecule from this side view. Bond lengths are in Å and the bond angle is in degrees. More detailed information is given in the papers by Ginsberg⁷⁹ and Bronger.¹¹²

Table 2.2: Equilibrium structural parameters for the isolated $[\text{ReH}_9]^{2-}$ dianion using different methods and basis sets. As described in the text, the basis sets VXZ = Re: cc-pVXZ-PP, H: cc-pVXZ (X = D, T, Q); aug-VTZ = Re: aug-cc-pVTZ-PP, H: aug-cc-pVTZ.

		$_{\mathrm{HF}}$		CCSD			CCSD(T)					Experiment (K_2ReH_9)		
$Parameter^{a}$	VDZ	VTZ	VQZ	VDZ	VTZ	VQZ	VDZ	VЛ	ĽΖ	aug-VTZ	VQZ	Ref. 79] ^b	Ref. 112^{c}	
$r_1(\text{Re}-\text{H}_{\text{cap}})$	1.673	1.668	1.668	1.683	1.676	1.677	1.688	3 1.6	81	1.686	1.682	1.68	1.674	
$r_2(\mathrm{Re-H}_{\mathrm{prism}})$	1.720	1.716	1.717	1.722	1.715	1.715	1.725	5 1.7	18	1.721	1.718	1.68	1.696	
Prism Angle θ	90.2	90.4	90.2	89.9	90.3	90.4	89.8	90	.3	90.4	90.4	93.6	88.7	

^a Bond lengths are in Å and the prism angle is in degrees. See Figure 2.1 for detailed definition of all geometrical parameters.

^c The experimental bond lengths and prism angle cited here are the average of the two sites. The two symmetry independent Re–H bonds are not averaged out. The bond angle is obtained from the atomic distances in Ref. [112].

In view of its low computational cost, the HF method makes reasonable predictions of the molecular structure, within 0.02 Å of experimental bond lengths. Previous all-electron,

^b The $[\text{ReH}_9]^{2-}$ dianions are reported to occupy two distinct sites in the crystal structure. The experimental geometry cited here is the average of the two sites and the two symmetry independent Re-H bonds.⁷⁹

Table 2.3: Comparison with previous research. Equilibrium structural parameters of the isolated $[\text{ReH}_9]^{2-}$ dianion using the HF method with different basis sets. As described in the text, the basis sets VXZ = Re: cc-pVXZ-PP, H: cc-pVXZ (X = D, T, Q)

	Γ	This wor	k ^a	Ref. 89 ^b				
Parameter ^c	VDZ	VTZ	VQZ	Basis I	Basis III	Basis V		
$r_1(\mathrm{Re-H_{cap}})$	1.673	1.668	1.668	1.689	1.687	1.687		
$r_2(\mathrm{Re-H_{prism}})$	1.720	1.716	1.717	1.741	1.742	1.743		
Prism Angle θ	90.2	90.4	90.2	89.5	89.5	89.6		

^a VDZ = cc-pVDZ-PP for Re(8s7p6d1f/4s4p3d1f) and cc-pVDZ for H(4s1p/2s1p); total of 83 basis functions. VTZ = ccpVTZ-PP for Re(10s9p8d2f1g/5s5p4d2f1g) and cc-pVTZ for H(5s2p1d/3s2p1d); total of 189 basis functions. VQZ = ccpVQZ-PP for Re(14s11p10d3f2g1h/6s6p5d3f2g1h) and cc-pVQZ for H(6s3p2d1f/4s3p2d1f); total of 369 basis functions.

^b An all-electron, non-relativistic *ab initio* HF method was applied. Basis I = DZ for Re(20s14p11d7f/17s11p8d2f) and TZ¹¹³ for H(5s/3s); total of 131 basis functions. Basis III = TZ for Re(23s17p14d9f/18s14p10d3f) and QZ2P¹¹⁴ for H(6s2p/4s2p); total of 221 basis functions. Basis V = TZP+ for Re(24s20p15d10f/19s17p11d4f) and QZ2P+ for H(7s2p/5s2p); total of 252 basis functions.

^c Bond lengths are in Å and the prism angle is in degrees. See Figure 2.1 for detailed definition of all structural parameters.

non-relativistic HF computations⁸⁹ also qualitatively agree with experiment, which may be enhanced by a fortuitous error cancelation between missing relativistic and electron correlation effects. On one hand, it is well-known that the non-relativistic methods strongly overestimate the bond lengths for transition metal hydrides.¹¹⁵ Table 2.3 illustrates the importance of relativistic effects (within the HF approximation) compared to previous research. A 0.02 - 0.03 Å overestimation for both the Re-H_{cap} and Re-H_{prism} bond lengths is found compared to the present computations with relativistic pseudopotentials. On the other hand, the HF method underestimates the bond lengths compared to the electron-correlated coupled-cluster method.¹¹⁶ Generally, increasing the treatment of dynamic correlation yields elongated Re-H_{cap} bond distances (Table 2.2). However, the improvement for the Re-H_{prism} distance is vague with respect to more complete treatments of electron correlation. Also note that the predicted $Re-H_{cap}$ bond lengths agree with experiment perfectly while $Re-H_{prism}$ bonds are constantly too long. This divergence might be due to the exclusion of counterions in our computations, a problem we explore later in this manuscript.

2.4.2 VIBRATIONAL FREQUENCIES

The $[\text{ReH}_9]^{2-}$ dianion has twenty-four vibrational normal modes, including nine Re-H stretching modes $(2A'_1 + 2E' + A''_2 + E'')$, two torsional modes $(A''_1 + A'_2)$ and thirteen bending modes $(A'_1 + 3E' + 2A''_2 + 2E'')$, which are described in Table 2.4. Both torsional motions are IR and Raman inactive, but have been measured using INS spectroscopy. Those vibrational modes with either E' or A''_2 symmetry are IR active. Normal modes of symmetry A'_1 , E' and E'' are Raman active.

Mode	Symmetry	Selection Rules ^a	$\mathrm{Description}^{\mathrm{b}}$
ν_1	E'	IR, R	$Re-H_{prism}$ scissoring and wagging, $Re-H_{cap}$ scissoring
ν_2	E'	IR, R	$\mathrm{Re-H_{prism}}$ scissoring and wagging, $\mathrm{Re-H_{cap}}$ scissoring
$ u_3$	$A_2^{\prime\prime}$	IR	$\mathrm{Re-H}_{\mathrm{prism}}$ and $\mathrm{Re-H}_{\mathrm{cap}}$ wagging
$ u_4 $	A_1''	ia	$Re-H_{prism}$ torsion
ν_5	$E^{\prime\prime}$	R	$\mathrm{Re-H_{prism}}$ scissoring and wagging, $\mathrm{Re-H_{cap}}$ twisting
$ u_6 $	$A_2^{\prime\prime}$	IR	$\mathrm{Re-H}_{\mathrm{prism}}$ and $\mathrm{Re-H}_{\mathrm{cap}}$ wagging
ν_7	A'_2	ia	Torsion between $\mathrm{Re-H_{cap}}$ and $\mathrm{Re-H_{prism}}$
ν_8	A'_1	R	Symmetric Re–H _{prism} wagging
$ u_9$	E'	IR, R	$Re-H_{cap}$ and $Re-H_{prism}$ scissoring
ν_{10}	$E^{\prime\prime}$	R	$Re-H_{prism}$ scissoring, $Re-H_{cap}$ twisting
ν_{11}	$A_2^{\prime\prime}$	IR	Asymmetric $\text{Re}-\text{H}_{\text{prism}}$ stretch with $\text{Re}-\text{H}_{\text{cap}}$ bend
ν_{12}	E'	IR, R	Asymmetric $\text{Re}-\text{H}_{\text{prism}}$ stretch with $\text{Re}-\text{H}_{\text{cap}}$ bend
ν_{13}	$E^{\prime\prime}$	R	Asymmetric $\text{Re}-\text{H}_{\text{prism}}$ stretch with $\text{Re}-\text{H}_{\text{cap}}$ bend
ν_{14}	A'_1	R	Out-of-phase symmetric $\mathrm{Re-H}_\mathrm{prism}$ and $\mathrm{Re-H}_\mathrm{cap}$ stretch
ν_{15}	E'	IR, R	Asymmetric $Re-H_{cap}$ stretch
ν_{16}	A'_1	R	Symmetric Re-H _{prism} and Re-H _{cap} stretch

Table 2.4: Symmetries and descriptions for the vibrational modes of the isolated $[ReH_9]^{2-}$ dianion.

^a IR: Infrared active, R: Raman active, ia: Inactive.

^b Description reported here is given from the view along the C_3 axis.

The harmonic vibrational frequencies are reported in Table 2.5 for the isolated $[ReH_9]^{2-}$ dianion. Since MOLPRO does not provide analytic gradients or analytic second derivatives

Table 2.5: Vibrational frequencies (cm^{-1}) for the isolated $[ReH_9]^{2-}$ dianion using different methods and basis sets. As described in the text, the basis sets VXZ = Re: cc-pVXZ-PP, H: cc-pVXZ (X = D, T, Q); aug-VTZ = Re: aug-cc-pVTZ-PP, H: aug-cc-pVTZ. Theoretical vibrational frequencies are harmonic; experimental frequencies include anharmonic effects.

		SC	CF		CCSD CCSD(T)						Expe	riment
											K ₂ ReH ₉	$BaReH_9$
Mode	VDZ	VTZ	VQZ^{a}	VDZ	VTZ	VQZ	VDZ	VTZ	aug-VTZ	VQZ	Ref. 87 ^b	Ref. 88 ^c
$\nu_1(E')$	391	389	388(18)	348	346	346	339	334	331	334	-	-
$\nu_2(E')$	724	723	719(337)	676	669	672	668	656	651	659	730?(IR)	684(IR)
$\nu_3(A_2'')$	739	734	738(535)	698	672	682	692	660	662	670	730?(IR)	740(IR)
$\nu_4(A_1'')$	875	878	864(0)	788	792	781	776	773	756	762	640(INS)	680?(INS)
$\nu_5(E'')$	904	908	901(0)	823	815	813	809	793	786	790	-	801?(INS)
$\nu_6(A_2'')$	981	990	980(0)	885	878	876	867	850	845	848	-	-
$\nu_7(A_2')$	1017	1030	1014(0)	904	913	909	883	884	873	881	810(INS)	860?(INS)
$\nu_8(A_1')$	1053	1040	1045(0)	992	955	961	978	933	927	938	991(R)	925(R)
$\nu_9(E')$	1087	1092	1077(2)	977	982	981	959	955	949	956	-	983(R)
$\nu_{10}(E'')$	1103	1110	1100(0)	992	992	997	973	965	959	970	1028(R)	1034(R)
$\nu_{11}(A_2'')$	1795	1769	1764(1665)	1798	1780	1776	1785	1770	1753	1766	1840(IR)	1830(IR)
$\nu_{12}(E')$	1801	1775	1769(975)	1812	1796	1793	1801	1788	1774	1785	-	1870(IR)
$\nu_{13}(E'')$	1842	1818	1814(0)	1851	1837	1837	1841	1828	1818	1829	1878(R)	-
$\nu_{14}(A_1')$	1906	1883	1880(0)	1905	1892	1890	1893	1881	1866	1880	1923(R)	-
$\nu_{15}(E')$	2014	1999	2000(330)	1979	1971	1968	1960	1952	1932	1949	1925(IR)	1956(IR)
$\nu_{16}(A_1')$	2106	2097	2104(0)	2020	2018	2022	1992	1988	1974	1991	1985(R)	1992(R)

^a The corresponding IR intensities (km/mol) at the HF/VQZ level of theory are given in parentheses.

- ^b The types of measurement are quoted in parentheses after each experimental value. The Raman spectrum cited was obtained from a single crystal at 90 K. The IR spectrum was recorded at 300 K from KBr discs. The INS data was originally measured on Na₂ReH₉ and K₂ReH₉ at 90 K by neutron energy loss using the beryllium filter spectrometer⁸⁶ and assigned by Creighton and Sinclair.⁸⁷ The assignment of 730 cm⁻¹ was uncertain in Ref. 87, so the value is listed twice in this table followed by a question mark to ν_2 or ν_3 .
- ^c The techniques of measurement are quoted in parentheses after each experimental frequency. The Raman spectrum was recorded from the BaReH₉ sample in the glass ampoule at room temperature. The IR spectrum was recorded at room temperature from KBr discs. The INS spectrum was recorded at 20K in an argon glovebox. Although the INS spectroscopy results for ν_4 , ν_5 and ν_7 could match the predicted values to some extent, they fail to match either the symmetry or description with our isolated [ReH₉]²⁻ computations. Thus we label the INS values with a question mark.

with effective core potentials, vibrational frequencies may suffer from numerical errors of a few wavenumbers. As expected, higher levels of theory yield lower frequencies for most vibrational modes as bond distances also lengthen. According to our HF/VQZ computations, it is not surprising that ν_1 , ν_5 , ν_6 and ν_9 are not detected via IR spectroscopy because of the low or vanishing IR intensities. The computations for the isolated $[\text{ReH}_9]^{2-}$ ion are harmonic frequencies and refer to gas phase species, while the experiments deduce fundamentals for the dianion in the solid state. Thus our theoretical results are not ready for precise comparisons with experimental value, yet several modes show adequate agreement with experiments.

However, there are two serious problems. The first is the dramatic differences between the present theory and the experiments by Parker and co-workers⁸⁸ for the Re–H_{prism} stretching modes ν_{11} and ν_{12} . More importantly, most of our harmonic frequencies are lower than the experimental fundamentals, suggesting a larger divergence when including the anharmonic corrections. This becomes more conspicuous in DFT calculations whose frequencies in the stretching region are smaller than the corresponding CCSD(T)/VQZ values by as much as 87 cm⁻¹.⁸⁸ As examined below, these deficiencies may also result from the missing counterions in our treatment.

We have also determined the anharmonic corrections to the fundamental frequencies for the dianion by employing second-order vibrational perturbation theory (VPT2). These predictions are reported in Table 2.6. In CFOUR, harmonic vibrational frequencies were computed from finite differences of analytic gradients, while in MOLPRO they were evaluated by the finite differences of energy points. The small differences ($\leq 1 \text{ cm}^{-1}$) between harmonic vibrational frequencies observed in Tables 2.5 and 2.6 result from the numerical errors in these different approaches. We note that no Fermi resonances were encountered. In general, anharmonicity contributes ~ 100 cm⁻¹ for stretching modes and ~ 45 cm⁻¹ for bending and torsional motions. The unphysically large correction for mode ν_1 indicates the large amplitude nature of this motion and the poor treatment that results from straightforward VPT2 treatment.
Table 2.6: Anharmonic second-order vibrational perturbation theory (VPT2) analysis for the $[ReH_9]^{2-}$ dianion at the CCSD(T)/VTZ level of theory. As described in the text, the basis set VTZ = Re: cc-pVTZ-PP, H: cc-pVTZ

			Theory	,a	Exper	Experiment ^b		
Mode	$\mathbf{Symmetry^{c}}$	ω	ν	$\nu - \omega$	$K_2 Re H_9^{87}$	$BaReH_9$ ⁸⁸		
$ u_1 $	$E'(\mathrm{IR, R})$	335	176	-159	-	-		
ν_2	$E'(\mathrm{IR, R})$	657	641	-16	730?(IR)	$684(\mathrm{IR})$		
ν_3	$A_2''(\mathrm{IR})$	661	652	-9	730?(IR)	$740(\mathrm{IR})$		
$ u_4 $	$A_1^{\prime\prime}(\mathrm{ia})$	774	734	-40	640(INS)	680?(INS)		
ν_5	$E''(\mathbf{R})$	794	739	-55	-	801?(INS)		
ν_6	$A_2''(\mathrm{IR})$	850	809	-41	-	-		
ν_7	$A_2'(ia)$	885	841	-44	810(INS)	860?(INS)		
ν_8	$A_1'(\mathbf{R})$	934	907	-27	991(R)	925(R)		
$ u_9$	$E'(\mathrm{IR, R})$	956	903	-53	-	983(R)		
ν_{10}	$E''(\mathbf{R})$	966	921	-44	1028(R)	1034(R)		
ν_{11}	$A_2''(\mathrm{IR})$	1769	1674	-95	$1840(\mathrm{IR})$	$1830(\mathrm{IR})$		
ν_{12}	$E'(\mathrm{IR, R})$	1788	1704	-84	-	$1870(\mathrm{IR})$		
ν_{13}	$E''(\mathbf{R})$	1829	1740	-89	1878(R)	-		
ν_{14}	$A_1'(\mathbf{R})$	1881	1784	-97	1923(R)	-		
ν_{15}	$E'(\mathrm{IR, R})$	1953	1836	-116	$1925(\mathrm{IR})$	$1956(\mathrm{IR})$		
ν_{16}	$A_1'(\mathbf{R})$	1988	1882	-107	1985(R)	1992(R)		

^a ω : harmonic frequencies, ν : anahrmonic frequencies.

^b The experimental techniques are quoted in parentheses after each value, and are summarized in detail in Table 2.5 notes b and c.

^c Selection rules are given in parentheses. IR: Infrared active, R: Raman active, ia: inactive.

2.4.3 Effects of Augmenting Basis Set

Often, in order to describe anionic species, specially designed diffuse basis sets are sought. Therefore, we have employed the mixed aug-VTZ basis set (H: aug-cc-pVTZ;⁴⁵ Re: aug-cc-pVTZ-PP⁹⁵) to re-optimize the geometry and compute the harmonic vibrational frequencies, as shown in Table 2.2 and 2.5. No basis set linear dependency issue is encountered as suggested by the smallest eigenvalue of the overlap matrix (1.8×10^{-5}) .¹¹⁷ Comparing to the CCSD(T)/VTZ and CCSD(T)/VQZ results, CCSD(T)/aug-VTZ level of theory predicts

0.003 - 0.005 Å longer bond distances and consequently lower (by as much as 20 cm⁻¹) vibrational frequencies. Since no dramatic change is observed when augmenting the basis set, we validate the sufficiency of using the non-augmented basis sets to describe the [ReH₉]²⁻ dianion.

2.4.4 M_2 ReH₉ (M = NA, K) SANDWICH COMPLEXES

As discussed earlier, the imperfect agreement between theory and experiment for bond lengths and several discrepancies in the vibrational frequencies may be related to the missing cations in our study. Since multiply-charged anions are rarely viable in the gas phase, a reasonable approach is to stabilize these species with counterions. One of the simplest corrections is to consider the M_2 ReH₉ (M =Na, K) sandwich complexes where [ReH₉]²⁻ is capped with two alkali metal cations along the molecular C_3 axis. As such, the D_{3h} symmetry is retained. However, this is not the experimentally observed structure in the solid state.^{79,112} From the above reported computations for [ReH₉]²⁻, the improvement is not substantial when increasing the basis set from VTZ to VQZ. Therefore, we optimized the geometries and evaluated the harmonic frequencies of the M_2 ReH₉ (M = Na, K) sandwich compounds at the CCSD(T)/VTZ (Re: cc-pVTZ-PP; H, Na, K: cc-pVTZ) level of theory with the frozen-core approximations.

The optimized geometries are shown in Figure 2.2 and 2.3. The distances between Re and the alkali metal atoms are 2.908 Å and 3.365 Å for Na and K at the respective equilibrium structures. Compared to the CCSD(T)/VTZ optimized $[ReH_9]^{2-}$ dianion, the Re-H_{cap} and Re-H_{prism} bond lengths are shortened by 0.016 and 0.004 Å for Na₂ReH₉, and 0.014 and 0.007 Å for K₂ReH₉. The relatively unchanged Re-H_{prism} bond lengths validate our computational methodology employed for the isolated dianion. Additionally, the more obvious changes in the Re-H_{cap} bond lengths result from neglecting the direct interaction between cations and H_{cap}, since in the crystal structure of K₂ReH₉, nine K neighbors of each $[ReH_9]^{2-}$ form a



Figure 2.2: The equilibrium structure of the Na₂ReH₉ molecule (D_{3h} symmetry) optimized at the CCSD(T)/VTZ level of theory. As described in the text, the basis set VTZ = Re: cc-pVTZ-PP; H, Na: cc-pVTZ. Only unique bond lengths (in Å) and the H-Re-H prism angle (in degrees) are shown.



Figure 2.3: The equilibrium structure of the K₂ReH₉ molecule (D_{3h} symmetry) optimized at the CCSD(T)/VTZ level of theory. As described in the text, the basis set VTZ = Re: cc-pVTZ-PP; H, K: cc-pVTZ. Only unique bond lengths (in Å) and the H-Re-H prism angle (in degrees) are shown.

faced-tricapped trigonal prism.⁷⁹

Table 2.7 reports the harmonic vibrational frequencies for the M_2 ReH₉ (M =Na, K) sandwich compounds. No imaginary vibrational frequency is encountered, indicating that the optimized structures are genuine minima. Since the equilibrium Re–H bonds are shortened in M_2 ReH₉, the vibrational frequencies become generally larger than the corresponding isolated [ReH₉]^{2–} values. The most substantial improvement is that all predictions involving Re–H stretching modes provide better agreement with the experiments. This illustrates the

Table 2.7: Vibrational frequencies (cm^{-1}) for the isolated $[ReH_9]^{2-}$ dianion and M_2ReH_9 (M = Na, K) at CCSD(T)/VTZ level of theory. As described in the text, the basis set VTZ = Re: cc-pVTZ-PP; H, Na, K: cc-pVTZ. Theoretical frequencies are harmonic; experimental frequencies include anharmonic effects.

			Theory		Expe	riment ^a	
Mode	Symmetry ^b	$[ReH_{9}]^{2-}$	Na_2ReH_9	K_2ReH_9	$K_2 Re H_9$ ⁸⁷	$BaReH_9$ ⁸⁸	Description ^c
$\nu_{\rm i}$	$E'(\mathrm{IR, R})$	-	63	43	-	-	Re-M scissoring
$ u_{\mathrm{ii}}$	$A_1'(\mathbf{R})$	-	236	166	-	-	Symmetric $\text{Re}-M$ stretch
$ u_{ m iii}$	$A_2^{\prime\prime}(\mathrm{IR})$	-	258	192	-	-	Asymmetric $\text{Re}-M$ stretch
$ u_{\mathrm{iv}}$	$E''(\mathbf{R})$	-	360	324	-	-	Re–bend coupled with $\text{Re}-M$ bend
ν_1	E'(IR, R)	334	571	554	-	-	${\rm Re-H_{prism}}$ scissoring and wagging, ${\rm Re-H_{cap}}$ scissoring
ν_2	$E'(\mathrm{IR, R})$	656	769	738	730?(IR)	684(IR)	${\rm Re-H_{prism}}$ scissoring and wagging, ${\rm Re-H_{cap}}$ scissoring
ν_3	$A_2^{\prime\prime}(\mathrm{IR})$	660	766	759	730?(IR)	$740(\mathrm{IR})$	$\mathrm{Re-H_{cap}}$ and $\mathrm{Re-H_{prism}}$ wagging
ν_4	$A_1^{\prime\prime}(\mathrm{ia})$	773	664	690	640(INS)	680?(INS)	$Re-H_{prism}$ torsion
ν_5	$E''(\mathbf{R})$	793	923	896	-	801?(INS)	$\mathrm{Re-H}_\mathrm{prism}$ scissoring and wagging, $\mathrm{Re-H}_\mathrm{cap}$ twisting
ν_6	$A_2^{\prime\prime}(\mathrm{IR})$	850	1034	975	-	-	$\mathrm{Re-H}_\mathrm{prism}$ and $\mathrm{Re-H}_\mathrm{cap}$ wagging
ν_7	$A_2'(ia)$	884	890	900	810(INS)	860?(INS)	Torsion between $\mathrm{Re-H_{cap}}$ and $\mathrm{Re-H_{prism}}$
ν_8	$A_1'(\mathbf{R})$	933	1129	1077	991(R)	925(R)	Symmetric Re–H _{prism} wagging
ν_9	$E'(\mathrm{IR, R})$	955	1026	1004	-	983(R)	$\mathrm{Re-H_{cap}}$ and $\mathrm{Re-H_{prism}}$ scissoring
ν_{10}	$E^{\prime\prime}(\mathbf{R})$	965	983	996	1028(R)	1034(R)	$\mathrm{Re-H_{prism}}$ scissoring, $\mathrm{Re-H_{cap}}$ twisting
ν_{11}	$A_2^{\prime\prime}(\mathrm{IR})$	1770	1847	1858	$1840(\mathrm{IR})$	$1830(\mathrm{IR})$	Asymmetric $\mathrm{Re-H_{prism}}$ stretch with $\mathrm{Re-H_{cap}}$ bend
ν_{12}	$E'(\mathrm{IR, R})$	1788	1834	1848	-	$1870(\mathrm{IR})$	Asymmetric Re– $\rm H_{prism}$ stretch with Re– $\rm H_{cap}$ bend
ν_{13}	$E^{\prime\prime}(\mathbf{R})$	1828	1877	1892	1878(R)	-	Asymmetric $\mathrm{Re-H_{prism}}$ stretch with $\mathrm{Re-H_{cap}}$ bend
ν_{14}	$A_1'(\mathbf{R})$	1881	1945	1956	1923(R)	-	Out-of-phase $\mathrm{Re-H}_\mathrm{prism}$ and $\mathrm{Re-H}_\mathrm{cap}$ stretch
ν_{15}	$E'(\mathrm{IR},\mathrm{R})$	1952	2072	2053	$1925(\mathrm{IR})$	1956(IR)	Asymmetric $Re-H_{cap}$ stretch
ν_{16}	$A_1'(\mathbf{R})$	1988	2081	2067	1985(R)	1992(R)	Symmetric $\mathrm{Re-H}_\mathrm{prism}$ and $\mathrm{Re-H}_\mathrm{cap}$ stretch

^a The experimental techniques are quoted in parentheses after each value, and are summarized in detail in Table 2.5 notes b and c.

^b Selection rules are given in parentheses. IR: Infrared active, R: Raman active, ia: inactive.

^c Descriptions for $\nu_{\rm i} - \nu_{\rm iv}$ are given from side view. The rest are given from top view along the C_3 axis.

significance of Coulomb interactions in predicting the structure and vibrations for multiplycharged anions. Obviously, our simple sandwich model is still incomplete for the description of the complicated bending region. Although the anharmonic frequencies for the sandwich complexes are not computed explicitly, we may qualitatively estimate the anharmonic contribution from our previous computations on the $[\text{ReH}_9]^{2-}$ dianion. It is expected that anharmonic corrections are able to explain the experimental values for modes ν_{15} and ν_{16} , yet inadequate to reproduce the whole spectrum. We note that previous theoretical work concerning the BaReH₉ unit cell has been reported from computations employing periodic DFT methods with plane-wave basis sets.^{83,88,91} The PBE functional of Perdew, Burke and Ernzerh¹¹⁸ predicts a geometry where the Re $-H_{cap}$ and Re $-H_{prism}$ distances differ by only 0.006 and 0.009 Å respectively, from the available K₂ReH₉ experimental data. For the unscaled harmonic vibrational frequencies, periodic DFT computations illustrate satisfactory agreement with experimental values,⁸⁸ but, analogous to our sandwich complexes, including the effects of an anharmonic potential energy surface will reduce this agreement. Additional high-level computations for the complete cell are encouraged to study the vibrational frequencies. However, this seems impractical at present with coupled-cluster theory.

2.4.5 Bonding

The NBO partial charges and Wiberg bond indices are reported in Tables 2.8 and 2.9. For the isolated dianion, the natural charge on Re is -0.71, compared to its formal +7 oxidation state. The prism hydrogens carry more electron density than the cap hydrogens, a result that agrees with earlier reported Mulliken populations.⁸⁹ As suggested by the Wiberg bond indices, Re $-H_{cap}$ and Re $-H_{prism}$ are genuine covalent bonds with similar bond orders. The small bond orders for the interactions between hydrogens confirms the assignment of [ReH₉]²⁻ as a polyhydide, where no bond is formed between hydrogens. For the sandwich complexes, the charges on Re and the Wiberg bond indices are very similar to those for the isolated dianion. From the charges on the alkali metals, the interactions between [ReH₉]²⁻ and M (M = Na, K) exhibit mainly ionic character, which further validates the present theoretical treatments for the [ReH₉]²⁻ dianion. This is also supported by the minimal bond indices between the alkali metal cation and the nearest prism hydrogens. Interestingly, the cap hydrogens become less negatively charged, showing a degree of electron density transfer to the prism hydrogens.

Table 2.8: NBO natural partial charges for $[\text{ReH}_9]^{2-}$ (D_{3h} symmetry) and the $M_2\text{ReH}_9$ (M = Na, K) sandwich compounds (D_{3h} symmetry) at the CCSD/LANL08(f) (Re), cc-pVTZ (H, Na, K) level of theory.

	$[{\rm ReH}_{9}]^{2-}$	Na_2ReH_9	$K_2 Re H_9$
Re	-0.706	-0.722	-0.696
$\mathrm{H}_{\mathrm{cap}}$	-0.098	+0.002	-0.014
$\mathrm{H}_{\mathrm{prism}}$	-0.167	-0.193	-0.200
M	N/A	+0.938	+0.969

Table 2.9: Wiberg NBO bond indices for $[\text{ReH}_9]^{2-}$ (D_{3h} symmetry) and the M_2 ReH₉ (M = Na, K) sandwich compounds (D_{3h} symmetry) at the CCSD/LANL08(f) (Re), cc-pVTZ (H, Na, K) level of theory.^a

	$[{\rm ReH}_9]^{2-}$	Na_2ReH_9	$K_2 Re H_9$
$\mathrm{Re-H_{cap}}$	0.52(1.665)	0.52(1.650)	0.52(1.652)
$\mathrm{Re-H}_{\mathrm{prism}}$	0.49(1.705)	0.48(1.704)	0.48(1.700)
$\rm H_{cap}{-}\rm H_{cap}$	$0.01 \ (2.884)$	$0.01 \ (2.858)$	$0.01 \ (2.861)$
$\rm H_{cap}{-}H_{prism}$	$0.07 \ (1.920)$	$0.07 \ (1.883)$	$0.07 \ (1.888)$
$\rm H_{cap}-\rm H'_{prism}$	0.05 (3.108)	0.05 (3.128)	$0.05 \ (3.119)$
$H_{\rm prism} - H_{\rm prism}$	$0.03\ (2.071)$	0.02(2.183)	$0.03 \ (2.154)$
$\rm H_{prism}-\rm H'_{prism}$	$0.01 \ (2.430)$	0.02(2.292)	$0.01 \ (2.319)$
$\mathrm{H}_{\mathrm{prism}} - \mathrm{H}''_{\mathrm{prism}}$	$0.07 \ (3.193)$	$0.07 \ (3.165)$	$0.07 \ (3.165)$
$M-\mathrm{Re}$	N/A	$0.01 \ (2.901)$	$0.01 \ (3.361)$
$M-\mathrm{H}_{\mathrm{prism}}$	N/A	0.02(2.161)	$0.01 \ (2.528)$

^a The corresponding inter-atomic distances (in Å) are given in parentheses. Only bond indices greater than 0.01 are shown. $H_{cap}-H_{prism}$ is the bond index between a cap H and one of its four nearest prism hydrogen atoms, while $H_{cap}-H'_{prism}$ is that between a cap H and one of its two most distant prism hydrogens. $H_{prism}-H_{prism}$ represents the two prism hydrogens that are on the same end of the prism triangular face. $H_{prism}-H'_{prism}$ denotes the two prism hydrogens that form the longer edge of the prism rectangular face. $H_{prism}-H''_{prism}$ refers to the two prism hydrogens that yield the diagonal of the prism rectangular face.

The NBO results are reported in Table 2.10, which confirm nine Re-H covalent bonds, with no bonding between hydrogens. The 5d, 6p and 6s orbitals of Re are responsible for the Re-H bond formation, in which rhenium 5d orbitals contribute ~ 60% of the hybridization. Comparing the M_2 ReH₉ (M = Na, K) sandwich compounds to the isolated dianion,

Table 2.10: Natural bond orbitals for $[\text{ReH}_9]^{2-}$ (D_{3h} symmetry) and the $M_2\text{ReH}_9$ (M = Na, K) sandwich compounds (D_{3h} symmetry) at the CCSD/LANL08(f) (Re), cc-pVTZ (H, Na, K) level of theory. Only bonding (BD) and anti-bonding (BD*) orbitals are shown.

	${\rm Re-H_{cap}~BD}$	${\rm Re-H_{prism}~BD}$	${\rm Re-H_{cap}~BD^*}$	${\rm Re-H_{prism}~BD^*}$
		$[{\rm ReH}_{9}]^{2-}$		
Occupancy	1.612	1.618	0.331	0.361
Re Hybrids	$sp^{2.50}d^{4.88}f^{0.01}$	$sp^{3.18}d^{5.12}f^{0.03}$	$sp^{2.50}d^{4.88}f^{0.01}$	$sp^{3.18}d^{5.12}f^{0.03}$
H Hybrids	$sp^{0.00}d^{0.00}$	$sp^{0.00}d^{0.00}$	$sp^{0.00}d^{0.00}$	$sp^{0.00}d^{0.00}$
		Na_2ReH_9		
Occupancy	1.560	1.614	0.315	0.383
Re Hybrids	$sp^{2.44}d^{4.85}f^{0.01}$	$sp^{3.03}d^{5.37}f^{0.05}$	$sp^{2.44}d^{4.85}f^{0.01}$	$sp^{3.03}d^{5.37}f^{0.05}$
H Hybrids	$sp^{0.01}d^{0.00}$	$sp^{0.00}d^{0.00}$	$sp^{0.01}d^{0.00}$	$sp^{0.00}d^{0.00}$
		$K_2 Re H_9$		
Occupancy	1.565	1.618	0.319	0.384
Re Hybrids	$sp^{2.45}d^{4.79}f^{0.01}$	$sp^{3.06}d^{5.34}f^{0.06}$	$sp^{2.45}d^{4.79}f^{0.01}$	$sp^{3.06}d^{5.34}f^{0.06}$
H Hybrids	$sp^{0.01}d^{0.00}$	$sp^{0.00}d^{0.00}$	$sp^{0.01}d^{0.00}$	$sp^{0.00}d^{0.00}$

significant changes on the occupancy are predicted, indicating charge transfer from $Re-H_{cap}$ bonding and $Re-H_{cap}$ anti-bonding orbitals to the $Re-H_{prism}$ anti-bonding orbitals.

2.5 Conclusions

In the current research, we have first predicted the equilibrium structure and vibrational frequencies of the isolated $[\text{ReH}_9]^{2-}$ dianion. The relativistic effects of the Re atom have been considered by employing the new Peterson energy-consistent pseudopotentials.⁹⁵ Reliable coupled-cluster methods have been applied to take into account the electron correlation effects. These computations reveal the importance of both effects in determining the structure of the isolated $[\text{ReH}_9]^{2-}$ dianion. Our geometry at the CCSD(T)/VQZ level of theory only differs by 0.008 and 0.022 Å from the most recent neutron diffraction experiments for the Re-H_{cap} and Re-H_{prism} bonds, respectively. Several harmonic frequencies for the isolated dianion demonstrate satisfactory agreement with experimental transitions. This agreement

diminishes when including anharmonicity. According to the NBO analysis, $[ReH_9]^{2-}$ is a polyhydride where hydrogens only form covalent bonds with the center Re. The Re-H bonding arises mainly from the 5*d* orbitals of Re and the 1*s* orbital of H.

The naive M_2 ReH₉ (M =Na, K) sandwich model slightly reduces the geometric differences with experiment, and improves the vibrational frequencies in the Re–H stretching region. Specifically for K₂ReH₉, the differences between our predictions and experiment are 0.007 and 0.015 Å for the Re–H_{cap} and Re–H_{prism} bond distances, respectively. The harmonic frequencies become 60 – 100 cm⁻¹ larger than those for the isolated dianion in the Re–H stretching region and anticipative of further anharmonic corrections. These features illustrate the importance of including the counterions in computations for such electronically dense systems. However, the VPT2 treatment is unlikely to reproduce the full experimental spectrum. It is hoped that this study will encourage further theoretical work on this unique transition metal hydride.

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2.7 Supporting Information

See supplementary material at http://pubs.acs.org/doi/suppl/10.1021/jp412003s/ suppl_file/jp412003s_si_001.pdf for Cartesian coordinates for all optimized structures.

Chapter 3

The Intricate Internal Rotation Surface and Fundamental Infrared Transitions of N-Propyl Radical*

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3.1 Abstract

The potential energy surface for methylene hindered internal rotation is examined for the *n*-propyl radical, a molecule fundamental to combustion chemistry. Six stationary points are identified, and four of them are unique: 1, 2, TS1 and TS2. The remaining two structures 1' and TS1' are mirror images with respect to 1 and TS1. Focal point analysis, converged to the complete basis set limit of coupled-cluster theory with single, double, triple and perturbative quadruple excitations [CCSDT(Q)], is employed to obtain the relative energies of these structures. A one-dimensional potential energy surface (PES) is constructed by explicitly mapping out a distinguished reaction path via constrained geometry optimizations. A "double-well" feature is observed on the electronic PES, but under the adiabatic approximation, the enthalpic (0 K) PES becomes a regular single-well potential with the expected 180° periodicity. The corresponding one-dimensional vibrational Schrödinger equation is solved using the Cooley-Numerov approach to obtain vibrational states of the methylene torsional motion. The predicted barrier for internal rotation is 105.5 cm^{-1} and 137.2 cm^{-1} for the electronic and enthalpic surfaces, respectively. Anharmonic (fundamental) vibrational frequencies are predicted for structure **1** using second-order vibrational perturbation theory, and the band origins for eleven modes are reported. Comparison with previous electron spin resonance and infrared spectroscopic work, in addition to other theoretical investigations, is made where possible.

3.2 INTRODUCTION

The *n*-propyl radical is an archetypical intermediate in both high and low temperature combustion chemistry. In the high temperature regime, it is the simplest alkyl radical that can undergo both C–C and C–H β -scission reactions.^{119–121} In cool flames, the reaction of *n*-propyl radical with multiple equivalents of O₂ is central to maintaining low-temperature combustion. Larger species can also undergo multiple oxidations, but *n*-propyl peroxy radical is the smallest species with enough degrees of freedom to isomerize to a •QOOH (hydroperoxy radical) intermediate via an energetically favorable six-membered ring transition state for intramolecular hydrogen-atom abstraction.^{122–128} As such, experimental and theoretical work on *n*-propyl radical can probe the reactivity observed in larger species with a compound that displays simpler spectra and is tractable with high-accuracy theoretical methods.



Figure 3.1: Sketch of the *n*-propyl radical structure. The out-of-plane angle of $C_{\beta}-H_1C_{\alpha}H_2$ is defined as χ to illustrate possible pyramidalization of the radical center.

Only four vibrational modes of the *n*-propyl radical have been observed. In a series of early matrix-isolation infrared (IR) spectroscopy studies, Pacansky and co-workers assigned three C-H stretching modes and a lower frequency mode corresponding to pyramidal bending of the radical center.^{129,130} The observed transitions were centered at 3100.0 and 3017.5 cm⁻¹ (α -CH₂), 2812.5 cm⁻¹ (β -CH₂), and 530.0 cm⁻¹ (see Figure 3.1 for labeling). These features reveal that the radical center possesses sp^2 hybridization and is easily distorted. The characteristic low vibrational frequency of the β -CH stretching mode also indicates an elongated C-H bond distance, when compared to a typical sp^3 hybridized C-H bond. Paddon-Row and Houk postulated that the analogous bond-lengthening effect seen in the ethyl radical was the result of hyperconjugation.¹³¹

Electron spin resonance (ESR) spectroscopy has also been utilized to study the methylene internal rotation of *n*-propyl radical, which is the rotation (angle θ , Figure 3.2) of the radical center around the carbon backbone ($-CH_2CH_3$). ESR spectra measured in solution at 93



Figure 3.2: Newman projection for the *n*-propyl radical along $C_{\alpha}-C_{\beta}$ axis. The half-filled p_{π} orbital on alpha carbon is perpendicular to the α -CH₂ plane. Note, if the out-of-plane angle χ is zero, $\theta - 90^{\circ}$ is equivalent to φ , else it differs by less than 2°. φ is the angle between the $C_{\alpha}C_{\beta}C_{\gamma}$ and $H_1C_{\alpha}H_2$ planes.

K and 133 K suggest a $\theta = 90^{\circ}$ conformation where the α hydrogen atoms on the radical center are in the plane containing all three carbon atoms and non-equivalent.^{132–134} This structure, which includes equivalent β hydrogen atoms by symmetry (C_s), was supported by an *ab initio* study from Ellinger *et al.*¹³⁵ A different ESR spectrum was obtained at lower temperatures (4 K) in an argon matrix.¹³⁶ This work by Adrian, Cochran and Bowers showed that the α hydrogen atoms are interchangeable due to internal rotation, and more than one equilibrium structure exists. As such, the α hydrogen atoms become magnetically equivalent on average and the β hydrogens are nonequivalent. Subsequent theoretical work by Pacansky and Dupuis at the Hartree-Fock (HF) level with a small basis set (4-31G) supported their assertion.¹³⁷ Discrepancies between the spectra observed in liquid and argon matrix environments are believed to be the result of increased radical-solvent interactions present in the liquid phase.^{137,138}

Later theoretical work aimed to predict the barrier for methylene internal rotation, which was experimentally estimated to be approximately 0.4 kcal mol⁻¹ by studying the temperature dependence of β hydrogen atom hyperfine splittings from ESR spectra.^{134,139} In 1988, Claxton and Graham¹⁴⁰ fitted several HF energy points to a Fourier series that included 0, 2, 4, and 6-fold symmetry terms. They obtained a barrier of 0.10 kcal mol⁻¹ including the zero-point energies under an adiabatic approximation. More recently, in 2010, Turovt-sev and Orlov reported a value of 0.313 kcal mol⁻¹ from 50 electronic energy points at the B3LYP/6-311++G(3df,3pd) level of theory represented with a Fourier series of the form $V = \sum_{n=0}^{12} V_n \cos n\tau_1$.¹⁴¹

In this research, we also examine the methylene hindered internal rotation and report geometric parameters for stationary points from computations at the coupled-cluster level of theory. Subsequently, we computed the relative energy differences between those points using focal point analysis (FPA)^{7,39–43} in order to extrapolate energies to the complete basis set (CBS) limit. We have also constructed a one-dimensional potential energy function, fitted by a Fourier series of the form $V = \sum_{n=0}^{16} V_n \cos 2n\tau$, with respect to the distinguished reaction coordinate for the methylene hindered internal rotation. The potential energy function was adopted in the vibrational Schrödinger equation to obtain the energy states of the methylene torsional motion. Finally, to augment the limited available IR spectroscopy data, we report eleven anharmonic (fundamental) frequencies of *n*-propyl radical from coupledcluster computations using second-order vibrational perturbation theory (VPT2).^{8,60}

3.3 Computational Methods

Optimized geometries for the stationary points along the methylene internal rotation coordinate were obtained using coupled-cluster theory with single, double and perturbative triple excitations [CCSD(T)].^{21,29,93,94} Tight convergence (RMS force $< 10^{-8} E_h/a_0$) was employed throughout. Dunning's correlation-consistent triple- ζ (cc-pVTZ) basis set⁴⁴ was used to describe the C and H atoms, and the 1*s*-like orbitals on the carbon atoms were frozen in the correlation energy computations in accordance with the design of this basis. An unrestricted Hartree-Fock (UHF) reference wave function was utilized since minimal spin contamination was encountered ($\langle S^2 \rangle \leq 0.763$). Stationary points were characterized by vibrational analysis; **1** and **2** are true minima while **TS1** and **TS2** are first-order saddle points. The single-reference nature of the molecular wave functions was verified by analyzing the coupled-cluster T_1 diagnostics^{98,99} ($T_1 = \sqrt{\frac{|t_{1\alpha}|^2 + |t_{1\beta}|^2}{N_{corr}}} \leq 0.014$) and the largest T_2 amplitudes ($T_{2,\max} \leq 0.022$).

Relative energy differences among the rotamers were obtained using focal point analysis (FPA), which gives a prescription for systematically extrapolating electronic energies to the *ab initio* limit. This procedure is described in detail elsewhere.^{7,39–43} Several corrections were appended to the extrapolated energies from our valence FPA results. A core correlation correction (Δ_{core}) from differencing all-electron CCSD(T)/cc-pCVTZ^{46,142} and frozen-core CCSD(T)/cc-pCVTZ energies was appended. A zero-point vibrational energy correction (Δ_{ZPVE}) was included from harmonic frequency computations at the CCSD(T)/ccpVTZ level of theory. Mass velocity and Darwin one-electron terms (Δ_{rel}) computed at the CCSD(T)/cc-pVTZ level of theory were also appended to account for the use of a nonrelativistic Hamiltonian.⁵⁶ Finally, a diagonal Born-Oppenheimer correction (Δ_{DBOC}), determined at the HF/cc-pVTZ level of theory, was included to account for the use of clamped nuclei.^{55,143}

To explicitly construct the PES for a description of the methylene hindered internal rotation, a distinguished reaction path (DRP) was generated by a series of constrained geometry optimizations at the MP2/cc-pVTZ level of theory. A linear combination of two torsional angles, $\tau_1(H_1-C_{\alpha}-C_{\beta}-C_{\gamma})$ and $\tau_2(H_2-C_{\alpha}-C_{\beta}-C_{\gamma})$ described in Figure 3.1, was chosen as the distinguished reaction coordinate, $\tau = \frac{1}{2}(\tau_1 + \tau_2 + 180)$ (in degrees). The electronic PES was first generated by CCSD(T)/cc-pVQZ single-point computations and then scaled slightly to reproduce the FPA relative energetics [SI, Eq. (5)]. Since τ dominates the total energy distribution of the methylene torsional motion, a DRP projected vibrational analysis¹⁴⁴ was employed to evaluate the ZPVE curve, obtained from harmonic MP2/ccpVTZ computations along the path. The resulting energy points were precisely fitted to a Fourier series of the form $\sum_{n=0}^{16} V_n \cos 2n\tau$ to express the potential energy V in terms of the reaction coordinate τ , as well as to ensure a smooth connection between the stationary points. We comment that the MP2/cc-pVTZ harmonic ZPVE corrections along the DRP are sufficiently accurate since they agree with the CCSD(T)/cc-pVTZ harmonic Δ_{ZPVE} values within 4 cm⁻¹ for the stationary points. The potential energy function $V(\tau)$ was subsequently employed in the vibrational Schrödinger equation to obtain several low-lying vibrational states of the methylene torsional motion using the Cooley-Numerov approach.¹⁴⁵⁻¹⁴⁷ The modulation of the reduced mass along the DRP was accounted for by utilizing a fitted function $G(\tau)$ [SI, Eq. (3)] and its derivative in the kinetic energy operator.

Anharmonic vibrational frequencies were computed for **1** using second-order vibrational perturbation theory (VPT2).^{8,60} First, harmonic frequencies were computed using CCSD(T) with an atomic natural orbital basis set¹⁴⁸ of C(13s8p6d4f/4s3p2d1f) and H(8s6p4d/4s2p1d) quality, termed ANO1. Recent work has shown that this generally contracted basis outperforms similarly sized Dunning basis sets⁴⁴ for the prediction of vibrational frequencies.¹⁴⁹ Requisite cubic and quartic components of the force field, among other parameters, were then obtained from finite differences of second derivatives computed using CCSD(T) with the smaller ANO0 basis [C(13s8p6d/3s2p1d) and H(8s6p/2s1p)]. Analytic second derivatives with a UHF reference were used throughout.¹⁵⁰

Restricted open-shell Hartree-Fock (ROHF) and second-order Z-averaged perturbation (ZAPT2)¹⁵¹ single-point energies were obtained using the MPQC 3.0.0 package.¹⁵² Coupledcluster computations were performed with CFOUR.⁹⁷ Higher-order CCSDT and CCSDT(Q) energies were obtained using the MRCC program of Kállay,^{153,154} interfaced with CFOUR. The projected frequency analyses along the DRP utilized the INTDER program.^{144,155} The Fourier fit of the PES and the Cooley-Numerov computations were performed using *Mathe*- matica 9.156

3.4 **Results and Discussions**

3.4.1 Stationary Points

We have identified six stationary points along the methylene hindered internal rotation coordinate at the CCSD(T)/cc-pVTZ level of theory. The fitted potential connecting these points relative to φ is depicted in Figure 3.3; the symmetry and "double well" nature of the electronic potential energy surface is clear. The internal rotation coordinate is demarcated with φ (in degrees), which is a measure of methylene rotation about the carbon backbone. Specifically, φ is a five-atom coordinate measuring the angle between the methylene plane and the plane containing all three carbon atoms. If the out-of-plane angle χ (defined in Figure 3.1) is zero, φ is equivalent to the τ angle defined in the Computational Methods section. Along the DRP, φ is very close to τ with discrepancies less than 2° (SI, Tables S4 - S7), and thus $V(\tau)$ and $V(\varphi)$ are indistinguishable in Figure 3.3. Note, that the distal methyl unit (γ -CH₃) always remains in a staggered position.

Of the six stationary points, four are unique: 1, TS1, 2 and TS2. The remaining two structures, 1' and TS1', are energetically equivalent to 1 and TS1, respectively, but are reflected over the mirror plane containing all three carbon atoms. Rotamers 1 and 1' are connected by TS2, and form a double well potential within the minimum region. Both 1 and 1' connect to the higher energy region, to rotamer 2, via TS1' and TS1, respectively. This electronic potential energy surface is analogous to that suggested by Turovtsev and Orlov.¹⁴¹

Our optimized stationary points are shown in Figure 3.4. The $C_{\alpha}-C_{\beta}$ bond lengths for all conformations are shorter than the experimental C–C single bond in propane (1.5209 Å),¹⁵⁷ indicating a bond order greater than one, which is in good agreement with previous



Figure 3.3: The fitted potential energy curve along the distinguished reaction coordinate τ . (a, blue) Electronic energy curve. (b, red) Enthalpic (0 K) energy curve. φ , which is the angle between the $C_{\alpha}C_{\beta}C_{\gamma}$ and $H_1C_{\alpha}H_2$ planes, differs from τ by less than 2°, and thus indistinguishable on the scale of the figure. See Tables S4 – S7 in SI for detailed φ and τ values along the DRP.

theoretical work.^{137,140,158} Except for **TS2**, which retains C_s symmetry, the other structures prefer small degrees of pyramidalization at the alpha carbon (C_{α}). The out-of-plane angle χ provides a measure of this distortion and varies in absolute value up to 9.52° (Figure 3.4). The preferred non-planar orientation can be interpreted as a result of hyperconjugation between the half-filled p_{π} orbital of the radical center (defined in Figure 3.2) and the σ orbitals involved in C–H or C–C bonding.¹³¹ For rotamer **1**, pyramidalization increases the favorable overlap between the singly-occupied p_{π} orbital and the C_{β}–H₃ σ orbital. The result is a longer C_{β}–H₃ bond length compared to the same methylene unit in propane. A hyperconjugation argument for pyramidal distortion is also supported by the stabilization energy from donor-acceptor interactions, which we find in natural bond orbital (NBO) analysis¹⁰⁶ (SI, Table S1). Curiously, σ - p_{π} overlap would be maximized if the two orbitals were



Figure 3.4: CCSD(T)/cc-pVTZ optimized stationary points of the *n*-propyl radical internal rotation about the radical center. Bond lengths are in Å and bond angles are in degrees. χ is the out-of-plane angle of C_{β} -H₁ C_{α} H₂. φ is the angle between the $C_{\alpha}C_{\beta}C_{\gamma}$ and H₁ C_{α} H₂ planes.

coplanar, but a dihedral angle $(p_{\pi}-C_{\alpha}-C_{\beta}-H_3)$ of -7.98° rather than 0° is preferred. This indicates the balance between favorable hyperconjugation and unfavorable steric repulsion from neighboring atoms.

Using a similar interpretation, the slight pyramidalization of conformer **2** is caused by the hyperconjugation between the p_{π} orbital of the α -CH₂ group and the σ orbital of C_{β}-C_{γ} bond. This conclusion is supported by comparing the $C_{\beta}-C_{\gamma}$ bond lengths between 2 (1.5423 Å) and **TS2** (1.5291 Å), recognizing that the $C_{\beta}-C_{\gamma}$ bond in **TS2** cannot hyperconjugate. Maximizing the C-C hyperconjugation results in rotamer 2 being slightly lower in energy than **TS1**, suggesting its importance in determining the geometry in the high-energy region. For the transition state **TS1**, H₂H₃ is nearly eclipsed and the overlap of p_{π} orbital of the radical center with either the $C_{\beta}-C_{\gamma}$ or $C_{\beta}-H \sigma$ orbital results in lesser degrees of pyramidalization.

3.4.2 Relative Energies

The small energy differences between rotamers necessitates a rigorous, high-accuracy treatment of the energy. We report the relative energies between stationary points from extrapolated single-point computations using coupled-cluster methods that include up to single, double, triple, and perturbative quadruple excitations with correlation-consistent basis sets up to cc-pV6Z.¹⁵⁹ The focal point analysis (FPA) approach was utilized for extrapolation, as described in the Computational Methods section. In each extrapolation we observe oscillatory convergence to within 2 cm⁻¹. Our results are listed Tables 3.1 - 3.3; the extrapolated electronic energy ($\Delta E[\text{CCSDT}(\mathbf{Q})/\text{CBS}]$) is shown in bold at the right of the table in the row labeled "CBS LIMIT", while the final electronic energy ($\Delta E_{\rm e}$), which includes core (Δ_{core}) , relativistic (Δ_{rel}) , and diagonal Born-Oppenheimer (Δ_{DBOC}) corrections, is shown below. The enthalpy at 0 K (ΔE_{final}) is also reported by adding the ZPVE correction to $\Delta E_{\rm e}$. We note that the ZPVE correction ($\Delta_{\rm ZPVE}$) contains an adiabatic approximation wherein the mode along the methylene internal rotation coordinate (ω_{24}) is omitted (ZPVE $=\frac{1}{2}\sum_{i=1}\omega_i$).^{140,160} This adiabatic approximation is supported by an obvious separation of classical time scales between the lowest-frequency mode (ω_{24}) and the other vibrations by at least a factor of two for all stationary points and structures along the DRP.

Claxton and Graham 140 predicted that rotamer ${\bf 2}$ is the local minimum on the electronic

Basis Set	$\Delta E_{\rm HF}$	δ [MP2]	δ [CCSD]	δ [CCSD(T)]	δ [CCSDT]	δ [CCSDT(Q)]	$\Delta E[\text{CCSDT}(\mathbf{Q})]$		
cc-pVDZ	-61.8	+35.6	-7.3	-3.0	-0.0	-0.2	[-36.8]		
cc- $pVTZ$	-58.3	+51.3	-13.1	-2.2	[-0.0]	[-0.2]	[-22.5]		
cc- $pVQZ$	-59.3	+58.2	-15.4	-1.3	[-0.0]	[-0.2]	[-18.0]		
cc-pV5Z	-59.5	+60.2	[-15.4]	[-1.3]	[-0.0]	[-0.2]	[-16.3]		
cc-pV6Z	-59.6	+61.4	[-15.4]	[-1.3]	[-0.0]	[-0.2]	[-15.0]		
CBS LIMIT	[-59.6]	[+63.2]	[-15.4]	[-1.3]	[-0.0]	[-0.2]	[-13.3]		
	4	$\Delta E_{\rm e} = \Delta I$	E[CCSDT($Q)/CBS] + \Delta_{co}$	$_{\rm ore}[{\rm CCSD}({\rm T})]$	/cc-pCVTZ]			
$+\Delta_{\rm rel}[{\rm CCSD}({\rm T})/{\rm cc}$ -pVTZ] $+\Delta_{\rm DBOC}[{\rm HF}/{\rm cc}$ -pVTZ]									
$= -13.3 + 1.5 - 0.2 - 0.3 = -12.3 \text{ cm}^{-1}$									
	ΔE_{final} :	$=\Delta E_{\rm e}+A$	$\Delta_{\rm ZPVE}[\rm CCS]$	SD(T)/cc-pVT	$[Z]^{a} = -12.3$	+22.3 = 10.0 cm	n^{-1}		

Table 3.1: Extrapolated energies (in cm^{-1}) for the relative energy difference between **TS2** and **1** of *n*-propyl radical.

^a The zero-point energy contribution from the vibration along the methylene internal rotation coordinate is excluded.

Table 3.2: Extrapolated energies (in cm^{-1}) for the relative energy difference between **2** to **TS1** of *n*-propyl radical.

Basis Set	$\Delta E_{\rm HF}$	δ [MP2]	δ [CCSD]	$\delta[\text{CCSD}(T)]$	δ [CCSDT]	$\delta[\text{CCSDT}(\mathbf{Q})]$	$\Delta E[\text{CCSDT}(\mathbf{Q})]$		
cc-pVDZ	+45.5	-36.8	+10.9	+2.0	+0.0	+0.2	[+21.8]		
cc- $pVTZ$	+41.3	-47.6	+15.2	+1.6	[+0.0]	[+0.2]	[+10.7]		
cc-pVQZ	+41.5	-54.9	+16.8	+0.9	[+0.0]	[+0.2]	[+4.5]		
cc-pV5Z	+41.4	-56.6	[+16.8]	[+0.9]	[+0.0]	[+0.2]	[+2.7]		
cc-pV6Z	+41.3	-57.2	[+16.8]	[+0.9]	[+0.0]	[+0.2]	[+2.0]		
CBS LIMIT $[+41.3]$ $[-58.1]$ $[+16.8]$ $[+0.9]$ $[+0.0]$ $[+0.2]$ $[+1.1]$									
$\Delta E_{\rm e} = \Delta E [\rm CCSDT(Q)/CBS] + \Delta_{\rm core} [\rm CCSD(T)/cc\text{-}pCVTZ]$									
		$+\Delta$	[CCSD(T)]	$/cc$ -pVTZ] + Λ	DDOG[HF/CC	-nVTZ]			

$$= 1.1 - 1.4 + 0.2 + 0.2 = 0.1 \text{ cm}^{-1}$$

 $\Delta E_{\rm final} = \Delta E_{\rm e} + \Delta_{\rm ZPVE} [\rm CCSD(T)/cc\text{-}pVTZ]^a = 0.1 - 19.3 = -19.2 \ \rm cm^{-1}$

^a The zero-point energy contribution from the vibration along the methylene internal rotation coordinate is excluded.

PES, lying 4.1 J mol⁻¹ (0.34 cm⁻¹) below **1** at the UHF/3-21G level of theory. Our focal point analysis, extrapolated to CCSDT(Q)/CBS, illustrates that **1** is actually 105.4 cm⁻¹ lower in energy than **2**. We find very small barriers for the transition state structures in both the low- and high-energy regions; 12.3 cm^{-1} for the transition of **1** to **TS2** and a striking 0.1

Basis Set	$\Delta E_{\rm HF}$	δ [MP2]	δ [CCSD]	$\delta[\text{CCSD}(\mathbf{T})]$	δ [CCSDT]	$\delta[\text{CCSDT}(\mathbf{Q})]$	$\Delta E[\text{CCSDT}(\mathbf{Q})]$			
cc-pVDZ	+29.8	+67.4	-47.1	-13.4	-0.6	-1.8	[+34.2]			
cc- $pVTZ$	+35.4	+98.3	-49.9	-12.6	[-0.6]	[-1.8]	[+68.8]			
cc-pVQZ	+32.2	+113.6	-49.8	-11.1	[-0.6]	[-1.8]	[+82.4]			
cc-pV5Z	+31.7	+114.6	[-49.8]	[-11.1]	[-0.6]	[-1.8]	[+82.9]			
cc-pV6Z	+31.8	+116.4	[-49.8]	[-11.1]	[-0.6]	[-1.8]	[+84.8]			
CBS LIMIT	[+31.8]	[+119.0]	[-49.8]	[-11.1]	[-0.6]	[-1.8]	[+87.4]			
$\Delta E_{\rm e} = \Delta E [\rm CCSDT(Q)/CBS] + \Delta_{\rm core} [\rm CCSD(T)/cc-pCVTZ]$										
$+\Delta_{\rm rel}[{\rm CCSD}({\rm T})/{\rm cc}$ -pVTZ] $+\Delta_{\rm DBOC}[{\rm HF}/{\rm cc}$ -pVTZ]										
$= 87.4 + 7.0 - 0.6 - 0.7 = 93.1 \text{ cm}^{-1}$										
	ΔE_{final}	$=\Delta E_{\rm e} + \Delta E_{\rm e}$	$\Delta_{\rm ZPVE}$ [CCS	SD(T)/cc-pVT	$Z]^{a} = 93.1 + 7$	77.3 = 170.4 cm	n^{-1}			

Table 3.3: Extrapolated energies (in cm⁻¹) for the relative energy difference between **TS2** to **2** of n-propyl radical.

^a The zero-point energy contribution from the vibration along the methylene internal rotation coordinate is excluded.

cm⁻¹ for the transition of **2** to **TS1**. The internal rotation barrier on the electronic PES is $105.5 \text{ cm}^{-1} (\mathbf{1} \rightarrow \mathbf{TS1})$, showing surprising agreement with a previous theoretical prediction (110 cm^{-1}) at the B3LYP/6-311++G(3df,3pd) level of theory.¹⁴¹

As previous research suggests,¹⁴⁰ the nature of the PES changes when including the ZPVE. By including the harmonic Δ_{ZPVE} correction at the CCSD(T)/cc-pVTZ level of theory, and using the adiabatic approximation, **TS2** becomes the global minimum instead of **1**. Furthermore, rotamer **2** becomes the highest energy species instead of **TS1**. As a consequence, the potential energy curve transforms from a double-well potential to a regular single-well potential with 180° periodicity (Figure 3.3). The ZPVE of the methylene torsional motion is 33.2 cm^{-1} , illustrated in Figure 3.5, obtained by solving the vibrational Schrödinger equation using the fitted enthalpic (0 K) potential energy function $V(\tau)$. This ZPVE value is subsequently appended to the FPA enthalpy change of **TS2** \rightarrow **2**. The barrier height that results is 137.2 cm^{-1} , a substantial improvement from the previous value of 428 J mol⁻¹ (35.8 cm⁻¹) obtained at the UHF/3-21G level¹⁴⁰ when compared to the ESR estimate \sim

0.4 kcal mol⁻¹ (140 cm⁻¹).^{134,139} Moreover, the energy ordering of the enthalpic PES agrees with ESR experiments in cyclopropane solution at 133 K, where rotamer **TS2** was suggested to be the preferred orientation.^{133,134} We note that even higher levels of theory and larger basis sets may be required to further quantify the nature of the PES. Recent development in explicitly correlated methods may be helpful for this kind of problem by including auxiliary corrections.



Figure 3.5: Vibrational wave functions for the methylene torsional motion of the *n*-propyl radical, superimposed on the fitted enthalpic (0K) potential energy curve along the distinguished reaction coordinate τ . The energy levels are: 33.2 cm⁻¹ (n = 0), 109.7 cm⁻¹ (n = 1), 161.9 cm⁻¹ (n = 2), and 277.2 cm⁻¹ (n = 3) where *n* is the vibrational quantum number.

Our primary goal in determining the correct ordering of the aforementioned stationary points is to identify an appropriate reference geometry for vibrational analysis so that we may augment existing data on *n*-propyl radical. In experiments, the minimum energy conformer is most likely to be observed, but we identify two such structures depending on whether the electronic or enthalpic PES is considered (1 or **TS2**, respectively). The difference in harmonic frequencies between 1 and **TS2** is shown at the CCSD(T)/cc-pVTZ and CCSD(T)/ANO1levels of theory in Table S2 of the SI. We find that for the twelve modes largely uncoupled from the methylene torsional motion (discussed in detail in the following section), only one (ω_6) yields a large difference between the two rotamers (> 25 cm⁻¹). Frequencies of the remaining eleven modes differ by only 1 cm⁻¹ on average. Consequently, and given the added difficulty in determining the anharmonic corrections for a transition state, we have chosen **1**, the global minimum on the electronic PES, for our analysis.

3.4.3 VIBRATIONAL FREQUENCIES

As discussed in the Computational Methods section, the fundamental frequencies for **1** were determined by appending an anharmonic correction obtained at the CCSD(T)/ANO0 level of theory to harmonic frequencies obtained at the CCSD(T)/ANO1 level. During the course of our VPT2 analysis, we encountered a large, unphysical anharmonic correction for the mode corresponding to torsional motion of the radical center about the carbon backbone. We previously observed this phenomenon in our analysis of the ethyl radical.¹⁶¹ As with that work, removing the offending mode (ν_{24} in this case) from the VPT2 analysis – that is, neglecting its contribution to the anharmonic constants χ_{rs} – highlights those modes that are strongly coupled with the methylene torsional motion. We find that after removal, ν_1 , ν_5 , ν_7 , ν_{15} and ν_{17} - ν_{23} shift on average by 30 cm⁻¹. The remaining twelve modes, are shifted by only 1.2 cm⁻¹ on average. We interpret those modes to be less coupled to the methylene torsional motion, and therefore our prediction of their fundamental frequencies should be more reliable. For instance, we suggest a value of 3021.2 cm⁻¹ for the predominantly uncoupled symmetric α -CH stretch (ν_2), which is in excellent agreement with the value from matrix-isolation studies (3017.5 cm⁻¹).^{129,130}

We report the anharmonic frequencies and harmonic intensities for eleven modes of 1 in Table 3.4, all of which are largely uncoupled from the torsional motion. One mode, ν_6 , has been omitted due to disagreement between the harmonic frequencies of 1 and **TS2**, as previously discussed. A list of frequencies for all the modes, including the change after removing ν_{24} , may be found in Table S3 of the SI, for reference. Among the modes listed in Table 3.4, no Fermi resonances were observed using the criteria $|\phi_{iik}| > 80 \text{ cm}^{-1}$ and $|2\omega_i - \omega_k| < 50 \text{ cm}^{-1}$ for Type I and $|\phi_{ijk}| > 80 \text{ cm}^{-1}$ and $|\omega_i + \omega_j - \omega_k| < 50 \text{ cm}^{-1}$ for Type II interactions. Resonances were observed among the remaining modes. Treatment is given in the SI using the standard procedure⁸ of diagonalizing the corresponding effective vibrational Hamiltonian where the deperturbed values are set to be the diagonal elements.

Table 3.4: Selected harmonic and anharmonic (fundamental) frequencies (cm^{-1}) for $\mathbf{1}$ (C_1) of the *n*-propyl radical.

				Experiment				
Mode	Description	$\omega_{\rm ANO0}{}^{\rm a}$	$\nu_{\rm ANO0}{}^{\rm b}$	$\Delta_{\rm ANO0}{}^{\rm c}$	$\omega_{\rm ANO1}{}^{\rm d}$	$ u^{\mathrm{e}}$	$\mathrm{Int.}^{\mathrm{f}}$	Ref. $[129]^{g}$
ν_2	symmetric α -CH stretch	3152.9	3025.8	-127.2	3148.3	3021.2	13.8	3017.5
ν_3	asymmetric $\gamma\text{-}\mathrm{CH}$ stretch	3131.9	2983.3	-148.6	3117.1	2968.5	26.1	
$ u_4$	asymmetric $\gamma\text{-}\mathrm{CH}$ stretch	3126.1	2978.9	-147.3	3110.6	2963.4	32.9	
ν_8	γ -CH ₃ scissor	1512.0	1499.7	-12.3	1508.6	1496.3	3.2	
$ u_9$	γ -CH ₃ twist	1505.7	1463.8	-41.9	1502.5	1460.6	6.0	
ν_{10}	β -CH ₂ scissor	1480.9	1435.2	-45.7	1476.4	1430.6	1.2	
ν_{11}	α -CH ₂ scissor	1470.5	1436.9	-33.6	1472.3	1438.8	2.1	
ν_{12}	γ -CH ₃ umbrella	1415.3	1381.6	-33.7	1410.0	1376.3	2.0	
ν_{13}	β -CH ₂ wag	1363.0	1329.2	-33.8	1363.6	1329.8	2.1	
ν_{14}	β -CH ₂ twist	1280.0	1246.6	-33.4	1276.7	1243.4	0.1	
ν_{16}	asymmetric C–C stretch	1091.7	1066.9	-24.8	1093.8	1069.1	0.1	

^a Harmonic vibrational frequencies obtained at the CCSD(T)/ANO0 level of theory.

^b Fundamentals computed at the CCSD(T)/ANO0 level of theory excluding the contribution of mode ν_{24} in VPT2 analysis.

 $^{\rm c}\Delta_{\rm ANO0} = \nu_{\rm ANO0} - \omega_{\rm ANO0}.$

^d Harmonic vibrational frequencies computed at CCSD(T)/ANO1 level.

 $^{\rm e}$ $\nu = \omega_{\rm ANO1} + \Delta_{\rm ANO0}.$

^f Harmonic IR intensities (km mol⁻¹) at the CCSD(T)/ANO1 level of theory.

 $^{\rm g}$ Observed in an argon matrix at 8 K.

Of the values reported in Table 3.4, we find the C–H stretching motions (ν_2 , ν_3 , and ν_4) to be the most intense. As such they should be readily observable in future experimental studies. Interestingly, the asymmetric C–C stretch along the carbon backbone (ν_{16}) has a small but non-zero intensity. If observed, this mode would provide an important benchmark for unsaturated molecules of this type. The analogous C–C mode in ethyl radical (C₂H₅),

for example, has been assigned to frequencies ranging from 1025 cm⁻¹ to 1185 cm⁻¹.^{161,162} We previously predicted that the origin of this ambiguity was the result of a nearly zero computed intensity. For reference, our reported value for the C–C stretching mode in ethyl radical (1047 cm⁻¹) falls roughly 20 cm⁻¹ lower than that for ν_{16} of *n*-propyl (1069 cm⁻¹); the C_{α}-C_{β} bond length increases by a thousandth of an Angström in propyl radical (from 1.4923 Å to 1.4932 Å).

Importantly, by solving the vibrational Schrödinger equation, we obtain the energy levels for the methylene torsional motion (ν_{24}). Four low-lying energy levels are found, which are 33.2 cm⁻¹ (n = 0), 109.7 cm⁻¹ (n = 1), 161.9 cm⁻¹ (n = 2), and 277.2 cm⁻¹ (n = 3), where n is the vibrational quantum number. The prediction for the fundamental transition of the torsional motion is thus 76.5 cm⁻¹, which is the energy difference between the first (n = 0) and the second (n = 1) energy levels. This fundamental transition lies in the far-infrared region and has not been observed so far. The first overtone, which is predicted to be 128.7 cm⁻¹, may also be observable. Far-infrared measurements of transitions between the highly anharmonic torsional states of n-propyl would not only have diagnostic merit but would also provide fundamental tests of vibrational adiabaticity for a multi-mode system.

3.5 SUMMARY

We report four unique stationary points (1, 2, TS1 and TS2) along the methylene hindered internal rotation coordinate of *n*-propyl radical using high-accuracy coupled cluster methods. Except for TS2, which possesses C_s symmetry, all other stationary points exhibit pyramidal distortion at the radical center. Relative energies between rotamers were determined by focal point analysis extrapolated to the CCSDT(Q)/CBS limit. Notably, the minimum energy rotamer shifts from 1 on the electronic potential energy surface (PES) to TS2 on the enthalpic (0 K) PES, clearly indicating the strong influence of the zero-point vibrational energy correction. Our final predictions place the barrier height for internal rotation at 137.2 cm⁻¹, which agrees with prior ESR experiments (~ 140 cm⁻¹). We also report eleven fundamental frequencies for *n*-propyl radical, those modes that we find to be largely uncoupled from the highly anharmonic torsional motion of the radical center. Comparison of our predicted symmetric α -CH stretching mode, for example, to available experimental spectra observed in an argon matrix yields agreement within 4 cm⁻¹. As only four modes have been previously reported from experimental work, our results significantly augment the available data. Finally, the anharmonic frequency for the methylene torsional motion is predicted to be 76.5 cm⁻¹ by explicitly solving the corresponding one-dimensional vibrational Schrödinger equation; yet this mode has not been observed experimentally. The results presented herein should serve to further guide characterization of this important molecule.

3.6 ACKNOWLEDGEMENTS

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3.7 Supporting Information

See supplementary material at http://pubs.acs.org/doi/suppl/10.1021/jp504764t/ suppl_file/jp504764t_si_001.pdf for Cartesian coordinates for stationary points and structures along the DRP, stabilization energies for donor-acceptor interactions using NBO, all computed modes for 1, a comparison of harmonic frequencies between 1 and TS2, the fitted potential energy functions, and the projected harmonic frequencies along the DRP.

Chapter 4

MULTIREFERENCE DRIVEN SIMILARITY RENORMALIZATION GROUP: A SECOND-ORDER PERTURBATIVE ANALYSIS*

^{*}C. Li, and F. A. Evangelista, accepted by J. Chem. Theory Comput., DOI: 10.1021/acs.jctc.5b00134Reprinted here with permission of the American Chemical Society.

4.1 Abstract

We introduce a multireference version of the driven similarity renormalization group (DSRG) approach [F. A. Evangelista, J. Chem. Phys. **141**, 054109 (2014)] based on a generalized reference wave function and operator normal ordering [W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **107**, 432 (1997)]. We perform a perturbative analysis of the corresponding equations at second order and derive a novel multireference perturbation theory, termed DSRG-MRPT2. The DSRG-MRPT2 energy equation can be written in a simple and compact form and can be solved via a non-iterative procedure that requires at most the three-body density cumulant of the reference. Importantly, even at the perturbation level, the multireference DSRG is free from the intruder-state problem. We propose an optimal range of the DSRG flow parameter that consistently yields reliable potential energy curves with minimal non-parallelism error. We find that the DSRG-MRPT2 can describe the potential energy curves of HF and N₂, and the singlet-triplet gap of *para*-benzyne with an accuracy similar to that of other multireference perturbation theories.

4.2 INTRODUCTION

Multireference (MR) electronic structure theories $^{163-165}$ are indispensable tools for accurately describing near-degenerate electronic states. Multireference methods usually separate electron correlation into two contributions: 166 (1) static correlation, which arises from the strong mixing of near-degenerate configurations (determinants), and (2) dynamic correlation, which is associated with small contributions of excited configurations that mostly model the short-range structure of the wave function and dispersion interactions. Static correlation effects can be captured by multideterminantal wave functions. $^{30,167-173}$ However, quantitatively accurate predictions require the simultaneous treatment of both static and dynamic electron correlation.

Dynamic correlation effects are commonly introduced via multireference versions of perturbation theory^{174–182} (MRPT), configuration interaction (MRCI),^{163,183,184} coupled cluster theory (MRCC),^{185–193} and other approaches.^{194–197} At the core of most multireference theories of dynamic correlation is the similarity transformation of the Hamiltonian (\hat{H}) via a wave operator $\hat{\Omega}$:

$$\hat{\Omega}: \hat{H} \to \bar{H} = \hat{\Omega}^{-1} \hat{H} \hat{\Omega}, \tag{4.1}$$

which yields a transformed Hamiltonian H. The purpose of the similarity transformation is to fold a large number of degrees of freedom into the *effective Hamiltonian*, a small part of \bar{H} that is "decoupled" from the rest of the operator. The effective Hamiltonian describes only a manageable number of states and can be diagonalized to obtain ground and excited state wave functions.

Multireference theories based on effective Hamiltonians are known to suffer from two important problems. The first is the intruder-state problem,^{198–200} which is encountered when states that lie within and outside the space spanned by the effective Hamiltonian become near degenerate. From the perspective of perturbation theory, intruders correspond to excited configurations with vanishing energy denominators. As a consequence, the first-order wave function contains unphysical (often diverging) contributions from excited configurations. The intruder-state problem may be alleviated in MRPT by introducing an empirical level-shift parameter that regularizes the offending denominators.^{201,202} For nonperturbative approaches, several techniques have been developed to deal with intruders.¹⁹⁸

The second difficulty faced by MR effective Hamiltonian theories is the mismatching between the number of wave function parameters and the number of conditions that can be derived from projections of the Schrödinger equation. For instance, state-specific MRCC theories^{186–189,203,204} contain redundant wave function parameters, and additional sufficiency conditions must be enforced to ensure a unique solution. Another example is that of internally-contracted multireference theories, $^{26,205-209}$ in which excitation operators are linearly dependent and must be orthonormalized. For nonlinear theories, the elimination of linear dependencies introduces numerical instabilities and leads to the appearance of "bumps" in potential energy surfaces.^{194,195,197,206,207} One solution to the problem of redundant parameterization is to impose *many-body conditions*. This approach originates in early works of Lindgren²¹⁰ and has been used by Nooijen and collaborators to formulate various coupled cluster approaches.^{191–193,211}



Figure 4.1: Example of the evolution of the two-body components of the transformed Hamiltonian $[\bar{H}_{pq}^{rs}(s)]$ as a function of the flow parameter s in the single-reference driven similarity renormalization group. $\bar{H}_{pq}^{rs}(s)$ is represented as a plot of the matrix $M_{[pq],[rs]}(s) = \bar{H}_{pq}^{rs}(s)$ where [pq] and [rs] are composite indices. The composite indices are divided into three sets: occupied-occupied ([ij]), occupied-virtual ([ia]), and virtual-virtual ([ab]), and the matrix plot shows nine distinct blocks that originate from various combinations of composite indices. For increasing values of s, the DSRG achieves an increasing decoupling of the block corresponding to $\bar{H}_{ab}^{ij}(s) = \langle \Phi_{ij}^{ab} | \bar{H}(s) | \Phi \rangle$, which is responsible for the coupling of the reference (Φ) to doubly excited determinants (Φ_{ij}^{ab}) .

Electron correlation approaches based on the renormalization group (RG) have recently found interesting applications in quantum chemistry. For example, the density-matrix renormalization group^{30,168–170} (DMRG) has been applied successfully to molecules that are beyond the scope of the traditional complete active space self-consistent field¹⁶⁷ (CASSCF) method.^{3,212,213} In this work we are concerned with a different RG technique introduced recently by one of us: the driven similarity renormalization group (DSRG).⁹ The DSRG builds on the similarity renormalization group (SRG), developed independently by Głazek and Wilson^{33,34} and Wegner.^{35,214} The DSRG is an alternative approach to treat dynamic correlation effects in many-body theories and is based on a series of infinitesimal unitary transformations of the Hamiltonian. The extent of this continuous transformation is controlled by a flow parameter s, which can be related to an energy cutoff.^{9,215,216} Figure 4.1 illustrates the DSRG transformation of a many-body operator—represented here as a matrix in which the elements are sorted according to the orbital energies. In this example, it can be seen that as the flow parameter increases, the DSRG transformation gradually zeros certain elements of $\bar{H}(s)$ that couple a closed-shell reference to doubly excited determinants $[\bar{H}_{ab}^{ij}(s)]$. As the DSRG transformation progresses, it reduces the elements of $\bar{H}_{ab}^{ij}(s)$ with large energy denominators and then proceeds to those with small denominators. In this way, if the DSRG transformation is halted at a finite value of s, it will never attempt to zero the elements of $\bar{H}_{ab}^{ij}(s)$ with zero energy denominators.

The SRG has found several applications in nuclear physics^{217–219} and in this context it was recently extended to treat open-shell nuclei.²²⁰ However, until recently the only application of the SRG to quantum chemistry consisted in a study of the water molecule by White.²¹⁵ In our previous work,⁹ the single-reference SRG and DSRG were implemented and benchmarked on ground state equilibrium properties of several diatomic molecules. Our study established that the SRG with one- and two-body operators [SRG(2)] has an accuracy that is intermediate between that of coupled cluster with singles and doubles^{23,24,92} (CCSD) and CCSD with pertubative triples corrections^{21,29,93,94} [CCSD(T)]. We also discovered that the SRG cannot easily converge calculations on C₂ and F₂, and it appears to predict a nonbonded energy minimum for F₂. These difficulties arise from the fact that the solutions of the SRG approach are found by numerical integration of a set of ordinary differential equations.^{9,34,35,215} In certain cases this set of differential equations is ill-conditioned and numerical integration stalls. This problem was the original motivation that lead us to develop the DSRG. In the DSRG, the unitary transformation of the Hamiltonian is parameterized indirectly by a source operator. The source operator can be written in a closed form, and thus, the DSRG equations consist of a set of polynomial equations that can be solved with well established numerical approaches developed for coupled cluster theory. In our benchmark study, the DSRG was shown to yield results that are similar to those obtained from the SRG. In addition, we found no instance in which the DSRG equations fail to converge or yields anomalous results.

The goal of this work is to extend the DSRG approach to a general multireference wave function. In order to explore the pivotal properties of the multireference DSRG (MR-DSRG) theory, we conduct a perturbative analysis of the corresponding equations at second order. The resulting DSRG second-order multireference perturbation theory (DSRG-MRPT2) has several attractive features: (1) it is size extensive, (2) it can be evaluated in a non-iterative fashion, and (3) it demands at most three-particle density cumulant.^{221–225} We will start by formulating the general DSRG approach based on a multireference wave function in Sec. 4.3.2, where the generalized normal ordered operators^{221,226,227} and many-body conditions^{191,210,211} are employed. In Sec. 4.3.3, we derive the DSRG-MRPT2 equations. What follows is a discussion of the formal properties of the MR-DSRG in Secs. 4.3.4 and 4.3.5. In Sec. 4.4, we apply the DSRG-MRPT2 to compute the dissociation curves of hydrogen fluoride and nitrogen molecules along with their spectroscopic constants, and the singlet-triplet separation of the *para*-benzyne molecule. Finally, in Sec. 4.5 we will discuss our findings and propose future extensions of the MR-DSRG theory.

4.3 Theory

4.3.1 Synopsis of the DSRG Theory

In the unitary DSRG formalism,⁹ the bare Hamiltonian (\hat{H}) is brought to a diagonal form by a continuous unitary transformation:

$$\hat{H} \to \bar{H}(s) = \hat{U}^{\dagger}(s)\hat{H}\hat{U}(s),$$
(4.2)

where $\bar{H}(s)$ is the transformed Hamiltonian and $\hat{U}(s)$ is a unitary operator that depends on a time-like parameter s defined in the range $[0, \infty)$. At the beginning of the transformation (s = 0) we require that $\hat{U}(0) = \hat{1}$ so that the DSRG Hamiltonian coincides with the bare Hamiltonian. In the limit of $s \to \infty$ we instead require that the unitary transformation exactly decouples the reference from excited states.

The unitary DSRG⁹ postulates that the flow of the Hamiltonian is *driven* by an Hermitian s-dependent source operator $\hat{R}(s)$. More specifically, the non-diagonal part of the transformed Hamiltonian $[\bar{H}(s)]_{\rm N}$, is equal to the source operator for all values of s:

$$[\bar{H}(s)]_{\mathrm{N}} = \hat{R}(s). \tag{4.3}$$

Therefore, once the source operator is specified, the DSRG equation [Eq. (4.3)] implicitly defines the unitary transformation $\hat{U}(s)$. The non-diagonal part of $\bar{H}(s)$ contains those Hugenholtz diagrams closed from the bottom and from the top, which correspond to pure excitation and de-excitation components of the Hamiltonian, respectively.^{36,37} The electronic energy is obtained by taking the expectation value of the transformed Hamiltonian:

$$E(s) = \langle \Phi | \bar{H}(s) | \Phi \rangle. \tag{4.4}$$

It is important to notice that the DSRG equation [Eq. (4.3)] and the energy [Eq. (4.4)] are evaluated at fixed values of the flow parameter and do not require numerical integration like in the case of the SRG.

4.3.2 Formulation of the DSRG Based on A Generalized Reference Wave Function

In this section, we will formulate a unitary version of the DSRG using the formalism of generalized normal ordering.^{221,226–229} For a detailed introduction to the generalized normal



Figure 4.2: Definition of orbital spaces and their corresponding orbital indices used in this work.

ordering we direct the reader to Refs. 203,221,226–229. Additionally, we provide a summary of this topic in the Supporting Information. Following the conventional definition of active space, the spin orbitals { ϕ^p , $p = 1, \dots, N$ } are partitioned into three distinct subsets: core (**C**), active (**A**), and virtual (**V**), of dimensions $N_{\mathbf{C}}$, $N_{\mathbf{A}}$, and $N_{\mathbf{V}}$, respectively. For convenience, we also consider the sets of generalized hole (**H**) and particle (**P**) spin orbitals, defined as $\mathbf{H} = \mathbf{C} \cup \mathbf{A}$ and $\mathbf{P} = \mathbf{A} \cup \mathbf{V}$, of size $N_{\mathbf{H}}$ and $N_{\mathbf{P}}$, respectively. Figure 4.2 summarizes the orbital spaces and the corresponding orbital index notation used in this work.

The generalized Fermi vacuum Φ used to define the operator normal ordering is a linear combination of Slater determinants (Φ_{μ}) weighted by the coefficients $\{c_{\mu}\}$,

$$\left|\Phi\right\rangle = \sum_{\mu=1}^{d} c_{\mu} \left|\Phi_{\mu}\right\rangle,\tag{4.5}$$

where, without loss of generality, $|\Phi\rangle$ is normalized to one. The determinants that enter in the definition of Φ are chosen to form a complete active space of dimension d, $M_0 = \{\Phi_{\mu}, \mu = 1, \dots, d\}$. That is, we consider all determinants Φ_{μ} with occupied core orbitals and a given number of active electrons (n_{act}) distributed in the active orbitals:

$$|\Phi_{\mu}\rangle = \underbrace{\hat{a}^{u}\hat{a}^{v}\cdots}_{n_{\text{act}}}\prod_{m}^{\mathbf{C}}\hat{a}^{m} |\rangle, \qquad (4.6)$$

where $|\rangle$ is the true vacuum and $\hat{a}^{p}(\hat{a}_{p})$ is a second quantized creation (annihilation) operator.

The second-quantized *bare* Hamiltonian written in the normal ordered form with respect to the vacuum Φ is

$$\hat{H} = E_0 + \sum_{pq} f_p^q \{\hat{a}_q^p\} + \frac{1}{4} \sum_{pqrs} v_{pq}^{rs} \{\hat{a}_{rs}^{pq}\},$$
(4.7)

where $E_0 = \langle \Phi | \hat{H} | \Phi \rangle$ is the energy of the reference Φ and f_p^q is the matrix element of the generalized Fock matrix. The latter is computed from the standard one-electron integrals $(h_q^p = \langle \phi_q | \hat{h} | \phi^p \rangle)$, the antisymmetrized two-electron integrals $(v_{rs}^{pq} = \langle \phi_r \phi_s | | \phi^p \phi^q \rangle)$, and the one-particle density matrix of the reference $(\gamma_q^p = \langle \Phi | \hat{a}^p \hat{a}_q | \Phi \rangle)$:

$$f_p^q = h_p^q + \sum_{rs} v_{pr}^{qs} \gamma_s^r.$$

$$\tag{4.8}$$

In Eq. (4.7), the creation and annihilation operators are written in a compact form,

$$\hat{a}_{ij\cdots}^{ab\cdots} = \hat{a}^a \hat{a}^b \cdots \hat{a}_j \hat{a}_i, \tag{4.9}$$

and normal ordering of the operators is indicated by curly braces.

The DSRG transformed Hamiltonian [H(s)] may be expressed in the normal ordered form with respect to Φ and in general it will be the sum of a scalar term $[\bar{H}_0(s)]$ and various *k*-body operators $[\bar{H}_k(s)]$ with rank *k* as high as the total number of electrons:^{9,191}

$$\bar{H}(s) = \bar{H}_0(s) + \bar{H}_1(s) + \bar{H}_2(s) + \bar{H}_3(s) + \cdots, \qquad (4.10)$$

where a generic k-body operator $\bar{H}_k(s)$ is defined as:

$$\bar{H}_{k}(s) = \frac{1}{(k!)^{2}} \sum_{pqrs\dots} \bar{H}_{pq\dots}^{rs\dots}(s) \{\hat{a}_{rs\dots}^{pq\dots}\}.$$
(4.11)

The unitary operator $\hat{U}(s)$ is conveniently parameterized as the exponential of an anti-Hermitian operator $\hat{A}(s)$:

$$\hat{U}(s) = e^{\hat{A}(s)},$$
(4.12)

where $\hat{A}(s)$ is truncated to a given substitution level *n*:

$$\hat{A}(s) = \sum_{k=1}^{n} \hat{A}_k(s).$$
(4.13)

Each k-body component of $\hat{A}(s)$ [$\hat{A}_k(s)$] is related to an excitation operator [$\hat{T}_k(s)$]:

$$\hat{A}_k(s) = \hat{T}_k(s) - \hat{T}_k^{\dagger}(s),$$
(4.14)

$$\hat{T}_k(s) = \frac{1}{(k!)^2} \sum_{ij\cdots}^{\mathbf{H}} \sum_{ab\cdots}^{\mathbf{P}} t_{ab\cdots}^{ij\cdots}(s) \{\hat{a}_{ij\cdots}^{ab\cdots}\}.$$
(4.15)

The cluster amplitudes $[t_{ab\cdots}^{ij\cdots}(s)]$ are tensors anti-symmetric with respect to the individual permutation of upper and lower indices. In the definition of \hat{T}_k , internal amplitudes corresponding to substitutions involving only active spin orbitals are excluded,

$$t_{uv\cdots}^{xy\cdots} = 0, \quad u, v, x, y \in \mathbf{A} \tag{4.16}$$

since their effect is to relax the coefficients that define the reference wave function (c_{μ}) .

The source operator $[\hat{R}(s)]$ contains contributions from normal ordered many-body op-
erators of different rank:

$$\hat{R}(s) = \hat{R}_1(s) + \hat{R}_2(s) + \cdots$$
(4.17)

There is no scalar contribution in Eq. (4.17) since $\hat{R}(s)$ contains only excitation and deexcitation operators. In accordance with the boundary conditions imposed onto $\hat{U}(s)$, we impose the following requirements onto $\hat{R}(s)$: (1) when s = 0, the non-diagonal component of \bar{H} is identical to the bare Hamiltonian,

$$\hat{R}(0) = [\bar{H}(0)]_{\rm N} = \hat{H}_{\rm N};$$
(4.18)

(2) when $s \to \infty$, the non-diagonal elements of the Hamiltonian vanish,

$$\hat{R}(\infty) = [\bar{H}(\infty)]_{\rm N} = 0.$$
 (4.19)

So far, we have not explicitly identified the expressions for the source operator. For $\hat{R}_k(s)$, we adopt the same parametrization as our previous work, which is determined from a perturbative analysis of the single-reference SRG equations,⁹

$$r_{ab\cdots}^{ij\cdots}(s) = [\bar{H}_{ab\cdots}^{ij\cdots}(s) + t_{ab\cdots}^{ij\cdots}(s)\Delta_{ab\cdots}^{ij\cdots}]e^{-s(\Delta_{ab\cdots}^{ij\cdots})^2}, \qquad (4.20)$$

and $r_{ij\cdots}^{ab\cdots}(s) = [r_{ab\cdots}^{ij\cdots}(s)]^*$. In Eq. (4.20) $\Delta_{ab\cdots}^{ij\cdots}$ is a generalized Møller–Plesset denominator defined in terms of the diagonal components of the Fock matrix ($\varepsilon_p = f_p^p$),

$$\Delta_{ab\cdots}^{ij\cdots} = \varepsilon_i + \varepsilon_j + \cdots - \varepsilon_a - \varepsilon_b - \cdots .$$
(4.21)

Eqs. (4.2)-(4.4) and (4.10)-(4.20) define our unitary multireference DSRG approach. Notice that the DSRG flow equation [Eq. (4.3)] is a set of *many-body* conditions, and it should be interpreted as equating the various normal ordered operator components of $[H(s)]_{\rm N}$ and $\hat{R}(s)$. When the left-hand-side of the DSRG flow equation [Eq. (4.3)] is expanded using the Baker–Campbell–Hausdorff (BCH) formula and the operator components are equated to that of the source operator, one obtains a set of polynomial equations in the amplitudes $t_{ab\cdots}^{ij\cdots}(s)$. In the unitary version of the DSRG, these equations do not truncate, so practical implementations have to resort to use an approximated BCH formula.^{194,230} Alternatively, it is possible to formulate a coupled cluster version of the multireference DSRG, in which the unitary transformation is replaced by a similarity transformation carried out by the exponential of an excitation operator. Nevertheless, these considerations do not affect the perturbative analysis of the DSRG equations carried out in this work. It is also not obvious that the MR-DSRG equations based on the source operator given in Eq. (4.20) always have a solution. However, our previous work⁹ on the single-reference DSRG showed that solutions of the non-perturbative equations can be found even in challenging cases. For example, the dissociation curve of H2O was computed with the single-reference DSRG without encountering convergence problems.

The source operator can be used to illustrate some of the features of the DSRG approach. In both the SRG and the DSRG, the time-like parameter s has a unit of [energy]⁻² and can be associated with an energy cutoff defined as $\Lambda = s^{-1/2}$.^{9,216} The many-body components of \bar{H} that couple the reference $|\Phi\rangle$ to internally-contracted excited configurations $\hat{a}_{ij\cdots}^{ab\cdots} |\Phi\rangle$ can be identified with the matrix elements $\bar{H}_{ab\cdots}^{ij\cdots}(s)$. For a fixed value of s, the elements of $\bar{H}_{ab\cdots}^{ij\cdots}(s)$ with $|\Delta_{ab\cdots}^{ij\cdots}|$ larger than Λ are approximately zero. On the contrary, if $|\Delta_{ab\cdots}^{ij\cdots}| \ll \Lambda$, then the corresponding $\bar{H}_{ab\cdots}^{ij\cdots}(s)$ is in general non-zero. Thus, in the DSRG (and SRG) the parameter s can be used to separate different energy scales of the Hamiltonian, which are expressed as the energy difference between the reference and its excitations or de-excitations. The partial decoupling of the Hamiltonian achieved by the DSRG sets this formalism apart from other nonperturbative many-body approaches. Moreover, this feature is also what guarantees the avoidance of the intruder-state problem in multireference many-body approaches based on the DSRG. This aspect is investigated further in Secs. 4.3.4 and 4.4.3.

4.3.3 Perturbative Analysis of the MR-DSRG Equations

Some of the features of the MR-DSRG theory can be appreciated by conducting a perturbative analysis of the corresponding equations. We will restrict this study to the case of a fixed reference, that is we ignore the relaxation of the coefficients c_{μ} that enter the definition of $|\Phi\rangle$ in Eq. (4.5). Our analysis begins by partitioning the bare Hamiltonian [Eq. (4.7)] into a zeroth-order term $\hat{H}^{(0)}$ plus a first-order perturbation $\hat{H}^{(1)}$ dependent on the parameter ξ ,

$$\hat{H} = \hat{H}^{(0)} + \xi \hat{H}^{(1)}. \tag{4.22}$$

The zeroth-order Hamiltonian includes the reference energy (E_0) and a one-body operator $[\hat{F}^{(0)}],$

$$\hat{H}^{(0)} = E_0 + \hat{F}^{(0)}, \tag{4.23}$$

where $\hat{F}^{(0)}$ contains the diagonal blocks of the Fock matrix corresponding to the core, active, and virtual orbitals:

$$\hat{F}^{(0)} = \sum_{mn}^{\mathbf{C}} f_m^n \{ \hat{a}_n^m \} + \sum_{uv}^{\mathbf{A}} f_u^v \{ \hat{a}_v^u \} + \sum_{ef}^{\mathbf{V}} f_e^f \{ \hat{a}_f^e \}.$$
(4.24)

This choice of $\hat{F}^{(0)}$ guarantees that $\hat{H}^{(0)}$ is invariant with respect to separate rotations of core, active, and virtual orbitals. To simplify the structure of $\hat{F}^{(0)}$, we work in the basis of semi-canonical orbitals, defined in such a way that the core, active, and virtual blocks of the generalized Fock matrix are diagonal.^{231,232} Thus, the zeroth-order generalized Fock

operator is simply

$$\hat{F}^{(0)} = \sum_{p} \varepsilon_p \{ \hat{a}_p^p \}, \qquad (4.25)$$

and it can be expressed using only a set of orbital energies $\{\varepsilon_p\}$, which are the diagonal elements of the generalized Fock matrix, $\varepsilon_p = f_p^p$. The resulting first-order Hamiltonian then contains the one- and two-body terms $\hat{F}^{(1)}$ and $\hat{V}^{(1)}$,

$$\hat{H}^{(1)} = \hat{H} - \hat{H}^{(0)} = \hat{F}^{(1)} + \hat{V}^{(1)}, \qquad (4.26)$$

where the one-body operator $\hat{F}^{(1)}$ involves only the off-diagonal contributions (e.g. coupling orbitals in **C** and **V**, etc.) and the two-body operator $\hat{V}^{(1)}$ corresponds to the full two-body operator $\hat{V} = \frac{1}{4} \sum_{pqrs} v_{pq}^{rs} \{\hat{a}_{rs}^{pq}\}.$

The perturbation theory derived from the many-body formulation of MR-DSRG is obtained by writing the DSRG energy and flow equations [Eqs. (4.3) and (4.4)] as depending on the perturbation ordering parameter ξ :

$$E(s,\xi) = \langle \Phi | \bar{H}(s,\xi) | \Phi \rangle, \qquad (4.27)$$

$$\hat{R}(s,\xi) = [\bar{H}(s,\xi)]_{\rm N} = [e^{-\hat{A}(s,\xi)}\hat{H}e^{\hat{A}(s,\xi)}]_{\rm N},$$
(4.28)

where the source operator $[\hat{R}(s,\xi)]$, the anti-Hermitian operator $[\hat{A}(s,\xi)]$, and the energy $[E(s,\xi)]$ are expanded in power series of ξ :

$$\hat{R}(s,\xi) = \hat{R}^{(0)}(s) + \xi \hat{R}^{(1)}(s) + \xi^2 \hat{R}^{(2)}(s) + \cdots, \qquad (4.29)$$

$$\hat{A}(s,\xi) = \hat{A}^{(0)}(s) + \xi \hat{A}^{(1)}(s) + \xi^2 \hat{A}^{(2)}(s) + \cdots, \qquad (4.30)$$

$$E(s,\xi) = E^{(0)}(s) + \xi E^{(1)}(s) + \xi^2 E^{(2)}(s) + \cdots$$
(4.31)

Expanding the transformed Hamiltonian $[\bar{H}(s,\xi)]$ and subsequently collecting terms with the same power of ξ yields the working equations for the MR-DSRG perturbation theory.

The zeroth-order DSRG equation is satisfied by the trivial solution $\hat{A}^{(0)}(s) = 0$, which implies that zeroth-order energy corresponds to the energy of the reference,

$$E^{(0)}(s) = \langle \Phi | \bar{H}^{(0)}(s) | \Phi \rangle = \langle \Phi | E_0 + \hat{F}^{(0)} | \Phi \rangle = E_0, \qquad (4.32)$$

where we have employed the fact that $\hat{F}^{(0)}$ is normal ordered with respect to the vacuum Φ .

The first-order contribution to the energy is null,

$$E^{(1)}(s) = \langle \Phi | \hat{H}^{(1)} + [\hat{H}^{(0)}, \hat{A}^{(1)}(s)] | \Phi \rangle = 0, \qquad (4.33)$$

since $\hat{H}^{(1)}$ is normal ordered with respect to Φ and $\hat{A}^{(1)}(s)$ does not contain internal excitations. The first-order DSRG equation

$$\hat{R}^{(1)}(s) = [\bar{H}^{(1)}(s)]_{\mathrm{N}} = \left(\hat{H}^{(1)} + [\hat{H}^{(0)}, \hat{A}^{(1)}(s)]\right)_{\mathrm{N}},\tag{4.34}$$

leads to the following expressions for the first-order amplitudes:

$$t_{a}^{i,(1)}(s) = \frac{\left[f_{a}^{i,(1)} + \sum_{ux}^{\mathbf{A}} \Delta_{u}^{x} t_{ax}^{iu,(1)}(s) \gamma_{u}^{x}\right] \left[1 - e^{-s(\Delta_{a}^{i})^{2}}\right]}{\varepsilon_{i} - \varepsilon_{a}},$$
(4.35)

$$t_{ab}^{ij,(1)}(s) = \frac{v_{ab}^{ij,(1)}[1 - e^{-s(\Delta_{ab}^{ij})^2}]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}.$$
(4.36)

Notice that when $|\Delta_{ab}^{ij}|$ (or $|\Delta_a^i|$) greater than the energy cutoff $\Lambda = s^{-1/2}$, the first-order amplitudes resemble the equations of open-shell perturbation theory. Eqs. (4.35) and (4.36) were derived using the generalized Wick's theorem, and details are provided in the Supporting Information. The first non-trivial correction to the energy appears at second-order with respect to the perturbation parameter ξ ,

$$E^{(2)}(s) = \langle \Phi | [\hat{H}^{(1)}, \hat{A}^{(1)}(s)] | \Phi \rangle + \frac{1}{2} \langle \Phi | [[\hat{H}^{(0)}, \hat{A}^{(1)}(s)], \hat{A}^{(1)}(s)] | \Phi \rangle$$

= $\frac{1}{2} \langle \Phi | [\tilde{H}^{(1)}(s), \hat{A}^{(1)}(s)] | \Phi \rangle, \qquad (4.37)$

where we used Eq. (4.34) to simplify the energy expression and introduced a modified firstorder effective Hamiltonian, $\tilde{H}^{(1)}(s) = \hat{H}^{(1)}(s) + \hat{R}^{(1)}(s)$, with *s*-dependent non-diagonal components:

$$\tilde{f}_{a}^{i,(1)}(s) = f_{a}^{i,(1)} [1 + e^{-s(\Delta_{a}^{i})^{2}}] + [\sum_{ux} \Delta_{u}^{x} t_{ax}^{iu,(1)}(s)\gamma_{u}^{x}] e^{-s(\Delta_{a}^{i})^{2}},$$
(4.38)

$$\tilde{v}_{ab}^{ij,(1)}(s) = v_{ab}^{ij,(1)} [1 + e^{-s(\Delta_{ab}^{ij})^2}].$$
(4.39)

The various terms that contribute to the DSRG-MRPT2 energy are reported in Table 4.1. These energy contributions are given in terms of the modified one- and two-body integrals $[\tilde{f}_a^{i,(1)}(s)]$ and $\tilde{v}_{ab}^{ij,(1)}(s)]$, the one-particle density matrix (γ) , the one-hole density matrix defined as the difference between identity matrix and one-particle density matrix $(\eta = 1 - \gamma)$, and the two- and three-body cumulants (λ_2, λ_3) of the reference wave function.

The first-order amplitude equations [Eqs. (4.35) and (4.36)] together with the expressions for the second-order energy [Eq. (4.37) and Table 4.1] define the second-order MR-DSRG perturbation theory (DSRG-MRPT2). It is worth pointing out several advantages of the DSRG-MRPT2 method. The first-order amplitudes and $E^{(2)}$ can be computed via an efficient non-iterative procedure that, in most common situations ($N_{\mathbf{A}} \ll N_{\mathbf{C}} < N_{\mathbf{V}}$) and excluding the cost of integral transformation, is dominated by a term proportional to $\mathcal{O}(N_{\mathbf{H}}^2 N_{\mathbf{P}}^2)$. Although our formulation of the DSRG-MRPT2 requires at most the threeparticle density cumulant (λ_3), resulting in a $\mathcal{O}(N_{\mathbf{A}}^6 N_{\mathbf{V}})$ scaling, this is not expected to be a major bottleneck when $N_{\mathbf{A}} < 20\text{--}30$ orbitals. However, we also consider an approximate version of the DSRG-MRPT2 in which the three-body cumulant is neglected from the $E^{(2)}$ equations. This approximation avoids the $\mathcal{O}(N_{\mathbf{A}}^6)$ memory cost required to store λ_3 and reduces the scaling of $E^{(2)}$ with respect to the number of active orbitals down to $\mathcal{O}(N_{\mathbf{A}}^4 N_{\mathbf{V}}^2)$. Also notice that a novel renormalization term $[\hat{R}^{(1)}(s)]$ appears in the expression of $E^{(2)}$. In our numerical studies we found that for finite values of s, $\hat{R}^{(1)}(s)$ has the net effect of increasing the magnitude of the second-order correlation energy. As $s \to \infty$, the energy contribution from $\hat{R}^{(1)}(s)$ gradually vanishes.

We end this section by pointing out connections between the $s \to \infty$ limit of the DSRG-MRPT2 and other perturbation theories. In the general case, DSRG-MRPT2 $(s \to \infty)$ is analogous to Brandow's second-order multireference many-body perturbation theory (MR-MBPT2),²³³ with the difference that in the former case the reference is a multideterminantal wave function instead of a core closed-shell determinant. When the model space consists of a single high-spin open-shell determinant, the DSRG-MRPT2 $(s \to \infty)$ reproduces the second-order restricted open-shell Møller–Plesset (ROMP) theory of Amos, Andrews, Handy and Knowles,²³⁴ while in the case of a single closed-shell determinant, the DSRG-MRPT2 $(s \to \infty)$ is identical to the second-order Møller–Plesset (MP2) energy.

4.3.4 Avoidance of Intruders in the DSRG

An analysis of the amplitude expressions of Eqs. (4.35) and (4.36) in the limit of small energy denominators elucidates the mechanism by which the MR-DSRG avoids the intruderstate problem. For example, as $|\Delta_{ab}^{ij}| \rightarrow 0$, the $t_{ab}^{ij,(1)}(s)$ amplitude can be expressed as a Taylor series of $f(z) = (1 - e^{-z^2})/z$ expanded in the dimensionless variable $z = \sqrt{s}\Delta_{ab}^{ij}$:

$$t_{ab}^{ij,(1)}(s) = v_{ab}^{ij,(1)}\sqrt{s}f(z) = s v_{ab}^{ij,(1)}\Delta_{ab}^{ij} + \mathcal{O}[s^{\frac{3}{2}}(\Delta_{ab}^{ij})^3],$$
(4.40)

Table 4.1: DSRG-MRPT2 zeroth- and second-order energy expressions. All quantities are given in terms of the one-particle density matrix (γ_q^p) , the one-hole density matrix (η_q^p) , the two-body cumulant (λ_{xy}^{uv}) , and the three-body cumulant (λ_{xyz}^{uvw}) of the reference (Φ) . The Einstein convention for the summation over the repeated indices is employed. See Figure 4.2 for the definition of the orbital spaces and their corresponding indices.

Term	Energy Expression
$E^{(0)}$	$f_p^q \gamma_q^p - \frac{1}{2} v_{pq}^{rs} \gamma_r^p \gamma_s^q + \frac{1}{4} v_{pq}^{rs} \lambda_{rs}^{pq}$
$\frac{1}{2} \langle [\tilde{F}^{(1)}(s), \hat{A}_1^{(1)}(s)] \rangle$	$+ \tilde{f}_{j}^{b,(1)}(s) t_{a}^{i,(1)}(s) \gamma_{i}^{j} \eta_{b}^{a}$
$\frac{1}{2} \langle [\tilde{V}^{(1)}(s), \hat{A}_1^{(1)}(s)] \rangle$	$+\frac{1}{2}\tilde{v}_{xy}^{ev,(1)}(s)t_{e}^{u,(1)}(s)\lambda_{uv}^{xy}$
	$-\frac{1}{2}\tilde{v}_{my}^{uv,(1)}(s)t_x^{m,(1)}(s)\lambda_{uv}^{xy}$
$\frac{1}{2} \langle [\tilde{F}^{(1)}(s), \hat{A}^{(1)}_2(s)] \rangle$	$+\frac{1}{2}\tilde{f}_{x}^{e,(1)}(s)t_{ey}^{uv,(1)}(s)\lambda_{uv}^{xy}$
	$-\tfrac{1}{2}\tilde{f}^{v,(1)}_m(s)t^{um,(1)}_{xy}(s)\lambda^{xy}_{uv}$
$\frac{1}{2} \langle [\tilde{V}^{(1)}(s), \hat{A}_{2}^{(1)}(s)] \rangle$	$+ \tfrac{1}{4} \tilde{v}_{kl}^{cd,(1)}(s) t_{ab}^{ij,(1)}(s) \gamma_{i}^{k} \gamma_{j}^{l} \eta_{c}^{a} \eta_{d}^{b}$
	$+ \frac{1}{8} \tilde{v}^{cd,(1)}_{xy}(s) t^{uv,(1)}_{ab}(s) \eta^a_c \eta^b_d \lambda^{xy}_{uv}$
	$+ \tfrac{1}{8} \tilde{v}_{kl}^{uv,(1)}(s) t_{xy}^{ij,(1)}(s) \gamma_i^k \gamma_j^l \lambda_{uv}^{xy}$
	$+\tilde{v}^{vb,(1)}_{jx}(s)t^{iu,(1)}_{ay}(s)\gamma^j_i\eta^a_b\lambda^{xy}_{uv}$
	$+ \tfrac{1}{4} \tilde{v}_{iz}^{uv,(1)}(s) t_{xy}^{iw,(1)}(s) \lambda_{uvw}^{xyz}$
	$+\frac{1}{4}\tilde{v}_{xy}^{wa,(1)}(s)t_{az}^{uv,(1)}(s)\lambda_{uvw}^{xyz}$

and similarly for the t_1 amplitude equation. Eq. (4.40) shows that for finite values of s small energy denominators cannot cause the DSRG-MRPT2 first-order amplitudes to diverge. As a consequence, $E^{(2)}(s)$ is also well behaved when one or more energy denominators approach or become equal to zero. This feature of the DSRG-MRPT2 is due to the term f(z) in Eq. (4.40), which may be viewed as a subtle way to regularize the energy denominators. We also notice that the function f(z) is odd with respect to z and goes to zero as $z \to 0$. For a fixed value of $v_{ab}^{ij,(1)}$ when the energy denominator Δ_{ab}^{ij} goes from zero to infinity, $t_{ab}^{ij,(1)}(s)$ first increases and then decreases. As a result, the DSRG regularization may introduce "ripples" in potential energy surfaces. However, this problem cannot be avoided because any odd regularization function that yields a finite amplitude in the limit $\Delta_{ab}^{ij} \to 0$ will have a discontinuity at the origin and—even worse—will introduce "jumps" in potential energy surfaces. This happens, for example, if the regularized denominator takes the form $g(z) = (1 - e^{-|z|})/z.$

Both the perturbative and non-perturbative versions of the DSRG (and the SRG) are inherently intruder free, and this feature differentiates them from regularization techniques commonly applied *a posteriori* to address the intruder-state problem in multireference perturbation theories.^{201,202,235} The DSRG-MRPT2 regularized denominator may also be related to the restrained denominator MP2 of Ohnishi, Ishimura, and Ten-no,²³⁶ which has been employed to improve the accuracy of intermolecular interaction energies computed with MP2. This approach uses a modified denominator of the form $\max(\tau, \Delta_{ab}^{ij})$, where τ is an energy threshold set equal to approximately 2.4 $E_{\rm h}$. Interestingly, this energy threshold falls within the optimal range of energy cutoff identified in this work ($\Lambda \in [1,3] E_{\rm h}$).

How should one choose the flow parameter s? This question will be addressed in two ways. Here we provide boundaries on s that are deduced by imposing conditions on the DSRG transformation, while in Sec. 4.4.3 we study how the choice of s affects the accuracy of the DSRG-MRPT2 energy. In general, the choice of s is dictated by two requirements. On one hand, the amount of correlation energy recovered by the DSRG increases with s, and so this quantity should be chosen to be as large as possible. On the other hand, if s is too large, the DSRG will be more sensitive to small energy denominators. Our objective is to determine an upper bound on s that guarantees that the DSRG transformation avoids the appearance of intruder states, corresponding to large t amplitudes. To this end, we seek a condition on s to ensure that the absolute value of the DSRG amplitudes is less than a certain maximum value (t_{max}):

$$\|t_{ab}^{ij,(1)}(s)\|_{\max} < t_{\max},\tag{4.41}$$

where $\|\cdot\|_{\text{max}}$ indicates the elementwise max norm of a tensor. To impose Eq. (4.41) we first

notice that the following inequality holds:

$$\|t_{ab}^{ij,(1)}(s)\|_{\max} \le \|v_{ab}^{ij,(1)}\|_{\max} \max_{z} |f(z)|\sqrt{s}.$$
(4.42)

A sufficiency condition that satisfies Eq. (4.41) can be derived by imposing:

$$\|v_{ab}^{ij,(1)}\|_{\max} \max_{z} |f(z)|\sqrt{s} < t_{\max}.$$
(4.43)

Using the fact that the maximum of |f(z)| with respect to z is $\max_{z} |f(z)| = (1 - e^{-c^2})/c = 0.6382$, where c = 1.1209, we arrive at the following condition:

$$s < \left[\frac{t_{\max}}{0.6382 \|v_{ab}^{ij,(1)}\|_{\max}}\right]^2.$$
(4.44)

Eq. (4.44) can be used to derive an upper bound for s. A reasonable choice of t_{max} is 0.1, which is equivalent to require that no excited configuration has a weight larger than 1%. Furthermore, we assume that the maximum value of two-electron integral for valencevalence excitations is around 0.1 $E_{\rm h}$ ($\|v_{ab}^{ij,(1)}\|_{\rm max} \approx 0.1$). Under these assumptions we obtain the condition $s < 2.46 E_{\rm h}^{-2}$, which is equivalent to an energy cutoff $\Lambda > 0.64 E_{\rm h}$. We take this result as an indication that s should be chosen to be of the order of one $E_{\rm h}^{-2}$ or less.

4.3.5 Formal Aspects of the MR-DSRG

In this section we discuss formal properties of the MR-DSRG, including the invariance of the energy with respect to orbital rotations, size consistency and extensivity, and vacuum relaxation effects. The source operator used in this work [Eq. (4.20)] is identical to the one previously used in the single-reference DSRG,⁹ and it is not orbital invariant. However, we have recently discovered that it is possible to write a more general version of the source operator that is orbital invariant and that coincides with Eq. (4.20) in a semi-canonical orbital basis. Since in the DSRG-MRPT2 it is always computationally advantageous to work with a diagonal zeroth-order operator, the issue of restoring orbital invariance has little practical importance. Therefore, we leave this topic for future work on nonperturbative versions of the MR-DSRG.

Since all quantities that enter the MR-DSRG energy and amplitude equations are connected, this theory and the DSRG-MRPT2 are size extensive. The connectivity of the MR-DSRG equations also implies that if the molecular orbital basis is *localized* on separate molecular fragments, then the sum of the energy of isolated fragments is equal to the energy computed on a supramolecular species composed of noninteracting fragments.²³⁷ Size consistency was confirmed numerically on the systems $H_2 \cdots H_2$ and $HF \cdots HF$ using a four-electron in four-orbital active space for the supramolecular species and a two-electron in two-orbital active space for the individual fragments.

Finally, we comment on the issue of relaxation of the reference in the MR-DSRG and other multireference theories based on generalized normal ordering. Any formalism that expresses the exact wave function $(|\Psi\rangle)$ as a wave operator $\hat{\Omega}$ applied to a multideterminantal reference, $|\Psi\rangle = \hat{\Omega} |\Phi\rangle$, must either allow the reference to relax by treating the expansion coefficients as variables, or include internal amplitudes that can change the weight of the reference determinants in $\hat{\Omega}$. The first option is usually the most convenient, and it produces theories that are numerically robust. For example, this approach is at the basis of recent formulations of the internally-contracted multireference theories.^{26,206–209,238} Reference relaxation effects can be introduced in the MR-DSRG following the same approach used in other internally-contracted multireference theories. In practice this requires solving the MR-DSRG equations and diagonalizing \bar{H} in the model space until a self-consistent solution is reached. As the reference changes, so do the density matrix, the cumulants, and the normal ordered operators. Alternatively, the DSRG transformed Hamiltonian can be diagonalized in a space of determinants (configurations)—generally much larger than the model space—that accounts for orbital and reference relaxation. This strategy is followed for example in several multireference coupled cluster methods developed by Nooijen and co-workers.^{190–193}

4.4 Results

4.4.1 Dissociations of Hydrogen Fluoride and Nitrogen

The accuracy of DSRG-MRPT2 was initially tested on the potential energy curves of the $X^{1}\Sigma^{+}$ state of hydrogen fluoride and the $X^{1}\Sigma_{g}^{+}$ state of the nitrogen molecule. A two-electron two-orbital CASSCF [CASSCF(2,2)] reference was employed for HF, while a six-electron in six-orbital CASSCF [CASSCF(6,6)] reference was used for N₂. Comparisons with second-order complete-active-space perturbation theory (CASPT2), ^{174,175,239} the partially contracted variant of second-order *n*-electron valence perturbation theory (pc-NEVPT2), ^{178–181} Mukherjee second-order perturbation theory (Mk-MRPT2), ^{186,187,203,204,240} internally-contracted multireference configuration interaction with singles and doubles ^{183,184} and Davidson's correction ²⁴¹ (ic-MRCISD+Q) and full configuration interaction (FCI) were made where possible. All computations employed Dunning's correlation-consistent cc-pVDZ basis set.⁴⁴ The 1*s*-like CASSCF molecular orbitals on nitrogen and fluorine atoms were excluded from the correlation treatment. The DSRG-MRPT2 method was implemented as a plugin to the PSI4²⁴² package. CASSCF, ^{243,244} CASPT2, pc-NEVPT2, ic-MRCISD+Q and FCI results were obtained using the MoLPRO 2010.1 package, ⁹⁶ while Mk-MRPT2 energies were computed with PSI4.²⁴²

The potential energy curves (PECs) for the lowest singlet state of HF and N₂ are depicted in the upper panel of Figures 4.3 and 4.4, respectively. In the case of N₂, we use ic-MRCISD+Q as the benchmark since it is more affordable and is known to provide highly parallel results compared to FCI.^{184,246} As illustrated in Figure 4.4, ic-MRCISD+Q (the black curve) deviates from FCI results²⁴⁵ (gray dots) by at most 1.8 m $E_{\rm h}$ at $r_{\rm N-N} = 4.2a_0$.



Figure 4.3: Potential energy curves for the $X^{1}\Sigma^{+}$ state of HF computed using various methods and the cc-pVDZ basis set. The upper panel shows the absolute energy, while the lower panel shows the energy deviation from the FCI. All multireference perturbation theories employed a CASSCF(2,2) reference. The fluorine 1s orbital was excluded from the correlation treatment. DSRG-MRPT2 and DSRG-MRPT2 ($\lambda_{3} = 0$) employed a flow parameter of $s = 0.5 E_{\rm h}^{-2}$, and the MR-MBPT2 curve is identical to the curve of DSRG-MRPT2 ($s \to \infty$).



Figure 4.4: Potential energy curves for the $X \, {}^{1}\Sigma_{g}^{+}$ state of N₂ computed using various methods and the cc-pVDZ basis set. The upper panel shows the absolute potential energy curves, while the lower panel illustrates the energy deviation from the ic-MRCISD+Q. FCI results taken from Ref. 245 are shown as dots in the top panel. All methods employed a CASSCF(6,6) reference and 1*s*-like orbitals on nitrogen atoms were excluded from the correlation treatment. DSRG-MRPT2 and DSRG-MRPT2 ($\lambda_{3} = 0$) employed a flow parameter of $s = 0.5 E_{\rm h}^{-2}$, and the MR-MBPT2 curve is identical to the curve of DSRG-MRPT2 ($s \to \infty$).

Potential energy curves for the multireference DSRG-MRPT2 were computed at s = 0.5 $E_{\rm h}^{-2}$, which corresponds to an energy cutoff $\Lambda = 1.4 E_{\rm h}$. We momentarily postpone a more detailed discussion of the choice of s to Sec. 4.4.3. However, our choice of the value of s is consistent with our finding that the optimal range for s is roughly [0.1,1] $E_{\rm h}^{-2}$. In addition to the DSRG-MRPT2 energy, we also show the potential curve computed at the MR-MBPT2 level of theory, which is obtained as the $s \to \infty$ limit of the DSRG-MRPT2.

Table 4.2: Spectroscopic constants for the $X^{1}\Sigma^{+}$ state of HF and the $X^{1}\Sigma_{g}^{+}$ state of N₂ computed using various methods and the cc-pVDZ basis set. Equilibrium distances (r_{e} , in Å), the harmonic frequencies (ω_{e} , in cm⁻¹), and anharmonicity constants ($\omega_{e}x_{e}$, in cm⁻¹) are given as deviations from reference values reported at the bottom of each section. The 1*s*-like molecular orbitals of fluorine and nitrogen were excluded from the correlation treatment. The value of the flow parameter *s* used in the DSRG-MRPT2 computations is indicated in parentheses.

Method	r_e	ω_e	$\omega_e x_e$	
HF				
CASSCF(2,2)	0.0008	-81.3	10.2	
CASPT2	0.0000	0.7	-0.1	
pc-NEVPT2	0.0035	-15.1	-8.2	
Mk-MRPT2	0.0041	-39.5	-6.1	
DSRG-MRPT2 (0.1)	-0.0004	24.2	-2.4	
DSRG-MRPT2 (0.5)	-0.0026	10.3	1.4	
DSRG-MRPT2 (1.0)	-0.0065	15.0	6.4	
DSRG-MRPT2 $(0.1, \lambda_3=0)$	-0.0010	40.3	-3.3	
DSRG-MRPT2 $(0.5, \lambda_3=0)$	-0.0036	38.5	-2.0	
DSRG-MRPT2 $(1.0, \lambda_3=0)$	-0.0075	41.6	1.5	
ic-MRCISD+Q	0.0000	-0.8	-0.1	
FCI	0.9203	4143.2	92.9	
\mathbf{N}_2				
CASSCF(6,6)	-0.0060	43.9	-0.3	
CASPT2	-0.0012	4.4	0.3	
pc-NEVPT2	0.0000	-4.1	0.6	
Mk-MRPT2	-0.0012	8.9	0.1	
DSRG-MRPT2 (0.1)	-0.0032	23.9	-0.0	
DSRG-MRPT2 (0.5)	-0.0013	-1.3	0.7	
DSRG-MRPT2 (1.0)	-0.0021	10.0	1.2	
DSRG-MRPT2 $(0.1, \lambda_3=0)$	-0.0046	38.7	-0.1	
DSRG-MRPT2 $(0.5, \lambda_3=0)$	-0.0040	30.5	0.2	
DSRG-MRPT2 $(1.0, \lambda_3=0)$	-0.0045	44.0	0.7	
ic-MRCISD+Q	1.1204	2321.4	14.9	

For both HF and N_2 , the DSRG-MRPT2 method yields continuous curves that parallel the benchmark results. On the contrary, it is striking to see that intruders are pervasive in the MR-MBPT2 curves. In the case of HF, intruders significantly shift the energy minimum to longer bond distances. In the case of N₂, intruders plague the entire potential energy curve and render it useless. Notice that in the vicinity of the intruders, both the MR-MBPT2 and DSRG-MRPT2 curves were sampled on a very fine grid, and that the latter shows no discontinuities. We also note that CASPT2, pc-NEVPT2 and Mk-MRPT2 yield smooth PECs for both the $X^{1}\Sigma^{+}$ state of HF and the $X^{1}\Sigma_{g}^{+}$ state of N₂. It is known in CASPT2 that the choice of zeroth-order Hamiltonian $[\hat{H}^{(0)}]$ affects the presence of the intruder state.¹⁸¹ For example, when $\hat{H}^{(0)}$ is a one-particle Hamiltonian, CASPT2 computations of excited states are prone to the intruder-state problem.²⁰¹ Mk-MRPT2 is guaranteed to be free from intruders only for the ground electronic states.²⁴⁰ In NEVPT2^{178,181} the absence of intruders is generally guaranteed by the use of Dyall Hamiltonian,²⁴⁷ which contains the active components of the two-body interaction.

The DSRG-MRPT2 is compared to other multireference perturbation theories in the lower panel of Figures 4.3 and 4.4, where we plot the energy error (ΔE) computed with respect to the benchmark curves. The DSRG-MRPT2 error remains fairly constant, and the resulting non-parallelism errors (NPE) are 4.5 and 18.1 m $E_{\rm h}$ for HF and N₂, respectively. The same figures for pc-NEVPT2 (6.7 and 2.2 m $E_{\rm h}$), Mk-MRPT2 (4.1 and 9.0 m $E_{\rm h}$), and CASPT2 (0.2 and 8.7 m $E_{\rm h}$) show that these methods tend to be more accurate than the DSRG-MRPT2, especially in the case of N₂. We also notice that neglecting the three-body cumulant in the DSRG-MRPT2 ($\lambda_3 = 0$), produces potential energy curves of HF and N₂ with larger absolute errors, especially at intermediate bond lengths. At large bond distances λ_3 appears to play a minor role. This is in agreement with prior observations that the oddrank density cumulants for N₂ vanish in the limit of infinite bond distance.²⁴⁸ The NPE for the DSRG-MRPT2 ($\lambda_3 = 0$) method also increases and it is about twice as large as that of DSRG-MRPT2: 7.7 and 27.1 m $E_{\rm h}$ for HF and N₂, respectively.

Table 4.2 reports the spectroscopic constants of HF and N_2 for different methods obtained

by a polynomial fitting of single point calculations. As in the case of the potential energy curves, our DSRG-MRPT2 theory yields results comparable to those obtained from other second-order perturbation theories. For example, the harmonic frequencies of HF and N₂ predicted by DSRG-MRPT2 (s = 0.5) only differ from the benchmark values by 10.3 and -1.3 cm^{-1} , respectively. Spectroscopic constants are relatively insensitive to the choice of s: computations that use $s = 0.5 E_{\rm h}^{-2}$ yield results that are in good agreement with the ones obtained using s = 0.1 and $1.0 E_{\rm h}^{-2}$. For N₂ we notice that the magnitude of the deviation of r_e and ω_e for different values of s is similar to the one observed in the uncorrected CASPT2 method with a level shift.²⁰¹

Results obtained neglecting the contributions of the three-body cumulants are also reported in Table 4.2. This approximation slightly deteriorates the quality of the properties, but the largest deviations in bond length and the vibrational frequency are smaller than 0.002 Å and 20 cm^{-1} , respectively. This observation suggests that neglecting the three-body cumulant might be a viable approximation that would be especially convenient when treating very large active spaces. However, additional benchmark results are necessary to assess the consequences that neglecting λ_3 has on the quality of the DSRG-MRPT2 results.

4.4.2 SINGLET-TRIPLET SPLITTINGS OF *p*-BENZYNE

As an example application of the DSRG-MRPT2 to medium-size molecules, we considered the singlet-triplet splitting ($\Delta E_{\rm ST}$) of *para*-benzyne, which has been studied extensively both experimentally²⁴⁹ and theoretically.^{204,208,209,250–255} The simplest active space for such diradical system is the two-electron in two-orbital complete active space CAS(2,2) that involves only the σ and σ^* orbitals. However, we also report results obtained with an active space that includes the six π orbitals [CAS(8,8)]. To examine the robustness of the current perturbation theory, we employed three values of the flow parameter (0.1, 0.5, 1.0 $E_{\rm h}^{-2}$) and compared the results of DSRG-MRPT2 with other MRPT methods including CASPT2, pc-



Figure 4.5: Equilibrium structures of *p*-benzyne optimized at the Mk-MRCCSD/cc-pVTZ level of theory in Ref. 208. Bond lengths are in Å and bond angles are in degrees. The 1*s*-like molecular orbitals on carbon atoms were kept frozen.

NEVPT2 and Mk-MRPT2. The singlet and triplet geometries were taken from Ref. 208 and are shown in Figure 4.5. These structures were optimized at the Mk-MRCCSD/cc-pVTZ level of theory using CASSCF(2,2) and ROHF references for the singlet and triplet states, respectively. All computations utilized the cc-pVTZ basis set⁴⁴ and the six 1*s*-like molecular orbitals on carbon atoms were excluded from the correlation treatment. The computed singlet-triplet splittings include a zero-point vibrational energy (ZPVE) correction (+0.3 kcal mol⁻¹) taken from Ref. 208.

The results of our computations are reported in Table 4.3. For the small active space, both CASPT2 and pc-NEVPT2 show satisfactory agreement with the photoelectron spectroscopy experiment, while the DSRG-MRPT2 (s = 0.5) and Mk-MRPT2 underestimate $\Delta E_{\rm ST}$ by more than 1.0 kcal mol⁻¹. In the case of Mk-MRPT2, relaxing the reference brings $\Delta E_{\rm ST}$ closer to values computed with nonperturbative methods like Mk-MRCCSD and ic-MRCCSD(T). The large relaxation effects observed for Mk-MRPT2 suggest that DSRG-MRPT2 might also benefit from the relaxation of the reference. However, as discussed earlier, this introduces some new aspects in the formulation of the theory. The singlet-triplet splitting computed with the DSRG-MRPT2 shows little variation when s goes from 0.5 to 1.0 $E_{\rm h}^{-2}$ (2.62 and 2.96 kcal mol⁻¹, respectively), however, the value obtained

Table 4.3: Adiabatic singlet-triplet splittings ($\Delta E_{\rm ST}$, in kcal mol⁻¹) of *p*-benzyne using various methods with cc-pVTZ basis set. ZPVE corrections $(+0.30 \text{ cm}^{-1})$ are included from Ref. 208. All results used the geometries taken from Ref. 208 and that are also reported in Figure 4.5. The value of the flow parameter s used in the DSRG-MRPT2 computations is indicated in parentheses.

Method	$\Delta E_{\rm ST}$			
CAS(2,2)				
CASSCF	0.32			
CASPT2	4.49			
pc-NEVPT2	3.66			
Mk-MRPT2	2.44			
Mk-MRPT2 (relaxed)	4.91			
DSRG-MRPT2 (0.1)	1.25			
DSRG-MRPT2 (0.5)	2.62			
DSRG-MRPT2 (1.0)	2.96			
DSRG-MRPT2 $(0.5, \lambda_3=0)$	2.10			
Mk-MRCCSD ^a	5.20			
$Mk-MRCCSD(T)^{a}$	4.45			
ic-MRCCSD $(T)^{b}$	5.18			
CAS(8,8)				
CASSCF	2.38			
CASPT2	5.72			
pc-NEVPT2	4.78			
DSRG-MRPT2 (0.1)	3.15			
DSRG-MRPT2 (0.5)	4.23			
DSRG-MRPT2 (1.0)	4.36			
DSRG-MRPT2 (0.5, $\lambda_3=0$)	3.33			
Exp. ^c	3.8 ± 0.4			
^a From Ref. 208.				

^b From Ref. 209.

^c From Ref. 249.

when $s = 0.1 E_{\rm h}^{-2}$ is smaller (1.25 kcal mol⁻¹). This is likely to be a consequence of the fact that the DSRG transformation computed with s = 0.1 neglects important contributions from low-lying excited configurations that fall under the energy cutoff $\Lambda = 3.2 E_{\rm h}$.

All $\Delta E_{\rm ST}$ values increase for the corresponding MRPT methods when employing the larger active space. The DSRG-MRPT2 (s = 0.5) method based on a CASSCF(8,8) reference



Figure 4.6: Energy error for the DSRG-MRPT2 [$\Delta E(r,s) = E_{\text{DSRG-MRPT2}}(r,s) - E_{\text{ref}}(r)$] for (a) HF against FCI and (b) N₂ against ic-MRCISD+Q as a function of the bond length (r) and flow parameter (s). Numerical ranges reported in the plot indicate the lower and upper limits of a contour area. Results were computed using the cc-pVDZ basis set. The CASSCF(2,2) and CASSCF(6,6) references were utilized for HF and N₂ computations, respectively. The fluorine and nitrogen 1s molecular orbitals were excluded from the correlation treatment.

predicts $\Delta E_{\rm ST} = 4.23$ kcal mol⁻¹, which is in excellent agreement with the 3.8 ± 0.4 kcal mol⁻¹ experimental estimate. Other MRPT methods yield results that are more in line with the state-of-the-art multireference coupled cluster results. Recent work has shown that the selection of the active space plays a less important role in nonperturbative theories. For example, $\Delta E_{\rm ST}$ of *p*-benzyne predicted by the ic-MRCCSD(T) theory with the cc-pVDZ basis set only differs by less than 0.2 kcal mol⁻¹ between CAS(2,2) and CAS(8,8).²⁰⁹

4.4.3 INTRUDER AVOIDANCE AND SENSITIVITY OF THE FLOW PARAMETER

In this section, we will discuss how the choice of the flow parameter s affects the accuracy of the DSRG-MRPT2 energy. Figure 4.6 show contour plots of $\Delta E(r, s)$, the energy differences between DSRG-MRPT2 and the benchmark methods as a function of the bond distance (r) and the flow parameter (s). The white region corresponds to $\Delta E(r, s) = 0$, while the areas in red and blue show regions where $\Delta E(r, s)$ is positive and negative, respectively.

The magnitude of this energy deviation is proportional to the saturation of the color.

As illustrated in Figure 4.6, when s is increased from 0 to about 0.1 $E_{\rm h}^{-2}$, the DSRG-MRPT2 gradually includes dynamical correlation effects and the error decreases. For $s > 10 E_{\rm h}^{-2}$, we notice a significant increase in the error and the appearance of valleys and hills. In the limit $s \to \infty$, we observe intruder states appear as an energy denominator becomes singular. An inspection of the contour plots in Figure 4.6 reveals that when s is in the range $[0.1, 1.0] E_{\rm h}^{-2}$ the DSRG-MRPT2 shows the smallest absolute error and provides potential energy curves with consistent deviations from the benchmark results.

We conclude this section with a more general discussion of the dependence of the DSRG results with respect to the flow parameter. It is important to point out that, above all, the DSRG is a technique to separate dynamical and static correlation effects. The former are included in the scalar energy [E(s)], while the latter are retained in the many-body components of H(s). Since the DSRG transformation is unitary, when the exact H(s) is diagonalized, its eigenvalues will show no dependence on the flow parameter. This discussion leads us to two observations. First, one way to reduce the dependence of the DSRG energy on the value of s is to retain certain components of H(s) and diagonalize the resulting approximate operator. The partial decoupling achieved by the DSRG transformation implies that as s grows, the matrix elements between the reference and excited configurations become sparser (for example, see Figure 4.1). Therefore, the effort required to reintroduce the contributions from near-degenerate configurations that are not included in E(s) is expected to be small. Second, since the perturbative theory derived in this work completely neglects the contributions of H(s), it provides a way to study the dependence of the DSRG energy on s in the worst case scenario. Our results then provide an upper bound for the dependence of the DSRG results on the choice of s.

4.5 Discussions and Conclusions

This work is a contribution to the development of electron correlation methods based on the renormalization group approach. We have proposed a multireference driven similarity renormalization group (MR-DSRG) theory to account for dynamic electron correlation in near-degenerate electronic states. The multireference DSRG is based on a multideterminantal reference wave function and uses the generalized operator normal-ordering of Mukherjee and Kutzelnigg.²²¹ The MR-DSRG approach is closely related to internally-contracted multireference theories, yet distinct in two crucial aspects. First, the MR-DSRG produces a continuous transformation of the Hamiltonian that is controlled by a flow parameter (s) that can be related to an energy cutoff ($\Lambda = s^{-1/2}$). For finite values of s the MR-DSRG suppresses those excitations that correspond to a denominator smaller than Λ . This is a common feature of *renormalization group* approaches and it permits the MR-DSRG to avoid the intruder-state problem. Second, the MR-DSRG is a many-body formalism, ^{190–192} and as such it avoids issues connected to linear dependence of the excitation operator found in other internally-contracted multireference theories.

As a preliminary study of the MR-DSRG, we derived and implemented a companion second-order perturbation theory (DSRG-MRPT2) based on a CASSCF reference wave function. The DSRG-MRPT2 equations are surprisingly simple. In the semi-canonical basis the energy and first-order amplitudes can be obtained via a non-iterative procedure, and the DSRG-MRPT2 requires at most the one-particle density matrix to evaluate the amplitudes and the three-particle density cumulant to compute the second-order correlation energy. A formal analysis of the DSRG-MRPT2 equations shows that divergences in the first-order amplitude equations are prevented by a term that regularizes the energy denominators.

A formal argument and a numerical study were used to establish a reliable range of the flow parameter. This is $s \in [0.1, 1] E_{\rm h}^{-2}$, or alternatively when expressed in terms of the energy cutoff, $\Lambda \in [1,3] E_{\rm h}$. Within this optimal range, the DSRG-MRPT2 gives results that are slightly inferior to those obtained with other multireference perturbation theories, including CASPT2, pc-NEVPT2, and Mk-MRPT2. For example, the equilibrium distance, the harmonic frequency, and the anharmonicity constant of HF computed at the DSRG-MRPT2 level differ from the FCI figures only by 0.0012 Å, 6.2 cm⁻¹, and 4.4 cm⁻¹, respectively. For the adiabatic singlet-triplet splitting ($\Delta E_{\rm ST}$) of *para*-benzyne, the prediction of DSRG-MRPT2 based on an eight-electron in eight-orbital active space is within 0.5 kcal mol⁻¹ from the experimental value²⁴⁹ and consistent for values of the flow parameter in the range [0.5,1.0] $E_{\rm h}^{-2}$. A simplified DSRG-MRPT2 method in which the three-particle cumulant is neglected¹⁹¹ has also been considered. This approximation reduces the computational complexity of DSRG-MRPT2 [from $\mathcal{O}(N_{\rm A}^6N_{\rm V})$ to $\mathcal{O}(N_{\rm A}^4N_{\rm V}^2)$] without compromising the separability properties of the energy. Our results show that neglecting λ_3 increases the nonparallelism error by a factor of two.

There are several aspects of the DSRG-MRPT2 (and the MR-DSRG) that can be improved and deserve further investigation. Given the fact that the final results are sensitive to the flow parameter used in a calculation, it might be desirable (especially in the case of the DSRG-MRPT2) to seek a procedure that reduces the sensitivity of the final results with respect to s.²⁰¹ We expect the nonperturbative MR-DSRG approach to be less sensitive to intruders. If this is the case, then it will be possible to perform computations with values of sthat are larger than the ones used for the DSRG-MRPT2, and no corrections due to the finite value of s will be required. Future work will also have to assess if it is possible to formulate improved source operators, and more importantly, find ways to reduce the s-dependence of the energy by retaining certain components of the DSRG transformed Hamiltonian.

In summary, our analysis of the DSRG-MRPT2 method motivates further developments of the DSRG approach, in particular of the nonperturbative version, which may be a competitor to other internally-contracted multireference theories. At the same time this work also suggests several new directions of inquiry. Given the simplicity of the DSRG-MRPT2 equations, this method should easily lend itself to very efficient implementations that take advantage of integral factorization techniques.^{256–260} Our results on *para*-benzyne motivate the formulation of the DSRG-MRPT2 with a relaxed reference. It would also be interesting to explore extension of the DSRG-MRPT2 to excited states, in particular to state-averaged or multi-state versions of the theory. These new methods may provide superior results when applied to study potential energy surfaces near conical intersections.

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4.7 Supporting Information

See supplementary material at http://pubs.acs.org/doi/suppl/10.1021/acs.jctc. 5b00134/suppl_file/ct5b00134_si_001.pdf for a synopsis of the generalized normal ordering, and the derivation of the first-order DSRG-MRPT2 amplitudes. Chapter 5

Concluding Remarks

Ab initio electronic structure theory is central to modern quantum chemistry, and its development has essentially benefited all fields of chemistry. Quantum chemistry is still evolving to tackle more challenging systems where all kinds of interesting chemistry occur. In this dissertation, we have demonstrated the interplay between the theory and experiment from different perspectives. On one hand, the highly reliable coupled cluster theory has been applied to construct the potential energy surface, on which the vibrational frequencies are obtained from the second-order vibrational perturbation theory. This approach is completely *ab initio* and the results can be systematically improved. Consequently, our computational results can assist experimentalists assigning and interpreting vibrational spectra. On the other hand, experimental values will always be the benchmark for any theoretical model. For instance, the DSRG-MRPT2 predicted value agrees well with the experimental singlettriplet gap of *p*-benzyne, which not only validates itself as a viable perturbation theory, but also motivates us for future developments of the DSRG theory.

In the first work on nonahydridorhenate dianion, we applied the state-of-the-art method to obtain the geometry and vibrational frequencies. As expected, the molecular dianion model is oversimplified, which fails to fully reproduce the experimental findings obtained from a potassium rhenium hydride crystal. To include the effect from the counterions, the nonahydridorhenate dianion is capped with two alkali metal cations to form a sandwich complex, and the results greatly improved from that of the dianion itself. However, the sandwich model is still naive because atoms are arranged periodically in crystals. This fundamental discrepancy can only be eliminated by computing the electronic structure under periodic boundary conditions. Although Hartree-Fock theory and density functional theory are available for periodic systems, they have made limited impact in the solid-state chemistry. On the contrary, correlated methods for such systems are largely undeveloped because of the devastating scalings. Thus, efficient implementations of these correlation methods seem very promising and may revolutionize the field of solid-state chemistry. In the second work, our initial goal is reporting anharmonic frequencies of the *n*-propyl radical to augment the experimental spectra. In order to find the reference geometry for vibrational analysis, we carefully studied the potential energy surface of the methylene internal rotation. This internal rotation is a large amplitude motion, which breaks down the harmonic approximation. As a result, second-order vibrational perturbation theory failed to reproduce the whole spectrum. Eventually, we are able to report the band origins of eleven modes that are largely uncoupled with the methylene torsional motion. The comparison of our predicted values to the available experimental spectrum in an argon matrix yields a perfect agreement. Other predicted anharmonic frequencies thus serve as a guidance for future experimental characterizations.

In the last work, we extended the driven similarity renormalization group approach to an arbitrary multireference wave function. We conducted a perturbative analysis of the MR-DSRG equations at the second order, resulting in the DSRG-MRPT2 theory. The proposed perturbation theory is size extensive, and its energy can be obtained in a noniterative fashion with the same asymptotic cost to the single reference MP2. Numerical results show that DSRG-MRPT2 performs similarly to other multireference perturbation theory including CASPT2, NEVPT2, and Mk-MRPT2. This encouraging result motivates us to further develop of the DSRG approach. The nonperturbative version of the theory is especially of interest, which may be competitive to other internally contracted multireference nonperturbative theories. In this case, a code generator seems necessary to address the considerable number of terms involved in the equations. From the DSRG-MRPT2 point of view, its simplicity should lend itself to highly efficient implementations with the help of density fitting. Furthermore, it would also be advantageous to choose other forms of the zeroth-order Hamiltonian and to incorporate the reference relaxation effect.

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