Hiking the valleys of quantum chemistry

by

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CHAPTER 1. GENERAL INTRODUCTION

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complex to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

P. A. M. Dirac, 1929¹

I. General Overview

Since the early twentieth century, when scientists realized that classical mechanics could not properly describe physical phenomena at the atomic level, quantum chemistry has flourished. The development of quantum chemical methods and the application of these methods to interesting chemical problems have resulted in many valuable tools and insights that affect the world around us. As an example, the medical imaging field has profoundly benefited by new spectroscopic techniques.

Much of quantum chemistry deals with valleys of potential energy surfaces and with methods of determining the "slope" and "elevation" of the hills. So, sit back, relax, and let me be your guide as we hike the landscape of quantum chemistry.

II. Dissertation Organization

This thesis is concerned with both the application and the extension of quantum chemical methods. Each chapter of the thesis represents a paper that has been published in or will be submitted to a scientific journal. The first three chapters of this thesis describe contributions made to chemistry through the use of quantum chemical methods, while the final two chapters illustrate the development of new methods.

Chapter 2 and Chapter 3 characterize a study of the electronic structure and magnetic properties of homodinuclear titanium(III) complexes, in order to determine trends related to

their potential use as molecular magnets. Chapter 2 focuses on hydride and halide bridging and terminal ligands, while Chapter 3 explores bridging ligands from other groups in the periodic table.

Chapter 4 portrays a study of the solvation of glycine. Microsolvation and continuum solvation approaches are investigated in order to study the structures of small glycine-water clusters and determine the energy difference between the zwitterionic and nonionized forms of glycine, the simplest amino acid.

Chapters 5 and 6 describe the implementation of analytic gradients, which are required for efficient molecular geometry optimizations, for two open-shell second-order perturbation theory methods. Chapter 5 discusses gradients for unrestricted Møller-Plesset perturbation theory, and Chapter 6 describes gradients for Z-averaged perturbation theory.

III. Theoretical Background

The non-relativistic time-dependent Schrödinger equation²⁻⁸ provides the basis for most quantum chemical methods. This equation is a complex partial differential equation involving both position $\vec{r}$ and time t :

$$\frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi(\vec{r}, t) \quad (1)$$

where $i = \sqrt{-1}$, $\hbar$ is Planck's constant divided by 2π , and $\hat{H}$ is the Hamiltonian operator.

The solution of equation (1) yields $\Psi(\vec{r}, t)$, which contains all obtainable information about the system. If the Hamiltonian is independent of time, the full time-dependent Schrödinger equation is not required and the simpler time-independent Schrödinger equation,

$$\hat{H} \Psi = E \Psi, \quad (2)$$

may be used. In equation (2), the wave function Ψ is an eigenfunction of the Hamiltonian with eigenvalue E . For a molecular system with n electrons and m nuclei, the Hamiltonian in atomic units may be expressed as

$$\hat{H} = -\sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{A=1}^m \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^n \sum_{A=1}^m \frac{Z_A}{r_{iA}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} + \sum_{A=1}^m \sum_{B>A}^m \frac{Z_A Z_B}{R_{AB}} \quad (3)$$

where ∇^2 is the Laplacian operator, M_A is the ratio of the mass of nucleus A to the mass of an electron, Z_A is the atomic number of nucleus A , r_{iA} is the distance between electron i and nucleus A , r_{ij} is the distance between electrons i and j , and R_{AB} is the distance between nuclei A and B . The first and second terms in equation (3) represent the kinetic energy of the electrons and the nuclei, respectively. The third term is the Coulomb attraction between electrons and nuclei. The fourth and fifth terms correspond to the repulsion between electrons and between nuclei, respectively.

The Born-Oppenheimer approximation⁹ is used to reduce the complexity of the system. Since nuclei are much heavier than electrons, they move much slower, and therefore the electrons in a molecule may be viewed as moving in a field of fixed nuclei. Because of this approximation, the second term in equation (3) may be neglected and the fifth term may be considered to be a constant. The remaining three terms constitute the electronic Hamiltonian:

$$\hat{H}_{elec} = -\sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{i=1}^n \sum_{A=1}^m \frac{Z_A}{r_{iA}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}. \quad (4)$$

The electronic wave function in the field of fixed nuclei may then be determined by

$$\hat{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec}. \quad (5)$$

The total energy is a sum of the electronic energy and the nuclear-nuclear repulsion energy:

$$E_{tot} = E_{elec} + \sum_{A=1}^m \sum_{B>A}^m \frac{Z_A Z_B}{R_{AB}} \quad (6)$$

Once the electronic problem has been solved for a particular configuration of nuclei, it is subsequently possible to solve for the motion of the nuclei. In essence, in the Born-Oppenheimer approximation the nuclei move on a potential energy surface that is obtained by solving the electronic problem. This potential energy surface is of fundamental importance to the study of equilibrium structures and chemical reactions.

For systems with three or more interacting particles, an exact solution to the Schrödinger equation cannot be obtained because the interparticle distances are not separable. Thus, approximate methods must be developed, and this is a major thrust of modern quantum chemistry. As a first approximation, the repulsions that depend on the interparticle distances are ignored; this yields the independent particle model. A product of one-electron wave functions called orbitals is used to approximate the full wave function. This product, called a Hartree product,^{10,12} is the origin of the tight-binding approximation, the extended Hückel approximation, and semi-empirical methods. An antisymmetric linear combination of Hartree products is used to form a Slater determinant^{13,14} in order to satisfy the antisymmetry principle. In a Slater determinant, the motion of electrons with parallel spin is correlated, but the motion of electrons with opposite spin remains uncorrelated.

According to the variational principle, the best single determinant ground state wave function $|\Psi_0\rangle$ is the one that gives the lowest possible energy E_0 , where

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle. \quad (7)$$

In the Hartree-Fock approximation,^{10,12,15,16} the complicated many-electron repulsion problem is replaced by multiple one-electron problems in which electron repulsions are treated in an

average way. Each electron is treated as though it moves in a potential field created by the nuclei and the average charge distribution of the other electrons. This averages out the instantaneous interactions between the electrons. Since the field seen by each electron depends on the orbitals of the other electrons, the Hartree-Fock equation is nonlinear and must be solved iteratively according to the self-consistent field (SCF) method. Trial orbitals for each electron are determined, and the electron density corresponding to these orbitals is calculated. New trial orbitals can then be determined. This procedure is repeated until the energy and trial functions do not change significantly.

In practice, each molecular orbital in the Hartree product may be expanded as a linear combination of basis functions. A molecular orbital ψ_i can be written as

$$\psi_i = \sum_{\mu=1}^N C_{\mu i} \phi_{\mu} \quad (8)$$

where $C_{\mu i}$ are the molecular orbital expansion coefficients, N is the number of basis functions in the expansion, and ϕ_{μ} are the basis functions. As the set of basis functions becomes larger and more complete, the molecular orbitals become more flexible and the Hartree-Fock energy E_0 approaches the complete basis set limit. In restricted Hartree-Fock (RHF) theory, α and β electrons that are paired with each other are given the same spatial orbital. In unrestricted Hartree-Fock (UHF) theory, α and β electrons have different spatial orbitals:

$$\psi_i^{\alpha} = \sum_{\mu=1}^N C_{\mu i}^{\alpha} \phi_{\mu}; \quad \psi_i^{\beta} = \sum_{\mu=1}^N C_{\mu i}^{\beta} \phi_{\mu}. \quad (9)$$

Since this enhances the flexibility of the wave function, the UHF energy will in principle be lower than the RHF energy. However, the UHF functions are not eigenfunctions of the total

spin operator, so they are contaminated by functions corresponding to states of higher spin multiplicity. The amount of spin contamination can provide a measure of the reliability of the UHF results.

The Hartree-Fock orbitals give the best possible single determinant description of the wave function. However, since the exact wave function is not truly a product of one-electron wave functions, there is a need for further improvement. The main drawback to the Hartree-Fock approximation is the neglect of electron correlation between electrons with opposite spins. This type of correlation is often termed dynamic electron correlation since it is related to the instantaneous correlations of electrons. The difference between the exact non-relativistic Born-Oppenheimer energy and the Hartree-Fock energy is called the correlation energy, and much of the effort in the field of electronic structure theory is aimed at approximating this value. In theory, a variational full configuration interaction (CI) calculation in which the exact wave function is represented as a linear combination of Slater determinants with a complete basis set will yield the exact energy. However, this is computationally intractable. Truncated CI methods can recover most of the correlation energy but they are not size-consistent, which means that the energy of a supermolecular system of two noninteracting molecules will not be the same as the sum of the energies of each molecule. Two size-consistent methods that recover much of the correlation energy include perturbation theory and coupled cluster methods. Coupled cluster (CC) methods provide good accuracy with a high computational cost, so they are currently useful primarily in single-point energy calculations, once geometries have been determined at a lower level of theory.

In the perturbation theory approach, the total Hamiltonian of the system is divided into two pieces:

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad (10)$$

$\hat{H}_0$ is the zeroth-order part of the Hamiltonian, which has known eigenfunctions and eigenvalues. The remainder of the Hamiltonian is identified as the perturbation $\hat{V}$. The exact energy may be formulated as an infinite sum of contributions involving eigenvalues of $\hat{H}_0$ and matrix elements of the perturbation with eigenfunctions of $\hat{H}_0$. Ideally, the perturbation $\hat{V}$ will be small and the perturbation expansion will converge quickly so that low orders of perturbation theory will yield energies that closely approximate the total energy. Commonly, the perturbation theory of Rayleigh and Schrödinger is chosen with the Hartree-Fock Hamiltonian as $\hat{H}_0$. This is also known as Møller-Plesset perturbation theory.¹⁷ Second-order Møller-Plesset (MP2) perturbation theory often provides a substantial portion of the correlation energy at a relatively low computational cost, so it has become widely used, particularly for geometry optimizations.

In addition to dynamic electron correlation, there exists a second type of correlation energy, often called nondynamic electron correlation, which is due to near degeneracies. Systems with transition metals often have degenerate or nearly degenerate molecular orbitals, so a method that accounts for this must be employed. A single Slater determinant does not adequately describe the system, so a multi-determinantal wave function is required. In the multiconfiguration self-consistent field (MCSCF) method, the variation principle is used to optimize the CI expansion coefficients and the orbitals for a wave function consisting of a relatively small number of determinants. Perturbation theory can be built on top of an

MCSCF wave function in order to further account for dynamic electron correlation. These methods include second-order multireference Møller-Plesset (MRMP2) perturbation theory,¹⁸⁻²⁰ multiconfigurational quasidegenerate perturbation theory (MCQDPT),^{21,22} and CASPT2.²³

As mentioned above, equation (1) represents the best non-relativistic description of a molecular system. Relativistic effects are particularly important for heavier atoms, since they contain relatively fast-moving electrons. In order to account for relativistic effects, the full relativistic Dirac equation may be used in place of the non-relativistic Schrödinger equation. However in practice, a spin-orbit interaction term is commonly added to the Hamiltonian from equation (3):

$$\hat{H}_{total} = \hat{H} + \hat{H}_{SO}. \quad (11)$$

The Pauli-Breit spin-orbit coupling operator²⁴ may be expressed as

$$\hat{H}_{SO} = \frac{\Omega^2}{2} \left\{ \sum_{i=1}^n \sum_{A=1}^m \frac{Z_A}{r_{iA}^3} [(\vec{r}_i - \vec{r}_A) \times \vec{p}_i] \cdot \vec{S}_i - \sum_{i=1}^n \sum_{j \neq i}^n \frac{1}{r_{ij}^3} [(\vec{r}_i - \vec{r}_j) \times \vec{p}_i] \cdot [\vec{S}_i + 2\vec{S}_j] \right\} \quad (12)$$

where Ω is the fine structure constant, $\vec{p}_i$ is the electron momentum operator, and $\vec{S}_i$ is the electron spin operator. The first term in equation (12) is known as the one-electron spin-orbit coupling (SOC) operator, while the second term is known as the two-electron SOC operator. Matrix elements may be formed over the Breit-Pauli operator with the unperturbed eigenstates as the basis, and then the matrix is diagonalized to yield spin-orbit coupled wave functions.

The electronic structure methods described so far in this section provide a systematically improvable way of approximating the Schrödinger equation. The one-electron

basis set in equation (8) may be progressively expanded. Higher orders of perturbation theory or a higher level of CI or CC theory may be used in order to recover a greater portion of the correlation energy and approach the full CI limit. However, the increased complexity of the basis set and the more accurate level of theory come with a greater computational cost. Hartree-Fock theory scales as order N^4 , where N is the size of the basis set. So, if the basis set size is doubled, the time required for the calculation will increase by a factor of 16. Second-order perturbation theory scales as order N^5 , so a similar growth in the basis set will increase the time requirements by a factor of 32. Higher levels of theory have larger scaling, so they quickly become impractical for systems with many atoms. Although computer power is rapidly rising, it does not keep pace with the desire to investigate bigger molecular systems. The implementation of distributed memory parallel codes will help to alleviate this and will enable the exploration of larger systems.

Another method for reducing the time requirements of a calculation involves replacing a portion of the system by a classical potential. This potential may be systematically improved if it is based on quantum mechanics and incorporates the important physical effects inherent in the system. The Effective Fragment Potential (EFP) method is a generalized potential derived from *ab initio* principles. The one-electron potentials are added to the *ab initio* electronic Hamiltonian. The original method (EFP1/HF) is specific to water and incorporates Coulombic interactions, induction/polarization interactions, and charge-transfer/exchange-repulsion terms.^{25,26} A density functional theory-based method (EFP1/DFT) includes some short-range correlation effects,²⁷ and a second-order perturbation theory-based method (EFP1/MP2) includes dispersion effects and a second-order correction to polarization.²⁸ In addition, a general effective fragment potential (EFP2) has also been

developed.²⁹⁻³⁴ These potentials are especially useful during the exploration of potential energy surfaces of solvated systems.

References

- (1) Dirac, P. A. M. *Proc. R. Soc. London, Ser. A* **1929**, 123, 714.
- (2) Schrödinger, E. *Ann. Phys.* **1926**, 79, 361.
- (3) Schrödinger, E. *Ann. Phys.* **1926**, 79, 489.
- (4) Schrödinger, E. *Ann. Phys.* **1926**, 79, 734.
- (5) Schrödinger, E. *Ann. Phys.* **1926**, 80, 437.
- (6) Schrödinger, E. *Ann. Phys.* **1926**, 81, 109.
- (7) Schrödinger, E. *Die Naturwissenschaften* **1926**, 14, 664.
- (8) Schrödinger, E. *Phys. Rev.* **1926**, 28, 1049.
- (9) Born, M.; Oppenheimer, J. R. *Ann. Phys.* **1927**, 84, 457.
- (10) Hartree, D. R. *Proc. Cambridge Philos. Soc.* **1928**, 24, 89.
- (11) Hartree, D. R. *Proc. Cambridge Philos. Soc.* **1928**, 24, 111.
- (12) Hartree, D. R. *Proc. Cambridge Philos. Soc.* **1928**, 24, 426.
- (13) Slater, J. C. *Phys. Rev.* **1929**, 34, 1293.
- (14) Slater, J. C. *Phys. Rev.* **1930**, 35, 509.
- (15) Fock, V. *Z. Phys.* **1930**, 61, 126.
- (16) Fock, V. *Z. Phys.* **1930**, 62, 795.
- (17) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, 46, 618.
- (18) Hirao, K. *Int. J. Quantum Chem. Symp.* **1992**, S26, 517.
- (19) Hirao, K. *Chem. Phys. Lett.* **1992**, 190, 374.
- (20) Hirao, K. *Chem. Phys. Lett.* **1992**, 196, 397.

- (21) Nakano, H. *Chem. Phys. Lett.* **1993**, 207, 372.
- (22) Nakano, H. *J. Chem. Phys.* **1993**, 99, 7983.
- (23) Anderson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, 96, 1218.
- (24) Bethe, H. A.; Salpeter, E. E. *Quantum Mechanics of the One and Two Electron Atoms*; Plenum: New York, 1977.
- (25) Jensen, J. H.; Day, P. N.; Gordon, M. S.; Basch, H.; Cohen, D.; Garmer, D. R.; Krauss, M.; Stevens, W. J. Effective Fragment Method for Modeling Intermolecular Hydrogen-Bonding Effects on Quantum Mechanical Calculations. In *Modeling the Hydrogen Bond*; Smith, D. A., Ed.; ACS Symposium Series: Washington DC, 1994; Vol. 569; pp 139.
- (26) Day, P. N.; Jensen, J. H.; Gordon, M. S.; Webb, S. P.; Stevens, W. J.; Krauss, M.; Garmer, D. R.; Basch, H.; Cohen, D. *J. Chem. Phys.* **1996**, 105, 1968.
- (27) Adamovic, I.; Freitag, M. A.; Gordon, M. S. *J. Chem. Phys.* **2003**, 118, 6725.
- (28) Song, J.; Gordon, M. S. *manuscript in preparation*.
- (29) Jensen, J. H. *J. Chem. Phys.* **1996**, 104, 7795.
- (30) Jensen, J. H.; Gordon, M. S. *Mol. Phys.* **1996**, 89, 1313.
- (31) Jensen, J. H.; Gordon, M. S. *J. Chem. Phys.* **1998**, 108, 4772.
- (32) Gordon, M. S.; Freitag, M. A.; Bandyopadhyay, P.; Jensen, J. H.; Kairys, V.; Stevens, W. J. *J. Phys. Chem. A* **2001**, 105, 293.
- (33) Adamovic, I.; Gordon, M. S. *Mol. Phys.* **2005**, 103, 379.
- (34) Li, H.; Jensen, J. H.; Gordon, M. S. *manuscript in preparation*.

CHAPTER 2. ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF

$\text{Y}_2\text{Ti}(\mu\text{-X})_2\text{TiY}_2$ (X, Y=H, F, Cl, Br) ISOMERS

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The electronic structure and magnetic properties of homodinuclear titanium(III) molecules with halide and hydride ligands have been studied using single and multi-reference methods. Natural orbital occupation numbers suggest that the singlet states are essentially diradical in character. Dynamic electron correlation is required for calculating quantitatively accurate energy gaps between the singlet and triplet states. Isotropic interaction parameters are calculated and three of the compounds studied are predicted to be ferromagnetic at the MRMP2/TZV(p) level of theory. Zero-field splitting parameters are determined using CASSCF and MCQDPT spin-orbit coupling with three different electron operator methods. Timings for these methods are compared. Calculated dimerization energies suggest that all dimers studied are lower in energy than corresponding monomers. Monomer structures and vibrational frequencies are reported.

1. Introduction

It has been noted that “the most important developments in molecular magnetism in the last two decades have concerned compounds where several magnetic centers interact” (Ref. 1, p. 103). Two of the greatest challenges include the synthesis of molecular ferromagnets that retain their ferromagnetism at very high temperatures and the design of systems with strong interactions between distant metal centers.² Since the bonding and magnetic properties of homodinuclear molecules arise from complex interactions between

the two metal centers and between the metal centers and the bridging and terminal ligands, it is important to understand how changes in the ligands affect the magnetic properties of the system. To this end, homodinuclear copper(II) d^9 molecules have been extensively studied, as they provide a molecular system with one unpaired electron on each metal atom.¹⁻¹⁷

Homodinuclear titanium(III) molecules also have one unpaired electron on each metal center and provide an essential contrast to the copper(II) d^9 molecules due to differences in orbital occupation for the unpaired electrons and to the greater radial extension of the Ti d orbitals.

Compounds containing titanium have long been studied for their interesting magnetic properties.¹⁸⁻²³ Recently, linear oxo-bridged heterodinuclear and homodinuclear compounds of titanium(III) have been examined using electron paramagnetic resonance (EPR), magnetic susceptibility studies, and *ab initio* calculations, and some compounds have been found to be ferromagnetic.²⁴⁻²⁶ Two possible explanations have been advanced for the origin of the Ti-Ti exchange interaction that is apparently responsible for the observed magnetic properties: the direct overlap of the occupied Ti d orbitals or an intramolecular superexchange pathway via the bridging ligands.²⁷ For an exchange pathway involving direct overlap of d orbitals, a decrease in the metal-metal distance generally leads to an increase in the magnitude of the antiferromagnetic interaction.²⁸ In a system with sizeable bridging ligands, the large Ti-Ti distance prevents the direct overlap of d orbitals and necessitates a superexchange pathway. Such pathways normally result in a smaller antiferromagnetic effect than does the direct overlap pathway.²⁸ A few of the oxo-bridged dinuclear compounds do not interact via a superexchange pathway and consequently have a very small metal-metal interaction.^{24,29} Most of the dinuclear titanium(III) complexes studied to this point are

antiferromagnetic,^{27,28,30-38} although two dinuclear complexes with extended ligand systems are also reported to be weakly ferromagnetic.³⁴

Many of the experimentally known ditanium(III) bridged compounds have a planar ring structure,^{27,30-32,35-37} so the D_{2h} isomers of $Ti_2X_2Y_4$ of interest in this work may be viewed as models for these compounds. Previous computational research has emphasized Ti_2H_6 as the simplest prototype for homodinuclear titanium(III) systems.^{39,40} In this work, we examine changes in magnetic properties and electronic structure due to variations in the bridging and terminal ligands in these systems, with $X, Y = H, F, Cl, Br$.

The dominant magnetic effect in most cases is the isotropic interaction. This is an electrostatic phenomenon that may be formally described as a coupling between local spin operators S_A and S_B . The Hamiltonian for the coupling may be written

$$\mathcal{H} = -2JS_A \cdot S_B.$$

The isotropic exchange interaction parameter is defined by

$$2J = E(S=0) - E(S=1),$$

where S is the spin quantum number for the system and the magnetic susceptibility is given by

$$\chi = \frac{2Ng^2\beta^2}{kT} [3 + \exp(\frac{-2J}{kT})]^{-1}$$

where N is Avogadro's number, g is the average electronic gyromagnetic ratio, β is the Bohr magneton, k is the Boltzmann constant, and T is the temperature. In molecules with two local doublets that interact through bridging ligands, the two local spin states S_A and S_B have singlet and triplet coupling. As long as the isotropic interaction is dominant, the total spin quantum number S is a good quantum number.¹ If the singlet ($S=0$) is the ground state ($J<0$),

the interaction is antiferromagnetic; if the triplet ($S=1$) is the ground state ($J>0$), the interaction is ferromagnetic. When the interaction is antiferromagnetic, the magnetic susceptibility goes through a maximum (the Néel temperature) as the temperature decreases. The temperature $T_{\max}$ at which this occurs is related to J by

$$|2J|/kT_{\max} = 1.599$$

where $k = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$. This relation may be used to compare experimentally observable susceptibility maxima with calculated isotropic interaction parameters.

If the isotropic interaction is small, other magnetic properties such as the dipolar interaction and anisotropic interaction (also called the pseudodipolar interaction) may become important. This may have especially important effects on the magnetic properties of the system if the triplet state is the ground state. In a dinuclear complex such as $D_{2h} \text{Ti}_2\text{X}_2\text{Y}_4$, the interaction of the two local doublets leads to a zero-field splitting (ZFS) of the triplet state. The electron paramagnetic resonance (EPR) spectrum of the triplet state may be described by the Hamiltonian

$$\mathcal{H} = \beta S \cdot g \cdot H + S \cdot \mathbf{D} \cdot S$$

where the first term accounts for the Zeeman perturbation due to the magnetic field H and the g -tensor, and the second term accounts for the dipolar and anisotropic interactions, where $\mathbf{D}$ is the ZFS tensor.¹⁰ The zero-field splitting parameters are calculated from the principal values of $\mathbf{D}$ by¹⁰

$$D = 3D_z/2$$

$$E = (D_x - D_y)/2$$

where D is the axial splitting parameter and E is the nonaxial (rhombic) splitting parameter. The dipolar term is often the minor contribution to D and is often reasonably estimated from the point dipole approximation.¹ The anisotropic (pseudodipolar) exchange interaction results from the synergistic effects of the local spin-orbit coupling (SOC) perturbations and the exchange interaction between the ground state of one magnetic center with the excited states of the other.^{1,35} In a symmetric dimer, the zero-field splitting parameters D and E are composed of the dipolar contributions D_d and E_d and the pseudodipolar contributions D_e and E_e according to³⁵

$$D = D_d + D_e$$

$$E = E_d + E_e$$

When the rhombic exchange parameter $|E_e|$ is larger than the axial exchange parameter $|D_e|$, SOC effects are larger perpendicular to the Ti-Ti axis than along it.

2. Computational Details

A triple-zeta with polarization (14s11p6d/10s8p3d) basis set was adopted for titanium, consisting of Wachter's basis set⁴¹ with two additional sets of p functions⁴² and an additional set of diffuse d functions.⁴³ In this notation (A/B), A and B refer to the primitive and contracted basis sets, respectively. For hydrogen, Dunning's (5s1p/3s1p) basis set was used.⁴⁴ For fluorine, the triple-zeta (10s6p/5s3p) basis set of Dunning was employed;⁴⁵ for chlorine, the triple-zeta (12s9p/6s5p) basis set of McLean and Chandler was employed;⁴⁶ and for bromine, the triple-zeta (14s11p5d/9s6p2d) basis set of Binning and Curtiss was employed.⁴⁷ Collectively, this basis set is referred to as TZV(p). All geometry optimizations were performed with this basis set.

In order to predict reasonable energy-related quantities, polarization functions were added to the TZV(p) basis set. The basis set referred to as TZVP(f) adds f functions to the titanium ($\alpha = 0.40$),⁴⁸ two sets of d polarization functions to the halides, and diffuse s and p functions to the halides as well. The 2d polarization and diffuse sp function exponents are the default values in GAMESS.⁴⁹ The basis set called TZVP(fg) retains the halide basis set from TZVP(f) and adds one set of f ($\alpha = 0.591$) and g ($\alpha = 0.390$) functions and a set of diffuse s ($\alpha = 0.035$), p ($\alpha = 0.239$), and d ($\alpha = 0.0207$) functions to the TZV(p) titanium basis. These exponents are optimized for correlated titanium atoms.⁵⁰

For the singlet homodinuclear titanium(III) molecules, preliminary geometry optimizations were carried out at the RHF level of theory. After convergence, modified virtual orbitals (MVOs) were generated by removing six electrons in the usual manner.⁵¹ The resulting orbitals were used as a starting point for a two configuration self-consistent field (TCSCF) geometry optimization. For the doublet and triplet states, geometry optimizations were performed at the ROHF level of theory.

Stationary points were characterized by calculating and diagonalizing the energy second-derivative (Hessian) matrix. Unless otherwise stated, these stationary points have no imaginary frequencies, so they are minima on their respective potential energy surfaces.

Dynamic electron correlation effects were included by carrying out multireference second-order perturbation theory (MRMP2)⁵² single-point energy calculations at the TCSCF singlet geometries and ROHF triplet geometries. These single-point energy calculations were repeated with the TZVP(f) and TZVP(fg) basis sets as a test of basis set convergence.

In order to obtain reasonable energies for the doublet states, Z-averaged perturbation theory (ZAPT2)⁵³ and MRMP2(1,1) calculations were carried out at the ROHF geometries.

Excited state calculations require fully optimized reaction space (FORS) multiconfigurational SCF (MCSCF) calculations⁵⁴ (also called CASSCF), in this case with an active space consisting of two electrons in ten orbitals. Spin-orbit coupling effects (SOC) are determined in three ways: a one-electron spin-orbit coupling operator method (HSO1),⁵⁵ a partial two electron and full one electron method (P2E),⁵⁶ and the full Pauli-Breit operator method (HSO2).⁵⁶ Both the complete active space SCF (CASSCF-SOC) and multiconfiguration quasi-degenerate perturbation spin-orbit coupling (MCQDPT-SOC)⁵⁷ techniques are used with each of the three methods.

All calculations were done using the electronic structure code GAMESS.⁴⁹ Molecules and orbitals were visualized using MacMolPlot,⁵⁸ a graphical interface to GAMESS.

3. Results and Discussion

Electronic Structure and Energetics. As noted in the earlier work on Ti_2H_6 , the ground-state minima are either triplets or they are singlets with a high degree of diradical character. The lowest energy singlet and triplet states are 1A_g and $^3B_{1u}$, respectively. The lowest energy structures for $\text{Ti}_2\text{F}_2\text{H}_4$ are an exception to the general pattern, and are discussed in the next section. The natural orbital analysis of the TCSCF/TZV(p) wave functions (Figure 1) shows that the lowest energy singlets all have at least 0.87 electrons in the lowest virtual orbitals. This suggests that these states are essentially singlet diradicals, probably with very small bonding interactions.

Dynamic electron correlation is required for calculating quantitatively accurate energy gaps between the singlet and triplet states (Table 1). At the TCSCF/TZV(p) level of

theory, five of the triplet states are predicted to lie slightly (<0.2 kcal/mol) below the singlet states. However, inclusion of dynamic electron correlation via second order perturbation theory lowers most of the singlet states preferentially. At the MRMP2/TZV(p) level of theory, three of the triplet states lie below the corresponding singlet states. As the basis set size is increased, the singlet-triplet splitting increases by up to 0.3 kcal/mol on going from TZV(p) to TZVP(f) and by up to an additional 0.6 kcal/mol from TZVP(f) to TZVP(fg).

The lowest energy singlet and triplet state geometries are shown in Table 2. Mulliken populations for the MCSCF and ROHF wavefunctions (Table 3) with the TZV(p) basis show positively charged Ti's, as expected with the anionic ligands. Charges on Ti range from +0.73 to +1.78, indicating highly polarized bonds. The Ti positive charges increase with the electronegativity of the ligands and with the number of electronegative ligands.

Although the orbitals for the $\text{Ti}_2\text{X}_2\text{Y}_4$ molecules are in principle able to form a direct Ti-Ti bond, there is apparently little such bonding based on the natural orbital occupation numbers (Figure 1). A similar conclusion was reached for singlet Ti_2H_6 .

Lowest energy structures for $\text{Ti}_2\text{F}_2\text{H}_4$. As for the other molecules in the series, the lowest energy D_{2h} singlet state for $\text{Ti}_2\text{F}_2\text{H}_4$ is a 1A_g state, while the lowest energy triplet state is a $^3B_{1u}$ state. Two low-lying orbital configurations can contribute to these states. For the singlet, these are $[(\sigma)(\sigma^*)]^2$ and $[(\delta)(\delta^*)]^2$. For the other molecules in the series, the $[(\sigma)(\sigma^*)]^2$ configuration dominates the ground state, while $[(\delta)(\delta^*)]^2$ is an excited singlet state. However, the $[(\delta)(\delta^*)]^2$ configuration dominates the $\text{Ti}_2\text{F}_2\text{H}_4$ ground state, while the $[(\sigma)(\sigma^*)]^2$ configuration, at 0.9 kcal/mol, dominates the first excited singlet state at the TCSCF/TZV(p) level of theory. MCSCF(2,10) calculations show that there is essentially no

mixing between the two configurations. The Generalized Valence Bond Perfect Pairing (GVB-PP(1))⁵⁹ method (equivalent to TCSCF) was used to calculate the analytical Hessian for the two states, and both have two imaginary frequencies. Displacements along the imaginary modes lead to a common C_{2h} structure (Figure 3). This structure is 0.3 and 1.2 kcal/mol lower than the two D_{2h} states at the TCSCF/TZV(p) level of theory (Table 4). GVB-PP analytic Hessian calculations show that it is a minimum on the potential energy surface. Vibrational frequencies are reported in Table 5. The plane containing the Ti and F atoms makes an angle of 83.3° with the plane containing the Ti and H atoms. Other geometrical parameters are reported in Table 2.

Monomer Structures and Vibrational Frequencies. A D_{3h} structure ($^2A_1'$ state) is found to be the lowest energy minimum for the titanium trihalides, TiX_3 . A C_{2v} structure (2A_1 state) is found to be the lowest energy minimum for both the TiX_2H and the $TiXH_2$ species. The C_{2v} state labels assume that z is the principal rotation axis and that the molecule lies in the yz plane. The ROHF/TZV(p) optimized geometries are given in Table 6.

In TiF_3 , the calculated Ti-F distance of 1.819 Å is close to previously reported distances of 1.79,⁶⁰ 1.7978,⁶¹ and 1.83⁶² Å. The computed vibrational frequencies agree well with prior estimates, calculations, and matrix isolation studies (see Table 7). This data provides additional evidence that the ν_3 band originally assigned to TiF_2 belongs to TiF_3 .^{63,64} In addition, the weak ν_1 symmetric stretch initially assigned to TiF_2 ⁶³ appears to belong to TiF_3 . The confusion seems to have occurred because TiF_3 both disproportionates and sublimates unchanged upon heating;⁶⁴ this results in a spectrum that contains bands due to both TiF_4 and TiF_3 rather than TiF_3 and TiF_2 as assigned.

For TiCl_3 , the calculated Ti-Cl distance of 2.272 Å differs considerably (~ 0.1 Å) from previously obtained Ti-Cl distances of 2.183⁶⁵ and 2.178⁶⁰ Å. Much of the available vibrational frequency data for TiCl_3 is for the solid state⁶⁶⁻⁷⁰. The few gas phase studies are summarized here. As seen in Table 7, the computed vibrational frequencies are similar to those found previously. ν_4 in this work is 38 cm^{-1} lower than ν_4 from Ref. 71, but is similar to that in references 60 and 65. ν_1 is 5-59 cm^{-1} higher than previously reported values, while ν_2 and ν_3 are within ± 28 cm^{-1} . Since the errors are not systematic and the previously reported frequencies vary significantly, the calculated frequencies have not been scaled.

For TiBr_3 , the metal-halide distance and vibrational frequencies have previously been estimated from the equilibrium structures, force fields, and vibrational frequencies of TiCl_3 and TiI_3 .⁶⁰ The previously estimated distance of 2.34 Å is 0.07 Å lower than the calculated distance of 2.414 Å. The vibrational frequencies differ from the previously estimated frequencies by 12, 8, 23, and 15 cm^{-1} for ν_1 - ν_4 (see Table 7).

Since the vibrational frequencies calculated for the titanium trihalides are in reasonable agreement with prior estimates, calculations, and matrix isolation studies, it is reasonable to assume a similar level of agreement for the predicted frequencies for the TiX_2H and TiXH_2 species (Table 8).

Of the TiX_2H and TiXH_2 species studied here, only calculations on TiHF_2 and TiHCl_2 have been reported in the literature to date. For TiHF_2 , Zakharov, et. al. found a Ti-H distance of 1.703 Å and a Ti-F distance of 1.741 Å with a calculated F-Ti-F angle of 129.0° using a 3-21G* basis set at the Hartree-Fock level of theory.⁷³ Vibrational data was not reported, although the stationary point was confirmed by diagonalizing the Hessian.⁷³

Determination of the ground state of this molecule is elusive. The occupation of a d_{x^2} ⁷⁴ orbital by a single electron on the Ti leads to a 2A_1 state while the occupation of a d_{xz} orbital leads to a 2B_1 state. At the ROHF/TZV(p) level, the C_{2v} 2B_1 state is 0.4 kcal/mol lower in energy than the C_{2v} 2A_1 state. At this level of theory, the 2B_1 state has a positive definite Hessian, while the 2A_1 state does not. At the ZAPT2/TZV(p)//ROHF/TZV(p) level of theory, the 2A_1 state is lower than the 2B_1 state by 1.2 kcal/mol. UHF/TZV(p) calculations predict that the 2B_1 state is 0.2 kcal/mol lower in energy than the 2A_1 state and that both are minima. However, at the UMP2/TZV(p) level of theory, the 2A_1 state is lower than the 2B_1 state by 1.0 kcal/mol. At this level of theory, the 2A_1 state has a positive definite Hessian while the 2B_1 state does not. The imaginary frequencies from the ROHF/TZV(p) 2A_1 and UMP2/TZV(p) 2B_1 state are out-of-plane bending modes. Calculations done in C_s symmetry show that these states end up converging to the lowest energy planar structures for the given level of theory.

For $TiHCl_2$, previous calculations using generalized valance bond methods and ECP basis sets predict a planar compound with a Ti-H distance of 1.68-1.70 Å, a Ti-Cl distance of 2.32-2.33 Å, and a Cl-Ti-Cl angle of 140-148°.^{75,76} The electronic state was not reported. In contrast, the Cl-Ti-Cl angle calculated in this work is 128.4°. In order to determine the origin of this difference, the minimum energy structures for the 2A_2 , 2B_1 , and 2B_2 states were calculated. The reported geometrical parameters in Ref. 75 agree well with our calculated geometry for the 2B_2 state, which is 24.6 kcal/mol higher in energy than the 2A_1 state at the ROHF level of theory and 27.4 kcal/mol higher at the ZAPT2//ROHF level of theory (See Table 9).

Vibrational Frequencies for Dimers. Vibrational frequencies for the Raman and IR active bands of the $Ti_2X_2Y_4$ molecules are listed in Table 5. Very little experimental data is

available for these compounds. Hastie, Hauge, and Margrave report an IR band at 745.5 cm^{-1} , which they attribute to a polymeric species such as $(\text{TiF}_3)_2$.⁶³ Two of our calculated frequencies for $\text{D}_{2h}\text{F}_2\text{Ti}(\mu\text{-F})_2\text{TiF}_2$ fall within a reasonable range of this band. For the triplet state, a peak at 747 cm^{-1} (745 cm^{-1} for the slightly higher energy singlet state) appears to be a likely candidate, but due to the symmetry of the vibration it is a Raman active peak and should not be IR active. A different peak at 764 cm^{-1} (762 cm^{-1} for the singlet) is within 19 cm^{-1} of the reported IR band and should be IR active. After correcting for matrix shift effects of up to 20 cm^{-1} ,⁶³ these values could be even closer.

Dimerization Energies. The calculated TiX_3 , TiX_2H , and TiXH_2 dimerization energies are listed in Table 10. Sørli and Øye report the presence of Ti_2Cl_6 in high-temperature absorption spectroscopy.⁷⁷ They suggest a distorted tetrahedral structure for Ti_2Cl_6 , in which two deformed tetrahedra share one edge. This structure would imply either C_{2v} or D_{2h} symmetry. Sørli and Øye found the enthalpy of dimerization to be in the range of -32.7 to 34.2 kcal/mol .⁷⁷ Previous experiments in other laboratories found the enthalpy of dimerization to be -31.9 kcal/mol ⁷⁸ and -40.6 kcal/mol .⁷⁹ The former values agree well with our calculated energy of dimerization of -32.8 kcal/mol for the D_{2h} structure using second order perturbation theory. In general, the D_{2h} structures of $\text{Ti}_2\text{X}_2\text{Y}_4$ are 32.7 - 54.4 kcal/mol lower in energy than their separated monomers (see Table 10). Dimerization energies were calculated from the lowest energy monomer structure to the lowest energy dimer structure at the MRMP2/TZV(p) level of theory.

Previous theoretical calculations were done by Martinsky and Minot, who found a dimerization energy of -73.4 kcal/mol for their lowest energy $\text{C}_s\text{Ti}_2\text{Cl}_6$ structure using density functional theory.⁸⁰ This is more than twice our predicted value. Their dibridged

compound lies 3.1 kcal/mol above the C_s compound.⁸⁰ The dimer spin state was not specified.

Magnetic Properties.

A. Isotropic interaction

Magnetic properties of dinuclear complexes with a single unpaired electron on each magnetic center depend on the intramolecular interaction between the two metal centers. This interaction is affected by both the bridging ligands and the terminal ligands. As the bridging ligand changes from H to Br to Cl to F, the MRMP2/TZVP(fg) interaction becomes more ferromagnetic (J becomes less negative) (Table 11). As the terminal ligand changes from H to Br to Cl to F, the interaction becomes more antiferromagnetic (J becomes more negative). The isotropic interactions for the halide series range from 41 cm^{-1} to -367 cm^{-1} at the MRMP2/TZVP(fg) level of theory. Note that dynamic correlation and larger basis sets have important effects on these predictions.

Experimentally observed J values for planar ring Ti compounds fall within the range predicted by MRMP2 calculations. For example, for $((C_5H_5)_2TiCl)_2$ and $((C_5H_5)_2TiBr)_2$, observed J values are -70 to -85 cm^{-1} and -125 cm^{-1} , respectively, after adjusting for the difference in the isotropic interaction parameter definition.³² These are similar to the corresponding values in Table 11. Based on a susceptibility maximum at 170 K, $((C_5H_5)_2TiCl)_2$ has an observed J value of -96 cm^{-1} .^{30,31} Stucky, et. al. found J values of -111 , -160 , and -138 cm^{-1} for $((C_5H_5)_2TiCl)_2$, $((CH_3C_4H_5)_2TiCl)_2$, and $((CH_3C_4H_5)_2TiBr)_2$, respectively.²⁷ Although the halide terminal ligands may have isotropic interactions that are different from the organic terminal ligands, the predicted trend of increasing antiferromaticity for a given terminal ligand as the bridging ligand changes from chloride to bromide is

consistent with the experiments.^{27,32} Also of note is the observation that no susceptibility maximum for $((\text{C}_5\text{H}_5)_2\text{TiF})_2$ was observed experimentally between 80 and 380K.³² The susceptibility maximum may be used experimentally to determine the antiferromagnetism of a compound. Since the theoretical calculations show that fluoride is a more ferromagnetic bridging ligand than chloride or bromide, this suggests that the isotropic interaction for $((\text{C}_5\text{H}_5)_2\text{TiF})_2$ is either slightly antiferromagnetic with $0 > J > -44 \text{ cm}^{-1}$ (80 K) or that the interaction is ferromagnetic.

An interesting correlation may be noted between the natural orbital occupation numbers for a series of compounds and the ferromagnetism of these compounds by comparing Figure 1 and Table 11. As the diradical character of the compound becomes more pronounced and the NOON becomes closer to one, the ferromagnetism of the compound increases. This is consistent with the increase in electronegativity of the bridging ligand.

B. Spin-Orbit Coupling Calculations

An initial state-averaged 2 electron, 10 orbital MCSCF calculation at the TCSCF/TZV(p) $^1\text{A}_g$ ground state geometry was used to obtain a set of starting orbitals. Then, a second 2 electron, 10 orbital MCSCF calculation was carried out with no orbital symmetry constraints and with each of the first 20 singlet states weighted equally. Using this wave function as a starting point, a 2 electron, 10 orbital MCSCF calculation with the core and virtual orbitals frozen was run at the same geometry to obtain the first 20 triplet states. The singlet and triplet state orbitals were used in the CASSCF spin-orbit coupling (CASSCF-SOC) calculations. The orbitals from the 20 singlet state calculation were used in the MCQDPT spin-orbit coupling (MCQDPT-SOC) calculations. The order and energies of the

excited states vary slightly for the different $\text{Ti}_2\text{X}_2\text{Y}_4$ molecules but are qualitatively similar to those reported for Ti_2H_6 .⁴⁰

Inspection of the eigenvectors of the spin-mixed states allows the identification of those adiabatic states that mix with the predominant state, as well as that angular momentum operator which is responsible for the mixing. These adiabatic states and operators are exactly the same as those previously reported for Ti_2H_6 , although the weightings vary slightly.⁴⁰ It is interesting to compare the performance of the three alternative methods for spin-orbit coupling calculations: the full two-electron (HSO2), partial two-electron (P2E) and the one-electron method with effective nuclear charges (HSO1). Compared with HSO2, for CASSCF-SOC and MCQDPT-SOC, the coefficients in the eigenvectors of the spin states are within ± 0.00002 for P2E and ± 0.002 for HSO1. Except for $\text{Ti}_2\text{F}_2\text{H}_4$, the energy levels calculated by P2E and HSO2 are practically the same and differ by no more than 0.008 cm^{-1} .

The principal axes X, Y, and Z for the T_1 (lowest triplet state) components can be determined from the coefficients of the eigenvectors. Then, the axial and rhombic pseudodipolar parameters D_e and E_e can be calculated as described previously.⁴⁰ These values are summarized in Table 12 for the six different methods used for determining spin-orbit coupling effects.

For the compounds with both bridging and terminal halide ligands, the spin-mixed triplet states are lower in energy than the lowest energy singlet state for all calculations except Ti_2Br_6 MCQDPT-SOC. This mirrors the pattern in singlet-triplet splitting for the TCSCF/TZV(p) and MRMP2/TZV(p) calculations, as expected. For most of the calculations, the magnitude of E_e is slightly larger than the magnitude of D_e by up to 0.014 cm^{-1} . The one exception occurs for MCQDPT-SOC calculations on Ti_2F_6 , for which $|D_e|$ is

0.015 cm^{-1} larger than $|E_e|$. In general, the magnitudes of D_e and E_e increase slightly as the method is improved from HSO1 to P2E to HSO2. For these compounds, the magnitudes of D_e and E_e decrease slightly as we go from CASSCF-SOC to MCQDPT-SOC calculations.

For the compounds with terminal halide ligands, all singlet states are lower in energy than the corresponding triplet states, as expected. In general, the magnitudes of D_e and E_e are similar. For the most part, $|D_e|$ is slightly larger than $|E_e|$ by up to 0.009 cm^{-1} for CASSCF-SOC or 0.031 cm^{-1} for MCQDPT-SOC. D_e becomes more negative and E_e becomes more positive for HSO2 relative to HSO1 and for MCQDPT-SOC relative to CASSCF-SOC.

For $\text{Ti}_2\text{Cl}_2\text{H}_4$ and $\text{Ti}_2\text{Br}_2\text{H}_4$, the magnitude of E_e is larger than the magnitude of D_e by up to 0.053 cm^{-1} for CASSCF-SOC calculations. However, this trend is reversed for MCQDPT-SOC calculations, for which $|D_e|$ is up to 0.071 cm^{-1} larger than $|E_e|$. D_e becomes more negative and E_e becomes more positive as the method improves from HSO1 to HSO2.

$\text{Ti}_2\text{F}_2\text{H}_4$ is the only compound that does not follow the general spin-orbit coupling patterns for $\text{Ti}_2\text{X}_2\text{Y}_4$ molecules. Its D_e values are an order of magnitude larger than other D_e values.

C. Spin-Orbit Coupling Timings

The relative times required for the various methods are given in Tables 13 and 14. Only timings for the σ, σ^* configuration of $\text{Ti}_2\text{F}_2\text{H}_4$ are included in the tables since this structure is analogous to the other $\text{Ti}_2\text{X}_2\text{Y}_4$ molecules. In general, the CASSCF-SOC method requires less time than the MCQDPT-SOC method. For the CASSCF-SOC calculations, the P2E state energies are almost exactly the same as the HSO2 energies, but the method requires roughly 46% of the CPU time required for the HSO2 method on a Sun UltraSPARC2 300 MHz processor. This is approximately the same whether or not the setup time is included in

the timings. For the MCQDPT-SOC calculations, the total time required for the P2E method is approximately 89% of the time required for the HSO2 method on a Compaq AXP EV6 500 MHz processor. However, the setup time for MCQDPT-SOC calculations is much greater than for CASSCF-SOC calculations. If only the times for the spin-orbit coupling parts of the calculations are compared, the P2E method requires only about 63% of the time required for the HSO2 method. For both CASSCF-SOC and MCQDPT-SOC calculations, the HSO1 method requires much less time than either the HSO2 or P2E method. As discussed in the previous section, the state energies vary slightly but the D_e and E_e values calculated by the HSO1 method are close to those calculated by the other two methods. There is a slight accuracy trade-off for a large computational time savings.

4. Conclusions

The compounds studied in this work have a high degree of diradical character. Dynamic electron correlation is required for calculating quantitatively accurate energy gaps between the singlet and triplet states. As the bridging ligand changes from H to Br to Cl to F, the interaction becomes more ferromagnetic; as the terminal ligand changes from H to Br to Cl to F, the interaction becomes more antiferromagnetic. Vibrational frequencies calculated for the monomers and dimers should help experimentalists determine whether these species are present in experiments. All dimers are predicted to be lower in energy than the corresponding separated monomers.

With the exception of $Ti_2F_2H_4$, spin-orbit coupling effects for these dinuclear titanium molecules are very similar to those for Ti_2H_6 . Energies calculated by the HSO2 and P2E methods are virtually the same, even though the latter method requires significantly less computer time for CASSCF-SOC and MCQDPT-SOC calculations.

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References and Notes

- (1) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993; Chapters 6-9.
- (2) Kahn, O. *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 834.
- (3) Hatfield, W. E. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R.D.; Gatteschi, D.; Kahn, O. Eds., NATO ASI Series: Reidel: Dordrecht. 1985; pp. 555-602.
- (4) Rodríguez-Forteza, A.; Alemany, P.; Alvarez, S.; Ruiz, E. *Chem. Eur. J.* 2001, 7, 627.
- (5) Escuer, A.; Mautner, F. A.; Peñalba, E.; Vicente, R. *Inorg. Chem.* **1998**, 37, 4190.
- (6) Acevedo-Chávez, R.; Costas, M. E.; Escudero, R. *Inorg. Chem.* **1996**, 35, 7430.
- (7) Slangen, P. M.; van Koningsbruggen, P. J.; Goubitz, K.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1994**, 33, 1121.
- (8) Emori, S.; Todoko, K. *Bull. Chem. Soc. Jpn.* **1993**, 66, 3513.
- (9) Oshio, H.; Nagashima, U.; *Inorg. Chem.* **1990**, 29, 3321.
- (10) Boillot, M-L.; Journaux, Y.; Bencini, A.; Gatteschi, D.; Kahn, O. *Inorg. Chem.* **1985**, 24, 263.
- (11) Charlot, M. F.; Verdager, M.; Journaux, Y.; de Loth, P.; Daudey, J. P. *Inorg. Chem.* **1984**, 23, 3802.
- (12) Julve, M.; Verdager, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, 23, 3808.

- (13) Charlot, M. F.; Jeannin, S.; Jeannin, Y.; Kahn, O.; Lucrece-Abaul, J.; Martin-Frere, J. *Inorg. Chem.* **1979**, *18*, 1675.
- (14) Charlot, M. F.; Kahn, O.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1411.
- (15) Crawford, V.H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E.; *Inorg. Chem.* **1976**, *15*, 2107.
- (16) Solomon, E. I. In *Copper Proteins*, Spiro, T. G., Ed.; Wiley-Interscience: New York. 1981; Chapter 2.
- (17) Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, *116*, 2728.
- (18) Fernandes, J. C.; Guimaraes, R. B.; Continentino, M. A.; Borges, H. A.; Valarelli, J. V.; Lacerda, A. *Phys. Rev. B* **1994**, *50*, 16754.
- (19) Machin, D. J.; Murray, K. S.; Walton, R. A. *J. Chem. Soc. A* **1968**, *1*, 195.
- (20) Fowles, G. W. A.; Lester, T. E.; Walton, R. A.; *J. Chem. Soc. A* **1968**, *1*, 198.
- (21) DeSavage, B. F.; Goff, J. F. *J. Appl. Phys.* **1967**, *38*, 1337.
- (22) Strnat, K. J. *AIP Conf. Proc.* **1972**, *5* (No. 2), 1047.
- (23) Manjusri, G.; Mohan Babu, T. V. S. M.; Kaul, S. N.; Lucinski, T. *J. Phys.: Condens. Matter* **1997**, *9*, 2085.
- (24) Lukens, W. W., Jr.; Andersen, R. A. *Inorg. Chem.* **1995**, *34*, 3440.
- (25) (a) Fink, K.; Fink, R.; Staemmler, V.; *Inorg. Chem.* **1994**, *33*, 6219. (b) Kolczewski, Ch.; Fink, K.; Staemmler, V. *Int. J. Quant. Chem.* **2000**, *76*, 137.
- (26) Ren, Q.; Chen, Z.; Ren, J.; Wei, H.; Feng, W.; Zhang, L. *J. Phys. Chem. A* **2002**, *106*, 6161.
- (27) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.
- (28) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.*, **1978**, *17*, 1841.

- (29) Lukens, W. W. Jr.; Matsunaga, P. T.; Andersen, R. A. *Organometallics* **1998**, *17*, 5240.
- (30) Martin, R. L.; Winter, G. J. *Chem. Soc.* **1965**, 4709.
- (31) Canty, A. J.; Coutts, R. S. P.; Wailes, P. C. *Aust. J. Chem.* **1968**, *21*, 807.
- (32) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *47*, 375.
- (33) (a) Fieselmann, B. F.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2074. (b) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078.
- (34) Francesconi, L. C.; Corbin, D. R.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 3074.
- (35) Samuel, E.; Harrod, J. F.; Gourier, D.; Dromzee, Y.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1992**, *31*, 3252.
- (36) Xin, S.; Harrod, J. F.; Samuel, E. J. *Am. Chem. Soc.* **1994**, *116*, 11562.
- (37) Dick, D. G.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 1146.
- (38) Chen, L.; Cotton, F. A.; Dunbar, K. R.; Feng, X.; Heintz, R. A.; Uzelmeir, C. *Inorg. Chem.* **1996**, *35*, 7358.
- (39) Webb, S. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 3846.
- (40) Webb, S. P.; Gordon, M. S. *J. Chem. Phys.* **1998**, *109*, 919.
- (41) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.
- (42) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1979**, *71*, 705.
- (43) Rappe, A. K.; Smedley, T. A.; Goddard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 2607.
- (44) Dunning, T. H.; Hay P. J. In *Methods of Electronic Structure Theory*, Schaefer H. F., III., Ed.; Plenum Press: New York. 1977; pp 1-27.
- (45) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.
- (46) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

- (47) (a) Binning, R. C.; Curtiss, L. A. *J. Comp. Chem.* **1990**, *11*, 1206. (b) Dunning, T. H., Jr. *J. Chem. Phys.* **1977**, *66*, 1382.
- (48) Webb, S. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 7197.
- (49) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Gordon, M. S.; Nguyen, K. A.; Su, S.; Windus, T. L.; Elbert, S. T.; Montgomery, J.; Dupuis, M. *J. Comput. Chem.* **1993**, *14*, 1347.
- (50) Glezakou, V.-A.; Gordon, M. S. *J. Phys. Chem.* **1997**, *101*, 8714.
- (51) Bauschlicher, C. W. *J. Chem. Phys.* **1980**, *72*, 880.
- (52) (a) Hirao, K. *Chem. Phys. Lett.* **1992**, *190*, 374. (b) Hirao, K. *Chem. Phys. Lett.* **1992**, *196*, 397. (c) Hirao, K. *Int. J. Quant. Chem.* **1992**, *S26*, 517. (d) Hirao, K. *Chem. Phys. Lett.* **1993**, *201*, 59.
- (53) (a) Jayatilaka, D.; Lee, T. J.; *Chem. Phys. Lett.* **1992**, *199*, 211. (b) Lee, T. J.; Jayatilaka, D. *Chem. Phys. Lett.* **1993**, *201*, 1.
- (54) (a) Sunberg, K. R.; Ruedenberg, K. In *Quantum Science*, Calais, J. L.; Goscinski, O.; Linderberg, J.; Öhrn Y. Eds.; Plenum Press: New York. 1976; p 505; (b) Cheung, L. M.; Sunberg, K. R.; Ruedenberg, K. *Int. J. Quantum Chem.* **1979**, *16*, 1103; (c) Ruedenberg, K.; Schmidt, M.; Gilbert, M. M.; Elbert, S. T.; *Chem. Phys.* **1982**, *71*, 41; (d) Roos, B. O.; Taylor, P.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.
- (55) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga, N. *J. Phys. Chem.* **1995**, *99*, 12764.
- (56) Fedorov, D. G.; Gordon, M. S. *J. Chem. Phys.* **2000**, *112*, 5611.
- (57) Fedorov, D. G.; Finley, J. P. *Phys. Rev. A* **2001**, *64*, 042502.
- (58) Bode B. M.; Gordon, M. S. *J. Mol. Graphics. Mod.* **1998**, *16*, 133.

- (59) Hunt, W. J.; Hay, P. J.; Goddard, W. A. *J. Chem. Phys.* **1972**, *57*, 738.
- (60) Giricheva, N. I.; Girichev, G. V.; Shlykov, S. A. *J. Struct. Chem.* **1991**, *32*, 602.
- (61) Solomonik, V. G.; Sliznev, V. V.; Balabanov, N. B. *Russ. J. Inorg. Chem.* **1997**, *42*, 430.
- (62) Yates, J. H.; Pitzer, R. M.; *J. Chem. Phys.* **1979**, *70*, 4049.
- (63) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *J. Chem. Phys.* **1969**, *51*, 2648.
- (64) Beattie I. R.; Jones, P. J.; Young, N. A. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 313.
- (65) Mamaeva, G. I.; Romanov, G. V.; Spiridonov, V. P.; Troyanov, S. I. *J. Struct. Chem.* **1987**, *28*, 846.
- (66) Fraser, G. V.; Chalmers, J. M.; Charlton, V.; Cudby, M. E. A. *Solid State Commun.* **1977**, *21*, 933.
- (67) Kanesaka, I.; Kawai, K.; Miyatake, T.; Kakugo, M. *Spectrochim. Acta, Part A* **1984**, *40A*, 705.
- (68) Kanesaka, I.; Yonezawa, M.; Kawai, K.; Miyatake, T.; Kakugo, M. *Spectrochim. Acta, Part A* **1986**, *42A* 1415.
- (69) Miyaoka, H.; Hasebe, K.; Sawada, M.; Sano, H.; Mori, H.; Mizutani, G.; Ushioda, S.; Otsuka, N.; Terano, M. *Vib. Spectrosc.* **1998**, *17*, 183.
- (70) Miyaoka, H.; Kuze, T.; Sano, H.; Mori, H.; Mizutani, G.; Ushioda, S.; Otsuka, N.; Terano, M. *J. Lumin.* **2000**, *87-89*, 709.
- (71) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *High Temp. Sci.* **1971**, *3*, 257.
- (72) Andersen, B.; Seip, H. M.; Strand, T. G.; Stolevik, R. *Acta Chem. Scand.* **1969**, *23*, 3224.
- (73) Zakharov, I. I.; Zhidomirov, G. M.; Zakharov, V. A. *J. Mol. Catal.* **1991**, *68*, 149.

- (74) This is referred to as d_{x^2} instead of d_{z^2} because of our choice of axis system.
- (75) Bierwagen, E. P.; Bercaw, J. E.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1994**, *116*, 1481.
- (76) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308.
- (77) Sørli, M.; Øye, H. A. *Inorg. Chem.* **1978**, *17*, 2473.
- (78) Polyachenok, L. D.; Novikov, G. I.; Polyachenok, O. G.; *Obshch. Prikl. Khim.* **1972**, *45*.
- (79) Sibbing E.; Schäfer, H. Z. *Anorg. Allg. Chem.* **1974**, *410*, 67.
- (80) Martinsky, C.; Minot, C. *Surf. Sci.* **2000**, *467*, 152.

TABLE 1: Calculated Singlet - Triplet Energy Gap ($E(\text{triplet}) - E(\text{singlet})$) in kcal/mol
 method/basis set for singlet/triplet calculation

molecule	TCSCF/TZV(p)	MRMP2/TZV(p)	MRMP2/TZVP(f)	MRMP2/TZVP(fg)
$\text{Ti}_2\text{H}_6^{\text{a}}$	0.56	1.33	1.40	1.43
Ti_2F_6	-0.12	-0.18	-0.23	-0.23
Ti_2Cl_6	-0.09	-0.01	0.27	0.90
Ti_2Br_6	-0.02	0.34	0.61	0.45
$\text{Ti}_2\text{H}_2\text{F}_4$	0.83	1.93	2.06	2.10
$\text{Ti}_2\text{H}_2\text{Cl}_4$	0.59	1.62	1.79	1.82
$\text{Ti}_2\text{H}_2\text{Br}_4$	0.52	1.53	1.68	1.70
$\text{Ti}_2\text{F}_2\text{H}_4^{\text{b}}$	-0.11	-0.18	-0.20	-0.20
$\text{Ti}_2\text{F}_2\text{H}_4^{\text{c}}$	0.12	0.24	0.28	0.28
$\text{Ti}_2\text{F}_2\text{H}_4^{\text{d}}$	0.08	0.17	0.21	0.24
$\text{Ti}_2\text{Cl}_2\text{H}_4$	-0.04	0.06	0.34	0.34
$\text{Ti}_2\text{Br}_2\text{H}_4$	0.02	0.30	0.57	0.87

^a Values from Reference 39. ^b D_{2h} $^1A_g[(\sigma)(\sigma^*)]^2/{}^3B_{1u}(\sigma,\sigma^*)$ state. ^c D_{2h} $^1A_g[(\delta)(\delta^*)]^2/{}^3B_{1u}(\delta,\delta^*)$ state. ^d C_{2h} 1A_u state.

TABLE 2: Geometrical Parameters for Lowest Energy Singlet and Triplet States^a

singlet states	distances (angstroms)				bond angles (degrees)	
	Ti-Ti	Ti-X	Ti-Y	Y-Y	Y-Ti-Y	X-Ti-X
Ti ₂ F ₆	3.249	2.020	1.814	3.289	130.1	72.9
Ti ₂ Cl ₆	3.703	2.491	2.267	4.038	125.9	84.0
Ti ₂ Br ₆	3.835	2.643	2.411	4.260	124.1	87.0
Ti ₂ H ₂ F ₄	2.963	1.905	1.815	3.322	132.4	77.9
Ti ₂ H ₂ Cl ₄	2.968	1.888	2.280	4.143	130.7	76.4
Ti ₂ H ₂ Br ₄	2.975	1.887	2.425	4.388	129.6	75.9
Ti ₂ F ₂ H ₄ ^b	3.269	2.030	1.759	3.075	121.9	72.8
Ti ₂ F ₂ H ₄ ^c	3.279	2.029	1.745	2.853	109.7	72.1
Ti ₂ F ₂ H ₄ ^d	3.274	2.029	1.748	2.914	112.9	72.4
Ti ₂ Cl ₂ H ₄	3.746	2.527	1.743	3.037	121.2	84.3
Ti ₂ Br ₂ H ₄	3.876	2.684	1.741	3.032	121.0	87.5

triplet states	distances (angstroms)				bond angles (degrees)	
	Ti-Ti	Ti-X	Ti-Y	Y-Y	Y-Ti-Y	X-Ti-X
Ti ₂ F ₆	3.246	2.019	1.814	3.289	130.1	73.0
Ti ₂ Cl ₆	3.712	2.491	2.268	4.039	125.9	83.7
Ti ₂ Br ₆	3.853	2.644	2.412	4.264	124.2	86.5
Ti ₂ H ₂ F ₄	2.989	1.909	1.815	3.317	132.1	77.0
Ti ₂ H ₂ Cl ₄	2.987	1.892	2.280	4.136	130.2	75.7
Ti ₂ H ₂ Br ₄	2.992	1.889	2.425	4.381	129.2	75.3
Ti ₂ F ₂ H ₄ ^a	3.268	2.030	1.759	3.075	121.9	72.8
Ti ₂ F ₂ H ₄ ^b	3.280	2.029	1.745	2.853	109.7	72.1
Ti ₂ F ₂ H ₄ ^c	3.274	2.029	1.749	2.922	113.3	72.4
Ti ₂ Cl ₂ H ₄	3.758	2.527	1.743	3.038	121.3	83.9
Ti ₂ Br ₂ H ₄	3.895	2.685	1.742	3.033	121.1	87.0

^a X is the bridging ligand in and Y is the terminal ligand in Ti₂X₂Y₄.

^b D_{2h} ¹A_g[(σ)(σ*)]²/B_{1u}(σ,σ*) state. ^c D_{2h} ¹A_g[(δ)(δ*)]²/B_{1u}(δ,δ*) state. ^d C_{2h} ¹A_u state.

TABLE 3: Mulliken Charges on Ti

molecule	singlet	triplet
Ti ₂ F ₆	1.78	1.78
Ti ₂ Cl ₆	0.93	0.94
Ti ₂ Br ₆	0.75	0.75
Ti ₂ H ₂ F ₄	1.46	1.46
Ti ₂ H ₂ Cl ₄	0.89	0.89
Ti ₂ H ₂ Br ₄	0.73	0.73
Ti ₂ F ₂ H ₄ ^a	1.12	1.12
Ti ₂ F ₂ H ₄ ^b	1.10	1.10
Ti ₂ F ₂ H ₄ ^c	1.11	1.11
Ti ₂ Cl ₂ H ₄	0.85	0.85
Ti ₂ Br ₂ H ₄	0.79	0.79

^a D_{2h} ¹A_g[(σ)(σ^*)]²/³B_{1u}(σ , σ^*) state. ^b D_{2h} ¹A_g[(δ)(δ^*)]²/³B_{1u}(δ , δ^*) state. ^c C_{2h} ¹A_u state.

TABLE 4: Relative Energies (kcal/mol) from lowest energy singlet (C_{2h}) for each basis set

	TCSCF/TZV(p)	MRMP2/TZV(p)	MRMP2/TZVP(f)	MRMP2/TZVP(fg)
$^1\text{Ti}_2\text{F}_2\text{H}_4^a$	1.17	1.77	2.64	3.06
$^3\text{Ti}_2\text{F}_2\text{H}_4^a$	1.05	1.59	2.44	2.86
$^1\text{Ti}_2\text{F}_2\text{H}_4^b$	0.30	0.46	0.28	0.18
$^3\text{Ti}_2\text{F}_2\text{H}_4^b$	0.41	0.70	0.55	0.47
$^1\text{Ti}_2\text{F}_2\text{H}_4^c$	0.00	0.00	0.00	0.00
$^3\text{Ti}_2\text{F}_2\text{H}_4^c$	0.08	0.17	0.21	0.24

^a D_{2h} $^1A_g[(\sigma)(\sigma^*)]^2/{}^3B_{1u}(\sigma,\sigma^*)$ state. ^b D_{2h} $^1A_g[(\delta)(\delta^*)]^2/{}^3B_{1u}(\delta,\delta^*)$ state. ^c C_{2h} 1A_u state.

TABLE 5: Theoretical Vibrational Frequencies (cm⁻¹) of Ti₂X₂Y₄ Molecules for Lowest Energy Singlet and Triplet States

Mode	Symmetry	Activity	Ti ₂ F ₂ ^a	Ti ₂ Cl ₂ ^a	Ti ₂ Br ₂ ^a	Ti ₂ H ₂ F ₂ ^a	Ti ₂ H ₂ Cl ₂ ^a	Ti ₂ H ₂ Br ₂ ^a	Ti ₂ F ₂ H ₂ ^a	Ti ₂ F ₂ Cl ₂ ^a	Ti ₂ F ₂ Br ₂ ^a	Ti ₂ Cl ₂ H ₂ ^a	Ti ₂ Br ₂ H ₂ ^a
Ti-Y stretching	a _g	Raman	700	432	334	689	432	362	1791	1796	1791	1814	1813
ring breathing	a _g	Raman	503	301	188	1369	1375	1369	484	492	490	294	218
bridge bending	a _g	Raman	302	171	116	289	240	172	255	276	267	150	111
Y-Ti-Y angle bending	a _g	Raman	126	70	44	118	70	44	658	641	536	657	653
bridge twisting	b _{1g}	Raman	148	89	54	580	508	481	948i	1207i	354	357	343
bridge stretching	b _{1g}	Raman	425	255	189	1284	1300	1304	411	325	341	240	175
Y-Ti-Y wagging	b _{1g}	Raman	160	108	78	162	115	104	399	429	427	369	356
Ti-Y stretching	b _{1g}	Raman	747	488	389	747	484	388	1690	1699	1698	1710	1711
Y-Ti-Y rocking	b _{1g}	Raman	90	69	50	85	48	35	279	230	245	284	291
Y-Ti-Y twisting	a _u	None	62	53	33	65	45	27	890i	1152i	278	350	341
Ti-Y stretching	b _{1u}	IR	671	407	309	660	380	266	1769	1773	1770	1799	1800
bridge stretching	b _{1u}	IR	528	297	187	1472	1488	1487	480	476	481	286	211
Y-Ti-Y bending	b _{1u}	IR	161	95	62	160	91	63	649	632	518	644	640
Ti-Y stretching	b _{2u}	IR	763	498	397	714	480	383	1704	1709	1710	1719	1717
bridge folding	b _{2u}	IR	247	132	83	827	762	747	119	113	115	80	61
Y-Ti-Y rocking	b _{2u}	IR	51	23	14	58	36	23	378	342	354	327	317
bridge stretching	b _{2u}	IR	439	317	253	1205	1205	1192	335	340	311	255	201
Y-Ti-Y wagging	b _{2u}	IR	131	83	55	139	87	71	493	481	462	425	409

Mode	Symmetry	Activity	Ti ₂ F ₂ ^a	Ti ₂ Cl ₂ ^a	Ti ₂ Br ₂ ^a	Ti ₂ H ₂ F ₂ ^a	Ti ₂ H ₂ Cl ₂ ^a	Ti ₂ H ₂ Br ₂ ^a	Ti ₂ F ₂ H ₂ ^a	Ti ₂ F ₂ Cl ₂ ^a	Ti ₂ F ₂ Br ₂ ^a	Ti ₂ Cl ₂ H ₂ ^a	Ti ₂ Br ₂ H ₂ ^a
Ti-Y stretching	a _g	Raman	700	431	335	689	434	367	1790	1797	1789	1811	1810
ring breathing	a _g	Raman	506	301	188	1370	1380	1374	487	492	490	294	218
bridge bending	a _g	Raman	306	178	121	295	244	174	258	277	265	156	116
Y-Ti-Y angle bending	a _g	Raman	125	69	44	120	69	43	659	641	526	660	658
bridge twisting	b _{1g}	Raman	146	84	52	570	496	467	674i	733i	355	258	284
bridge stretching	b _{1g}	Raman	425	255	188	1271	1288	1295	411	325	341	239	175
Y-Ti-Y wagging	b _{1g}	Raman	159	109	78	160	115	103	400	428	426	370	357
Ti-Y stretching	b _{1g}	Raman	747	489	389	744	483	386	1690	1699	1698	1714	1715
Y-Ti-Y rocking	b _{1g}	Raman	88	69	50	79	44	32	280	229	246	250	239
Y-Ti-Y twisting	a _u	None	62	42	27	62	33	22	672i	1987i	281	244	254
Ti-Y stretching	b _{1u}	IR	671	407	308	660	381	266	1769	1774	1769	1796	1796
bridge stretching	b _{1u}	IR	528	297	187	1466	1483	1484	481	476	477	285	210
Y-Ti-Y bending	b _{1u}	IR	160	95	62	160	89	63	649	632	508	646	643
Ti-Y stretching	b _{2u}	IR	764	499	397	713	479	382	1703	1710	1709	1722	1721
bridge folding	b _{2u}	IR	247	132	83	829	766	751	120	110	114	64	48
Y-Ti-Y rocking	b _{2u}	IR	49	21	13	54	30	18	378	341	356	299	251
bridge stretching	b _{2u}	IR	440	315	251	1183	1188	1180	336	340	316	254	200
Y-Ti-Y wagging	b _{2u}	IR	131	83	55	138	86	69	494	479	455	424	410

^a Results from MCSCF numerical Hessian calculation with double differencing and projection. ^b Results from GVB analytic Hessian calculation. ^c Results from ROHF analytic Hessian calculation. ^d Results from ROHF numerical Hessian calculation with double differencing and projection. ^e D_h 'A_g[(σ*)²]/B_h(σ,σ*) state. ^f D_h 'A_g[(δ*)²]/B_h(δ,δ*) state. ^g C_{2v} 'A₁ state.

TABLE 6: ROHF/TZV(p) Geometries for the Titanium Monomers

Molecule	Symmetry/State	Ti-X ^a	Ti-H ^a	X-Ti-X or H-Ti-H angle ^b
TiF ₃	D _{3h} ² A ₁ '	1.819		120.0
TiHF ₂	C _{2v} ² A ₁	1.821	1.754	127.6
TiH ₂ F	C _{2v} ² A ₁	1.824	1.764	116.5
TiCl ₃	D _{3h} ² A ₁ '	2.272		120.0
TiHCl ₂	C _{2v} ² A ₁	2.292	1.723	128.4
TiH ₂ Cl	C _{2v} ² A ₁	2.315	1.749	116.0
TiBr ₃	D _{3h} ² A ₁ '	2.414		120.0
TiHBr ₂	C _{2v} ² A ₁	2.436	1.720	129.2
TiH ₂ Br	C _{2v} ² A ₁	2.461	1.748	116.0

^a bond distances in angstroms ^b bond angles in degrees

TABLE 7: Theoretical and Experimental Vibrational Frequencies (cm⁻¹) of TiX₃ molecules (D_{3h})

Mode	sym stretch A ₁ '	out-of-plane A ₂ ''	asym stretch E'	asym bend E'
Molecule	ν_1	ν_2	ν_3	ν_4
TiF ₃	639	142	738	164
	630 ^a	150 ^a	735 ^a	160 ^a
	643 ^b		740.6 ^{b,c}	
		140.6 ^c		
	665 ^d	146 ^d	764 ^d	172 ^d
TiCl ₃	355	101	484	97
	296(15) ^a	120(6) ^a	505 ^a	95(5) ^a
	338(17) ^a	118(6) ^a	465(24) ^a	91(5) ^a
		110±12 ^f	505±10 ^f	135±12 ^f
	350±30 ^g	110±15 ^g	500±10 ^g	135±15 ^g
	320(30) ^h	129(20) ^h	498(16) ^h	107(7) ^h
TiBr ₃	218	88	388	63
	230 ^a	80 ^a	355 ^a	58 ^a

^aEstimated in Ref. 60. ^bReference 63. ^cReference 64. ^dReference 61. ^eReference 62.

^fReference 71. ^gReference 65,72. ^hReference 65.

TABLE 8. Theoretical Vibrational Frequencies (cm⁻¹) of TiHX₂ and TiH₂X molecules (C_{2v})

Mode	Ti-H stretch	Ti-X stretch	X-Ti-X bend	Ti-F stretch	angle bend	out-of-plane
Symmetry	a ₁	a ₁	a ₁	b ₁	b ₁	b ₂
TiHF ₂	1646	647	163	755	519	89
TiHCl ₂	1689	358	85	411	534	213
TiHBr ₂	1683	240	62	348	489	248

Mode	Ti-H stretch	Ti-X stretch	H-Ti-H bend	Ti-H stretch	angle bend	out-of-plane
Symmetry	a ₁	a ₁	a ₁	b ₁	b ₁	b ₂
TiH ₂ F	1737	584	727	1684	375	293
TiH ₂ Cl	1759	396	611	1732	369	309
TiH ₂ Br	1716	298	610	1682	288	268

TABLE 9: ROHF/TZV(p) Geometries for the Different States of TiHCl_2

State	Ti-X	Ti-H	X-Ti-X angle	relative energy (kcal/mol)
$^2\text{A}_1$ (ground)	2.292	1.723	128.4	0.00
$^2\text{B}_1$	2.296	1.710	136.7	1.72
$^2\text{A}_2$	2.316	1.723	120.8	5.29
$^2\text{B}_2$	2.335	1.689	147.4	24.63
	2.32 ^a	1.68 ^a	147.8 ^a	

^a values from reference 75

TABLE 10: Energy of Dimerization (kcal/mol) using TZV(p) basis

Molecule	ΔE_{elec} MRMP2	ΔZPE (MCSCF)	$\Delta H_{\text{dimerization}}$ (MRMP2)
$\text{Ti}_2\text{F}_6^{\text{a}}$	-42.3	1.5	-40.7
$\text{Ti}_2\text{Cl}_6^{\text{a}}$	-33.7	0.9	-32.8
Ti_2Br_6	-33.3	0.6	-32.7
$\text{Ti}_2\text{H}_2\text{F}_4$	-45.7	4.1	-41.6
$\text{Ti}_2\text{H}_2\text{Cl}_4$	-34.3	3.2	-31.1
$\text{Ti}_2\text{H}_2\text{Br}_4$	-34.8	3.0	-31.8
$\text{Ti}_2\text{F}_2\text{H}_4^{\text{b}}$	-53.9	2.2	-51.6
$\text{Ti}_2\text{Cl}_2\text{H}_4$	-54.0	2.2	-51.8
$\text{Ti}_2\text{Br}_2\text{H}_4$	-56.3	2.0	-54.3

^a Calculations for triplet state (lowest energy state at MRMP2/TZV(p) level of theory)

^b Calculations for C_{2h} structure

TABLE 11: $J(\text{cm}^{-1}) = E(\text{singlet}) - E(\text{triplet})$

Molecule	TCSCF/TZV(p)	MRMP2/TZV(p)	MRMP2/TZVP(f)	MRMP2/TZVP(fg)
Ti_2H_6	-98	-233	-246	-250
Ti_2F_6	20	32	40	41
Ti_2Cl_6	15	2	-47	-157
Ti_2Br_6	4	-59	-107	-78
$\text{Ti}_2\text{H}_2\text{F}_4$	-144	-337	-360	-367
$\text{Ti}_2\text{H}_2\text{Cl}_4$	-103	-283	-313	-318
$\text{Ti}_2\text{H}_2\text{Br}_4$	-90	-268	-294	-298
$\text{Ti}_2\text{F}_2\text{H}_4^{\text{a}}$	20	32	35	35
$\text{Ti}_2\text{F}_2\text{H}_4^{\text{b}}$	-20	-42	-49	-50
$\text{Ti}_2\text{F}_2\text{H}_4^{\text{c}}$	-14	-30	-37	-41
$\text{Ti}_2\text{Cl}_2\text{H}_4$	7	-10	-59	-60
$\text{Ti}_2\text{Br}_2\text{H}_4$	-4	-52	-100	-153

^a $\text{D}_{2h} \text{ } ^1\text{A}_g[(\sigma)(\sigma^*)]^2/\text{B}_{1u}(\sigma, \sigma^*)$ state. ^b $\text{D}_{2h} \text{ } ^1\text{A}_g[(\delta)(\delta^*)]^2/\text{B}_{1u}(\delta, \delta^*)$ state. ^c $\text{C}_{2h} \text{ } ^1\text{A}_u$ state.

TABLE 12: Spin-Orbit Coupling

molecule		CASSCF-SOC/TZV(p)			MCQDPT-SOC/TZV(p)		
		HSO1	HSO2P	HSO2	HSO1	HSO2P	HSO2
Ti ₂ F ₆	S ₀	-7.491	-8.355	-8.355	-6.706	-7.589	-7.589
	T ₁ X	-52.848	-53.697	-53.693	-45.358	-46.202	-46.198
	T ₁ Y	-52.915	-53.771	-53.771	-45.415	-46.270	-46.269
	T ₁ Z	-52.911	-53.766	-53.770	-45.430	-46.268	-46.271
	D _e	-0.030	-0.032	-0.038	-0.044	-0.032	-0.038
	E _e	0.034	0.037	0.039	0.029	0.034	0.035
Ti ₂ Cl ₆	S ₀	-8.927	-9.995	-9.995	-7.557	-8.686	-8.687
	T ₁ X	-48.611	-49.658	-49.655	-37.103	-38.211	-38.208
	T ₁ Y	-48.689	-49.745	-49.744	-37.159	-38.279	-38.278
	T ₁ Z	-48.676	-49.731	-49.734	-37.147	-38.265	-38.268
	D _e	-0.026	-0.030	-0.035	-0.016	-0.020	-0.025
	E _e	0.039	0.043	0.044	0.028	0.034	0.035
Ti ₂ Br ₆	S ₀	-6.663	-7.774	-7.774	-5.460	-6.592	-6.592
	T ₁ X	-18.562	-19.651	-19.649	19.473	18.350	18.352
	T ₁ Y	-18.619	-19.718	-19.717	19.429	18.295	18.296
	T ₁ Z	-18.607	-19.704	-19.707	19.439	18.307	18.305
	D _e	-0.016	-0.020	-0.024	-0.012	-0.016	-0.019
	E _e	0.028	0.034	0.034	0.022	0.027	0.028
Ti ₂ H ₂ F ₄	S ₀	-6.072	-6.622	-6.622	-5.872	-6.599	-6.599
	T ₁ X	304.086	303.563	303.566	491.004	490.447	490.450
	T ₁ Y	303.914	303.380	303.380	490.792	490.212	490.213
	T ₁ Z	303.913	303.378	303.374	490.786	490.207	490.203
	D _e	-0.087	-0.094	-0.099	-0.112	-0.123	-0.129
	E _e	0.086	0.091	0.093	0.106	0.118	0.118
Ti ₂ H ₂ Cl ₄	S ₀	-7.709	-8.483	-8.484	-6.901	-7.881	-7.882
	T ₁ X	215.218	214.450	214.457	446.386	445.533	445.538
	T ₁ Y	215.044	214.261	214.266	446.154	445.265	445.268
	T ₁ Z	215.045	214.262	214.257	446.133	445.242	445.237
	D _e	-0.086	-0.093	-0.104	-0.137	-0.157	-0.166
	E _e	0.087	0.094	0.096	0.116	0.134	0.135
Ti ₂ H ₂ Br ₄	S ₀	-7.234	-8.042	-8.043	-6.706	-7.703	-7.704
	T ₁ X	188.937	188.106	188.114	416.105	415.191	415.197
	T ₁ Y	188.760	187.918	187.923	415.875	414.930	414.933
	T ₁ Z	188.761	187.920	187.914	415.853	414.904	414.900
	D _e	-0.088	-0.092	-0.105	-0.137	-0.156	-0.165
	E _e	0.089	0.094	0.096	0.115	0.130	0.132

S₀, T₁ X, T₁ Y, and T₁ Z are the energies (cm⁻¹) of the spin-mixed states for the lowest energy singlet and X, Y, and Z components of the lowest energy triplet state, respectively. D_e and E_e (cm⁻¹) are the axial and rhombic ZFS parameters, respectively.

^a D_{2h} ¹A_g[(σ)(σ*)]²/²B_{1u}(σ,σ*) state. ^b D_{2h} ¹A_g[(δ)(δ*)]²/²B_{1u}(δ,δ*) state. ^c C_{2h} ¹A_u state.

TABLE 12: (cont.)

molecule		CASSCF-SOC/TZV(p)			MCQDPT-SOC/TZV(p)		
		HSO1	HSO2P	HSO2	HSO1	HSO2P	HSO2
$\text{Ti}_2\text{F}_2\text{H}_4^a$	S_0	-53.091	-56.216	-56.232	-98.661	-105.397	-105.420
	$T_1 X$	-91.490	-94.270	-94.226	-49.704	-57.300	-57.223
	$T_1 Y$	-91.567	-94.358	-94.317	-49.634	-57.142	-57.064
	$T_1 Z$	-90.612	-93.364	-93.381	-47.979	-55.561	-55.588
	D_e	0.916	0.950	0.890	1.690	1.660	1.556
	E_e	0.038	0.044	0.045	-0.035	-0.079	-0.079
$\text{Ti}_2\text{F}_2\text{H}_4^b$	S_0	-28.829	-30.636	-30.644	-19.192	-21.147	-21.152
	$T_1 X$	11.685	9.742	9.772	58.295	56.227	56.246
	$T_1 Y$	11.683	9.740	9.768	58.253	56.125	56.145
	$T_1 Z$	12.205	10.289	10.278	58.494	56.433	56.426
	D_e	0.521	0.548	0.508	0.220	0.257	0.230
	E_e	0.001	0.001	0.002	0.021	0.051	0.050
$\text{Ti}_2\text{F}_2\text{H}_4^c$	S_0	-29.488	-31.381	-31.39	-21.186	-23.351	-23.358
	$T_1 X$	2.680	0.668	0.697	59.049	56.375	56.396
	$T_1 Y$	2.672	0.659	0.686	59.285	56.839	56.861
	$T_1 Z$	3.213	1.227	1.215	59.418	56.767	56.758
	D_e	0.537	0.564	0.524	0.251	0.160	0.130
	E_e	0.004	0.005	0.005	-0.118	-0.232	-0.232
$\text{Ti}_2\text{Cl}_2\text{H}_4$	S_0	-12.999	-14.299	-14.299	-14.334	-16.292	-16.293
	$T_1 X$	-30.231	-31.506	-31.501	-36.987	-38.759	-38.753
	$T_1 Y$	-30.327	-31.615	-31.613	-37.076	-38.874	-38.871
	$T_1 Z$	-30.271	-31.556	-31.560	-36.953	-38.74	-38.745
	D_e	0.008	0.004	-0.003	0.078	0.076	0.067
	E_e	0.048	0.054	0.056	0.044	0.058	0.059
$\text{Ti}_2\text{Br}_2\text{H}_4$	S_0	-11.483	-12.813	-12.814	-12.727	-14.424	-14.425
	$T_1 X$	-0.004	-1.307	-1.303	5.237	3.569	3.573
	$T_1 Y$	-0.077	-1.397	-1.396	5.172	3.483	3.485
	$T_1 Z$	-0.019	-1.336	-1.340	5.308	3.626	3.622
	D_e	0.022	0.016	0.009	0.104	0.100	0.093
	E_e	0.037	0.045	0.047	0.033	0.043	0.044

TABLE 13: CASSCF-SOC Timings

molecule	method	Total CPU Time	Spin Orbit Coupling ^b	% Total Time	% SOC Time ^b
Ti ₂ F ₆	HSO1	229.6	56.4	1.58	0.39
	HSO2P	6355.8	6180.5	43.8	43.1
	HSO2	14514.2	14352.0	100.0	100.0
Ti ₂ Cl ₆	HSO1	472.9	167.0	1.50	0.53
	HSO2P	10179.6	9871.1	32.2	31.5
	HSO2	31599.6	31304.0	100.0	100.0
Ti ₂ Br ₆	HSO1	1780.0	1028.7	2.38	1.39
	HSO2P	35267.4	34429.9	47.1	46.4
	HSO2	74895.0	74137.5	100.0	100.0
Ti ₂ Br ₆ ^a	HSO1	531.5	256.6	3.22	1.58
	HSO2P	6621.7	6348.8	40.1	39.2
	HSO2	16492.6	16198.1	100.0	100.0
Ti ₂ H ₂ F ₄	HSO1	178.2	37.2	2.33	0.49
	HSO2P	4292.3	4153.0	56.1	55.1
	HSO2	7656.3	7536.3	100.0	100.0
Ti ₂ H ₂ Cl ₄	HSO1	270.4	81.2	1.91	0.58
	HSO2P	6052.6	5859.5	42.8	42.1
	HSO2	14141.1	13926.8	100.0	100.0
Ti ₂ H ₂ Br ₄	HSO1	861.3	359.1	2.88	1.22
	HSO2P	17408.1	16962.5	58.2	57.5
	HSO2	29914.1	29515.7	100.0	100.0
Ti ₂ F ₂ H ₄ ^c	HSO1	108.1	21.6	1.89	0.38
	HSO2P	3043.9	2956.8	53.1	52.4
	HSO2	5728.6	5640.9	100.0	100.0
Ti ₂ Cl ₂ H ₄	HSO1	147.8	34.5	1.66	0.39
	HSO2P	3617.5	3505.1	40.5	39.8
	HSO2	8921.2	8806.7	100.0	100.0
Ti ₂ Br ₂ H ₄	HSO1	294.2	91.8	1.99	0.63
	HSO2P	6466.5	6265.6	43.7	42.9
	HSO2	14799.7	14598.1	100.0	100.0

Timings for a 300 MHz UltraSPARC2 computer. ^a Timings for a 500 MHz AXP EV6 computer. ^b This category includes time required for integral transformations and spin-orbit matrix element calculation. ^c D_{2h} [(σ)(σ*)]² state.

TABLE 14: MCQDPT-SOC Timings

molecule	method	Total CPU Time	Spin Orbit Coupling ^a	% Total Time	% SOC Time ^a
Ti ₂ F ₆	HSO1	3863.2	90.3	62.6	3.7
	HSO2P	5111.1	1500.7	82.8	62.2
	HSO2	6174.1	2412.8	100.0	100.0
Ti ₂ Cl ₆	HSO1	9560.4	181.9	73.3	4.2
	HSO2P	11137.3	2471.3	85.4	56.5
	HSO2	13048.7	4374.7	100.0	100.0
Ti ₂ Br ₆	HSO1	50172.1	800.1	81.7	7.1
	HSO2P	63878.7	6745.2	104.1	59.7
	HSO2	61380.2	11304.2	100.0	100.0
Ti ₂ H ₂ F ₄	HSO1	2191.8	58.1	59.4	3.8
	HSO2P	3170.8	1022.4	85.9	67.3
	HSO2	3692.1	1519.2	100.0	100.0
Ti ₂ H ₂ Cl ₄	HSO1	4471.8	105.3	68.4	4.6
	HSO2P	6022.4	1579.2	92.2	68.8
	HSO2	6533.6	2296.9	100.0	100.0
Ti ₂ H ₂ Br ₄	HSO1	18638.0	363.9	81.0	6.4
	HSO2P	20682.6	3366.0	89.9	59.2
	HSO2	22996.9	5682.4	100.0	100.0
Ti ₂ F ₂ H ₄ ^b	HSO1	1620.4	42.7	60.2	3.9
	HSO2P	2320.5	711.9	86.1	65.5
	HSO2	2693.6	1086.2	100.0	100.0
Ti ₂ Cl ₂ H ₄	HSO1	2103.7	56.5	62.8	4.3
	HSO2P	2908.5	859.7	86.8	65.8
	HSO2	3350.1	1307.2	100.0	100.0
Ti ₂ Br ₂ H ₄	HSO1	4797.0	111.8	67.1	4.7
	HSO2P	6212.8	1538.0	86.9	64.4
	HSO2	7150.8	2388.1	100.0	100.0

Timings for a 500 MHz AXP EV6 computer. ^a This category includes time required for integral transformations and spin-orbit matrix element calculation. ^b D_{2h} [(σ)(σ*)]² state.

Figure 1. Three-dimensional plots of the natural orbitals from a 2 electron, 2 orbital MCSCF/TZV(p) calculation. The orbital contour value for the plots is $0.06 \text{ bohr}^{3/2}$. The z-axis is defined by the Ti-Ti axis. The orbitals shown are for $\text{Ti}_2\text{F}_2\text{H}_4$. Natural orbital occupations numbers (NOON's) are shown above.

Figure 2. Three-dimensional plots of the natural orbitals for singlet $\text{Ti}_2\text{F}_2\text{H}_4$ from a 2 electron, 2 orbital MCSCF/TZV(p) calculation. The orbital contour value for the plots is $0.06 \text{ bohr}^{3/2}$. The z-axis is defined by the Ti-Ti axis. Natural orbital occupations numbers (NOON's) are shown above.

Figure 3. Three-dimensional plots of the natural orbitals for singlet $\text{Ti}_2\text{F}_2\text{H}_4$ with C_{2h} symmetry from a 2 electron, 2 orbital MCSCF/TZV(p) calculation. The orbital contour value for the plots is $0.06 \text{ bohr}^{3/2}$. The z-axis is defined by the Ti-Ti axis. Natural orbital occupations numbers (NOON's) are shown above.

CHAPTER 3. INFLUENCE OF MULTI-ATOM BRIDGING LIGANDS ON THE ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF HOMODINUCLEAR TITANIUM MOLECULES

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The electronic structure and magnetic properties of homodinuclear titanium(III) molecules with bridging ligands from groups 14, 15, and 16 are examined. Single- and multireference methods with triple- ζ plus polarization basis sets are employed. Dynamic electron correlation effects are included via second-order multireference perturbation theory. Isotropic interaction parameters are calculated, and two of the complexes studied are predicted to be ferromagnetic based on multi-reference second-order perturbation (MRMP2) theory, using the TZVP(fg) basis set. Zero-field splitting parameters are determined using spin-orbit coupling obtained from complete active space (CAS) SCF and multiconfigurational quasidegenerate perturbation theory (MCQDPT) wave functions. Three Breit-Pauli-based spin coupling methods were employed: Full Breit-Pauli (HSO2), the partial two-electron method (P2E), and the semi-empirical one-electron method (HSO1). Timings for these three methods are compared.

1. Introduction

The interaction of multiple metal centers in molecular complexes, solid-state compounds, and enzymes has become a rapidly expanding field of study over the last few years.¹⁻⁶ In particular, the design of single-molecule ferromagnets and antiferromagnetic superconductors with high critical temperatures are significant challenges in the area of

materials science. The relationship between magnetic and electronic properties is also a growing field of study in bioinorganic chemistry.⁷

The magnetization of a material depends on the magnetic field acting on it. The magnetic susceptibility, χ , is a property of the material and relates the magnetization, M , to the strength of the magnetic field, H . For relatively low values of H ,

$$M = \chi H.$$

If the magnetic susceptibility is negative, it is independent of temperature and the material is diamagnetic. If the susceptibility is positive, it varies with temperature. This is the case for paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic materials. In ferromagnetic materials, the susceptibility increases as the temperature decreases. In antiferromagnetic materials, the magnetic susceptibility passes through a maximum at the Néel temperature and goes to zero as the temperature approaches absolute zero.

The magnetic behavior of transition metal complexes in which more than one metal atom has unpaired electrons depends on the strength of the interaction between the metal centers. When strong metal-metal bonds occur in a dimer, the molecule will be diamagnetic. If the metal centers do not interact, the magnetic properties of the dimer are unchanged from those of the monomer. In a weakly interacting complex, the weak coupling of the electrons leads to low-lying excited states of different spin. In dinuclear complexes with one unpaired electron on each metal center, the two local spin states S_A and S_B can interact through the bridging ligands with either singlet or triplet coupling. If singlet coupling is favored, the interaction is antiferromagnetic; if triplet coupling is favored, the interaction is

ferromagnetic. If this isotropic interaction is the dominant magnetic effect, the total spin quantum number S is a good quantum number.⁸

The Hamiltonian that describes the coupling between local spin operators S_A and S_B was introduced by Heisenberg.⁹ It may be written as

$$\mathcal{H} = -2JS_A \cdot S_B,$$

where the isotropic exchange interaction parameter J is defined by

$$2J = E(S=0) - E(S=1).$$

The isotropic interaction parameter is related to the magnetic susceptibility by

$$\chi = \frac{2Ng^2\beta^2}{kT} [3 + \exp(\frac{-2J}{kT})]^{-1}$$

where N is Avogadro's number, g is the average electronic gyromagnetic ratio, β is the Bohr magneton, k is the Boltzmann constant, and T is the temperature. Moreover, for antiferromagnetic compounds the isotropic interaction parameter is proportional to the Néel temperature $T_{\max}$ according to

$$|2J|/kT_{\max} = 1.599$$

where $k = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$. This relation may be used to compare calculated isotropic interaction parameters with experimentally observable susceptibility maxima.

The isotropic exchange interaction usually has a greater effect on the magnetic properties than other phenomena such as the spin-orbit coupling and the magnetic dipole-dipole interaction. However, if the singlet-triplet splitting is small or if the triplet state is the ground state, these other interactions may become essential for an accurate description of the system. In addition, these effects may be seen in an electron paramagnetic resonance (EPR)

spectrum of the triplet state, since they result in a zero-field splitting (ZFS) of the M_s components. The Hamiltonian for these terms may be written

$$\mathcal{H} = S \cdot \mathbf{D} \cdot S + \beta S \cdot \mathbf{g} \cdot H$$

where the first term accounts for the dipolar and anisotropic exchange interactions due to the zero-field splitting tensor $\mathbf{D}$ and the second term accounts for the Zeeman perturbation with the $\mathbf{g}$ (gyromagnetic) tensor. The principal (diagonal) values of $\mathbf{D}$ and $\mathbf{g}$ are fit to the experimental data. The principal values of $\mathbf{D}$ are used to calculate the axial and nonaxial (rhombic) zero-field splitting parameters D and E according to¹⁰

$$D = 3D_z/2$$

$$E = (D_x - D_y)/2$$

The anisotropic exchange tensor $\mathbf{D}_e$ may be found by

$$\mathbf{D}_e = \mathbf{D} - \mathbf{D}_d$$

where $\mathbf{D}_d$ is the dipole-dipole interaction tensor. The dipolar term is often the minor contribution to $\mathbf{D}$ and can often be reasonably estimated from the point dipole approximation.⁸ The axial and rhombic exchange interaction parameters, D_e and E_e , are related to the spin-orbit coupling and may be calculated by

$$D = D_d + D_e$$

$$E = E_d + E_e$$

In 1934, Kramers introduced the idea of superexchange in order to explain how transition metal ions in solids could interact at long distances.¹¹ He proposed that the neighboring non-magnetic atoms could play a role in the magnetic interaction mechanism through an exchange spin-coupling. In the 1950s, Anderson and Nesbet developed basic

qualitative models of exchange interactions in solid-state materials.¹²⁻¹⁵ The Anderson model has been successful in predicting the sign of the magnetic interaction, but does not quantitatively reproduce its magnitude. Early *ab initio* calculations on the ionic solid KNiF_3 confirmed the ideas of the Anderson model, but yielded a magnetic coupling value that was much too small.¹⁶

In 1952, Bleaney and Bowers discovered that superexchange is not limited to solids, but also occurs in binuclear or polynuclear metal complexes such as copper acetate.¹⁷ In the mid-1970s, Hay, Thibault, and Hoffmann (HTH)¹⁸ and Kahn and Briat^{19,20} discussed a semi-quantitative equivalent of the Anderson model for molecular complexes and other systems based on extended Hückel calculations. One reason that the Anderson and HTH models produce J values that are too small relative to experimental values is that they neglect dynamic correlation contributions. An important advance toward a quantitative examination of magnetic coupling came in 1981, when de Loth et al. used perturbation theory in order to include the effect of excited configuration state functions that contribute to the energy difference between the lowest energy singlet and triplet states.²¹ Since this time, perturbation theory methods built on a multireference zeroth-order wavefunction have been used to examine the magnetic coupling in a variety of metal complexes and materials.²²⁻⁴⁰ Other theoretical methods for calculating the magnetic coupling for biradicals and binuclear complexes have been discussed recently.⁴¹

Ab initio calculations can provide new insights into the interactions between metal centers and ligands. Homodinuclear complexes with one unpaired electron on each metal center, such as d^1 Ti(III) complexes, are some of the simplest model compounds for investigating spin-spin interactions. Experimentally, dititanium(III) compounds with a linear

oxo-bridge,⁴²⁻⁴⁵ organic bridge,⁴⁶⁻⁵⁷ face-sharing bioctahedral tribridge,^{58,59} or dibridge (ring) structure have been characterized. Complexes with a ring structure include hydrido-,⁶⁰⁻⁶² halo-,⁶³⁻⁷⁴ amido-,⁷⁵⁻⁷⁸ hydroxy-,^{74,79} alkoxy-,^{76,80} phosphido-,⁸¹ silyl-,⁸² sulfato-,⁸³ and thio-bridged species.⁷⁶ Some of the rings are essentially planar^{63,66,77,80,81} while others are buckled.^{61,79}

The magnetic properties of linear oxo-bridged compounds have been investigated using CASSCF, MC-CEPA, and ACPF calculations^{84,85} and density functional theory calculations.⁸⁶ The Ti-Ti bonding interaction, isotropic interaction, and zero-field splitting parameters of D_{2h} $H_2Ti(\mu-H)_2TiH_2$, a simple model of the flat ring compounds, were studied in detail using multireference methods.^{29,30} The effects of halide bridging and terminal ligands on the magnetic properties of homodinuclear titanium(III) compounds were also examined using multireference methods.³⁴ In the present study, the effects of other bridging ligands such as OH, SH, NH_2 , PH_2 , NNN, CN, OCN, CNO, SCN, NO, and NO_2 on the magnetic properties will be discussed.

2. Computational Details

Geometry optimizations for triplet states were carried out at the restricted open-shell Hartree-Fock (ROHF) level of theory. The triplet orbitals were used as a starting point for a two configuration self-consistent field (TCSCF) optimization for the singlet states. The basis set used in the geometry optimizations is denoted TZV(p). It consists of a triple- ζ with polarization (14s11p6d/10s8p3d) basis set for titanium, which is comprised of Wachter's basis set⁸⁷ with two additional sets of p functions⁸⁸ and an additional set of diffuse d functions.⁸⁹ In the notation (A/B), A is the primitive basis set and B is the contracted basis

set. For hydrogen, Dunning's (5s1p/3s1p) basis set was employed;⁹⁰ for carbon, nitrogen, and oxygen, the Dunning (10s6p/5s3p) basis set was used.⁹¹ The McLean and Chandler (12s9p/6s5p) basis set was utilized for phosphorus and sulfur.⁹²

The energy second-derivative (Hessian) matrix was calculated and diagonalized at all stationary points. Unless otherwise stated, all stationary points have zero imaginary frequencies and are minima on their respective potential energy surfaces.

Two larger basis sets denoted TZVP(f) and TZVP(fg) were also used in this study. For both, diffuse s and p functions and two sets of d polarization functions were added to the main group elements. The diffuse sp function and 2d polarization function exponents are the default values in GAMESS.^{93,94} The basis set called TZVP(f) adds an f function ($\alpha = 0.40$)⁹⁵ to the titanium atom. The basis set referred to as TZVP(fg) adds a set of f ($\alpha = 0.591$) and g ($\alpha = 0.390$) polarization functions, as well as a set of diffuse s ($\alpha = 0.035$), p ($\alpha = 0.239$), and d ($\alpha = 0.0207$) functions, to the TZV(p) titanium basis. These exponents in the TZVP(fg) basis set are optimized for correlated titanium atoms.⁹⁶

The effects of dynamic electron correlation were included by carrying out second-order multireference perturbation theory (MRMP2)⁹⁷⁻¹⁰⁰ single-point energy calculations at the TCSCF and ROHF geometries. Single-point energy calculations were repeated with the TZVP(f) and TZVP(fg) basis sets as a test of basis set convergence.

For excited states, fully optimized reaction space (FORS) multiconfigurational SCF (MCSCF) calculations¹⁰¹⁻¹⁰³ (also called complete active space SCF (CASSCF)¹⁰⁴) with an active space consisting of 2 electrons in 10 or more orbitals are required. Spin-orbit coupling (SOC) effects are determined using both the complete active space SCF (CASSCF-SOC) and

multiconfiguration quasi-degenerate perturbation theory (MCQDPT-SOC)¹⁰⁵ methods. Three different operators are used in the calculations: a semi-empirical one-electron spin-orbit coupling operator (HSO1),¹⁰⁶ a partial two-electron/full one-electron operator (P2E),¹⁰⁷ and the full Pauli-Breit operator (HSO2).¹⁰⁷

The electronic structure code GAMESS^{93,94} was used for all calculations. Orbitals were visualized using MacMolPlt,¹⁰⁸ a graphical interface to GAMESS.

3. Results and Discussion

Electronic Structure and Energetics

OH

The hydroxide ligand is isoelectronic with fluoride, so it provides a good first comparison with hydride and halide bridging ligands. Indeed, the complex $\text{Ti}_2(\mu\text{-OH})_2\text{H}_4$ follows the electronic structure and energetic trends discussed in previous work on Ti_2H_6 ²⁹ and $\text{Ti}_2\text{X}_2\text{Y}_4$ (X,Y=H,F,Cl,Br).³⁴ Mulliken populations (Table 1) for the TCSCF and ROHF wave functions with the TZV(p) basis show that the titanium atoms are positively charged. The lowest energy D_{2h} singlet and triplet states are determined to be 1A_g and $^3B_{1u}$, respectively. The molecular orbitals that create these states are primarily formed from the σ and σ^* combination of the $d_{x^2-z^2}$ orbitals on the two Ti atoms (Figure 1), where the Ti atoms lie along the z-axis and the OH ligands lie along the x-axis. The two configurations that are responsible for the singlet state may be expressed as $[(\sigma)(\sigma^*)]^2$, or:

Config. #	σ	σ^*
1	2	0
2	0	2

The singlet state has a high degree of diradical character; a natural orbital analysis of the TCSCF/TZV(p) wave function (Table 2) shows that there are 0.92 electrons in the lowest virtual orbital. This suggests that although the molecule is in principle able to form a direct Ti-Ti bond, the singlet state is essentially a singlet diradical with very little bonding interaction.

The TCSCF/TZV(p) energy difference between the singlet and triplet states is only 0.2 kcal/mol (Table 3). The inclusion of dynamic electron correlation via second-order perturbation theory lowers the singlet state preferentially. The MRMP2/TZV(p) energy difference increases to 0.7 kcal/mol. As the basis set size is increased, the singlet-triplet splitting increases by an additional 0.1 kcal/mol to 0.8 kcal/mol at the MRMP2/TZVP(fg) level of theory, and is still very small.

SH

The hydrosulfido ligand is isoelectronic with chloride, so one might think that it would follow a similar electronic structure pattern. Unlike $\text{Ti}_2(\mu\text{-OH})_2\text{H}_4$, the analogous $\text{Ti}_2(\mu\text{-SH})_2\text{H}_4$ D_{2h} structure is not a local minimum. Imaginary frequencies lead to C_{2v} and C_{2h} structures. The relative energies for these structures are shown in Table 4. The C_{2v} structure is lower in energy than the C_{2h} structure by 1.1 kcal/mol. Geometrical parameters are presented in Table 5. Although it has a lower symmetry, the general electronic structure of $\text{Ti}_2(\mu\text{-SH})_2\text{H}_4$ can be related to that of $\text{Ti}_2(\mu\text{-OH})_2\text{H}_4$. The frontier molecular orbitals that create the 1A_1 and 3B_2 states are derived from the Ti d_{xz-zy} atomic orbitals. The “modified” σ and σ^* molecular orbitals have a_1 and b_2 symmetry, respectively. The singlet state is essentially a singlet diradical with 0.96 electrons in the lowest virtual orbital (Table 2).

At the TCSCF/TZV(p) level of theory, the singlet state is predicted to be only 0.01 kcal/mol lower in energy than the triplet state (Table 3). The inclusion of dynamic electron correlation at the MRMP2/TZV(p) level further stabilizes the singlet state by 0.2 kcal/mol. As the basis set is improved, the singlet-triplet splitting grows to 0.5 kcal/mol at the MRMP2/TZVP(fg) level of theory.

NH₂

For D_{2h} $Ti_2(\mu-NH_2)_2H_4$, the $[(\sigma)(\sigma^*)]^2$ orbital configuration is not the dominant configuration in the ground state. Instead, the $[(\delta)(\delta^*)]^2$ orbital configuration (Figure 2) created from the Ti d_{xy} atomic orbitals dominates the ground state and the $[(\sigma)(\sigma^*)]^2$ orbital configuration corresponds to an excited state. This behavior was noted earlier for $Ti_2(\mu-F)_2H_4$.³⁴ MCSCF(2,10) calculations show that the $[(\sigma)(\sigma^*)]^2$ and $[(\delta)(\delta^*)]^2$ configurations essentially do not mix, even though they belong to the same irreducible representation. However, the singlet state comprised of σ orbitals and the triplet state dominated by δ orbitals are not local minima. Imaginary frequencies lead to a C_{2h} structure for both singlet and triplet states (Figure 3). At the MRMP2/TZV(p) level of theory, this structure is 0.3 and 5.7 kcal/mol lower in energy than the singlet D_{2h} states with orbital configurations $[(\delta)(\delta^*)]^2$ and $[(\sigma)(\sigma^*)]^2$, respectively (Table 4).

PH₂

The lowest energy singlet and triplet states for $Ti_2(\mu-PH_2)_2H_4$ with D_{2h} symmetry are 1A_g and $^3B_{1u}$. The D_{2h} triplet state is not a minimum on the potential energy surface. The imaginary frequency ($38i\text{ cm}^{-1}$) leads to a structure with C_{2v} symmetry. The lowest energy C_{2v} singlet is 1.0 kcal/mol lower in energy than the lowest energy D_{2h} singlet (Table 4). The

ground state of this molecule is more similar to SH than NH₂. The molecular orbitals are formed primarily from the Ti d_{x²-y²} orbitals, similar to OH and SH, rather than the d_{xy} orbitals seen in NH₂.

NNN

The azido ligand can act as a bridge between the titanium atoms in two ways: a μ -1,1 ("end-on") mode or a μ -1,3 ("linear") mode. These bridging modes are shown in Figure 4. Both of these bridging modes have been seen experimentally in copper(II) dinuclear compounds.⁸ For both modes, the D_{2h} structure is a local minimum. The ground state of these molecules is ¹A_g, and the lowest energy triplet state is ³B_{1u}. The molecular orbitals follow the pattern established for hydroxide. According to a natural orbital analysis of the TCSCF/TZV(p) wave function, there are 0.85 electrons in the lowest virtual orbital of the end-on structure and 0.95 electrons in the lowest virtual orbital of the linear structure (Table 2). The TCSCF/TZV(p) singlet-triplet splitting for the end-on structure is calculated to be 1.1 kcal/mol, and increases to 3.2 kcal/mol at the MRMP2/TZVP(fg) level (Table 3). For the linear structure, the TCSCF/TZV(p) singlet-triplet splitting is 0.2 kcal/mol and 0.5 kcal/mol at the MRMP2/TZVP(fg) level. The MRMP2/TZVP(fg) end-on structure is more stable than the linear structure by 1.7 kcal/mol.

Experimentally for the copper compounds, the end-on azido-bridged structures are ferromagnetic, while the linear structures are strongly antiferromagnetic.^{109,110} In contrast, the end-on Ti₂(μ -1,1-NNN)₂H₄ is very antiferromagnetic and the linear Ti₂(μ -1,3-NNN)₂H₄ is slightly antiferromagnetic. The atomic orbitals available to form metal-metal bonds are different on copper and titanium. For copper, the unpaired electron density is in the d_{xz}

orbital, rather than $d_{x^2-z^2}$. This difference may be used to explain the dramatic difference in the magnetic coupling observed for the two bonding modes with the different metals. The HOMO and LUMO orbitals for titanium complexes are oriented along the Ti-Ti axis, whereas the orbitals in copper complexes are oriented along the Cu-ligand bonds.

CN

The cyano ligand can bridge the titanium atoms in three ways: two end-on structures (μ -1,1-CN and μ -1,1-NC) and one linear structure (μ -1,2-CN) (Figure 5). Experimentally, the cyano ligand has been observed to bind in a bidentate fashion using both the carbon and nitrogen, or preferentially through the carbon when it bonds in an end-on fashion.¹¹¹ The end-on structure with D_{2h} symmetry is predicted to be a local minimum. For the linear structure, the highest possible symmetry is C_{2h} . (A structure with equally high C_{2v} symmetry could be imagined. However, since the two titanium atoms are in different environments, the C_{2v} structures were not considered in this study.) For all three structures, the active orbitals are composed primarily of Ti $d_{x^2-z^2}$ orbitals, as discussed for the OH bridging ligand. Regardless of basis set, the MRMP2 calculations predict that the μ -1,2 arrangement is lower in energy than the μ -1,1-N structure by approximately 18 kcal/mol. The μ -1,1-C arrangement is the highest energy bridging structure. These calculations suggest that the linear bonding structure will be preferred for the cyano ligand in this type of system.

OCN/ONC

The cyanato and fulminato ligands also have three available bridging modes. Experimentally, when it bonds in an end-on fashion the cyanato ligand tends to bind through the nitrogen atom¹¹² and the fulminato ligand tends to bind through the carbon atom.¹¹¹ For all

of these structures, the usual D_{2h} or C_{2h} structure is a local minimum. The singlet states are essentially diradicals, with 0.85 to 1.00 electrons in the lowest virtual orbital (Table 2). For most of these compounds, the singlet state is the lowest in energy. However, the MRMP2 triplet state of $Ti_2(\mu-1,3-ONC)_2H_4$ is predicted to be 0.03 kcal/mol lower in energy than the lowest energy singlet state (Table 3).

Larger basis sets and dynamic electron correlation also affect the isomeric orderings of these ligands. For the cyanato compounds at the MRMP2/TZV(p) level, $Ti_2(\mu-1,1-NCO)_2H_4$ is 1.9 kcal/mol lower in energy than $Ti_2(\mu-1,3-OCN)_2H_4$. The inclusion of higher polarization functions also stabilizes $Ti_2(\mu-1,1-NCO)_2H_4$ with respect to $Ti_2(\mu-1,3-OCN)_2H_4$. At the MRMP2/TZVP(fg) level, the relative energy is 9.6 kcal/mol. $Ti_2(\mu-1,1-OCN)_2H_4$ is predicted to be much higher in energy than either of the other two compounds. For the fulminato compounds, at the MRMP2/TZV(p) level, the $Ti_2(\mu-1,3-ONC)_2H_4$ compound is 12.2 kcal/mol lower in energy than the $Ti_2(\mu-1,1-ONC)_2H_4$ compound. Multireference perturbation theory suggests that the $\mu-1,1-CNO$ and $\mu-1,1-ONC$ structures have similar energies. The calculations suggest that for this system, the cyanato ligand will bind through the nitrogen atom in an end-on fashion and the fulminato ligand will bind in a linear fashion.

Many experimentally observed compounds with fulminato ligands are known to be explosive.¹¹¹ Indeed, the calculations on the compounds in this study show that the fulminato-bridged compounds are over 140 kcal/mol higher in energy than the cyanato-bridged compounds (Table 6), which suggests that the isomerization of these molecules would be highly exothermic.

SCN

The thiocyanate ligand also has three possible bridging modes. All three bridging structures have been observed experimentally in metal complexes.¹¹³ The μ -1,3-SCN bridging structure has a C_{2h} local minimum. The bond angles for this compound are quite different from the bond angles for OCN (Table 5). The μ -1,1-N bridging mode has a local minimum with D_{2h} symmetry. However, the compound with the μ -1,1-S bridging mode in D_{2h} symmetry has one imaginary frequency for the singlet state and two for the triplet state. The lowest energy singlet with C_{2v} symmetry is 0.3 kcal/mol lower in energy than the related C_{2h} structure and 1.1 kcal/mol lower in energy than the D_{2h} structure (Table 6). The molecular orbitals in the active space are formed primarily from the Ti $d_{x^2-y^2}$ orbitals, as noted for the SH ligand. At the MRMP2/TZV(p) level, the singlet state is predicted to lie 0.03 kcal/mol below the triplet state (Table 3). As the basis set size is increased, the singlet is stabilized by a further 0.1 kcal/mol. At the MRMP2/TZVP(fg) level, the μ -1,1-NCS bridged structure is predicted to be 1.1 kcal/mol lower in energy. The μ -1,1-SCN bridged structure is predicted to be the highest in energy.

NO

Nitrosyl is an interesting ligand. Again, this ligand can bridge the titanium atoms in three possible ways. Two of these bridging modes (μ -1,1-NO and μ -1,2-NO) result in compounds with an electronic structure previously unseen in this study. The third bonding mode (μ -1,1-ON) has an electronic structure analogous to that described for the hydroxide complex.

The lowest energy singlet and triplet states for $\text{Ti}_2(\mu\text{-}1,1\text{-NO})_2\text{H}_4$ are $^1\text{A}_g$ and $^3\text{B}_{3u}$. The frontier molecular orbitals that form these states have b_{2u} and b_{1g} symmetry and are shown in Figure 6. Rather than having unpaired electrons on the titanium atoms, this compound has the unpaired electron density mostly on the oxygen atoms. The two active molecular orbitals are principally formed from atomic p_y orbitals on the oxygen atoms. There are 0.87 electrons in the lowest virtual orbital, so the molecule is essentially a singlet diradical. At the MRMP2/TZV(p) level of theory, this ground state singlet is 42.8 kcal/mol lower in energy than the first excited singlet state, which is composed of the normal titanium σ/σ^* orbitals (Table 6). MCSCF (2,14) calculations show that these states do not mix. The lowest energy triplet state is 2.8 kcal/mol higher in energy than the ground state singlet at the MRMP2/TZV(p) level of theory. When the basis set size is increased, the state with the “normal” titanium σ/σ^* orbitals is predicted to lie approximately 40 kcal/mol higher in energy than the state created by the oxygen p_y orbitals. For $\text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4$, the lowest energy singlet and triplet states have $^1\text{A}_g$ and $^3\text{B}_u$ symmetry, respectively. The frontier molecular orbitals for these states have b_g and a_u symmetry and are shown in Figure 7. For this molecule, the unpaired electron density is located primarily on the nitrogen atoms. The two active molecular orbitals are formed from the nitrogen p_z orbitals, where the z -axis is the principal axis. At the MRMP2/TZV(p) level of theory, the triplet is predicted to be 0.1 kcal/mol lower in energy than the singlet (Table 3).

Of the three bonding modes, the triplet state of $\text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4$ is predicted to be the lowest in energy. At the MRMP2/TZV(p) level, $\text{Ti}_2(\mu\text{-}1,1\text{-NO})_2\text{H}_4$ and $\text{Ti}_2(\mu\text{-}1,1\text{-ON})_2\text{H}_4$ are calculated to lie 14.0 and 96.8 kcal/mol above $\text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4$, respectively. With the

larger basis set, the MRMP2 level of theory predicts that the $\text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4$ triplet structure will be lowest in energy. According to these calculations, the molecule is ferromagnetic and the magnetic susceptibility is predicted to increase as the temperature decreases. The effects of spin-orbit coupling on the singlet-triplet energy gap will be considered below.

NO₂

The nitrite ion is an electronegative ligand. While this ligand has many possible bonding modes (including $\mu\text{-}1,2\text{-ONO}$ and $\mu\text{-}1,3\text{-ONO}$), the lowest energy local minimum found in this study is shown in Figure 8. The lowest energy singlet and triplet states are $^1\text{A}_g$ and $^3\text{B}_{3u}$, respectively. The frontier molecular orbitals are also shown in Figure 8. As seen in the $\mu\text{-}1,2\text{-NO}$ structure, the unpaired electron density is primarily located on the p_y orbitals of nitrogen, where the titanium atoms lie along the z-axis and the nitrogen atoms lie along the x-axis. The lowest energy singlet state has 0.99 electrons in the lowest virtual orbital, based on a natural orbital occupation analysis of the TCSCF/TZV(p) wave function (Table 2), so it is essentially a singlet diradical. The singlet-triplet splitting is 0.03 kcal/mol at the MPMP2/TZVP(fg) level of theory (Table 3).

Magnetic Properties

A. Isotropic Interaction

The isotropic interaction between the titanium atoms in these dinuclear complexes is proportional to the calculated singlet-triplet energy gap, in the absence of spin-orbit coupling and magnetic dipole-magnetic dipole effects. The isotropic interaction parameters for these compounds are shown in Table 7. As noted earlier,³⁴ as the diradical character of the

dinuclear complex becomes more pronounced and the natural orbital occupation numbers of the HOMO and LUMO approach 1, the ferromagnetism of the complex increases. At the MRMP2/TZVP(fg) level of theory, the interaction becomes more ferromagnetic (J becomes more positive) in the order $\text{Ti}_2(\mu\text{-}1,1\text{-NO})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-CNO})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-NNN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-NCO})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-NCS})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-CN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-NC})_2\text{H}_4 < \text{Ti}_2(\mu\text{-H})_2\text{H}_4^{29} < \text{Ti}_2(\mu\text{-Br})_2\text{H}_4^{34} < \text{Ti}_2(\mu\text{-OH})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,2\text{-CN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-SH})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,3\text{-NNN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-OCN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-ONC})_2\text{H}_4 < \text{Ti}_2(\mu\text{-PH}_2)_2\text{H}_4 < \text{Ti}_2(\mu\text{-Cl})_2\text{H}_4^{34} < \text{Ti}_2(\mu\text{-}1,1\text{-ON})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,1\text{-SCN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-NH}_2)_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,3\text{-SCN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,3\text{-OCN})_2\text{H}_4 < \text{Ti}_2(\mu\text{-NO}_2)_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,3\text{-ONC})_2\text{H}_4 < \text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4 < \text{Ti}_2(\mu\text{-F})_2\text{H}_4^{34}.$

For copper compounds, an experimentally-determined linear relationship was found between the isotropic interaction parameter J and the metal-ligand-metal angle.¹¹⁴ However, the homodinuclear titanium compounds examined in this study show no such relationship (Table 8).

B. Spin-Orbit Coupling Calculations

For the homodinuclear titanium molecules of interest in this study, it is necessary to consider 2 electrons in at least 10 orbitals in order to develop correct descriptions of the excited states.³⁰ The Ti-Ti bonding and antibonding interactions of the $\sigma\sigma^*$, $\pi\pi^*$, and $\delta\delta^*$ type arising from the atomic d orbitals must be treated. For all molecules except those with NO and NO₂ bridging ligands, an initial state-averaged 2-electron, 10-orbital MCSCF calculation was carried out at the ground state geometry. For $\text{Ti}_2(\mu\text{-}1,3\text{-ONC})_2\text{H}_4$, the ground state is predicted to be a triplet based on the TCSCF and MRMP2 calculations reported above, so the ROHF/TZV(p) geometry was used. For the other molecules, the

calculations were performed at the TCSCF/TZV(p) singlet geometry. The resulting orbitals were used in a second state-averaged 2-electron, 10-orbital MCSCF calculation with no orbital symmetry restraints and with each of the first 20 states weighted equally. These orbitals were used in both the CASSCF spin-orbit coupling (CASSCF-SOC) and MCQDPT spin-orbit coupling (MCQDPT-SOC) calculations.

For most of the homodinuclear titanium molecules considered in this study, the excited states and spin-orbit coupling effects are qualitatively similar to those previously reported for hydride and halide ligands.^{30,34} However, the complexes with μ -1,1-NO, μ -1,2-NO, and μ -NO₂ ligands do not follow the customary trends. For the NO and NO₂ bridging ligands, more than 10 orbitals are needed to treat the low-lying excited states. To obtain starting orbitals, modified virtual orbitals were generated by removing six electrons in the usual manner.¹¹⁵ For the μ -1,1-NO case, molecular orbitals formed primarily from atomic p orbitals on the oxygen atoms and antibonding molecular orbitals on NO were used in addition to the Ti d orbitals (see Figure 9). At the CASSCF-SOC level, the primary adiabatic states that mix to form the first spin state are S₀, T₂, T₉, and T₇ (see Table 9). T₁ is the primary component of spin states 2, 3, and 4. However, the inclusion of dynamic electron correlation dramatically alters these results. At the MCQDPT-SOC level, the first spin state is produced by a nearly equal mixture of S₈ and S₀. The principal adiabatic state that creates spin states 2, 3, and 4 is T₆. The primary configuration state functions (CSF's) (and their weightings) that contribute to these states are shown in Table 10. In Table 10, the occupancy of the 14 active orbitals (molecular orbitals 39-53, where orbital 39 is the HOMO) in each CSF is represented by an ordered pair of numbers. A 2 or a 0 indicates that the orbital is

doubly occupied or unoccupied, respectively. A + or a - indicates that a single electron occupies the orbital. The antisymmetric spin function (for the singlet state) is denoted by a + and a -, while the symmetric spin function (for the triplet state) is denoted by + +.

For $\text{Ti}_2(\mu\text{-1,2-NO})_2\text{H}_4$, the ground state is predicted to be a triplet based on the TCSCF and MRMP2 calculations, so the ROHF/TZV(p) geometry was used. The 14 orbitals used in the SOC calculations are shown in Figure 10. The CASSCF-SOC calculations predict that the first spin state is primarily formed from the S_0 adiabatic state, while the next three spin states are primarily formed from the T_1 adiabatic state (see Table 11). At the MCQDPT-SOC level, the first spin state is composed of adiabatic states S_0 , S_{15} , S_7 , and S_{14} , while the next three spin states are composed of T_1 , T_4 , T_{20} , and T_5 . The configuration state functions that create these states are shown in Table 12.

For $\text{Ti}_2(\mu\text{-NO}_2)_2\text{H}_4$, the ground state is predicted to be a triplet based on the TCSCF calculations, so the ROHF/TZV(p) geometry was used. The 16 orbitals used in the SOC calculations are shown in Figure 11. These include 10 orbitals primarily created from the Ti d atomic orbitals, two orbitals formed from N p orbitals, and four antibonding NO_2 orbitals. As shown in Table 13, the principal adiabatic states that form the first four spin states are S_0 and T_1 for CASSCF-SOC, and S_0 and T_7 for MCQDPT-SOC. CSF's for these states are shown in Table 14.

The principal axes X, Y, and Z for the T_1 (lowest energy triplet state) components can then be determined from the coefficients of the eigenvectors. The axial and rhombic pseudodipolar parameters D_e and E_e can be calculated as discussed previously.³⁰ These values are presented in Table 15. In general, the one-electron operator (HSO1) and the

partial two-electron operator (P2E) track the full two-electron operator (HSO2) closely. The magnitude of the state energies for the lowest singlet and triplet states calculated by HSO1 varies from HSO2 by up to 2.5 cm^{-1} , but details of the splittings are qualitatively correct. The energies calculated by P2E are practically the same as those of HSO2, and differ by no more than 0.021 cm^{-1} . In general, the magnitude of D_e and E_e increases as the spin-orbit coupling operator varies from HSO1 to P2E to HSO2. The magnitude of the zero-field splitting parameters from MCQDPT-SOC calculations is usually larger than the magnitude from CASSCF-SOC calculations. In general, the effect of dynamic correlation on the SOC parameters is much larger than is the effect of the SOC method.

C. Spin-Orbit Coupling Timings

The CPU time required for spin-orbit coupling calculations on a Sun UltraSPARC3 900 MHz processor is reported in Tables 16 and 17. For CASSCF-SOC, the one-electron operator method requires only 2.1-3.5% of the time needed for a full two-electron calculation. Most of this time is due to the setup routines; the actual integral transformations and spin-orbit coupling calculations with HSO1 take only 4.2 – 15.6 seconds for the molecules in this study. The partial two-electron operator calculation requires 46.6 - 71.6% of the time for a full two-electron calculation. The average savings is approximately 36%.

Overall, the MCQDPT-SOC method requires more time than the CASSCF-SOC method. The setup for MCQDPT is much more expensive. In addition, the cost of the spin-orbit coupling computation increases somewhat, particularly for the HSO2 method. For MCQDPT-SOC, the one-electron operator requires 50% of the time needed for a full two-electron operator calculation. When the setup time is not considered, HSO1 requires 2.5 - 3.8% and P2E requires 43.0 - 67.9% of the time required for HSO2.

4. Conclusions

The influence of multi-atom bridging ligands from groups 14, 15, and 16 of the periodic table on the magnetic properties of homodinuclear titanium complexes has been examined. These compounds are prototypes for many experimentally observed compounds. The compounds studied in this work have a high degree of diradical character, and there is little or no Ti-Ti bonding. Dynamic electron correlation is required for accurate predictions of the singlet-triplet splitting. In contrast to most of the ligands, NO^- and NO_2^- have the unpaired density on the ligands rather than the titanium atoms. The ferromagnetism of the complexes studied in this work is closely related to the natural orbital occupation numbers of the HOMO and LUMO, but is not related to the titanium-ligand-titanium angle. The addition of dynamic correlation via second order perturbation theory greatly increases the mixing of spin states, but there is very little singlet-triplet splitting.

The partial two-electron operator method tracks the full two-electron operator closely in the spin-orbit coupling calculations while dynamic correlation has a very large effect. The zero-field splitting parameters calculated by each operator method are very similar, although the magnitude tends to increase in the order $\text{HSO1} < \text{P2E} < \text{HSO2}$. The zero-field splitting parameters from MCQDPT-SOC calculations are slightly larger than those from CASSCF-SOC calculations. The time required for MCQDPT-SOC calculations is much greater than CASSCF-SOC calculations. HSO1 requires only 2-3% of the time required for HSO2, while P2E requires 50-70% of the time.

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References

- (1) Gatteschi, D.; Sessoli, R. *J. Magnetism and Magnetic Materials* **2004**, 272-276, 1030.
- (2) Coronado, E.; Forment-Aliaga, A.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J.; Martínez-Ferrero, E.; Nuez, A.; Romero, F. M. *Solid State Sci.* **2003**, 5, 917.
- (3) *Magnetism: Molecules to Materials IV*; Miller, J. S.; Drillon, M., Eds.; WILEY-VCH: Weinheim, 2003.
- (4) Miller, J. S.; Epstein, A. J. *MRS Bulletin* **2000**, 25, 21.
- (5) *Metal-Organic and Organic Molecular Magnets*; Day, P.; Underhill, A. E., Eds.; The Royal Society of Chemistry: Cambridge, 1999.
- (6) *Molecular Magnetism: New Magnetic Materials*; Itoh, K.; Kinoshita, M., Eds.; Gordon and Breach: Amsterdam (Kodansha: Tokyo), 2000.
- (7) Girerd, J.-J.; Journaux, Y. Molecular Magnetism in Bioinorganic Chemistry. In *Physical Methods in Bioinorganic Chemistry*; Que Jr., L., Ed.; University Science Books: Sausalito, CA, 2000; pp 321.
- (8) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
- (9) Heisenberg, W. *Z. Phys.* **1928**, 49, 619.
- (10) Boillot, M.-L.; Journaux, Y.; Bencini, A.; Gatteschi, D.; Kahn, O. *Inorg. Chem.* **1985**, 24, 263.

- (11) Kramers, H. A. *Physica* **1934**, *1*, 182.
- (12) Anderson, P. W. *Phys. Rev.* **1950**, *79*, 350.
- (13) Nesbet, R. K. *Ann. Phys.* **1958**, *4*, 87.
- (14) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2.
- (15) Nesbet, R. K. *Phys. Rev.* **1960**, *119*, 658.
- (16) Wachters, A. J. H.; Nieuwpoort, W. C. Crystalfield Splitting and Magnetic Interaction in KNiF₃. In *Selected Topics in Molecular Physics*; Clementi, E., Ed.; Verlag-Chemie: Weinheim, Germany, 1972; pp 135.
- (17) Bleaney, B.; Bowers, K. D. *Proc. Royal Soc. London A* **1952**, *214*, 451.
- (18) Hay, P. J.; Thibault, J. C.; Hoffmann, R. J. *Am. Chem. Soc.* **1975**, *97*, 4884.
- (19) Kahn, O.; Briat, B. J. *Chem. Soc., Faraday Trans. II* **1976**, *72*, 268.
- (20) Kahn, O.; Briat, B. J. *Chem. Soc., Faraday Trans. II* **1976**, *72*, 1441.
- (21) de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. **1981**.
- (22) Illas, F.; Casanovas, J.; García-Bach, M. A.; Caballol, R.; Castell, O. *Phys. Rev. Lett.* **1993**, *71*, 3549.
- (23) Pierloot, K.; Van Praet, E.; Vanquickenborne, L. G. *J. Phys. Chem.* **1993**, *97*, 12220.
- (24) Casanovas, J.; Illas, F. *J. Chem. Phys.* **1994**, *100*, 8257.
- (25) de Graaf, C.; Illas, F.; Broer, R.; Nieuwpoort, W. C. *J. Chem. Phys.* **1996**, *106*, 3287.
- (26) Sousa, C.; de Jong, W. A.; Broer, R.; Nieuwpoort, W. C. *J. Chem. Phys.* **1997**, *106*, 7162.
- (27) de Graaf, C.; Broer, R.; Nieuwpoort, W. C. *Chem. Phys. Lett.* **1997**, *271*, 372.

- (28) Moedl, M.; Povill, A.; Rubio, J.; Illas, F. J. *Phys. Chem. A* **1997**, *101*, 1526.
- (29) Webb, S. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 3846.
- (30) Webb, S. P.; Gordon, M. S. *J. Chem. Phys.* **1998**, *109*, 919.
- (31) de Graaf, C.; de P. R. Moreira, I.; Illas, F.; Martin, R. L. *Phys. Rev. B* **1999**, *60*, 3457.
- (32) Suaud, N.; Bolvin, H.; Daudey, J. P. *Inorg. Chem.* **1999**, *38*, 6089.
- (33) de Graaf, C.; Sousa, C.; de P. R. Moreira, I.; Illas, F. J. *Phys. Chem. A* **2001**, *105*, 11371.
- (34) Aikens, C. M.; Gordon, M. S. *J. Phys. Chem. A* **2003**, *107*, 104.
- (35) Taratiel, D.; Cabrero, J.; de Graaf, C.; Caballol, R. *Polyhedron* **2003**, *22*, 2409.
- (36) Herebian, D.; Wieghardt, K. E.; Neese, F. *J. Am. Chem. Soc.* **2003**, *125*, 10997.
- (37) de Graaf, C.; Hozoi, L.; Broer, R. J. *Chem. Phys.* **2004**, *120*, 961.
- (38) Wang, B.; Chen, Z. *Chem. Phys. Lett.* **2004**, *387*, 395.
- (39) Muñoz, D.; de Graaf, C.; Illas, F. J. *Comp. Chem.* **2004**, *25*, 1234.
- (40) Paulovic, J.; Cimpoesu, F.; Ferbinteanu, M.; Hirao, K. *J. Am. Chem. Soc.* **2004**, *126*, 3321.
- (41) Illas, F.; de P. R. Moreira, I.; de Graaf, C.; Barone, V. *Theor. Chem. Acc.* **2000**, *104*, 265.
- (42) Bodner, A.; Jeske, P.; Weyhermueller, T.; Wieghardt, K. E.; Dubler, E.; Schmalke, H.; Nuber, B. *Inorg. Chem.* **1992**, *31*, 3737.
- (43) Jeske, P.; Wieghardt, K. E.; Nuber, B. *Inorg. Chem.* **1994**, *33*, 47.

- (44) Lukens Jr., W. W.; Andersen, R. A. *Inorg. Chem.* **1995**, *34*, 3440.
- (45) Kempe, R.; Spannenberg, A.; Penlecke, N.; Rosenthal, U. *Z. Kristallogr.* **1998**, *213*, 423.
- (46) Carr, S. G.; Boyd, P. D. W.; Smith, T. D. *J. Chem. Soc., Dalton Trans.* **1972**, 1491.
- (47) Cookson, D. J.; Smith, T. D.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1396.
- (48) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 1841.
- (49) Fieselmann, B. F.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2074.
- (50) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078.
- (51) Francesconi, L. C.; Corbin, D. R.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 3074.
- (52) Fachinetti, G.; Biran, C.; Floriani, C.; Villa, A. C.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 5.
- (53) Corbin, D. R.; Atwood, J. L.; Stucky, G. D. *Inorg. Chem.* **1986**, *25*, 98.
- (54) Harris, H. A.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1987**, *109*, 4739.
- (55) Harris, H. A.; Kanis, D. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 8602.
- (56) Rosenthal, U.; Goerls, H. *J. Organomet. Chem.* **1992**, *439*, C36.
- (57) Cotton, F. A.; Dikarev, E. V.; Murillo, C. A.; Petrukhina, M. A. *Inorg. Chim. Acta* **2002**, *332*, 41.

- (58) Briat, B.; Kahn, O.; Morgenstern-Badarau, I.; Rivoal, J. C. *Inorg. Chem.* **1981**, *20*, 4193.
- (59) Chen, L.; Cotton, F. A.; Dunbar, K. R.; Feng, X.; Heintz, R. A.; Uzelmeir, C. *Inorg. Chem.* **1996**, *35*, 7358.
- (60) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1969**, *91*, 7301.
- (61) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182.
- (62) Xin, S.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1994**, *116*, 11562.
- (63) Martin, R. L.; Winter, G. *J. Chem. Soc.* **1965**, 4709.
- (64) Canty, A. J.; Coutts, R. S. P.; Wailes, P. C. *Aust. J. Chem.* **1968**, *21*, 807.
- (65) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *47*, 375.
- (66) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.
- (67) Olthof, G. J. *J. Organomet. Chem.* **1977**, *128*, 367.
- (68) Perevalova, E. G.; Urazowski, I. F.; Lemenovskii, D. A.; Slovokhotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1985**, *289*, 319.
- (69) Hill, J. E.; Nash, J. M.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 1617.
- (70) Sobota, P.; Ejfler, J.; Utko, J.; Lis, T. *J. Organomet. Chem.* **1991**, *410*, 149.
- (71) Cotton, F. A.; Wojtczak, W. A. *Gazz. Chim. Ital.* **1993**, *123*, 499.
- (72) Yu, P.; Murphy, E. F.; Roesky, H. W.; Lubini, P.; Schmidt, H.-G.; Noltemeyer, M. *Organomet.* **1997**, *16*, 313.
- (73) Hao, S.; Feghali, K.; Gambarotta, S. *Inorg. Chem.* **1997**, *36*, 1745.

- (74) Smith, S. B.; Stephan, D. W. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, 2004; Vol. 4; pp 31.
- (75) Lappert, M. F.; Sanger, A. R. *J. Chem. Soc. A* **1971**, 874.
- (76) Lappert, M. F.; Sanger, A. R. *J. Chem. Soc. A* **1971**, 1314.
- (77) Armor, J. N. *Inorg. Chem.* **1978**, *17*, 203.
- (78) Vroegop, C. T.; Teuben, J. H.; van Bolhuis, F.; van der Linden, J. G. M. *J. Chem. Soc. Chem. Commun.* **1983**, 550.
- (79) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137.
- (80) Samuel, E.; Harrod, J. F.; Gourier, D.; Dromzee, Y.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1992**, *31*, 3252.
- (81) Dick, D. G.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 1146.
- (82) Heneken, G.; Weiss, E. *Chem. Ber.* **1973**, *106*, 1747.
- (83) Thewalt, U.; Schinnerling, P. J. *Organomet. Chem.* **1991**, *418*, 191.
- (84) Fink, K.; Fink, R.; Staemmler, V. *Inorg. Chem.* **1994**, *33*, 6219.
- (85) Kolczewski, C.; Fink, K.; Staemmler, V. *Int. J. Quant. Chem.* **2000**, *76*, 137.
- (86) Ren, Q.; Chen, Z.; Ren, J.; Wei, H.; Feng, W.; Zhang, L. *J. Phys. Chem. A* **2002**, *106*, 6161.
- (87) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.
- (88) Hood, D. M.; Pitzer, R. M.; Schaefer III, H. F. *J. Chem. Phys.* **1979**, *71*, 705.
- (89) Rappe, A. K.; Smedley, T. A.; Goddard III, W. A. *J. Phys. Chem.* **1981**, *85*, 2607.
- (90) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; pp 1.

- (91) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.
- (92) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
- (93) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Gordon, M. S.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery Jr., J. A. *J. Comp. Chem.* **1993**, *14*, 1347.
- (94) Gordon, M. S.; Schmidt, M. W. *J. Mol. Struct. (THEOCHEM)* **in press**.
- (95) Webb, S. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 7197.
- (96) Glezakou, V.-A.; Gordon, M. S. *J. Phys. Chem. A* **1997**, *101*, 8714.
- (97) Hirao, K. *Chem. Phys. Lett.* **1992**, *190*, 374.
- (98) Hirao, K. *Chem. Phys. Lett.* **1992**, *196*, 397.
- (99) Hirao, K. *Int. J. Quant. Chem.* **1992**, *S26*, 517.
- (100) Hirao, K. *Chem. Phys. Lett.* **1993**, *201*, 59.
- (101) Sunberg, K. R.; Ruedenberg, K. MCSCF Studies of Chemical Reactions: Natural Reaction Orbitals and Localized Reaction Orbitals. In *Quantum Science*; Calais, J.-L., Goscinski, O., Linderberg, J., Öhrn, Y., Eds.; Plenum: New York, 1976; pp 505.
- (102) Cheung, L. M.; Sunberg, K. R.; Ruedenberg, K. *J. Quant. Chem.* **1979**, *16*, 1103.
- (103) Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41.
- (104) Roos, B. O.; Taylor, P.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.
- (105) Fedorov, D. G.; Finley, J. P. *Phys. Rev. A* **2001**, *64*, 042502.
- (106) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga, N. *J. Phys. Chem.* **1995**, *99*, 12764.

- (107) Fedorov, D. G.; Gordon, M. S. *J. Chem. Phys.* **2000**, *112*, 5611.
- (108) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics and Modeling* **1998**, *16*, 133.
- (109) Comarmond, J.; Plumere, P.; Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O. *J. Am. Chem. Soc.* **1982**, *104*, 6330.
- (110) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490.
- (111) Sharpe, A. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 2; pp 7.
- (112) Schönherr, T. *Inorg. Chem.* **1986**, *25*, 171.
- (113) Vrieze, K.; Van Koten, G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 2; pp 189.
- (114) Crawford, V. M.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 3175.
- (115) Bauschlicher, C. W. *J. Chem. Phys.* **1980**, *72*, 880.

TABLE 1: Mulliken Charges on Ti for the Lowest-Energy Singlet and Triplet States

molecule	bonding mode	singlet	triplet
Ti ₂ (OH) ₂ H ₄	1,1-μ-O	1.10	1.11
Ti ₂ (SH) ₂ H ₄	1,1-μ-S	0.87	0.88
Ti ₂ (NH ₂) ₂ H ₄	1,1-μ-N	1.06	1.06
Ti ₂ (PH ₂) ₂ H ₄	1,1-μ-P	0.79	0.79
Ti ₂ (NNN) ₂ H ₄	1,1-μ	1.07	1.07
Ti ₂ (NNN) ₂ H ₄	1,3-μ	0.96	0.96
Ti ₂ (CN) ₂ H ₄	1,1-μ-C	1.11	1.12
Ti ₂ (CN) ₂ H ₄	1,1-μ-N	1.09	1.09
Ti ₂ (CN) ₂ H ₄	1,2-μ	1.03	1.03
Ti ₂ (OCN) ₂ H ₄	1,1-μ-O	1.14	1.14
Ti ₂ (OCN) ₂ H ₄	1,1-μ-N	1.07	1.07
Ti ₂ (OCN) ₂ H ₄	1,3-μ	1.10	1.10
Ti ₂ (ONC) ₂ H ₄	1,1-μ-O	1.07	1.07
Ti ₂ (ONC) ₂ H ₄	1,1-μ-C	1.12	1.13
Ti ₂ (ONC) ₂ H ₄	1,3-μ	1.01	1.01
Ti ₂ (SCN) ₂ H ₄	1,1-μ-S	0.87	0.87
Ti ₂ (SCN) ₂ H ₄	1,1-μ-N	1.05	1.05
Ti ₂ (SCN) ₂ H ₄	1,3-μ	0.83	0.83
Ti ₂ (NO) ₂ H ₄	1,1-μ-N ^a	1.16	1.16
Ti ₂ (NO) ₂ H ₄	1,1-μ-N ^b	1.00	1.00
Ti ₂ (NO) ₂ H ₄	1,1-μ-O	1.08	1.08
Ti ₂ (NO) ₂ H ₄	1,2-μ	1.09	1.09
Ti ₂ (NO ₂) ₂ H ₄	1,3-μ-ONO	1.31	1.31

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b a_g and b_{1u} frontier molecular orbitals.

TABLE 2: Natural Orbital Occupation Numbers (NOONs) from a Natural Orbital Analysis of the MCSCF(2,2) Wavefunction

molecule	bonding mode	HOMO		LUMO	
		NOON	sym	NOON	sym
Ti ₂ (OH) ₂ H ₄	1,1-μ-O	1.08	a _g	0.92	b _{1u}
Ti ₂ (SH) ₂ H ₄	1,1-μ-S	1.04	a ₁	0.96	b ₂
Ti ₂ (NH ₂) ₂ H ₄	1,1-μ-N	1.02	a _u	0.98	a _g
Ti ₂ (PH ₂) ₂ H ₄	1,1-μ-P	1.05	a ₁	0.95	b ₂
Ti ₂ (NNN) ₂ H ₄	1,1-μ	1.15	a _g	0.85	b _{1u}
Ti ₂ (NNN) ₂ H ₄	1,3-μ	1.05	a _g	0.95	b _{1u}
Ti ₂ (CN) ₂ H ₄	1,1-μ-C	1.12	a _g	0.88	b _{1u}
Ti ₂ (CN) ₂ H ₄	1,1-μ-N	1.12	a _g	0.88	b _{1u}
Ti ₂ (CN) ₂ H ₄	1,2-μ	1.06	b _u	0.94	a _g
Ti ₂ (OCN) ₂ H ₄	1,1-μ-O	1.06	a _g	0.94	b _{1u}
Ti ₂ (OCN) ₂ H ₄	1,1-μ-N	1.15	a _g	0.85	b _{1u}
Ti ₂ (OCN) ₂ H ₄	1,3-μ	1.02	a _g	0.98	b _u
Ti ₂ (ONC) ₂ H ₄	1,1-μ-O	1.05	a _g	0.95	b _{1u}
Ti ₂ (ONC) ₂ H ₄	1,1-μ-C	1.13	a _g	0.87	b _{1u}
Ti ₂ (ONC) ₂ H ₄	1,3-μ	1.00	a _g	1.00	b _u
Ti ₂ (SCN) ₂ H ₄	1,1-μ-S	1.03	a ₁	0.97	b ₂
Ti ₂ (SCN) ₂ H ₄	1,1-μ-N	1.13	a _g	0.87	b _{1u}
Ti ₂ (SCN) ₂ H ₄	1,3-μ	1.02	b _u	0.98	a _g
Ti ₂ (NO) ₂ H ₄	1,1-μ-N ^a	1.13	b _{2u}	0.87	b _{1g}
Ti ₂ (NO) ₂ H ₄	1,1-μ-N ^b	1.05	a _g	0.95	b _{1u}
Ti ₂ (NO) ₂ H ₄	1,1-μ-O	1.05	a _g	0.95	b _{1u}
Ti ₂ (NO) ₂ H ₄	1,2-μ	1.03	b _g	0.97	a _u
Ti ₂ (NO ₂) ₂ H ₄	1,3-μ-ONO	1.01	b _{1g}	0.99	b _{2u}

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b a_g and b_{1u} frontier molecular orbitals.

TABLE 3: Calculated Singlet-Triplet Energy Gap ($E(\text{triplet}) - E(\text{singlet})$) in kcal/mol

molecule	bonding mode	MCSCF/ TZV(p)	MCSCF/ TZVP(f)	MCSCF/ TZVP(fg)	MRMP2/ TZV(p)	MRMP2/ TZVP(f)	MRMP2/ TZVP(fg)
Ti ₂ (OH) ₂ H ₄	1,1- μ -O	0.2	0.2	0.2	0.7	0.8	0.8
Ti ₂ (SH) ₂ H ₄	1,1- μ -S	0.01	0.3	0.3	0.2	0.5	0.5
Ti ₂ (NH) ₂ H ₄	1,1- μ -N	0.03	0.03	0.03	0.05	0.07	0.07
Ti ₂ (PH) ₂ H ₄	1,1- μ -P	0.01	0.04	0.03	0.2	0.4	0.4
Ti ₂ (NNN) ₂ H ₄	1,1- μ	1.0	1.0	0.9	3.0	3.2	3.2
Ti ₂ (NNN) ₂ H ₄	1,3- μ	0.2	0.07	0.08	0.6	0.5	0.5
Ti ₂ (CN) ₂ H ₄	1,1- μ -C	0.8	0.8	0.8	2.2	2.4	2.5
Ti ₂ (CN) ₂ H ₄	1,1- μ -N	0.8	0.6	0.6	1.9	2.1	2.1
Ti ₂ (CN) ₂ H ₄	1,2- μ	0.2	0.1	0.1	0.7	0.6	0.6
Ti ₂ (OCN) ₂ H ₄	1,1- μ -O	0.2	0.1	0.1	0.5	0.5	0.5
Ti ₂ (OCN) ₂ H ₄	1,1- μ -N	1.1	0.9	0.9	3.0	3.1	3.1
Ti ₂ (OCN) ₂ H ₄	1,3- μ	0.03	0.00	0.01	0.09	0.06	0.06
Ti ₂ (ONC) ₂ H ₄	1,1- μ -O	0.08	0.08	0.08	0.3	0.4	0.4
Ti ₂ (ONC) ₂ H ₄	1,1- μ -C	0.9	1.0	1.0	3.0	3.3	3.3
Ti ₂ (ONC) ₂ H ₄	1,3- μ	-0.01	-0.01	-0.01	-0.03	-0.03	-0.03
Ti ₂ (SCN) ₂ H ₄	1,1- μ -S	-0.02	0.02	0.02	0.03	0.1	0.1
Ti ₂ (SCN) ₂ H ₄	1,1- μ -N	0.9	0.8	0.7	2.6	2.8	2.8
Ti ₂ (SCN) ₂ H ₄	1,3- μ	0.01	0.02	0.02	0.02	0.06	0.06
Ti ₂ (NO) ₂ H ₄	1,1- μ -N ^a	0.9	1.6	1.6	3.2	4.8	4.7
Ti ₂ (NO) ₂ H ₄	1,1- μ -N ^b	0.06	0.06	0.06	0.3	0.3	0.3
Ti ₂ (NO) ₂ H ₄	1,1- μ -O	0.06	0.04	0.04	0.2	0.2	0.2
Ti ₂ (NO) ₂ H ₄	1,2- μ	-0.05	-0.1	-0.1	-0.1	-0.2	-0.2
Ti ₂ (NO) ₂ H ₄	1,3- μ -ONO	-0.02	-0.03	-0.03	0.02	0.04	0.03

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b a_g and b_{1u} frontier molecular orbitals.

TABLE 4: Relative MRMP2/TZV(p) Energies (kcal/mol) for Ligands without Local Minimum D_{2h} σ,σ^* Structure

Ligand/Structure	State	
μ -SH	singlet	triplet
D_{2h}	2.3	2.3
C_{2h}	1.1	1.1
C_{2v}	0.0	0.2
μ -NH ₂	singlet	triplet
D_{2h} σ,σ^*	5.7	7.8
D_{2h} δ,δ^*	0.3	0.4
C_{2h}	0.0	0.05
μ -PH ₂	singlet	triplet
D_{2h}	1.0	1.2
C_{2v}	0.0	0.2
1,1- μ -SCN	singlet	triplet
D_{2h}	2.2	2.2
C_{2h}	0.8	0.7
C_{2v}	0.0	0.03

TABLE 5. Geometrical Parameters for the Lowest Energy Structure of $Ti_2(\mu-L)_2H_4$

	symmetry	distances (Å)			bond angles (deg)		dihedral angles (deg)	
		Ti-H	Ti-H	Ti-L	L-Ti-L	Ti-L-Ti	H-Ti-Ti-L	Ti-L-Ti-L
$Ti_2(1,1-\mu-L)_2H_4$	D_{2h}	1.743		2.341	3.337	89.1	90.9	
$Ti_2(1,1-\mu-CN)_2H_4$	D_{2h}	1.746		2.326	3.356	87.7	92.3	
$Ti_2(1,1-\mu-CNO)_2H_4$	D_{2h}	1.765		2.142	3.193	83.6	96.4	
$Ti_2(1,1-\mu-NC)_2H_4$	D_{2h}	1.754		2.185	3.265	83.3	96.7	
$Ti_2(1,1-\mu-NCS)_2H_4$	D_{2h}	1.758		2.167	3.242	83.1	96.9	
$Ti_2(1,1-\mu-NO)_2H_4^a$	D_{2h}	1.696		1.928	2.935	80.9	99.1	
$Ti_2(1,1-\mu-NNN)_2H_4$	D_{2h}	1.777		2.112	3.226	80.4	99.6	
$Ti_2(1,1-\mu-OH)_2H_4$	D_{2h}	1.779		2.037	3.175	77.6	102.4	
$Ti_2(1,1-\mu-OCN)_2H_4$	D_{2h}	1.753		2.089	3.296	75.8	104.2	
$Ti_2(1,1-\mu-NO)_2H_4^b$	D_{2h}	1.766		2.214	3.552	73.3	106.7	
$Ti_2(1,1-\mu-ON)_2H_4$	D_{2h}	1.762		2.083	3.353	72.9	107.1	
$Ti_2(1,1-\mu-ONC)_2H_4$	D_{2h}	1.756		2.081	3.363	72.2	107.8	83.6
$Ti_2(1,1-\mu-NH_2)_2H_4$	C_{2h}	1.780		2.151	3.218	83.2	96.8	-21.5
$Ti_2(1,1-\mu-SH)_2H_4$	C_{2v}	1.753	1.755	2.575	3.837	79.6	96.3	-18.9
$Ti_2(1,1-\mu-PH_2)_2H_4$	C_{2v}	1.765	1.767	2.702	3.937	83.3	93.5	-26.7
$Ti_2(1,1-\mu-SCN)_2H_4$	C_{2v}	1.738	1.740	2.628	3.991	74.9	98.8	

	symmetry	distances (Å)			bond angle (deg)	
		Ti-H	Ti-X	Ti-Z	Ti-Ti	X-Ti-Z
$Ti_2(1,2-\mu-XZ)_2H_4$ or $Ti_2(1,3-\mu-XYZ)_2H_4$	C_{2h}	1.756	2.334	2.157	4.573	80.9
$Ti_2(1,2-\mu-CN)_2H_4$	C_{2h}	1.759	2.153	2.153	5.400	88.4
$Ti_2(1,3-\mu-NNN)_2H_4$	C_{2h}	1.762	2.079	2.130	5.419	87.0
$Ti_2(1,3-\mu-OCN)_2H_4$	C_{2h}	1.760	2.038	2.315	5.562	88.2
$Ti_2(1,3-\mu-ONC)_2H_4^c$	C_{2h}	1.754	2.641	2.117	5.743	94.1
$Ti_2(1,3-\mu-SCN)_2H_4$	C_{2h}	1.688	1.985	1.783	3.834	96.8
$Ti_2(1,2-\mu-NO)_2H_4^c$	D_{2h}	1.675	1.797	1.797	4.234	110.6

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b a_g and b_{1u} frontier molecular orbitals. ^c Triplet state.

TABLE 6: Relative Energies (kcal/mol) for Lowest-Energy Singlet and Triplet States

compound	singlet			triplet		
	MRMP2/ TZV(p)	MRMP2/ TZVP(f)	MRMP2/ TZVP(fg)	MRMP2/ TZV(p)	MRMP2/ TZVP(f)	MRMP2/ TZVP(fg)
H ₂ Ti(1,1- μ -NNN) ₂ TiH ₂	0.0	0.0	0.0	3.0	3.2	3.2
H ₂ Ti(1,3- μ -NNN) ₂ TiH ₂	5.1	1.1	1.7	5.7	1.6	2.2
H ₂ Ti(1,1- μ -CN) ₂ TiH ₂	30.3	30.7	30.5	32.5	33.1	33.0
H ₂ Ti(1,1- μ -NC) ₂ TiH ₂	17.3	18.9	18.4	19.2	20.9	20.4
H ₂ Ti(1,2- μ -CN) ₂ TiH ₂	0.0	0.0	0.0	0.7	0.6	0.6
H ₂ Ti(1,1- μ -OCN) ₂ TiH ₂	26.3	49.5	49.4	26.8	50.0	49.9
H ₂ Ti(1,1- μ -NCO) ₂ TiH ₂	0.0	0.0	0.0	3.0	3.1	3.1
H ₂ Ti(1,3- μ -OCN) ₂ TiH ₂	1.9	9.3	9.6	2.0	9.3	9.7
H ₂ Ti(1,1- μ -ONC) ₂ TiH ₂	152.2	178.6	178.4	152.6	179.0	178.7
H ₂ Ti(1,1- μ -CNO) ₂ TiH ₂	170.7	176.6	177.0	173.7	179.9	180.3
H ₂ Ti(1,1- μ -ONC) ₂ TiH ₂	140.0	157.5	157.8	140.0	157.4	157.8
H ₂ Ti(1,1- μ -SCN) ₂ TiH ₂	47.4	46.7	47.1	47.5	46.8	47.2
H ₂ Ti(1,1- μ -NCS) ₂ TiH ₂	2.7	0.0	0.0	5.3	2.8	2.8
H ₂ Ti(1,3- μ -SCN) ₂ TiH ₂	0.0	0.7	1.1	0.0	0.7	1.1
H ₂ Ti(1,1- μ -NO) ₂ TiH ₂ ^a	14.0	13.0	13.3	17.2	17.8	18.1
H ₂ Ti(1,1- μ -NO) ₂ TiH ₂ ^b	56.8	55.0	57.3	57.1	55.3	57.6
H ₂ Ti(1,1- μ -ON) ₂ TiH ₂	96.8	111.5	113.6	97.0	111.8	113.8
H ₂ Ti(1,2- μ -NO) ₂ TiH ₂	0.1	0.2	0.2	0.0	0.0	0.0

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b a_g and b_{1u} frontier molecular orbitals.

TABLE 7: Isotropic Interaction Parameter J (cm⁻¹)

molecule	bonding mode	MCSCF/ TZV(p)	MCSCF/ TZVP(f)	MCSCF/ TZVP(fg)	MRMP2/ TZV(p)	MRMP2/ TZVP(f)	MRMP2/ TZVP(fg)
Ti ₂ (OH) ₂ H ₄	1,1-μ-O	-40	-43	-41	-118	-137	-135
Ti ₂ (SH) ₂ H ₄	1,1-μ-S	-1	-47	-47	-32	-87	-87
Ti ₂ (NH ₂) ₂ H ₄	1,1-μ-N	-5	-5	-6	-8	-12	-12
Ti ₂ (PH ₂) ₂ H ₄	1,1-μ-P	-2	-6	-6	-34	-62	-62
Ti ₂ (NNN) ₂ H ₄	1,1-μ	-183	-166	-164	-526	-566	-566
Ti ₂ (NNN) ₂ H ₄	1,3-μ	-34	-13	-13	-103	-84	-86
Ti ₂ (CN) ₂ H ₄	1,1-μ-C	-146	-133	-133	-391	-425	-430
Ti ₂ (CN) ₂ H ₄	1,1-μ-N	-142	-99	-98	-337	-359	-362
Ti ₂ (CN) ₂ H ₄	1,2-μ	-40	-21	-21	-115	-108	-110
Ti ₂ (OCN) ₂ H ₄	1,1-μ-O	-29	-17	-17	-88	-84	-85
Ti ₂ (OCN) ₂ H ₄	1,1-μ-N	-198	-162	-160	-518	-546	-547
Ti ₂ (OCN) ₂ H ₄	1,3-μ	-6	-1	-1	-16	-10	-10
Ti ₂ (ONC) ₂ H ₄	1,1-μ-O	-13	-14	-14	-55	-62	-63
Ti ₂ (ONC) ₂ H ₄	1,1-μ-C	-163	-175	-175	-528	-575	-581
Ti ₂ (ONC) ₂ H ₄	1,3-μ	2	2	2	5	5	5
Ti ₂ (SCN) ₂ H ₄	1,1-μ-S	3	-4	-4	-6	-24	-24
Ti ₂ (SCN) ₂ H ₄	1,1-μ-N	-155	-131	-130	-446	-490	-492
Ti ₂ (SCN) ₂ H ₄	1,3-μ	-1	-3	-3	-4	-11	-11
Ti ₂ (NO) ₂ H ₄	1,1-μ-N ^a	-158	-276	-276	-558	-831	-828
Ti ₂ (NO) ₂ H ₄	1,1-μ-N ^b	-11	-10	-10	-49	-57	-57
Ti ₂ (NO) ₂ H ₄	1,1-μ-O	-11	-7	-6	-35	-42	-42
Ti ₂ (NO) ₂ H ₄	1,2-μ	8	24	24	26	34	35
Ti ₂ (NO ₂) ₂ H ₄	1,3-μ-ONO	4	5	5	-3	-6	-6

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b a_g and b_{1u} frontier molecular orbitals.

TABLE 8: Comparison of Metal-Ligand-Metal Angle and Isotropic Interaction Parameters for D_{2h} Structures at the TCSCF/TZV(p) Level of Theory

	Ti-L-Ti angle	J (cm ⁻¹)
Ti ₂ (1,1-μ-NCO) ₂ H ₄	96.4	-198
Ti ₂ (1,1-μ-NNN) ₂ H ₄	99.6	-183
Ti ₂ (1,1-μ-CNO) ₂ H ₄	92.3	-163
Ti ₂ (1,1-μ-NO) ₂ H ₄ ^a	99.1	-158
Ti ₂ (1,1-μ-NCS) ₂ H ₄	96.9	-155
Ti ₂ (1,1-μ-CN) ₂ H ₄	90.9	-146
Ti ₂ (1,1-μ-NC) ₂ H ₄	96.7	-142
Ti ₂ (μ-H) ₂ H ₄ ^b	103.7	-98
Ti ₂ (μ-OH) ₂ H ₄	102.4	-40
Ti ₂ (1,1-μ-OCN) ₂ H ₄	104.2	-29
Ti ₂ (1,1-μ-ONC) ₂ H ₄	107.8	-13
Ti ₂ (1,1-μ-ON) ₂ H ₄	107.1	-11
Ti ₂ (1,1-μ-NO) ₂ H ₄ ^c	106.7	-11
Ti ₂ (μ-Br) ₂ H ₄ ^d	92.5	-4
Ti ₂ (μ-Cl) ₂ H ₄ ^d	95.7	7

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b Values from Reference 29.

^c a_g and b_{1u} frontier molecular orbitals. ^d Values from Reference 34.

TABLE 9: The First Four Spin States Obtained from the 20 Singlet, 20 Triplet SOC Calculation for $\text{Ti}_2(\mu\text{-}1,1\text{-NO})_2\text{H}_4$. Adiabatic State Weightings are from the Eigenvectors Resulting from the Diagonalization of the SOC Matrix.

CASSCF-SOC with HSO2 operator				
spin state	principal axes	energy relative to adiabatic ground state S_0 (cm^{-1})	CASSCF adiabatic state	eigenvector weighting
1		-12	S_0	0.9790
			T_2	0.0206
			T_9	0.0002
			T_7	0.0001
2	X	237	T_1	0.9951
			T_3	0.0045
			T_6	0.0002
			T_{10}	0.0002
3	Y	237	T_1	0.9952
			T_3	0.0045
			T_{10}	0.0002
			S_6	0.0001
4	Z	237	T_1	0.9956
			S_3	0.0039
			T_6	0.0002
			S_{11}	0.0002

MCQDPT-SOC with HSO2 operator

spin state	principal axes	energy relative to adiabatic ground state S_0 (cm^{-1})	CASSCF adiabatic state	eigenvector weighting
1		-2	S_8	0.5436
			S_0	0.4502
			S_{10}	0.0049
			S_2	0.0013
			T_7	0.0001
2	Z	9387	T_6	0.9996
			S_4	0.0002
			S_{15}	0.0001
3	Y	9387	T_6	0.9996
			T_5	0.0002
			T_{13}	0.0001
4	X	9388	T_6	0.9997
			T_5	0.0002
			T_{13}	0.0001

TABLE 10: Principal Configuration State Functions in CASSCF Adiabatic States for $\text{Ti}_2(\mu\text{-1,1-NO})_2\text{H}_2$.

State	Coefficient	Active Orbital Occupancy
S_0	0.172679	20000000000000
	-0.056019	+0000000000-00
	-0.439273	02000000000000
	0.509953	0+00000000-000
	0.640762	00020000000000
	-0.317496	00000000002000
S_8	-0.756819	20000000000000
	0.468181	+0000000000-00
	0.098792	02000000000000
	0.147722	0+00000000-000
	0.174700	00020000000000
	0.345678	00000020000000
	-0.098964	00000000002000
T_1	-0.118790	00000000000200
	0.749618	0+0+0000000000
T_6	0.661282	000+000000+000
	-0.692251	++000000000000
	0.449596	+000000000+000
	-0.253080	0+000000000+00
	0.464420	000+00+0000000
	0.197247	0000000000++00

The occupancy of the 14 active orbitals in the primary CSF's is shown for four CASSCF adiabatic states. A 2 indicates that the orbital is doubly occupied in the CSF. A + or a - indicates that a single electron occupies the orbital.

TABLE 11: The First Four Spin States Obtained from the 20 Singlet, 20 Triplet SOC Calculation for $\text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4$. Adiabatic State Weightings are from the Eigenvectors Resulting from the Diagonalization of the SOC Matrix.

CASSCF-SOC with HSO2 operator				
spin state	principal axes	energy relative to adiabatic ground state S_0 (cm^{-1})	CASSCF adiabatic state	eigenvector weighting
1		-2.870	S_0	0.9997
			T_2	0.0002
			T_6	0.0001
2	Y	887.082	T_1	0.9997
			T_3	0.0001
			T_7	0.0001
3	X	887.089	T_1	0.9997
			S_2	0.0001
			S_5	0.0001
4	Z	887.110	T_1	0.9997
			T_3	0.0002
			T_7	0.0001
MCQDPT-SOC with HSO2 operator				
spin state	principal axes	energy relative to adiabatic ground state S_0 (cm^{-1})	CASSCF adiabatic state	eigenvector weighting
1		-0.730	S_0	0.5106
			S_{15}	0.3281
			S_7	0.1425
			S_{14}	0.0179
2	X	246.512	T_1	0.4628
			T_4	0.4238
			T_{20}	0.109
			T_5	0.0044
3	Y	246.630	T_1	0.4628
			T_4	0.4238
			T_{20}	0.109
			T_5	0.0044
4	Z	246.735	T_1	0.4628
			T_4	0.4238
			T_{20}	0.109
			T_5	0.0044

TABLE 12: Principal Configuration State Functions in CASSCF Adiabatic States for $\text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4$.

State	Coefficient	Active Orbital Occupancy
S_0	0.203232	20000000000000
	-0.313720	+000-000000000
	0.072045	+0000000000-00
	-0.530604	02000000000000
	0.147667	0+00000-000000
	-0.496062	0+0000000-0000
	0.472163	00002000000000
	-0.115934	0000+000000-00
	0.101962	0000000+0-0000
	-0.239314	00000000020000
S_7	-0.382972	20000000000000
	0.318757	+000-000000000
	-0.308719	+0000000000-00
	-0.460314	0+00000-000000
	-0.238212	0+0000000-0000
	0.352217	00002000000000
	0.298433	0000+000000-00
	0.179306	00000002000000
	-0.309574	0000000+0-0000
	-0.191792	00000000020000
S_{14}	-0.095493	00000000000200
	0.076820	20000000000000
	0.060769	+000-000000000
	0.059639	+0000000000-00
	0.106808	00200000000000
	-0.618625	00+00000-00000
	0.113697	00+0000000000-
	0.074314	000+00-0000000
	0.593462	000+000000-000
	-0.088849	000+00000000-0
	-0.280126	00000+00-00000
	-0.253416	000000+000-000
	-0.054223	00000002000000
	-0.142897	00000000200000
	-0.159228	00000000+0000-
	0.080294	00000000002000

The occupancy of the 14 active orbitals in the primary CSF's is shown for eight CASSCF adiabatic states. A 2 indicates that the orbital is doubly occupied in the CSF. A + or a - indicates that a single electron occupies the orbital.

TABLE 12: cont.

State	Coefficient	Active Orbital Occupancy
S ₁₅	0.508497	20000000000000
	0.395347	+000-000000000
	0.389969	+0000000000-00
	-0.167991	02000000000000
	-0.196134	0+00000-000000
	0.054622	0+0000000-0000
	0.091912	00+00000-00000
	-0.092015	000+000000-000
	0.304653	0000+000000-00
	-0.362371	00000002000000
	-0.295368	0000000+0-0000
	0.165713	00000000000200
T ₁	-0.458774	++000000000000
	0.102646	+000000+000000
	-0.280084	+00000000+0000
	-0.636168	0+00+000000000
	0.156088	0+000000000+00
	-0.186759	0000+00+000000
	0.474139	0000+0000+0000
	0.102556	000000000+0+00
T ₄	0.524968	++000000000000
	-0.234767	+000000+000000
	0.207394	+00000000+0000
	-0.395514	0+00+000000000
	-0.302571	0+000000000+00
	0.067400	00++0000000000
	0.364747	0000+00+000000
	0.440483	0000+0000+0000
	0.114145	0000000+000+00
	-0.176248	000000000+0+00
T ₅	-0.801000	00++0000000000
	0.306229	00+000+0000000
	-0.067194	00+0000000+000
	-0.068473	00+000000000+0
	0.376414	000+0+00000000
	0.125356	000+0000+00000
	0.223942	000+000000000+
	0.161946	00000++0000000
	-0.092945	000000+000000+

TABLE 12: (continued)

State	Coefficient	Active Orbital Occupancy
T_{20}		
	-0.104177	++000000000000
	-0.739346	+000000+000000
	-0.197710	+00000000+0000
	-0.231158	0000+00+000000
	-0.074468	0000+0000+0000
	0.573987	0000000+000+00
	0.113080	000000000+0+00

TABLE 13: The First Four Spin States Obtained from the 20 Singlet, 20 Triplet SOC Calculation for $\text{Ti}_2(\mu\text{-NO}_2)_2\text{H}_4$. Adiabatic State Weightings are from the Eigenvectors Resulting from the Diagonalization of the SOC Matrix.

CASSCF-SOC with HSO2 operator				
spin state	principal axes	energy relative to adiabatic ground state S_0 (cm^{-1})	CASSCF adiabatic state	eigenvector weighting
1		-4.358	S_0	0.9995
			T_5	0.0004
			T_8	0.0001
2	Y	1281.284	T_1	0.9993
			T_6	0.0005
			T_3	0.0001
			T_7	0.0001
			S_7	0.0001
3	X	1281.292	T_1	0.9993
			T_6	0.0005
			T_3	0.0001
			T_9	0.0001
			S_{10}	0.0001
4	Z	1281.295	T_1	0.9993
			S_5	0.0005
			S_2	0.0001
			T_7	0.0001
			T_9	0.0001
MCQDPT-SOC with HSO2 operator				
spin state	principal axes	energy relative to adiabatic ground state S_0 (cm^{-1})	CASSCF adiabatic state	eigenvector weighting
1		-2.862	S_0	0.9998
			T_5	0.0001
2	Z	1650.370	T_7	0.9998
			T_1	0.0001
			T_3	0.0001
3	Y	1650.378	T_7	0.9998
			S_2	0.0001
			T_1	0.0001
4	X	1651.108	T_7	0.9999
			T_3	0.0001

TABLE 14: Principal Configuration State Functions in CASSCF Adiabatic States for $\text{Ti}_2(\mu\text{-NO}_2)_2\text{H}_4$.

State	Coefficient	Active Orbital Occupancy
S_0	0.383051	2000000000000000
	-0.560557	+0000000-0000000
	-0.063039	0200000000000000
	-0.606029	0000020000000000
	0.409274	0000000020000000
T_1	0.654701	+0000+0000000000
	0.755765	00000+00+0000000
T_7	0.481309	++00000000000000
	-0.397813	+0000000000+0000
	0.404633	0+000000+0000000
	-0.541849	00000+000+000000
	0.390828	00000000+00+0000

The occupancy of the 16 active orbitals in the primary CSF's is shown for three CASSCF adiabatic states. A 2 indicates that the orbital is doubly occupied in the CSF. A + or a - indicates that a single electron occupies the orbital.

TABLE 15: Spin-Orbit Coupling

			CASSCF-SOC/TZV(p)			MCQDPT-SOC/TZV(p)		
			HSO1	P2E	HSO2	HSO1	P2E	HSO2
Ti ₂ (OH) ₂ H ₄	1,1-μ-O	S	-12.563	-13.581	-13.584	-11.905	-13.413	-13.415
		T X	84.555	83.399	83.412	129.866	128.280	128.292
		T Y	84.507	83.345	83.355	129.847	128.279	128.288
		T Z	84.865	83.726	83.719	130.431	128.913	128.906
		D _e	0.334	0.354	0.335	0.575	0.634	0.616
		E _e	0.024	0.027	0.029	0.010	0.001	0.002
Ti ₂ (SH) ₂ H ₄	1,1-μ-S	S	-10.554	-11.521	-11.522	-10.229	-11.515	-11.516
		T X	-4.436	-5.397	-5.400	8.088	6.832	6.829
		T Y	-4.475	-5.439	-5.437	8.030	6.759	6.761
		T Z	-4.439	-5.400	-5.396	8.085	6.848	6.851
		D _e	0.016	0.018	0.023	0.026	0.052	0.056
		E _e	0.019	0.021	0.019	0.029	0.036	0.034
Ti ₂ (NH ₂) ₂ H ₄	1,1-μ-N	S	-7.831	-8.486	-8.488	-7.454	-8.413	-8.414
		T X	6.814	6.132	6.138	22.425	21.408	21.414
		T Y	6.816	6.135	6.142	22.413	21.390	21.397
		T Z	6.932	6.259	6.256	22.539	21.558	21.555
		D _e	0.117	0.126	0.116	0.120	0.159	0.150
		E _e	-0.001	-0.002	-0.002	0.006	0.009	0.009
Ti ₂ (PH ₂) ₂ H ₄	1,1-μ-P	S	-11.862	-12.953	-12.954	-12.488	-14.118	-14.119
		T X	-3.208	-4.280	-4.284	10.070	8.497	8.494
		T Y	-3.264	-4.341	-4.339	9.969	8.373	8.376
		T Z	-3.221	-4.293	-4.289	10.006	8.424	8.428
		D _e	0.015	0.018	0.023	-0.013	-0.011	-0.007
		E _e	0.028	0.031	0.028	0.051	0.062	0.059
Ti ₂ (NNN) ₂ H ₄	1,1-μ	S	-7.402	-8.058	-8.058	-7.225	-8.020	-8.021
		T X	461.455	460.679	460.684	828.690	827.341	827.347
		T Y	461.412	460.632	460.634	828.648	827.253	827.255
		T Z	461.549	460.779	460.775	829.038	827.682	827.677
		D _e	0.115	0.124	0.116	0.369	0.385	0.376
		E _e	0.022	0.023	0.025	0.021	0.044	0.046
Ti ₂ (NNN) ₂ H ₄	1,3-μ	S	-11.649	-12.601	-12.601	-12.457	-13.903	-13.903
		T X	67.021	66.044	66.046	128.215	126.546	126.548
		T Y	66.993	66.013	66.014	128.122	126.450	126.451
		T Z	67.001	66.021	66.019	128.097	126.423	126.421
		D _e	-0.006	-0.008	-0.011	-0.072	-0.075	-0.078
		E _e	0.014	0.015	0.016	0.046	0.048	0.049

^a b_{2u} and b_{1g} frontier molecular orbitals. ^b a_g and b_{1u} frontier molecular orbitals.

TABLE 15: (continued)

			CASSCF-SOC/TZV(p)			MCQDPT-SOC/TZV(p)		
			HSO1	P2E	HSO2	HSO1	P2E	HSO2
$\text{Ti}_2(\text{CN})_2\text{H}_4$	1,1- μ -C	S	-12.995	-14.158	-14.159	-14.109	-15.881	-15.882
		T X	321.646	320.422	320.431	502.173	500.197	500.207
		T Y	321.476	320.237	320.240	501.995	500.034	500.040
		T Z	321.527	320.293	320.286	502.140	500.196	500.188
		D _e	-0.034	-0.037	-0.049	0.056	0.081	0.064
		E _e	0.085	0.093	0.095	0.089	0.082	0.083
$\text{Ti}_2(\text{CN})_2\text{H}_4$	1,1- μ -N	S	-12.462	-13.579	-13.580	-13.642	-15.251	-15.253
		T X	328.904	327.584	327.595	520.840	518.461	518.476
		T Y	328.828	327.501	327.507	520.795	518.443	518.454
		T Z	329.055	327.746	327.739	521.706	519.452	519.444
		D _e	0.189	0.203	0.188	0.889	1.000	0.979
		E _e	0.038	0.042	0.044	0.023	0.009	0.011
$\text{Ti}_2(\text{CN})_2\text{H}_4$	1,2- μ	S	-11.809	-12.825	-12.826	-12.167	-13.660	-13.660
		T X	75.418	74.358	74.359	117.219	115.218	115.220
		T Y	75.423	74.364	74.362	117.199	115.196	115.193
		T Z	75.439	74.381	74.384	118.485	116.650	116.653
		D _e	0.018	0.020	0.024	1.276	1.443	1.447
		E _e	-0.002	-0.003	-0.002	0.010	0.011	0.014
$\text{Ti}_2(\text{OCN})_2\text{H}_4$	1,1- μ -O	S	-10.496	-11.416	-11.417	-10.834	-12.141	-12.143
		T X	55.346	54.387	54.395	131.234	129.821	129.829
		T Y	55.312	54.349	54.353	131.202	129.784	129.789
		T Z	55.372	54.413	54.408	131.319	129.914	129.908
		D _e	0.043	0.045	0.034	0.101	0.111	0.099
		E _e	0.017	0.019	0.021	0.016	0.019	0.020
$\text{Ti}_2(\text{OCN})_2\text{H}_4$	1,1- μ -N	S	-9.734	-10.610	-10.611	-12.287	-13.814	-13.815
		T X	488.024	486.918	486.927	401.018	400.416	400.425
		T Y	487.965	486.853	486.858	398.687	397.956	397.960
		T Z	488.252	487.163	487.157	398.883	398.159	398.152
		D _e	0.258	0.278	0.264	-0.970	-1.027	-1.041
		E _e	0.030	0.032	0.035	1.165	1.230	1.233
$\text{Ti}_2(\text{OCN})_2\text{H}_4$	1,3- μ	S	-13.701	-14.829	-14.829	-16.872	-18.807	-18.808
		T X	-1.015	-2.142	-2.140	4.975	2.471	2.473
		T Y	-1.004	-2.131	-2.132	5.164	3.211	3.209
		T Z	-1.005	-2.130	-2.129	7.156	5.350	5.354
		D _e	0.005	0.006	0.007	2.087	2.509	2.513
		E _e	-0.005	-0.006	-0.004	-0.095	-0.370	-0.368

TABLE 15: (continued)

			CASSCF-SOC/TZV(p)			MCQDPT-SOC/TZV(p)		
			HSO1	P2E	HSO2	HSO1	P2E	HSO2
$\text{Ti}_2(\text{ONC})_2\text{H}_4$ 1,1- μ -O	S		-9.700	-10.545	-10.547	-9.542	-10.683	-10.684
	T X		17.453	16.586	16.593	70.534	69.318	69.325
	T Y		17.425	16.555	16.559	70.518	69.318	69.323
	T Z		17.459	16.592	16.587	70.563	69.368	69.364
	D _e		0.020	0.021	0.011	0.037	0.050	0.040
	E _e		0.014	0.015	0.017	0.008	0.000	0.001
$\text{Ti}_2(\text{ONC})_2\text{H}_4$ 1,1- μ -C	S		-11.744	-12.792	-12.792	-12.287	-13.814	-13.815
	T X		379.475	378.345	378.352	401.018	400.416	400.425
	T Y		379.338	378.195	378.198	398.687	397.956	397.960
	T Z		379.403	378.266	378.260	398.883	398.159	398.152
	D _e		-0.004	-0.004	-0.015	-0.970	-1.027	-1.041
	E _e		0.069	0.075	0.077	1.165	1.230	1.233
$\text{Ti}_2(\text{ONC})_2\text{H}_4$ 1,3- μ	S		-10.414	-11.322	-11.322	-11.883	-13.484	-13.484
	T X		-15.050	-15.955	-15.955	-17.540	-19.094	-19.094
	T Y		-15.042	-15.947	-15.948	-17.529	-19.107	-19.108
	T Z		-15.043	-15.948	-15.946	-17.539	-19.120	-19.118
	D _e		0.003	0.003	0.006	-0.005	-0.020	-0.017
	E _e		-0.004	-0.004	-0.003	-0.005	0.006	0.007
$\text{Ti}_2(\text{SCN})_2\text{H}_4$ 1,1- μ -S	S		-10.252	-11.198	-11.198	-10.260	-11.554	-11.554
	T X		-16.854	-17.796	-17.799	-1.767	-3.059	-3.062
	T Y		-16.875	-17.818	-17.817	-1.780	-3.076	-3.075
	T Z		-16.848	-17.789	-17.786	-1.748	-3.028	-3.024
	D _e		0.017	0.018	0.022	0.026	0.040	0.045
	E _e		0.011	0.011	0.009	0.007	0.008	0.007
$\text{Ti}_2(\text{SCN})_2\text{H}_4$ 1,1- μ -N	S		-10.913	-11.898	-11.900	-11.318	-12.619	-12.620
	T X		370.799	369.618	369.627	634.494	632.402	632.414
	T Y		370.738	369.552	369.557	634.483	632.371	632.379
	T Z		370.950	369.780	369.774	635.265	633.240	633.233
	D _e		0.182	0.195	0.182	0.776	0.853	0.836
	E _e		0.030	0.033	0.035	0.006	0.016	0.017
$\text{Ti}_2(\text{SCN})_2\text{H}_4$ 1,3- μ	S		-9.990	-10.885	-10.885	-9.973	-11.178	-11.178
	T X		-8.571	-9.466	-9.466	-1.810	-3.039	-3.039
	T Y		-8.562	-9.455	-9.456	-1.786	-3.013	-3.014
	T Z		-8.559	-9.452	-9.451	-1.658	-2.853	-2.852
	D _e		0.008	0.008	0.010	0.140	0.173	0.175
	E _e		-0.005	-0.005	-0.005	-0.012	-0.013	-0.013

TABLE 15: (continued)

			CASSCF-SOC/TZV(p)			MCQDPT-SOC/TZV(p)		
			HSO1	P2E	HSO2	HSO1	P2E	HSO2
$\text{Ti}_2(\text{NO})_2\text{H}_4$	1,1- μ -N ^a	S	-10.529	-11.705	-11.710	-1.362	-2.193	-2.193
		T X	237.869	237.282	237.290	9388.05	9387.80	9387.80
		T Y	237.631	237.034	237.042	9387.54	9387.21	9387.20
		T Z	237.935	237.372	237.369	9387.38	9386.90	9386.90
		D _e	0.185	0.214	0.203	-0.419	-0.602	-0.599
		E _e	0.119	0.124	0.124	0.255	0.296	0.2965
$\text{Ti}_2(\text{NO})_2\text{H}_4$	1,1- μ -N ^b	S	-13.672	-14.858	-14.861	-22.868	-25.789	-25.795
		T X	12.587	11.379	11.389	68.302	65.277	65.297
		T Y	12.556	11.344	11.352	68.268	65.23	65.248
		T Z	12.644	11.439	11.434	68.255	65.211	65.203
		D _e	0.0725	0.0775	0.0635	-0.03	-0.0425	-0.0695
		E _e	0.0155	0.0175	0.0185	0.017	0.0235	0.0245
$\text{Ti}_2(\text{NO})_2\text{H}_4$	1,1- μ -O	S	-13.718	-14.865	-14.868	-15.753	-17.59	-17.594
		T X	7.204	6.012	6.024	54.265	52.184	52.199
		T Y	7.176	5.982	5.991	54.227	52.138	52.151
		T Z	7.268	6.08	6.074	54.418	52.347	52.34
		D _e	0.078	0.083	0.0665	0.172	0.186	0.165
		E _e	0.014	0.015	0.0165	0.019	0.023	0.024
$\text{Ti}_2(\text{NO})_2\text{H}_4$	1,2- μ	S	-2.692	-2.87	-2.87	-0.684	-0.73	-0.73
		T X	887.267	887.088	887.089	246.625	246.511	246.512
		T Y	887.261	887.081	887.082	246.678	246.63	246.63
		T Z	887.288	887.108	887.109	246.827	246.735	246.735
		D _e	0.024	0.0235	0.0235	0.1755	0.1645	0.164
		E _e	0.003	0.0035	0.0035	-0.0265	-0.0595	-0.059
$\text{Ti}_2(\text{NO}_2)_2\text{H}_4$	1,3- μ -ONO	S	-4.102	-4.357	-4.358	-2.539	-2.861	-2.862
		T X	1281.62	1281.29	1281.29	1651.12	1651.11	1651.11
		T Y	1281.61	1281.28	1281.28	1650.49	1650.38	1650.38
		T Z	1281.62	1281.3	1281.3	1650.49	1650.37	1650.37
		D _e	0.008	0.01	0.007	-0.319	-0.372	-0.373
		E _e	0.005	0.004	0.004	0.318	0.365	0.365

TABLE 16: CASSCF-SOC Timings^a

molecule	method	total CPU time	spin-orbit coupling ^b	% total time	% SOC time ^b
Ti ₂ (1,1-μ-OH) ₂ H ₄	HSO1	47.1	4.2	2.5	0.2
	P2E	1340.3	1296.7	71.6	70.9
	HSO2	1871.9	1829.0	100.0	100.0
Ti ₂ (1,1-μ-SH) ₂ H ₄	HSO1	75.6	6.7	2.9	0.3
	P2E	1609.2	1534.6	62.1	60.8
	HSO2	2591.4	2522.6	100.0	100.0
Ti ₂ (1,1-μ-NH ₂) ₂ H ₄	HSO1	85.4	5.0	2.7	0.2
	P2E	1910.9	1833.8	59.5	58.5
	HSO2	3212.9	3132.6	100.0	100.0
Ti ₂ (1,1-μ-PH ₂) ₂ H ₄	HSO1	94.0	7.7	2.7	0.2
	P2E	2025.7	1939.2	57.6	56.6
	HSO2	3515.0	3425.7	100.0	100.0
Ti ₂ (1,1-μ-NNN) ₂ H ₄	HSO1	107.0	10.7	2.1	0.2
	P2E	3406.5	3310.3	68.1	67.5
	HSO2	5000.2	4904.8	100.0	100.0
Ti ₂ (1,3-μ-NNN) ₂ H ₄	HSO1	102.9	10.7	2.2	0.2
	P2E	3313.0	3222.8	69.5	68.9
	HSO2	4769.4	4674.5	100.0	100.0
Ti ₂ (1,1-μ-CN) ₂ H ₄	HSO1	63.4	5.9	2.2	0.2
	P2E	2003.7	1944.0	68.3	67.6
	HSO2	2935.3	2877.0	100.0	100.0
Ti ₂ (1,1-μ-NC) ₂ H ₄	HSO1	66.8	6.0	2.2	0.2
	P2E	2079.4	2019.2	67.7	67.0
	HSO2	3073.0	3012.3	100.0	100.0
Ti ₂ (1,2-μ-CN) ₂ H ₄	HSO1	99.4	5.9	3.3	0.2
	P2E	2010.0	1915.4	67.2	66.1
	HSO2	2990.8	2896.4	100.0	100.0
Ti ₂ (1,1-μ-OCN) ₂ H ₄	HSO1	109.8	10.7	2.1	0.2
	P2E	3457.5	3359.0	67.4	66.8
	HSO2	5131.9	5032.0	100.0	100.0
Ti ₂ (1,1-μ-NCO) ₂ H ₄	HSO1	114.6	10.8	2.3	0.2
	P2E	3412.1	3314.3	67.3	66.6
	HSO2	5072.6	4975.3	100.0	100.0
Ti ₂ (1,3-μ-OCN) ₂ H ₄	HSO1	173.5	10.7	3.4	0.2
	P2E	3439.0	3276.6	68.0	66.9
	HSO2	5059.4	4897.1	100.0	100.0
Ti ₂ (1,1-μ-ONC) ₂ H ₄	HSO1	110.4	10.6	2.2	0.2
	P2E	3473.6	3373.4	68.1	67.5
	HSO2	5098.4	4999.7	100.0	100.0
Ti ₂ (1,1-μ-NCO) ₂ H ₄	HSO1	103.2	10.6	2.2	0.2
	P2E	3251.7	3159.2	68.9	68.2
	HSO2	4721.5	4629.6	100.0	100.0

^a Timings for a 900-MHz UltraSPARC3 computer. ^b This category includes the time required for integral transformations and spin-orbit matrix element calculations.

^c b_{2u} and b_{1g} frontier molecular orbitals. ^d a_g and b_{1u} frontier molecular orbitals.

TABLE 16: (continued)

molecule	method	total CPU time	spin-orbit coupling ^b	% total time	% SOC time ^b
$\text{Ti}_2(1,3\text{-}\mu\text{-ONC})_2\text{H}_4$	HSO1	171.8	10.6	3.5	0.2
	P2E	3374.0	3215.0	67.8	66.7
	HSO2	4976.6	4816.9	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-SCN})_2\text{H}_4$	HSO1	184.2	15.5	2.2	0.2
	P2E	3831.0	3661.0	46.6	45.6
	HSO2	8213.8	8034.6	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-NCS})_2\text{H}_4$	HSO1	133.8	15.5	1.9	0.2
	P2E	3943.5	3817.6	55.2	54.4
	HSO2	7141.0	7022.9	100.0	100.0
$\text{Ti}_2(1,3\text{-}\mu\text{-SCN})_2\text{H}_4$	HSO1	225.9	15.6	3.3	0.2
	P2E	3910.1	3699.4	57.4	55.8
	HSO2	6816.8	6624.7	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-NO})_2\text{H}_4^c$	HSO1	77.4	7.7	2.3	0.2
	P2E	2094.3	2024.7	61.6	60.8
	HSO2	3398.7	3328.3	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-NO})_2\text{H}_4^d$	HSO1	73.0	7.7	2.3	0.3
	P2E	1960.9	1895.2	63.0	62.2
	HSO2	3114.6	3048.5	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-ON})_2\text{H}_4$	HSO1	61.0	6.4	2.1	0.2
	P2E	1991.9	1938.5	68.6	68.0
	HSO2	2902.9	2848.8	100.0	100.0
$\text{Ti}_2(1,2\text{-}\mu\text{-NO})_2\text{H}_4$	HSO1	121.7	7.6	3.4	0.2
	P2E	2115.3	2002.7	59.6	58.3
	HSO2	3550.0	3437.8	100.0	100.0
$\text{Ti}_2(\mu\text{-NO}_2)_2\text{H}_4$	HSO1	130.3	14.1	2.2	0.2
	P2E	3437.4	3317.7	56.8	55.9
	HSO2	6055.4	5936.6	100.0	100.0

TABLE 17: MCQDPT-SOC Timings^a

molecule	method	total CPU time	spin-orbit coupling ^b	% total time	% SOC time ^b
Ti ₂ (1,1-μ-OH) ₂ H ₄	HSO1	1953.6	64.2	49.2	3.1
	P2E	3289.0	1408.4	82.9	67.9
	HSO2	3967.7	2074.5	100.0	100.0
Ti ₂ (1,1-μ-SH) ₂ H ₄	HSO1	3030.5	94.6	55.3	3.6
	P2E	4548.4	1667.4	83.0	64.0
	HSO2	5481.2	2606.4	100.0	100.0
Ti ₂ (1,1-μ-NH ₂) ₂ H ₄	HSO1	3082.4	92.4	50.8	2.9
	P2E	4862.2	1949.4	80.2	60.6
	HSO2	6062.8	3218.8	100.0	100.0
Ti ₂ (1,1-μ-PH ₂) ₂ H ₄	HSO1	4035.6	120.4	55.0	3.4
	P2E	6036.4	2121.3	82.2	59.9
	HSO2	7342.0	3538.9	100.0	100.0
Ti ₂ (1,1-μ-NNN) ₂ H ₄	HSO1	5256.9	163.0	45.4	2.5
	P2E	8585.8	3489.0	74.2	53.8
	HSO2	11571.7	6486.2	100.0	100.0
Ti ₂ (1,3-μ-NNN) ₂ H ₄	HSO1	5514.1	165.3	49.7	2.7
	P2E	8399.8	3390.7	75.7	55.8
	HSO2	11091.0	6078.9	100.0	100.0
Ti ₂ (1,1-μ-CN) ₂ H ₄	HSO1	2802.8	92.1	46.6	2.9
	P2E	4798.2	2094.6	79.8	65.0
	HSO2	6012.0	3221.1	100.0	100.0
Ti ₂ (1,1-μ-NC) ₂ H ₄	HSO1	2760.5	92.1	45.9	2.8
	P2E	4861.0	2171.5	80.9	65.1
	HSO2	6011.0	3337.4	100.0	100.0
Ti ₂ (1,2-μ-CN) ₂ H ₄	HSO1	2997.0	101.0	49.4	3.2
	P2E	4968.1	2053.8	81.8	64.6
	HSO2	6072.3	3177.5	100.0	100.0
Ti ₂ (1,1-μ-OCN) ₂ H ₄	HSO1	5683.1	164.9	46.7	2.4
	P2E	8821.1	3532.4	72.4	52.1
	HSO2	12180.0	6776.2	100.0	100.0
Ti ₂ (1,1-μ-NCO) ₂ H ₄	HSO1	5380.7	163.6	48.2	2.7
	P2E	8386.7	3341.4	75.1	55.3
	HSO2	11168.4	6045.0	100.0	100.0
Ti ₂ (1,3-μ-OCN) ₂ H ₄	HSO1	5832.5	176.6	46.4	2.7
	P2E	9086.1	3463.1	72.3	52.6
	HSO2	12569.7	6586.3	100.0	100.0
Ti ₂ (1,1-μ-ONC) ₂ H ₄	HSO1	5500.0	164.1	46.6	2.5
	P2E	8865.8	3553.0	75.1	54.0
	HSO2	11799.5	6574.4	100.0	100.0
Ti ₂ (1,1-μ-NCO) ₂ H ₄	HSO1	5296.0	164.3	45.9	2.7
	P2E	8601.9	3347.4	74.6	54.1
	HSO2	11534.2	6182.5	100.0	100.0

^a Timings for a 900-MHz UltraSPARC3 computer. ^b This category includes the time required for integral transformations and spin-orbit matrix element calculations.

^c b_{2u} and b_{1g} frontier molecular orbitals. ^d a_g and b_{1u} frontier molecular orbitals.

TABLE 17: (continued)

molecule	method	total CPU time	spin-orbit coupling ^b	% total time	% SOC time ^b
$\text{Ti}_2(1,3\text{-}\mu\text{-ONC})_2\text{H}_4$	HSO1	6161.3	177.4	50.8	2.9
	P2E	9421.7	3388.8	77.7	54.5
	HSO2	12119.5	6216.5	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-SCN})_2\text{H}_4$	HSO1	9390.9	221.9	54.0	2.7
	P2E	12985.5	3961.1	74.7	47.6
	HSO2	17374.7	8318.0	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-NCS})_2\text{H}_4$	HSO1	7343.0	207.2	50.3	2.8
	P2E	11226.6	4094.0	76.9	55.3
	HSO2	14607.0	7403.4	100.0	100.0
$\text{Ti}_2(1,3\text{-}\mu\text{-SCN})_2\text{H}_4$	HSO1	8370.3	220.9	56.3	3.2
	P2E	11819.0	3962.5	79.5	57.4
	HSO2	14868.5	6898.4	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-NO})_2\text{H}_4^c$	HSO1	10992.8	119.6	75.0	3.2
	P2E	13051.1	2164.0	89.1	57.1
	HSO2	14653.3	3790.2	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-NO})_2\text{H}_4^d$	HSO1	11202.1	120.6	75.7	3.5
	P2E	13125.5	2021.4	88.7	58.1
	HSO2	14798.9	3478.0	100.0	100.0
$\text{Ti}_2(1,1\text{-}\mu\text{-ON})_2\text{H}_4$	HSO1	10554.0	118.9	74.7	3.3
	P2E	12605.1	2097.3	89.2	58.1
	HSO2	14126.0	3609.1	100.0	100.0
$\text{Ti}_2(1,2\text{-}\mu\text{-NO})_2\text{H}_4$	HSO1	11275.4	150.0	73.9	3.8
	P2E	13441.6	2191.7	88.1	55.0
	HSO2	15253.9	3985.7	100.0	100.0
$\text{Ti}_2(\mu\text{-NO}_2)_2\text{H}_4$	HSO1	29299.6	236.8	78.0	2.8
	P2E	32852.8	3630.9	87.5	43.0
	HSO2	37540.7	8437.5	100.0	100.0

Figure 1. Three-dimensional plots of the σ and σ^* natural orbitals from a two-electron, two-orbital MCSCF/TZV(p) calculation for singlet $\text{Ti}_2(\text{OH})_2\text{H}_4$. The orbital contour value for the plots is $0.06 \text{ bohr}^{3/2}$.

Figure 2. Three-dimensional plots of the δ and δ^* natural orbitals for singlet $\text{Ti}_2(\text{NH}_2)_2\text{H}_4$ from a two-electron, two-orbital MCSCF/TZV(p) calculation. The orbital contour value for the plots is $0.06 \text{ bohr}^{3/2}$.

Figure 3. Three-dimensional plots of the natural orbitals for singlet $\text{Ti}_2(\text{NH}_2)_2\text{H}_4$ with C_{2h} symmetry from a two-electron, two-orbital MCSCF/TZV(p) calculation. The orbital contour value for the plots is 0.06

Figure 4. Three-dimensional plots of “end-on” $\text{Ti}_2(\mu\text{-}1,1\text{-NNN})_2\text{H}_4$ and “linear” $\text{Ti}_2(\mu\text{-}1,3\text{-NNN})_2\text{H}_4$ from a two-electron, two-orbital MCSCF/TZV(p) calculation.

Figure 5. Three-dimensional plots of $\text{Ti}_2(\mu\text{-}1,1\text{-CN})_2\text{H}_4$, $\text{Ti}_2(\mu\text{-}1,1\text{-NC})_2\text{H}_4$, and $\text{Ti}_2(\mu\text{-}1,2\text{-CN})_2\text{H}_4$ from a two-electron, two-orbital MCSCF/TZV(p) calculation.

Figure 6. Three-dimensional plots of the natural orbitals for singlet $\text{Ti}_2(\mu\text{-}1,1\text{-NO})_2\text{H}_4$ from a two-electron, two-orbital MCSCF/TZV(p) calculation. The orbital contour value for the plots is $0.1 \text{ bohr}^{3/2}$.

Figure 7. Three-dimensional plots of the frontier orbitals for triplet $\text{Ti}_2(\mu\text{-}1,2\text{-NO})_2\text{H}_4$ from a ROHF/TZV(p) calculation. The orbital contour value for the plots is $0.1 \text{ bohr}^{3/2}$.

Figure 8. Three-dimensional plots of the natural orbitals from a two-electron, two-orbital MCSCF/TZV(p) calculation for singlet $\text{Ti}_2(\text{NO})_2\text{H}_4$. The orbital contour value for the plots is $0.1 \text{ bohr}^{3/2}$.

Figure 9. Three-dimensional plots of the 14 active molecular orbitals for $\text{Ti}_2(\mu\text{-}1,1\text{-NO})_2\text{H}_4$ used in the spin-orbit coupling calculations. Orbital 39 is the HOMO.

Figure 10. Three-dimensional plots of the 14 active molecular orbitals for $\text{Ti}_2(\mu\text{-1,2-NO})_2\text{H}_4$ used in the spin-orbit coupling calculations. Orbital 39 is the HOMO.

Figure 11. Three-dimensional plots of the 16 active molecular orbitals for $\text{Ti}_2(\mu\text{-NO}_2)_2\text{H}_4$ used in the spin-orbit coupling calculations. Orbital 47 is the HOMO.

CHAPTER 4. SYSTEMATIC INVESTIGATION OF THE SOLVATION OF NONIONIZED AND ZWITTERIONIC GLYCINE

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Microsolvation and combined microsolvation-continuum approaches are employed in order to examine the solvation of glycine. Glycine(H_2O)_n supermolecular clusters with $n = 1-7$ are studied with effective fragment potentials, Hartree-Fock, second-order perturbation theory, and the polarizable continuum model in order to determine the structures and relative energies of nonionized and zwitterionic glycine clusters. Bridging structures are predicted to be the global minima after 3-5 discrete water molecules are included in the calculations, depending on the level of theory. Second-order perturbation theory stabilizes the zwitterionic structures by about 8-9 kcal/mol relative to the nonionized structures regardless of the number of discrete water molecules considered. Continuum calculations stabilize the zwitterionic structures relative to nonionized structures, and this effect decreases as the number of discrete water molecules is increased. Seven water molecules do not fully solvate glycine.

Introduction

Since most chemical reactions and biological processes take place in solution, an accurate treatment of solvent effects is increasingly important in quantum chemistry. The two main approaches to solvation include dielectric continuum methods and discrete microsolvation methods, and each has its own advantages and disadvantages. Most common solvation models are based on a continuum approach, in which the solvent is treated in bulk

as a polarizable medium.¹ These models include the self-consistent reaction field (SCRF) or Onsager cavity model,^{2,3} the polarizable continuum model (PCM),⁴ the COSMO⁵ and GCOSMO⁶ models, the solvation model 5 (SM5)^{7,8}, and other variants of these methods. Continuum methods are fast, relatively simple, and designed to satisfactorily reproduce bulk properties of the solvent. However, they can be very sensitive to the choice of the parameters such as the shape of the cavity in which the solute is embedded. Their description of important electronic effects is generally not adequate. In addition, they cannot describe the individual interactions between solute and solvent molecules, which may be particularly important when the solvent and solute can form hydrogen bonds.

In a discrete approach, individual solvent molecules are explicitly treated. This successfully accounts for the intermolecular solute-solvent interactions. However, if *ab initio* solvent molecules are used, the calculation may be very computationally demanding. A number of quantum mechanical/molecular mechanical (QM/MM) methods have been developed in order to reduce the computational cost associated with discrete solvation approaches.⁹ A generalized potential derived from first principles known as the effective fragment potential method has been developed by Stevens, Jensen, Gordon, and co-workers.^{10,11} The original method (EFP1/HF) was designed specifically for water and is represented by a set of one-electron potentials that are added to the *ab initio* electronic Hamiltonian.^{10,11} It contains three energy terms, including Coulombic interactions, induction/polarization interactions, and charge-transfer/exchange-repulsion terms between solvent molecules and between solvent and solute molecules. Charge penetration is included to correct for the pointwise nature of the electrostatic expansion. The first two terms are determined from *ab initio* calculations on the water monomer, and the third term is fit to a

quantum mechanical water dimer potential, so the method can be systematically improved. The EFP1/HF method has been found to closely reproduce Hartree-Fock results for a variety of systems. Other effective fragment potential methods have been developed, including a density functional theory-based model (EFP1/DFT) that includes some short-range correlation effects,¹² and an EFP1/MP2 model that incorporates dispersion effects and a second-order correction to polarization.¹³ A general effective fragment potential model (EFP2) has also been developed.¹⁴⁻¹⁷ This method is applicable to any solvent, and may be applied across covalent bonds. No fitting is used in this procedure, and the existing model includes terms for exchange repulsion, electrostatic interaction and charge penetration, polarization, dispersion¹⁸ and charge transfer.¹⁹

As the number of discrete solvent molecules increases, the number of degrees of freedom in the system also increases. Since numerous minima exist in the configuration space, methods such as molecular dynamics or Monte Carlo simulations must be employed in order to extensively sample this space. Some three-layer approaches have been developed that combine the microsolvation and continuum approaches.²⁰⁻²⁶ These methods may reduce the number of explicit solvent molecules required (and hence the computational cost) and may allow for an accurate description of long-range interactions.

Interactions between water molecules and amino acids and the effects of hydrogen bonding between them are of significant interest to chemists, particularly with regard to structures and vibrational spectra. Depending on the pH, amino acids such as glycine may be neutral, anionic, or cationic. Neutral amino acids exist predominantly in their nonionized form (N) in the gas phase, while in solution or in crystals they occur in the zwitterionic form (Z).^{27,28} The relative stability of these two forms of glycine is of increasing interest. The

intermolecular hydrogen bonding interaction leads to a considerably larger stability of the zwitterionic form compared to the nonionized form; consequently, the experimental free energy and enthalpy for the process $Z(aq) \rightarrow N(aq)$ are 7.3 and 10.3 kcal/mol, respectively.²⁹

As the smallest amino acid, glycine has been the object of many theoretical investigations. The nonionized structure for glycine has three internal rotational degrees of freedom: the rotation of the amino group around the C-N bond, the rotation of the C-C bond, and the rotation of the hydroxyl group around the C-O bond. Initial studies examined various C_s and C_1 stationary points on the conformational potential energy surface of nonionized gas phase glycine.^(30,31 and references therein) Continuum solvation models have been employed in several studies. Bonaccorsi et al. showed that electrostatic solute-solvent interactions stabilize zwitterionic glycine with respect to the nonionized form using continuum-only calculations.³² Tortonda et al. found that the combination of correlation energy and continuum calculations makes the zwitterionic form lower in energy than the nonionized form.³³ In addition, they found that solvent effects change the relative stabilities of the gas phase conformers, and that the most stable conformer in solution is well-suited for intramolecular proton transfer.³³

Previous theoretical studies in the gas phase predicted that the zwitterion is not a minimum if basis sets including polarization functions on the hydrogen atoms are used.³⁴ A complex of zwitterionic glycine with one discrete water molecule is a minimum at the RHF level of theory, but is not a minimum at the MP2 level of theory.^{35,36} Two discrete water molecules are required in order for the zwitterion to be a minimum at the MP2 level of theory.³⁵ Low energy structures for the zwitterion with one or two water molecules have also

been of interest to other researchers.^{37,38} In addition, low energy structures have been examined for the nonionized form with one or two water molecules.^{35,37,39-41}

The lowest energy zwitterionic structure with three waters was first reported by Kassab et al. in 2000 using DFT.⁴² This group also reported one nonionized structure relating to proton transfer. Bandyopadhyay et al. examined the energy difference between this structure and the global minima for zwitterionic and nonionized species using *ab initio* RHF and MP2 calculations, EFP1/HF potentials, and PCM.²⁵ Adamovic et al. extended this work to consider the effects of DFT and EFP1/DFT potentials.¹² Other zwitterionic and nonionized tri-hydrated structures were examined by Ramaekers et al.⁴¹

A few other studies have explored supermolecular complexes with more than three discrete water molecules, but many of these did not fully sample the configuration space. Ramaekers et al. looked at nonionized and zwitterionic structures with four and five water molecules.⁴¹ Yamabe et al. examined intermolecular proton transfer pathways for glycine(H₂O)_n (n = 1-4, 11, 17) using density functional theory (DFT) and DFT+Onsager methods.⁴³ They considered structures based on three conformers (N3, N5, and N8 defined below), which included the lowest energy structure in solution but did not include the lowest energy gas phase structure. Only bridged structures were examined, and no configurational sampling was reported.

Fernández-Ramos et al. examined the proton transfer reaction for a six-water complex in an Onsager dielectric continuum.²⁴ They started with several arrangements of the six-water complex and used the lowest energy configuration they found upon optimization at the HF/6-31G(d) level.

Rzepa and Yi found starting structures for complexes with 7 and 15 waters using Monte Carlo searches with a molecular mechanics force field, and then optimized these structures with semi-empirical models.²¹ They found that the zwitterionic form is more stable than the nonionized form for the glycine(H₂O)₁₅ supermolecular complex and for the glycine(H₂O)₇ complex in a self-consistent reaction field.

Bandyopadhyay et al. looked at the glycine(H₂O)₈ complex using three-layer models that combined the effective fragment potential with the Onsager and PCM models.^{23,25} In the first study, eight water molecules in the solvation shell were selected from a molecular dynamics calculation, and this structure was optimized.²³ In the second study, MC with local minimization was used in order to find a low energy configuration.²⁵ Cui used an approach similar to the former in order to examine the effects of TIP3P waters.²⁶ Using the three-layer approach, the zwitterion is predicted to be more stable than the nonionized species when a reliable continuum method is used.^{23,25,26}

Theoretically predicted spectra may be useful in the analysis of experimentally determined spectra of small hydrogen-bonded complexes such as the glycine-water complex. Theoretical methods have previously been applied to Raman²⁴ and IR⁴¹ spectra. Anharmonic vibrational spectroscopy of the glycine(H₂O) complex has also been considered.⁴⁴ Neutral complexes of glycine and water molecules may be isolated in a matrix environment. Related ionic complexes may be segregated using mass spectrometric techniques. Xu et al. note that only [Gly(H₂O)_n]⁺ species with $n \geq 5$ are seen in their mass spectrometry experiments, and they attribute this to the formation of a zwitterionic species.⁴⁵ On the other hand, Diken et al. were later able to synthesize the bare glycine anion and the smaller hydrates Gly⁻•(H₂O)₁₋₂.⁴⁶

Theoretical calculations may be useful in determining at what point the zwitterionic species will become more stable than the nonionized form.

The goal of the present work is to determine the equilibrium structures for small glycine-water clusters and determine which conformers dominate as the size of the cluster increases. In addition, the present work will determine at what point the zwitterionic form is predicted to be more stable than the nonionized form, and how the inclusion of correlation energy affects this result. The convergence of the zwitterionic-nonionized energy difference will be considered. The effect of adding a bulk solvent will be discussed, as well as how this is affected by increasing the number of discrete water molecules. The number of waters needed to completely solvate glycine will be considered in an effort to determine the number of waters in the first solvent shell. Previous studies have investigated a first solvation shell consisting of 5,⁴⁷ 6,^{21,24,48} 8,^{23,26} or 11⁴³ water molecules.

Computational Methods

Molecular structures for water and eight nonionized glycine minima were determined at the restricted Hartree-Fock (RHF) level of theory using the 6-31G(d,p) basis set. Four of the nonionized glycine structures have C_s symmetry and four structures have C_1 symmetry. (See Ref. 30) MP2/6-31++G(d,p) single-point energies were used to refine the relative energies. For zwitterionic glycine, the Polarizable Continuum Model (PCM) was employed with a geometry optimization at the RHF/6-31G(d,p) level to calculate a minimum energy structure. General effective fragment potentials (EFP2's) that include exchange repulsion, electrostatic interaction and charge penetration effects were constructed for water, the eight nonionized minima, the zwitterionic minimum, and three other zwitterionic structures constructed by introducing torsion around the C-C bond.

For 1-3 discrete water molecules, a Monte Carlo (MC) simulation with local minimization⁴⁹ “basin-hopping” approach was used to find minima on the potential energy surface. Starting structures for MC runs were constructed by adding a water molecule in various positions relative to structures determined from previous runs with one fewer water molecule. For complexes involving one water molecule, 30 steps were allowed in each local optimization. For two and three water molecules, 60 steps were allowed. General effective fragment potentials (EFP2's) were used for glycine and water in order to reduce the computational cost. Structures obtained from the MC runs were used as a starting point for geometry optimizations with glycine treated at the RHF/6-31++G(d,p) level of theory and water molecules treated with the EFP1/HF potential (this will be referred to as an efp-ab optimization). These structures were then fully optimized at the RHF/6-31++G(d,p) level of theory (this will be referred to as an ab-ab optimization). At each step, duplicate minima were removed. As a test of this two-part optimization, full *ab initio* RHF/6-31++G(d,p) optimizations were performed on selected structures from the MC runs with one discrete water molecule. Single point calculations incorporating the conductor-like polarizable continuum model (C-PCM)⁵⁰ were performed on the efp-ab and ab-ab optimized structures. For one and two water molecules, optimizations incorporating C-PCM were also run. Single point MP2 calculations were performed on the ab-ab optimized structures. In addition, single point MP2 energies were calculated using C-PCM orbitals and orbital energies to integrate correlation effects with bulk solvent effects.⁵¹⁻⁵⁴ MP2 and B3LYP geometry optimizations were performed for selected ab-ab structures. Imaginary frequencies were detected by diagonalizing the energy second-derivative (Hessian) matrix.

For four discrete water molecules, a simulated annealing Monte Carlo with local minimization approach was used to find minima on the potential energy surface.⁵⁵ *Ab initio* atoms were not allowed to move during the MC steps, but were allowed to move during the minimization procedure. Starting structures were generated by adding a water molecule to unique structures with three water molecules. The water molecules were represented by the EFP1/HF potential and the RHF/6-31++G(d,p) level of theory was used for glycine in order to allow the molecule to sample torsional degrees of freedom. The initial and final temperatures used in the simulation were 10000K and 200K, respectively. Fifty temperatures were used in the simulation, and 300 geometries were evaluated at each temperature. Local optimizations were carried out after 150 MC steps, with a maximum of 150 optimization steps. The maximum step size was held constant and the *ab initio* atoms were not allowed to move during the MC steps. All structures within 3.0 kcal/mol of the global nonionized and zwitterionic minima were subjected to a full RHF/6-31++G(d,p) geometry optimization. Single-point MP2 and C-PCM calculations were performed on the unique ab-ab minima.

For five or more discrete waters, a similar simulated annealing MC with local minimization approach was employed. The initial temperature was set at 5000K. Two hundred temperatures were used in the simulation and 200 geometries were evaluated at each temperature. Ten translational steps were permitted in each block. Three fragments were allowed to move during each MC step. The box dimensions for periodic boundary conditions were slightly increased to 23x19.5x20. Local optimizations were performed after 100 MC steps, with a maximum of 200 steps in each. Full RHF/6-31++G(d,p) geometry optimizations were performed on a few lowest energy nonionized and zwitterionic structures. Single-point MP2 and C-PCM calculations were performed on the ab-ab minima.

All calculations were performed with the electronic structure code GAMESS,⁵⁶ which is freely available from Iowa State University at www.msg.ameslab.gov. Structures were visualized with MacMolPlt,⁵⁷ a graphical interface to GAMESS.

Results and Discussion

Glycine

The eight nonionized glycine conformers determined in the geometry optimizations correspond to the eight minima found in Ref. 30. These gas phase structures and their relative energies are shown in Figure 1.

Glycine(H₂O)

A single water molecule can interact with each glycine conformer to form a wide variety of structures. It may interact with the carboxylic acid group, the amino group, or the saturated carbon, or it may act as a bridge between the carboxylic acid and amino groups. 66 distinct structures were observed for nonionized EFP2 glycine and 25 structures were found for zwitterionic EFP2 glycine interacting with a single EFP2 water molecule. Upon efp-ab optimization, there are 47 unique structures for the nonionized form ranging from 0.0 to 13.7 kcal/mol relative to the lowest energy structure and 6 unique structures for the zwitterionic form ranging from 24.2 to 28.2 kcal/mol above the lowest energy nonionized minimum for glycine (see Table 1 and Figure 2). The reduction in the number of isomers may be due in part to relaxation from the frozen EFP2 geometries. After ab-ab optimization, 44 unique nonionized structures and 5 unique zwitterionic structures remain. These unique structures are named according to the following convention. The name of each structure has the form *mNn*-alpha or *mZ*-alpha, where *m* designates the number of water molecules surrounding the glycine core, *Nn* represents the *n*th nonionized glycine conformer, *Z* indicates the zwitterion,

and “alpha” is an alphabetical letter used to label the structures. The complexes are labeled alphabetically from the lowest energy structure at the mixed efp-ab level of theory, so structures close to “a” are relatively low in energy.

EFP1/HF waters do a good job of reproducing the RHF relative energy ordering, particularly for the lowest energy structures. In the six lowest energy structures (1N1-a, 1N2-a, 1N6-a, 1N6-b, 1N8-a, and 1N8-b) (shown in Figure 2), the water interacts with the carboxylic acid functionality of the glycine molecule. The five zwitterionic structures found in this work (1Z-a, 1Z-b, 1Z-c, 1Z-d, and 1Z-e in Figure 3) are similar to those found in Ref. 35 (Z1a, Z1b, and i, iv, and iii in Figure 2 of that reference). A frequency analysis shows that the four lowest energy structures are minima on the RHF/6-31++G(d,p) potential energy surface. The fifth structure has an imaginary frequency of $6i\text{ cm}^{-1}$. The two lowest energy structures have the water molecule bridging the protonated amino group and the carboxylate group. They differ in that the water molecule bonds to the oxygen that is *cis* to the nitrogen for 1Z-a, and to the oxygen *trans* to the nitrogen for 1Z-b.

Some of the nonionized structures found here have been previously reported in the literature. Most of these studies were largely concerned with a few conformers. Basch and Stevens examined five structures with C_s symmetry, and as a result a few of their structures are saddle points.³⁹ Their structures came from four gas phase conformers. Kwon et al. examined two monohydrated minima that were derived from the most stable gas phase conformer.³⁷ Jensen and Gordon found eight nonionized minima from multiple conformers.³⁵ Wang et al. examined four monohydrated structures based on a single gas phase conformer.⁴⁰ Rameakers et al. determined 16 nonionized structures that were derived from three gas phase conformers.⁴¹ The present and previous studies agree that cyclic 1N1-a is the most stable

structure. However, most 1:1 glycine-water complexes examined in this work have not been seen previously, including four of the five structures that lie within 3.0 kcal/mol of 1N1-a at the RHF/6-31++G(d,p) level of theory. Six of the 47 nonionized structures found in this study have imaginary frequencies ranging from $5\text{--}67i\text{ cm}^{-1}$, so they are saddle points at this level of theory. Since the potential energy surface appears to be shallow and other levels of theory may predict slightly different results (as previously reported for gas phase glycine), these structures are retained here.

On average, the inclusion of correlation via MP2 single point energies lowers the energy of nonionized structures by 0.3 kcal/mol relative to the lowest energy N structure. The relative energies were raised by up to 0.7 kcal/mol or lowered by up to 2.4 kcal/mol. This effect is more dramatic for zwitterionic structures, whose relative energies decrease by 8.1-9.2 kcal/mol relative to the lowest energy N structure. MP2 optimizations on zwitterions with only one discrete water result in proton transfer leading to nonionized structures, in agreement with Ref. 35. Optimizations of nonionized structures with second-order perturbation theory changed bond lengths slightly, but did not change energy orderings or general structure aspects substantially.

Single point calculations using C-PCM with the RHF/6-31++G(d,p) structures simulate the effect of adding a bulk solvent around the glycine(H_2O) complex. These calculations stabilize the zwitterionic structures by 21.0-23.7 kcal/mol relative to the lowest energy nonionized structure; nonetheless, the nonionized form is predicted to be the lowest in energy. Although geometry optimization inside a continuum solvent has a negligible effect on the structure of the nonionized glycine, there are large effects on the zwitterionic structure. These effects have been seen previously.⁵⁸ If one intends to determine structures

of the zwitterion in solution rather than in small water clusters, optimization in the presence of solvent is important. Single point energy calculations at the combined C-PCM+MP2 level of theory predict that the zwitterionic species is 3.6 kcal/mol lower in energy than the nonionized species when one discrete water is considered inside the bulk.

Glycine(H₂O)₂

For glycine with two water molecules, 238 nonionized and 86 zwitterionic structures were found in the EFP2 Monte Carlo simulations. After efp-ab optimization, 155 nonionized and 19 zwitterionic structures remain. Upon ab-ab optimization, 132 unique nonionized structures and 11 unique zwitterionic structures were found. Ten of the nonionized and two of the zwitterionic structures were found in previous studies (see Table 2 and Figures 4,5). As found in earlier studies,^{35,41} the water molecules bridge the COO⁻ and NH₃⁺ groups in the lowest energy zwitterionic structures (Figure 5). Most levels of theory agree that a complex with a bridge consisting of two water molecules (such as 2Z-a, 2Z-b, and 2Z-c) is slightly lower in energy than a complex with two single-water bridges (such as 2Z-d and 2Z-e), although the RHF/6-31++G(d,p) level of theory predicts that the latter is 0.1 kcal/mol lower in energy. The nonionized-zwitterion energy difference is 20.2 kcal/mol at the efp-ab level of theory, in very good agreement with the RHF energy differences of 19.7 kcal/mol for 2Z-d and 19.8 kcal/mol for 2Z-a. MP2 single point energies stabilize the zwitterionic form with respect to the nonionized glycine by 7.0-9.4 kcal/mol. Nonetheless, the global minimum is found to be the nonionized species. Upon optimization at the MP2 level of theory, the two zwitterionic structures without a bridging water molecule (2Z-j and 2Z-k) become nonionized structures. Structures 2Z-g and 2Z-h optimize to the same structure. After optimization at the MP2 level of theory, eight unique zwitterionic structures remain.

C-PCM single point energies stabilize the zwitterion(H_2O)₂ complex by 16.0-23.1 kcal/mol. This stabilization is less than that seen for the glycine(H_2O) complex, but the inclusion of bulk solvent effects continues to have a dramatic consequence for the energy difference with two explicit water molecules. Combined C-PCM+MP2 single point energy calculations predict that the zwitterionic species is 4.7 kcal/mol lower in energy than the nonionized species, so the consideration of a second explicit water molecule inside the bulk increased the Z-N energy difference by 1.1 kcal/mol.

In the lowest energy nonionized complexes (2N1-a, 2N1-b, 2N2-a, 2N6-a, 2N6-b, 2N2-b, 2N6-c, 2N8-a, 2N8-b, and 2N8-c), the water molecules form a ring with carboxylic acid end of glycine (Figure 4). This motif was found in an earlier study by Jensen and Gordon.³⁵ This structure may be visualized with the two oxygen atoms in glycine essentially substituting for two of the oxygen atoms in a cluster of four water molecules. The di-hydrated nonionized structure found by Kwon et al. is either 2N1-e or 2N1-f; these structures lie 4.8 and 5.5-5.6 kcal/mol above the global minimum at the RHF/6-31++G(d,p) and MP2//RHF/6-31++G(d,p) levels of theory, respectively. The lowest energy structure reported by Rameakers et al. is 2N1-c, which is 4.5 and 4.8 kcal/mol above the global minimum at the RHF/6-31++G(d,p) and MP2//RHF/6-31++G(d,p) levels of theory, respectively. At the B3LYP/6-31++G(d,p) level of theory, 2N1-c is 5.2 kcal/mol higher in energy than 2N1-a.

Glycine(H_2O)₃

For the glycine complex with three water molecules, 824 nonionized and 212 zwitterionic structures were found in the EFP2 Monte Carlo calculations. After optimization with *ab initio* glycine and EFP1/HF waters, 450 nonionized and 42 zwitterionic complexes were found. Full *ab initio* optimizations lead to 349 nonionized and 24 zwitterionic

structures. 24 of the nonionized structures are predicted to lie within 3.0 kcal/mol of the global minimum (Table 3). The lowest energy structures fall into two groups. The global minimum structure 1N1-a (see Figure 6) consists of three water molecules interacting with the carboxylic acid end of glycine in a ring similar to the water pentamer. This global minimum was previously reported by Bandyopadhyay and Gordon.²⁵ The other primary motif seen in the low energy structures is a chain of three waters that bridges the carboxylic acid and amino groups (see 3N6-a and 3N6-c in Figure 6). A similar cyclic bridging structure was seen by Yamabe et al.⁴³ This type of structure is stabilized by 2.0-3.0 kcal/mol relative to ring structures when electron correlation is included via MP2 single point energies. Optimization at the MP2 level of theory further stabilizes the cyclic structures. At the MP2/6-31++G(d,p) level of theory, 3N6-c is predicted to lie 0.8 kcal/mol lower in energy than 3N1-a, so it is predicted to be the global minimum at this level of theory. The B3LYP level of theory also stabilizes the cyclic structures relative to the ring structures with respect to RHF calculations, although not as dramatically as MP2 calculations. After optimization at the B3LYP/6-31++G(d,p) level of theory, 3N6-c is 1.4 kcal/mol higher in energy than 3N1-a.

The relative energies for the cyclic and the ring structures with *ab initio* glycine and EFP1/HF waters are somewhat different than the energies from full *ab initio* calculations. Interestingly, the EFP1/HF water relative energies are closer to the MP2 single point values. For most other structures, the EFP and RHF relative energies agree to within 1.0 kcal/mol.

Two other previous studies have examined minima for complexes with nonionized glycine and three water molecules. Kassab et al. were interested in the minimum that resulted from intramolecular proton transfer rather than the global minimum.⁴² This structure (3N3-h in Figure 6) is 6.5 kcal/mol higher in energy than the global minimum at the RHF/6-

31++G(d,p) level of theory. Rameakers et al. purport to find the global minimum.⁴¹

However, this structure (3N1-ar in Figure 6) is 7.1 kcal/mol higher than the global minimum at the RHF/6-31++G(d,p) level of theory. After optimizations at the B3LYP/6-31++G(d,p) level of theory, 3N1-ar is 8.5 kcal/mol higher in energy than 3N1-a.

The lowest energy efp-ab zwitterionic glycine complex with three water molecules (3Z-a) is shown in Figure 7. At the RHF/6-31++G(d,p) level of theory, two structures found in this work (3Z-d and 3Z-f in Figure 7) are predicted to be 0.1 kcal/mol lower in energy than 3Z-a. Neither of these structures has been previously reported. Structure 3Z-a was previously reported in the literature,^{25,42} as were three higher energy structures.^{41,43} The energy ordering predicted by the MP2 single point energies suggests that 3Z-a is the global zwitterionic minimum. This structure is 14.7 kcal/mol higher in energy than the global nonionized minimum with EFP1/HF waters and RHF/6-31++G(d,p) glycine, 15.6 kcal/mol higher in energy at the RHF/6-31++G(d,p) level of theory, and 5.2 kcal/mol higher in energy at the MP2//RHF/6-31++G(d,p) level of theory. In general, MP2 single point calculations stabilize the zwitterionic structures by 6.7-10.4 kcal/mol. C-PCM calculations stabilize the zwitterionic structures with respect to the nonionized structures by 12.1-18.7 kcal/mol. C-PCM+MP2 calculations predict that the zwitterionic form is 6.9 kcal/mol lower in energy than the nonionized form, so the inclusion of a third explicit water molecule increases the Z-N energy difference by 2.2 kcal/mol. In general, the efp-ab method predicts relative energies that are in very good agreement with the fully RHF values. For three waters, the global minimum is predicted to be a nonionized structure at all levels of theory except C-PCM+MP2.

Glycine(H₂O)₄

In a glycine(H₂O)₄ complex, the number of low energy local minima increases substantially. This prompted the procedural change described in the Computational Methods section above. At least 26 nonionized complexes of gas phase glycine conformer 1 with four water molecules are predicted to lie within 3.0 kcal/mol of the global minimum based on the Monte Carlo calculations. The lowest energy RHF/6-31++G(d,p) nonionized structure (4N1-a in Figure 8) is analogous to the water hexamer “book” structure. The lowest energy structure based on gas phase conformer 6 (4N6-a in Figure 8) has a cyclic structure similar to 3N6-a. At the RHF/6-31++G(d,p) level of theory, this structure is 0.8 kcal/mol higher in energy than 4N1-a. However, MP2 single point energies predict that it is 1.0 kcal/mol more stable. MP2 optimizations on these structures increase this energy difference in favor of the cyclic isomer to 1.7 kcal/mol. Bond lengths for both structures decrease upon MP2 optimization.

The lowest energy zwitterionic complex is shown in Figure 8. At the RHF/6-31++G(d,p) level of theory, this structure is predicted to be 11.7 kcal/mol less stable than the global minimum nonionized structure. The inclusion of dynamic electron correlation via MP2 single point energies decreases this to 1.6 kcal/mol. In general, MP2 single point energies stabilize zwitterionic structures with four waters by 8.5-11.7 kcal/mol. C-PCM calculations stabilize the zwitterionic structures by 10.0-14.7 kcal/mol. C-PCM+MP2 single point energy calculations predict that 4Z-a is 7.7 kcal/mol lower in energy than 4N1-a and 6.7 kcal/mol lower in energy than 4N6-a. The Z-N energy difference for four explicit waters is within 1 kcal/mol of the difference for three explicit waters, which suggests that the C-

PCM+MP2 Z-N energy difference may be converging with respect to the number of discrete water molecules considered inside the bulk.

A previous investigation on the energy difference between the nonionized and zwitterionic structures predicted the zwitterion to be more stable when four discrete water molecules were considered in the calculations.⁴¹ However, this study did not sample the configuration space, so the “global minima” reported are in fact high energy structures. At the B3LYP/6-31++G(d,p) level of theory, 4N6-a is predicted to be 0.2 kcal/mol lower in energy than 4N1-a and 16.3 kcal/mol lower in energy than the structure reported in Ref. 41; 4Z-a is predicted to lie 5.0 kcal/mol above 4N6-a, and the zwitterionic structure reported in Ref. 41 is predicted to lie 9.6 kcal/mol above 4N6-a. In addition, the structures reported in the Yamabe et al. study on intermolecular proton transfer⁴³ are somewhat higher in energy than the global minima reported here. All levels of theory examined here agree that the global minimum for the four water complex is a nonionized structure when it is not embedded in bulk water. As noted previously, relative energies obtained using EFP waters are in good agreement with those from fully quantum mechanical calculations.

Glycine(H₂O)₅

With five water molecules, the number of low energy local minima escalates further. Only the global minimum and a few selected low energy minima from the Monte Carlo “basin-hopping” procedure are discussed here.

For the glycine(H₂O)₅ complex, the efp-ab method predicts relative energies that are in good agreement with the fully *ab initio* calculations. The RHF/6-31++G(d,p) global minimum nonionized structure is predicted to be a bridge-like species (see 5N6-a in Figure 9) similar to 3N6-a and 4N6-a, rather than a structure consisting of a water cluster at the

carboxylic acid end of glycine (see 5N1-a in Figure 9). This 5N6-a structure can be considered to be more solvated, as the waters are in closer proximity to the glycine molecule. The nonplanar gas phase conformer 6 can accept hydrogen bonds, and this appears to encourage bridge-like structures. The lowest energy zwitterionic structure is also a bridged structure. It is predicted to lie 9.5 kcal/mol higher than the global minimum at the RHF/6-31++G(d,p) level of theory. Incorporation of electron correlation reduces this value to 0.4 kcal/mol at the MP2//RHF/6-31++G(d,p) level of theory. The use of C-PCM with RHF stabilizes the zwitterion by 8.7 kcal/mol, but still predicts that it is 0.8 kcal/mol higher in energy than the global minimum. C-PCM+MP2 calculations predict that 5Z-a is 7.3 kcal/mol lower in energy than 5N6-a.

The only previous calculation we are aware of on this system predicted the zwitterion to be more stable by 6.6 kcal/mol,⁴¹ but the minima reported are not the lowest energy structures. The nonionized structure reported in Ref. 41 is predicted to lie 13.2 kcal/mol higher in energy than 5N6-a at the RHF/6-31++G(d,p) level of theory, and 18.0 kcal/mol higher in energy at the B3LYP/6-31++G(d,p) level of theory. The zwitterionic structure reported in Ref. 41 is predicted to lie 9.5 kcal/mol higher in energy than 5N6-a at the B3LYP/6-31++G(d,p) level of theory.

Glycine(H₂O)₆

The lowest energy nonionized complexes with six water molecules found in this study have a cubic structure (Figure 10). The lowest energy zwitterionic structure corresponds to the addition of the water labeled "x" to 5Z-a with subsequent expansion of the structure. At the RHF/6-31++G(d,p) level of theory, the zwitterion is predicted to be 8.4 kcal/mol higher in energy than the global minimum. This energy difference is reduced to 0.8

kcal/mol at the MP2// RHF/6-31++G(d,p) level of theory. Addition of bulk solvent effects through the use of C-PCM single point energy calculations stabilizes the zwitterion by 8.6 kcal/mol, which means it is predicted to lie 0.2 kcal/mol lower in energy than the lowest energy nonionized structure. Integration of correlation energy via C-PCM+MP2 single point energy calculations increases this energy difference to 6.9 kcal/mol.

Fernández-Ramos et al. examined the proton transfer energy difference for the glycine(H_2O)₆ complex using RHF and MP2 methods with and without an Onsager SCRF, and found that their zwitterionic structure lies lower in energy than their nonionized structure for all levels of theory.²⁴ However, they only probed a few starting structures and did not report cubic structures.

Glycine(H₂O)₇

Low energy nonionized and zwitterionic structures for the glycine(H_2O)₇ supermolecular complex are shown in Figure 11. The efp-ab method and the RHF/6-31++G(d,p) level of theory predict the global minimum to be a nonionized prismatic structure based on gas phase conformer 1 (7N1-a). The lowest energy structure based on gas phase conformer 8 (7N8-a) is 1.2 kcal/mol higher in energy at the RHF/6-31++G(d,p) level of theory, while the lowest energy structure based on conformer 6 (7N6-a) is 1.3 kcal/mol higher in energy. However, the inclusion of correlation energy via MP2 single point energy calculations stabilizes 7N8-a and 7N6-a with respect to 7N1-a. At this level of theory, 7N8-a and 7N6-a are predicted to lie 1.0 and 0.7 kcal/mol lower in energy than 7N1-a, respectively.

The efp-ab method predicts that the zwitterionic structures 7Z-a, 7Z-b, and 7Z-f lie 7.3, 7.4, and 8.9 kcal/mol higher in energy than 7N1-a. However, this differs slightly from the full RHF/6-31++G(d,p) results. At this level of theory, the lowest energy zwitterionic

structure is predicted to be 7Z-f, followed by 7Z-b and 7Z-a (8.4, 8.5, and 9.0 kcal/mol higher than 7N1-a, respectively). With seven discrete water molecules, many structures fall within 1 kcal/mol of the lowest energy zwitterionic structure, so it may be necessary to examine multiple structures in order to interpret experimental results for this system.

MP2 single point energy calculations again stabilize the zwitterionic structures by about 9 kcal/mol. These calculations predict that the global minimum structure will be 7Z-b. It lies 0.3 kcal/mol lower in energy than 7N8-a at the MP2//RHF/6-31++G(d,p) level of theory. C-PCM single point energy calculations stabilize the zwitterionic structures by about 9 kcal/mol. These calculations also predict that 7Z-b will be the global minimum. The integration of correlation energy and C-PCM bulk solvation effects further stabilizes the zwitterionic structures. At this level of theory, 7Z-b is predicted to lie 8.8 kcal/mol lower in energy than both 7N1-a and 7N8-a. Overall, 7Z-b is predicted to be the global minimum for the correlated methods discussed here.

The zwitterionic structures seen in this work appear to be qualitatively similar to the PM3 and AM1 structures reported previously.²¹ The structures show a high degree of hydrogen bonding. In addition, the solvent molecules are asymmetrically clustered around the zwitterionic glycine solute, in contrast to the highly symmetrical ordering seen around the nonionized glycine. The N-H...O bond is effectively broken, and the CO₂⁻ group is twisted with respect to the NH₃⁺ group. In addition, the semi-empirical calculations on the glycine(H₂O)₇ system predicted the nonionized structure to be lower in energy than the zwitterion by 4.0 kcal/mol and the combined semi-empirical/SCRF approach predicted the zwitterionic structure to be lower in energy than the nonionized structure by 1.4 kcal/mol.²¹

This is in good agreement with our combined RHF/C-PCM approach, which predicts 7Z-b to be 0.5 kcal/mol lower in energy than the nonionized structures.

Conclusions

In general, the EFP1/HF water potentials track RHF structures and energy orderings well. The global minimum structure is the same for both methods for the numbers of water molecules examined in this study. Since there are a large number of low energy structures, configurational sampling is important. Multiple gas phase conformers must be considered. These species are highly fluxional, so multiple structures will likely be important for a physical description of the system.

The effect of systematically increasing the level of solvation is observed. The convergence of each method as the number of water molecules increases is summarized in Table 8. As the number of discrete water molecules increases, a different, "more solvated," structure becomes the global minimum nonionized structure. The internal structure of glycine in this complex is not the lowest energy gas phase conformer. This change occurs for three water molecules at the MP2/6-31++G(d,p) level of theory and for five water molecules at the RHF/6-31++G(d,p) level of theory. When seven discrete water molecules are considered, the lowest energy structure at the RHF/6-31++G(d,p) level of theory has an internal structure of gas phase conformer 1; however, the lowest energy nonionized structure at the MP2//RHF/6-31++G(d,p) level of theory is based on gas phase conformer 8.

Correlation effects included via second order perturbation theory typically stabilize the zwitterion about 8-9 kcal/mol with respect to the nonionized form. Even so, the nonionized form is lowest in energy for complexes with up to six water molecules. The zwitterionic structure is the global minimum for a supermolecular complex with seven

discrete water molecules at the MP2//RHF/6-31++G(d,p) level of theory. As the number of discrete water molecules increases, the effect of a continuum solvent on the energy difference between the nonionized and zwitterionic forms decreases. However, it still has a significant effect for clusters with seven waters, so these clusters do not completely recover long-range interactions with bulk solvent. Seven water molecules do not fully solvate the glycine molecule. The integration of correlation with the continuum solvent effects through C-PCM+MP2 single point energy calculations suggests that the zwitterionic species is 6.7-8.8 kcal/mol lower in energy than the neutral species in solution, which agrees well with the experimental free energy. At least three discrete water molecules are needed in order to obtain converged results within this level of theory.

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References

- (1) Cramer, C. J.; Truhlar, D. G. In *Reviews in Computational Chemistry*; Boyd, D. B., Lipkowitz, K. B., Eds.; VCH: New York, 1995; Vol. 6.
- (2) Kirkwood, J. G. *J. Chem. Phys.* **1934**, 2, 351.
- (3) Onsager, L. *J. Am. Chem. Soc.* **1936**, 58, 1486.
- (4) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, 55, 117.
- (5) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, II, 799.
- (6) Truong, T. N.; Stefanovich, E. V. *Chem. Phys. Lett.* **1995**, 240, 253.
- (7) Li, J.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. *Chem. Phys. Lett.* **1998**, 288, 293.

- (8) Hawkins, G. D.; Zhu, T.; Li, J.; Chambers, C. C.; Giesen, D. J.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. In *Combined Quantum Mechanical and Molecular Mechanical Methods*; Gao, J., Thompson, M. A., Eds.; ACS: Washington DC, 1998; Vol. 712; pp 201.
- (9) Gao, J. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 7.
- (10) Jensen, J. H.; Day, P. N.; Gordon, M. S.; Basch, H.; Cohen, D.; Garmer, D. R.; Krauss, M.; Stevens, W. J. Effective Fragment Method for Modeling Intermolecular Hydrogen-Bonding Effects on Quantum Mechanical Calculations. In *Modeling the Hydrogen Bond*; Smith, D. A., Ed.; ACS Symposium Series: Washington DC, 1994; Vol. 569; pp 139.
- (11) Day, P. N.; Jensen, J. H.; Gordon, M. S.; Webb, S. P.; Stevens, W. J.; Krauss, M.; Garmer, D. R.; Basch, H.; Cohen, D. *J. Chem. Phys.* **1996**, *105*, 1968.
- (12) Adamovic, I.; Freitag, M. A.; Gordon, M. S. *J. Chem. Phys.* **2003**, *118*, 6725.
- (13) Song, J.; Gordon, M. S. *manuscript in preparation*.
- (14) Jensen, J. H. *J. Chem. Phys.* **1996**, *104*, 7795.
- (15) Jensen, J. H.; Gordon, M. S. *Mol. Phys.* **1996**, *89*, 1313.
- (16) Jensen, J. H.; Gordon, M. S. *J. Chem. Phys.* **1998**, *108*, 4772.
- (17) Gordon, M. S.; Freitag, M. A.; Bandyopadhyay, P.; Jensen, J. H.; Kairys, V.; Stevens, W. J. *J. Phys. Chem. A* **2001**, *105*, 293.
- (18) Adamovic, I.; Gordon, M. S. *Mol. Phys.* **2005**, *103*, 379.
- (19) Li, H.; Jensen, J. H.; Gordon, M. S. *manuscript in preparation*.
- (20) Russell, S. T.; Warshel, A. *J. Mol. Bio.* **1985**, *185*, 389.
- (21) Rzepa, H. S.; Yi, M. *J. Chem. Soc., Perkin Trans.* **1991**, *2*, 531.

- (22) De Vries, A. H.; Van Duijnen, P. T.; Juffer, A. H.; Rullmann, J. A. C.; Dijkman, J. P.; Merenga, H.; Thole, B. T. *J. Comp. Chem.* **1995**, *16*, 37.
- (23) Bandyopadhyay, P.; Gordon, M. S. *J. Chem. Phys.* **2000**, *113*, 1104.
- (24) Fernández-Ramos, A.; Smedarchina, Z.; Siebrand, W.; Zgierski, M. Z. *J. Chem. Phys.* **2000**, *113*, 9714.
- (25) Bandyopadhyay, P.; Gordon, M. S.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **2002**, *116*, 5023.
- (26) Cui, Q. *J. Chem. Phys.* **2002**, *117*, 4720.
- (27) Albrecht, G.; Corey, R. B. *J. Am. Chem. Soc.* **1939**, *61*, 1087.
- (28) Jonsson, P. G.; Kvick, A. *Acta Crystallogr. B* **1972**, *28*, 1827.
- (29) Wada, G.; Tamura, E.; Okina, M.; Nakamura, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3064.
- (30) Jensen, J. H.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 7917.
- (31) Hu, C.-H.; Shen, M.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1993**, *115*, 2923.
- (32) Bonaccorsi, R.; Palla, P.; Tomasi, J. *J. Am. Chem. Soc.* **1984**, *106*, 1945.
- (33) Tortonda, F. R.; Pascual-Ahuir, J. L.; Silla, E.; Tuñón, I. *Chem. Phys. Lett.* **1996**, *260*, 21.
- (34) Ding, Y.; Krogh-Jespersen, K. *Chem. Phys. Lett.* **1992**, *199*, 261.
- (35) Jensen, J. H.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 8159.
- (36) Ding, Y.; Krogh-Jespersen, K. *J. Comp. Chem.* **1996**, *17*, 338.
- (37) Kwon, O. Y.; Kim, S. Y.; No, K. T. *Bull. Korean Chem. Soc.* **1995**, *16*, 410.
- (38) Wang, W.; Pu, X.; Zheng, W.; Wong, N.-B.; Tian, A. *J. Mol. Struct. Theochem.* **2003**, *626*, 127.

- (39) Basch, H.; Stevens, W. J. *Chem. Phys. Lett.* **1990**, *169*, 275.
- (40) Wang, W.; Zheng, W.; Pu, X.; Wong, N.-B.; Tian, A. *J. Mol. Struct. Theochem.* **2002**, *618*, 235.
- (41) Ramaekers, R.; Pajak, J.; Lambie, B.; Maes, G. *J. Chem. Phys.* **2004**, *120*, 4182.
- (42) Kassab, E.; Langlet, J.; Evleth, E.; Akacem, Y. *J. Mol. Struct. Theochem.* **2000**, *531*, 267.
- (43) Yamabe, S.; Ono, N.; Tsuchida, N. *J. Phys. Chem. A* **2003**, *107*, 7915.
- (44) Chaban, G. M.; Gerber, R. B. *J. Chem. Phys.* **2001**, *115*, 1340.
- (45) Xu, S.; Nilles, J. M.; Bowen Jr., K. H. *J. Chem. Phys.* **2003**, *119*, 10696.
- (46) Diken, E. G.; Hammer, N. I.; Johnson, M. A. *J. Chem. Phys.* **2004**, *120*, 9899.
- (47) Kokpol, U.; Doungdee, P. B.; Hannongbua, S. V.; Rode, B. M. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1789.
- (48) Förner, W.; Otto, P.; Bernhart, J.; Ladik, J. *Theor. Chim. Acta* **1981**, *60*, 269.
- (49) Li, Z.; Scheraga, H. A. *Proc. Nat. Acad. Sci.* **1987**, *84*, 6611.
- (50) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.
- (51) Olivares del Valle, F. J.; Tomasi, J. *Chem. Phys.* **1991**, *150*, 139.
- (52) Aguilar, M. A.; Olivares del Valle, F. J.; Tomasi, J. *Chem. Phys.* **1991**, *150*, 151.
- (53) Olivares del Valle, F. J.; Aguilar, M. A.; Tolosa, S. *J. Mol. Struct. Theochem.* **1993**, *279*, 223.
- (54) Olivares del Valle, F. J.; Aguilar, M. A. *J. Mol. Struct. Theochem.* **1993**, *280*, 25.

- (55) Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P. *Science* **1983**, 220, 671.
- (56) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Gordon, M. S.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery Jr., J. A. *J. Comp. Chem.* **1993**, 14, 1347.
- (57) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics and Modeling* **1998**, 16, 133.
- (58) Truong, T. N.; Stefanovich, E. V. *J. Chem. Phys.* **1995**, 103, 3709.

TABLE 1: Structures and relative energies for glycine(H₂O)

Structure	Refs	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)	water interaction	imaginary frequencies
1N1-a	a*,b,c,d,e,g	0.0	0.0	0.0	0.0	0.0	COOH	
1N6-a		1.5	1.5	1.2	1.7	1.4	COOH	
1N2-a	a*,b,d	1.5	1.5	1.2	1.3	1.1	COOH	
1N6-b		1.7	1.7	1.4	1.7	1.5	COOH	
1N8-a		2.3	2.4	2.0	2.3	2.0	COOH	
1N8-b		2.5	2.6	2.2	2.4	2.1	COOH	
1N1-b	c,d	2.6	3.3	3.2	-0.2	0.1	NH ₂	
1N1-c	a,b,c,d,e,g	3.1	3.1	3.6	1.6	2.1	bridge between C=O and N-H	
1N6-c	b	3.8	4.4	3.8	1.3	1.1	bridge between C=O and N	
1N6-d		4.4	4.5	4.6	2.6	2.9	bridge between C=O and N-H	
1N2-b	d	4.8	5.4	5.0	1.2	1.4	NH ₂	
1N3-b		5.0	5.0	3.9	1.2	0.8	CH ₂	6
1N3-a	d	5.0	5.0	3.9	1.2	0.8	CH ₂	
1N2-c		5.1	5.2	5.0	4.4	4.2	bridge between C=O and N-H	
1N3-c		5.1	5.0	3.8	1.2	0.8	CH ₂	
1N3-d	b,d	5.4	5.8	4.0	2.9	2.0	bridge between O-H and N-H	
1N2-d	d	5.5	5.5	6.2	2.4	3.2	CH ₂	21
1N2-e		5.5	5.6	6.3	2.3	3.2	CH ₂	
1N8-c		5.8	6.4	6.0	2.0	2.2	NH ₂	
1N1-d	c,d,g	5.9	6.1	6.4	2.5	3.1	CH ₂	
1N8-d		6.0	6.0	6.5	3.5	4.1	CH ₂	
1N3-e	b,d	6.3	6.1	5.5	0.7	1.0	C=O only	
1N3-f	a	6.3	6.2	5.5	0.6	1.0	C=O only	64
1N3-g		6.4	6.3	5.9	0.3	0.9	C=O only	67
1N3-h		6.6	6.9	5.8	1.8	1.9	NH ₂	
1N2-f	d	7.0	7.2	6.8	4.0	4.1	bridge between O-H and N-H	
1N4-a		7.1	7.7	7.3	1.1	1.5	OH	33
1N6-e		7.1	7.4	8.0	3.7	4.8	NH ₂	

a. Ref. 39 b. Ref. 35 c. Ref. 40 d. Ref. 41 e. Ref. 37 f. Ref. 38 g. Ref. 44

h. Ref. 43 i. Ref. 36 *Related C_s structure.

TABLE 1: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)	water interaction	imaginary frequencies
1N8-e		7.2	7.4	7.0	4.6	4.6	bridge between O-H and N-H	
1N6-f		7.4	7.6	7.9	3.8	4.5	CH ₂	
1N8-f		7.9	8.1	8.6	4.5	5.5	NH ₂	
1N7-a		8.8	9.4	8.7	3.1	3.3	OH	
1N5-a		9.1	10.0	9.1	3.3	3.4	bridge between O-H and N-H	14
1N4-b		9.2	9.7	8.9	2.8	3.0	NH ₂	
1N4-c		9.4	9.3	9.0	4.1	4.5	bridge between C=O and N-H	
1N7-b	b,d	10.3	7.1	4.7	2.7	1.4	bridge between O-H and N	
1N4-e		11.0	10.9	11.5	2.9	4.3	C=O only	
1N4-d		11.0	10.9	11.4	3.2	4.6	C=O only	
1N7-c		11.1	11.2	10.6	5.4	5.6	bridge between C=O and N-H	
1N7-d		11.7	11.2	10.6	5.5	5.7	bridge between C=O and N-H	
1N7-e		12.8	12.7	13.1	4.9	6.2	C=O only	
1N7-f		12.9	12.7	12.9	5.4	6.5	C=O only	
1N5-b		12.9	13.4	12.6	3.7	4.5	NH ₂	
1N7-g		13.7	14.0	13.9	6.6	7.6	NH ₂	
1Z-a	b,e,f,h,i	24.2	23.5	15.3	2.4	-3.6	bridge between C=O and N-H	
1Z-b	b	25.9	25.9	16.9	4.9	-2.0	bridge between C=O and N-H	6
1Z-d	b,i	27.2	26.7	17.5	4.8	-2.2	CH ₂	
1Z-c	b,f	27.2	26.7	17.5	4.9	-2.2	CH ₂	
1Z-e	b,e,f,i	28.2	28.0	19.4	4.5	-1.7	COO	

TABLE 2: Structures and relative energies for glycine(H_2O)₂

Structure	Refs	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)	water interaction
2N1-a	a	0.0	0.0	0.0	0.0	0.0	water ring on COOH
2N1-b		0.5	0.4	0.6	0.3	0.6	water ring on COOH
2N2-a	a	1.4	1.3	1.1	1.3	1.1	water ring on COOH
2N6-a		1.5	1.5	1.2	1.6	1.3	water ring on COOH
2N6-b		1.6	1.6	1.3	1.7	1.4	water ring on COOH
2N2-b		1.9	1.7	1.7	1.5	1.6	water ring on COOH
2N6-c		1.9	1.8	1.7	1.8	1.8	water ring on COOH
2N8-a		2.3	2.3	2.0	2.4	2.1	water ring on COOH
2N8-b		2.7	2.6	2.5	2.6	2.6	water ring on COOH
2N8-c		3.0	2.4	2.0	2.4	2.1	water ring on COOH
2N1-c	b	4.2	4.5	4.8	1.9	2.4	COOH, NH ₂
2N1-d		4.2	4.4	5.3	1.9	3.1	two water chain on COOH
2N8-d		4.6	5.7	3.7	4.8	3.4	two water bridge between N and OH
2N1-e	a	5.0	4.8	5.6	3.6	4.2	COOH, bridge
2N3-a	a	5.1	5.2	3.6	4.5	3.4	two water bridge between NH and C=O
2N3-b		5.1	5.1	3.6	4.3	3.3	two water bridge between NH and C=O
2N1-f	b,c	5.1	4.8	5.5	3.6	4.2	COOH, bridge
2N6-d		5.2	6.3	4.3	5.9	4.5	two water bridge between N and OH
2N6-e	a	5.3	5.6	5.4	3.2	3.1	COOH, NH ₂
2N1-g		5.3	5.3	6.1	3.6	4.4	two water bridge between NH and C=O
2N1-h		5.3	5.7	5.2	4.1	4.1	water ring on NH ₂
2N1-i		5.4	5.9	5.6	3.0	3.2	two water chain on NH ₂
2N1-j		5.4	5.8	5.2	4.2	4.2	water ring on NH ₂
2N1-k		5.5	5.3	6.0	4.1	4.7	two water bridge between NH and C=O
2N6-f		5.5	5.7	5.6	3.3	3.3	COOH, NH ₂

a. Ref. 35 b. Ref. 41 c. Ref. 37

TABLE 2: (continued)

EFP1/HF and									
Structure	Refs	RHF/6-31++G(d,p)	Full RHF/6-31++G(d,p)	MP2//RHF/6-31++G(d,p)	PCM+RHF//RHF/6-31++G(d,p)	PCM+MP2//RHF/6-31++G(d,p)	water interaction		
2N6-g		5.7	5.9	6.5	3.7	4.5	two water chain on COOH		
2N8-e		5.7	6.4	4.6	4.3	3.4	two water bridge between N and OH		
2N6-h		5.7	6.5	5.5	4.4	3.8	single water bridge plus dangling water		
2N2-c		5.8	5.9	6.5	3.3	4.3	two water chain on COOH		
2N6-i		6.0	6.1	6.7	3.7	4.7	two water chain on COOH		
2N6-j		6.2	6.0	6.4	4.7	5.0	COOH, bridge		
2N6-k		6.3	6.7	6.4	5.4	5.4	water ring on NH ₂		
2N1-l		6.4	6.3	7.5	3.0	4.3	two water chain on COOH		
2N6-l		6.5	6.6	6.1	4.8	4.8	water ring on NH ₂		
2N2-d	a	6.6	6.6	7.0	5.5	5.7	two water bridge between NH and C=O		
2N6-m		6.7	7.5	7.3	5.1	5.3	two water bridge between N and C=O		
2N8-f		6.7	7.1	6.7	4.1	4.0	COOH, NH ₂		
2N7-a		6.8	7.7	4.4	5.4	3.1	two water bridge between N and OH		
2N3-c		6.9	6.7	5.9	3.9	3.6	two water chain on CH ₂		
2N8-g		7.0	7.2	7.0	4.2	4.3	COOH, NH ₂		
2N2-e		7.0	6.7	7.6	4.3	5.2	COOH, CH ₂		
2N1-m		7.0	6.9	7.5	4.3	5.0	COOH, CH ₂		
2N6-n		7.0	7.0	7.4	4.8	5.6	two water bridge between NH and C=O		
2N2-f		7.0	6.7	7.6	4.4	5.1	COOH, CH ₂		
2N1-n	b	7.1	7.3	8.0	3.5	4.4	bridge, NH ₂		
2N6-o		7.1	6.6	7.1	5.0	5.5	COOH, bridge		
2N2-g		7.1	6.8	6.7	6.6	6.4	COOH, bridge		
2N2-h		7.2	7.5	6.8	5.4	5.3	water ring on NH ₂		
2N1-o		7.2	7.0	7.6	4.6	5.3	COOH, CH ₂		
2N2-i		7.3	7.6	7.0	5.2	5.3	water ring on NH ₂		
2N6-p		7.5	8.0	8.3	4.4	4.7	two water bridge between N and C=O		
2N6-q		7.5	8.0	8.2	4.5	4.8	two water bridge between N and C=O		

TABLE 2: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)	water interaction
2N8-h		7.6	7.4	8.1	5.6	6.2	COOH, CH ₂
2N8-i		7.7	7.4	8.1	5.6	6.2	COOH, CH ₂
2N8-j		7.8	8.0	7.3	6.1	6.0	water ring on NH ₂
2N6-r		7.8	7.7	8.6	4.8	5.8	two water chain on COOH
2N6-s		7.9	7.7	8.6	4.6	5.7	two water chain on COOH
2N8-k		7.9	8.1	7.5	6.0	5.9	water ring on NH ₂
2N6-t		8.0	7.8	8.7	4.8	5.8	two water chain on COOH
2N8-l		8.0	8.9	7.8	5.5	4.9	two water bridge between N and C=O
2N2-j		8.1	7.8	7.8	5.9	6.1	COOH, bridge
2N2-k		8.1	7.7	7.7	5.9	6.1	COOH, bridge
2N8-m		8.3	8.1	8.0	6.8	6.6	COOH, bridge
2N6-u		8.4	8.3	8.2	5.0	5.0	bridge, bridge
2N8-n		8.4	8.3	8.2	6.7	6.8	COOH, bridge
2N6-v		8.5	8.3	8.8	5.8	6.5	COOH, CH ₂
2N8-o		8.5	8.3	7.6	6.1	5.6	two water bridge between N and OH
2N6-w		8.5	8.4	8.9	5.9	6.5	COOH, CH ₂
2N8-p		8.5	9.0	8.5	6.2	6.3	water ring on NH ₂
2N2-l		8.6	8.5	9.2	6.2	7.0	COOH, NH ₂
2N1-p		8.6	8.8	8.5	5.8	5.7	two water bridge between NH and OH
2N8-q		8.6	9.1	8.8	5.3	5.2	two water bridge between N and C=O
2N8-r		8.6	8.5	9.5	6.3	7.1	two water chain on CH ₂
2N8-s		8.6	8.5	9.5	6.4	7.2	two water chain on CH ₂
2N7-b	a	8.8	9.4	7.0	7.4	5.7	bridge, bridge
2N1-q		8.9	8.6	10.0	4.6	6.2	single water bridge plus dangling water
2N1-r		8.9	9.8	10.8	3.3	5.0	two water chain on NH ₂
2N1-s		9.0	9.4	10.8	4.4	6.1	two water bridge between NH and C=O
2N8-t		9.0	8.9	10.0	6.5	7.4	two water chain on CH ₂

TABLE 2: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)	water interaction
2N1-t	9.0	9.4	9.2	6.0	6.0	6.0	two water bridge between NH and OH
2N4-a	9.0	8.9	8.6	5.5	5.7	5.7	water ring on OH
2N3-d	9.1	8.9	8.1	4.8	5.2	5.2	water ring on OH
2N5-a	9.1	9.3	6.9	6.3	4.7	4.7	two water bridge between N and OH
2N1-u	9.2	10.0	11.0	4.3	5.8	5.8	water ring on NH ₂
2N8-u	9.5	9.4	8.9	6.7	7.0	7.0	two water bridge between NH and OH
2N8-v	9.5	9.3	10.3	6.9	8.0	8.0	COOH, NH ₂
2N1-v	9.6	9.8	10.4	5.8	6.6	6.6	two water chain on CH ₂
2N7-c	9.6	8.8	8.1	4.8	5.0	5.0	water ring on OH
2N4-b	9.6	9.7	8.6	6.4	6.2	6.2	two water bridge between N and OH
2N8-w	9.7	9.5	10.4	7.0	8.0	8.0	COOH, NH ₂
2N1-w	10.0	10.6	11.1	5.0	6.0	6.0	NH ₂ , CH ₂
2N2-m	10.1	10.4	11.2	5.2	6.3	6.3	NH ₂ , CH ₂
2N5-b	10.3	10.4	9.3	7.9	7.0	7.0	two water bridge between NH and OH
2N2-n	10.4	10.5	11.8	4.6	6.2	6.2	NH ₂ , CH ₂
2N8-x	10.5	10.8	11.1	6.1	6.7	6.7	NH ₂ , CH ₂
2N3-e	10.5	10.2	9.9	6.3	6.3	6.3	CH ₂ , CH ₂
2N3-f	10.6	9.9	10.4	4.0	5.1	5.1	C=O, CH ₂
2N2-o	10.6	10.9	10.9	6.7	7.2	7.2	two water bridge between NH and OH
2N7-d	10.6	10.7	9.9	7.3	7.3	7.3	water ring on OH
2N5-c	10.7	10.9	9.8	7.8	7.3	7.3	two water bridge between NH and OH
2N8-y	10.7	11.2	11.5	5.9	6.5	6.5	NH ₂ , CH ₂
2N4-c	10.8	10.6	10.0	8.8	8.5	8.5	two water bridge between OH and C=O
2N2-p	10.8	11.3	12.1	6.3	7.4	7.4	two water bridge between NH and C=O
2N7-e	10.8	10.8	10.2	7.4	7.4	7.4	water ring on OH
2N5-d	10.9	10.9	9.7	8.6	7.9	7.9	two water bridge between NH and C=O
2N4-d	10.9	10.8	10.4	7.2	7.0	7.0	two water bridge between NH and C=O

TABLE 2: (continued)

Structure	Refs	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)	water interaction
2N6-x		10.9	10.9	11.3	7.0	7.6	two water chain on CH ₂
2N8-z		10.9	11.1	11.1	7.4	7.9	two water bridge between NH and OH
2N4-e		11.1	10.9	10.5	7.3	7.1	two water bridge between NH and C=O
2N4-f		11.2	11.2	11.6	4.8	5.7	bridge, CH ₂
2N3-g		11.7	11.5	11.8	5.0	6.1	OH, CH ₂
2N6-y		11.7	11.7	13.4	6.3	8.5	two water chain on NH ₂
2N4-g		12.0	12.1	12.9	4.4	5.9	C=O, OH
2N2-q		12.1	11.9	11.8	8.9	9.0	bridge, bridge
2N7-f		12.8	13.0	13.1	6.2	7.0	bridge, CH ₂
2N7-g		13.1	12.8	12.2	10.8	10.5	two water bridge between OH and C=O
2N8-aa		13.2	13.0	13.7	7.3	8.6	single water bridge plus dangling water
2N7-h		13.6	13.5	13.4	7.4	8.0	two water bridge between NH and C=O
2N7-i		13.6	14.6	13.7	8.4	8.3	two water bridge between N and C=O
2N7-j		13.7	13.4	13.2	7.3	7.9	two water bridge between NH and C=O
2N5-e		13.7	14.1	14.5	6.5	7.5	bridge, CH ₂
2N7-k		13.8	13.9	14.4	6.3	7.6	C=O, OH
2N7-l		13.8	13.9	14.8	5.7	7.3	C=O, OH
2N5-f		14.0	14.3	15.1	6.1	7.6	C=O, bridge
2N5-g		14.1	14.4	14.8	6.7	7.9	C=O, bridge
2N7-m		14.2	13.9	13.5	9.0	9.0	single water bridge plus dangling water
2N7-n		14.9	15.3	14.1	7.1	6.7	two water bridge between N and C=O
2N4-h		15.5	15.6	16.1	6.3	8.1	two water chain on NH ₂
2N7-o		16.2	16.7	17.4	7.7	9.2	NH ₂ , CH ₂
2N5-h		19.0	18.7	20.0	7.8	9.9	C=O, NH ₂
2N7-p		19.2	19.0	20.6	9.6	11.9	C=O, NH ₂
2N7-q		19.3	19.0	20.4	10.0	12.1	C=O, NH ₂

TABLE 2: (continued)

Structure	Refs	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)	water interaction
2Z-a	a,b	20.2	19.8	10.8	2.4	-4.7	two water bridge between NH and C=O
2Z-b		20.6	20.6	11.3	3.0	-4.4	two water bridge between NH and C=O
2Z-c		20.9	20.6	11.4	3.4	-3.9	two water bridge between NH and C=O
2Z-e		21.3	19.7	11.4	2.8	-3.7	bridge, bridge
2Z-d	a	21.3	19.7	11.4	2.7	-3.7	bridge, bridge
2Z-f		23.3	21.9	12.5	5.9	-1.8	bridge, bridge
2Z-g		25.4	24.5	17.6	3.8	-1.2	bridge, NH ₂
2Z-h		26.0	24.6	17.6	3.8	-1.2	bridge, NH ₂
2Z-i		27.2	27.0	19.2	3.9	0.5	bridge, NH ₂
2Z-j		29.3	29.0	20.9	7.3	1.2	water ring on C=O
2Z-k		29.7	28.7	21.2	6.5	0.9	C=O, CH ₂

TABLE 3: Structures and relative energies for glycine(H_2O)₃

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N1-a	c	0.0	0.0	0.0	0.0	0.0
3N1-b		0.4	1.3	1.0	1.9	1.6
3N6-a		1.1	2.9	0.2	2.3	0.1
3N6-b		1.3	2.6	0.1	3.2	1.0
3N8-a		1.3	3.1	0.3	2.0	-0.1
3N6-c		1.3	2.7	0.1	3.2	1.0
3N6-d		1.4	2.9	0.9	3.7	2.0
3N6-e		1.5	3.2	0.5	2.9	0.8
3N2-a		1.5	2.4	1.9	3.0	2.5
3N8-b		1.7	3.5	0.5	3.2	0.7
3N6-f		1.8	2.7	2.1	3.4	2.9
3N1-c		1.9	2.7	2.4	0.5	0.3
3N8-c		2.0	3.7	0.7	3.2	0.8
3N1-d		2.3	3.0	2.3	2.6	1.7
3N6-g		2.4	1.4	1.0	1.5	1.2
3N1-e		2.4	3.1	3.0	0.7	0.8
3N8-d		2.4	2.4	2.0	2.4	2.1
3N1-f		2.4	3.0	3.3	0.9	1.4
3N1-g		2.5	3.2	2.8	2.9	2.6
3N8-e		2.6	3.5	2.8	4.2	3.6
3N2-b	c	2.8	1.2	1.0	1.1	1.0
3N1-h		2.8	3.3	3.7	1.0	1.5
3N6-h		2.8	4.3	3.3	4.9	3.9
3N1-i		2.9	3.3	3.6	1.0	1.5
3N6-i		3.2	3.6	3.2	4.2	3.9
3N1-j		3.3	3.5	3.5	2.4	2.1
3N1-k		3.3	4.4	2.8	3.1	2.0
3N8-f		3.3	4.8	2.3	5.0	2.9
3N1-l		3.3	4.1	3.3	1.7	1.4
3N6-j		3.4	4.0	2.9	4.0	2.8
3N2-c		3.4	4.2	3.5	1.7	1.3
3N1-m		3.4	4.1	4.5	2.1	2.4
3N1-n		3.5	3.3	3.2	2.4	2.1
3N6-k		3.5	3.8	3.0	1.8	1.0
3N1-o		3.5	4.1	3.5	1.5	1.5
3N1-p		3.6	4.2	3.5	4.0	3.1
3N8-g		3.6	5.1	4.1	5.9	4.9
3N8-h		3.7	5.0	2.6	5.1	3.2
3N1-q		3.7	4.2	4.6	1.4	1.8
3N1-r		3.7	5.3	5.5	2.9	3.2
3N3-a		3.8	4.0	2.0	3.7	2.2
3N3-b		3.8	4.1	2.2	3.7	2.3
3N1-s		3.9	4.8	3.4	3.4	2.5

a. Lowest energy structure in Ref. 41 b. Ref. 42 c. Ref. 25

TABLE 3: (continued)

Structure	Refs.	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N4-a		3.9	4.7	2.0	1.8	0.0
3N1-t		4.0	4.2	4.3	4.0	4.3
3N8-i		4.0	5.2	2.9	5.6	3.6
3N2-d		4.1	4.8	4.1	4.1	3.7
3N1-u		4.1	4.2	4.3	4.1	4.4
3N6-l		4.1	4.9	4.1	4.6	4.1
3N6-m		4.1	4.5	4.3	3.2	3.1
3N6-n		4.1	4.9	3.2	4.3	3.0
3N2-e		4.2	4.4	4.4	2.1	2.4
3N7-a		4.2	5.6	1.8	3.3	0.4
3N6-o		4.2	5.2	3.9	4.1	3.2
3N3-c		4.2	4.5	2.5	3.9	2.5
3N3-d		4.2	4.5	2.5	4.0	2.6
3N3-e		4.3	3.9	2.1	3.6	2.2
3N3-f		4.3	4.5	2.8	3.6	2.4
3N8-j		4.3	2.2	1.8	2.3	2.0
3N1-v		4.3	4.7	5.5	1.6	2.4
3N6-p		4.3	5.9	4.8	5.1	4.2
3N6-q		4.3	5.2	3.7	4.2	3.2
3N2-f		4.4	4.8	4.8	2.4	2.7
3N6-r		4.4	6.0	4.8	5.3	4.3
3N1-w		4.6	5.1	4.4	4.8	4.2
3N6-s		4.6	5.0	4.9	2.7	2.9
3N1-x		4.6	5.0	5.0	2.8	2.8
3N8-k		4.6	6.0	3.5	6.8	4.8
3N6-t		4.6	5.7	4.5	4.5	3.6
3N1-y		4.6	6.1	4.2	4.6	3.2
3N2-g	c	4.6	5.5	4.7	5.1	4.1
3N1-aa		4.7	5.4	5.5	4.6	4.5
3N1-z		4.7	5.0	4.9	3.2	3.0
3N2-h		4.7	5.4	5.5	3.2	3.4
3N6-u		4.7	5.5	5.5	3.5	3.7
3N6-v		4.8	6.0	4.5	4.7	3.7
3N6-w		4.8	5.0	4.7	3.9	3.4
3N3-g		4.9	5.6	2.9	5.4	3.2
3N2-i		4.9	5.5	5.0	4.4	3.9
3N6-x		4.9	5.7	4.7	3.5	3.0
3N6-y		4.9	6.1	4.7	4.4	3.5
3N8-l		4.9	5.7	4.9	5.3	4.8
3N2-j		5.0	5.6	4.7	5.6	4.6
3N6-z		5.1	1.6	1.3	1.5	1.3
3N2-k		5.1	6.2	4.4	4.3	3.2
3N2-l		5.1	5.6	5.9	2.5	2.9
3N2-m		5.1	5.5	4.8	5.2	4.3
3N2-n		5.2	5.8	5.9	2.8	3.0

TABLE 3: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N6-aa		5.2	5.6	5.9	2.9	3.2
3N2-o		5.2	5.2	4.5	5.3	4.3
3N6-ab		5.2	6.8	5.3	4.1	3.3
3N8-m		5.2	6.3	4.8	4.1	2.8
3N6-ac		5.2	5.7	5.9	2.9	3.2
3N6-ad		5.3	6.0	3.5	6.8	4.6
3N2-p		5.3	5.5	4.8	4.4	3.7
3N1-ab		5.3	5.7	6.0	4.2	4.3
3N1-ac		5.4	5.7	6.1	4.2	4.3
3N6-ae		5.4	5.0	3.6	3.6	2.7
3N8-n		5.4	5.5	5.5	3.3	3.5
3N1-ad		5.4	5.8	5.2	5.2	4.5
3N2-q		5.5	6.3	4.8	4.4	3.5
3N1-ae		5.5	5.6	6.2	4.4	4.9
3N3-h	b,c	5.5	6.5	3.9	6.7	4.3
3N6-af		5.5	6.3	5.0	5.3	4.0
3N8-o		5.5	6.2	6.3	4.3	4.4
3N3-i		5.5	6.8	3.9	6.9	4.5
3N2-r		5.5	6.3	5.1	3.3	2.8
3N1-af		5.5	5.7	6.1	4.4	4.6
3N2-s		5.6	6.3	4.8	4.4	3.5
3N1-ag		5.6	5.9	6.3	4.6	4.8
3N1-ah		5.6	5.7	5.9	4.6	4.7
3N6-ag		5.6	5.7	5.5	5.8	5.8
3N1-ai		5.6	5.9	5.4	5.1	4.5
3N6-ah		5.7	5.8	5.6	5.7	5.8
3N8-p		5.7	6.0	5.9	4.1	3.9
3N1-aj		5.7	6.9	6.0	5.0	4.6
3N6-ai		5.7	6.0	5.2	5.4	4.8
3N6-aj		5.7	7.0	5.9	5.1	4.1
3N7-b		5.7	6.9	3.2	7.3	4.0
3N6-ak		5.8	6.4	5.7	5.8	5.3
3N6-al		5.8	6.9	6.1	5.3	4.8
3N6-am		5.8	6.8	6.2	5.3	4.9
3N6-an		5.8	6.1	5.3	5.6	5.0
3N8-q		5.8	6.2	5.5	5.2	4.5
3N2-t		5.8	5.7	5.4	5.3	5.4
3N2-u		5.8	6.2	6.1	5.1	4.9
3N6-ao		5.8	6.6	6.8	5.5	5.9
3N6-ap		5.9	6.2	6.1	4.2	4.1
3N6-aq		5.9	6.5	5.8	5.9	5.4
3N2-v		5.9	5.8	5.2	4.4	3.8
3N8-r		5.9	6.4	6.6	3.6	3.9
3N8-s		5.9	6.7	5.0	4.8	3.8
3N2-w		5.9	6.3	5.4	5.8	4.9

TABLE 3: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N6-ar		5.9	6.1	5.1	5.7	5.0
3N1-ak		5.9	6.9	6.4	6.5	6.0
3N6-as		5.9	6.9	6.3	5.3	4.9
3N8-t		6.0	6.5	6.7	3.6	3.9
3N6-at		6.0	6.2	5.4	5.8	5.3
3N6-au		6.0	6.3	6.2	4.4	4.3
3N8-u		6.1	8.2	5.5	6.9	4.9
3N3-j		6.1	7.3	4.4	7.0	4.8
3N6-av		6.1	7.2	6.4	5.2	4.5
3N6-aw		6.1	5.8	5.6	5.8	5.8
3N8-v		6.2	5.2	3.9	4.1	3.3
3N5-a		6.2	7.2	3.6	4.1	1.6
3N2-x		6.2	6.5	6.2	6.1	5.4
3N2-y		6.2	6.6	5.6	6.0	5.3
3N1-al		6.2	6.8	6.7	6.0	6.2
3N8-w		6.2	7.4	5.0	7.0	4.9
3N1-am		6.2	7.7	6.5	5.9	5.3
3N1-an		6.2	7.8	6.9	5.0	4.6
3N4-b		6.3	6.6	4.9	5.4	4.0
3N1-ao		6.3	6.6	6.9	5.5	5.9
3N4-c		6.3	6.3	4.9	3.5	2.8
3N2-z		6.4	6.8	7.3	5.4	5.9
3N8-x		6.5	6.7	5.1	5.1	4.1
3N1-ap		6.5	7.1	7.5	5.8	6.4
3N8-y		6.5	6.6	6.3	6.4	6.4
3N8-z		6.5	6.1	5.4	5.2	4.5
3N8-aa		6.5	6.7	6.4	6.4	6.4
3N2-aa		6.5	6.9	7.0	5.5	5.5
3N6-ax		6.6	7.7	7.1	6.3	6.2
3N1-aq		6.6	7.2	7.5	4.1	4.3
3N8-ab		6.6	7.9	5.0	7.6	5.4
3N2-ab		6.6	7.2	6.5	7.2	6.2
3N1-ar	a	6.6	7.1	7.3	4.1	4.2
3N2-ac		6.7	7.8	6.7	6.7	5.7
3N1-as		6.7	6.9	8.0	3.8	4.9
3N8-ac		6.7	7.9	6.3	5.6	4.3
3N6-ay		6.8	8.2	7.0	6.9	6.1
3N8-ad		6.8	8.3	6.8	7.3	6.1
3N8-ae		6.9	7.3	6.4	6.7	6.1
3N3-k		6.9	7.9	5.8	6.3	4.7
3N1-at		6.9	7.8	8.9	5.8	6.8
3N8-af		6.9	7.3	6.3	6.5	5.9
3N8-ag		6.9	7.3	6.3	6.7	6.1
3N5-b		6.9	7.5	5.3	6.6	5.0
3N8-ah		7.0	7.5	6.6	7.3	6.4

TABLE 3: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N1-au		7.0	7.9	8.5	5.9	6.6
3N7-c		7.1	8.2	5.6	6.5	4.5
3N8-ai		7.1	8.1	6.7	6.0	4.8
3N8-aj		7.1	7.4	7.6	6.2	6.4
3N8-ak		7.1	8.1	5.2	7.1	4.8
3N6-az		7.1	9.0	7.3	6.0	4.9
3N1-av		7.1	7.9	8.2	5.2	5.5
3N1-aw		7.2	8.0	7.9	4.9	4.8
3N8-al		7.2	7.5	7.9	5.3	5.8
3N6-ba		7.2	7.7	7.8	6.2	6.5
3N8-am		7.2	7.3	6.4	6.7	6.1
3N1-ax		7.3	8.0	7.8	5.1	5.1
3N8-an		7.3	7.4	7.7	6.5	6.7
3N1-ay		7.3	7.5	7.7	4.1	4.3
3N5-c		7.3	8.1	6.2	6.4	5.1
3N1-az		7.3	7.9	7.7	5.3	5.3
3N2-ad		7.4	8.3	7.4	7.9	7.1
3N7-d		7.4	8.3	4.9	6.8	4.1
3N3-l		7.4	7.4	6.1	4.3	3.9
3N1-ba		7.4	8.6	8.9	6.6	7.0
3N5-d		7.5	8.1	6.0	5.7	4.3
3N8-ao		7.5	8.1	6.7	5.0	4.4
3N1-bb		7.5	7.5	8.3	5.6	6.6
3N6-bb		7.5	8.5	7.4	6.7	5.5
3N8-ap		7.5	8.4	7.5	6.6	6.2
3N3-m		7.5	7.9	6.5	6.5	5.3
3N2-ae		7.5	7.8	8.2	5.7	5.9
3N1-bc		7.5	7.5	8.2	5.6	6.6
3N2-af		7.6	8.4	7.9	6.1	5.7
3N8-aq		7.6	9.1	7.7	5.5	4.7
3N7-e		7.6	8.1	5.9	6.9	5.2
3N6-bc		7.6	8.4	8.3	5.0	5.0
3N2-ag		7.7	8.6	8.9	3.6	4.5
3N7-f		7.7	8.1	6.4	5.6	4.6
3N5-e		7.8	8.4	6.5	6.1	4.8
3N6-bd		7.8	8.3	9.0	5.0	5.9
3N6-be		7.8	8.2	8.1	6.5	6.4
3N7-g		7.9	4.1	2.3	3.6	2.3
3N2-ah		7.9	8.7	8.4	5.8	5.6
3N2-ai		7.9	9.0	8.6	5.9	5.6
3N8-ar		8.0	8.2	8.6	6.5	6.7
3N6-bf		8.0	8.7	9.3	6.7	7.4
3N8-as		8.0	8.3	7.6	6.8	6.6
3N6-bg		8.0	8.2	7.9	5.2	5.0
3N3-n		8.0	9.1	6.3	6.9	4.9

TABLE 3: (continued)

Structure	Refs	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N7-h		8.0	8.0	6.4	5.4	4.5
3N7-i		8.1	8.4	6.9	5.8	5.0
3N8-at		8.1	9.0	8.1	5.7	5.0
3N7-j		8.1	9.8	6.3	8.2	5.6
3N7-k		8.2	8.5	6.6	7.2	5.8
3N8-au		8.2	8.4	8.9	6.5	6.8
3N8-av		8.2	8.4	9.0	6.7	7.0
3N8-aw		8.3	8.5	9.0	6.6	6.9
3N8-ax		8.3	8.5	9.0	6.8	7.2
3N8-ay		8.3	9.6	8.7	6.3	5.6
3N8-az		8.3	8.9	8.8	6.7	6.6
3N1-bd		8.4	8.9	10.0	4.6	5.8
3N1-be		8.4	9.0	8.4	6.0	5.9
3N8-ba		8.4	8.6	7.9	7.0	6.3
3N6-bh		8.4	8.8	8.5	5.3	5.7
3N2-aj		8.4	9.2	9.3	5.0	5.2
3N8-bb		8.4	9.7	9.0	6.3	5.9
3N1-bf		8.5	8.5	9.7	5.2	6.3
3N2-ak		8.5	8.9	10.1	4.4	5.7
3N8-bc		8.5	8.9	8.7	7.3	7.0
3N1-bg		8.6	9.5	8.7	7.4	7.1
3N2-al		8.6	9.2	8.5	7.2	6.4
3N8-bd		8.7	8.9	9.6	6.8	7.4
3N8-be		8.7	8.9	9.4	6.8	7.1
3N6-bi		8.7	9.5	9.3	5.9	6.3
3N2-am		8.7	9.3	9.5	7.3	7.7
3N8-bf		8.7	8.5	9.0	6.8	7.1
3N2-an		8.8	9.3	8.8	7.1	6.7
3N8-bg		8.8	8.8	7.5	5.1	4.1
3N7-l		8.9	10.4	6.6	7.4	4.7
3N1-bh		8.9	10.0	9.5	5.1	5.0
3N2-ao		9.0	9.3	8.8	7.1	6.7
3N8-bh		9.0	9.6	10.5	5.7	6.7
3N2-ap		9.1	9.4	9.1	7.0	6.8
3N6-bj		9.1	8.9	9.2	6.9	7.7
3N8-bi		9.1	9.2	10.2	6.9	7.8
3N8-bj		9.2	9.6	9.5	8.7	8.3
3N3-o		9.2	9.7	8.6	7.0	6.5
3N1-bi		9.2	9.3	10.6	5.4	6.6
3N8-bk		9.2	9.9	9.9	8.4	8.6
3N8-bl		9.2	9.8	10.0	8.1	8.6
3N3-p		9.2	9.6	8.6	6.9	6.4
3N1-bj		9.3	9.5	9.9	4.8	5.6
3N8-bm		9.3	9.7	10.7	5.8	6.9
3N6-bk		9.3	10.2	8.5	7.6	6.5

TABLE 3: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N7-m		9.3	10.3	7.7	6.9	5.1
3N8-bn		9.4	9.5	10.5	7.1	8.0
3N6-bl		9.6	9.8	9.8	7.1	7.3
3N3-q		9.6	10.1	9.4	7.4	6.9
3N8-bo		9.6	10.4	9.7	8.3	8.4
3N3-r		9.6	9.9	8.9	7.2	6.6
3N6-bm		9.6	10.4	11.4	5.9	7.2
3N2-aq		9.6	10.0	10.1	6.2	6.7
3N8-bp		9.7	10.5	11.4	8.3	9.3
3N4-d		9.7	10.7	8.3	6.4	5.1
3N8-bq		9.8	10.4	9.2	9.6	8.5
3N3-s		9.8	9.6	8.8	5.2	5.4
3N6-bn		9.9	10.1	10.5	7.2	7.7
3N6-bo		9.9	11.7	9.8	9.0	7.9
3N6-bp		10.0	10.6	10.5	6.8	7.1
3N2-ar		10.2	11.2	11.9	8.1	8.5
3N8-br		10.2	10.5	10.1	8.4	8.1
3N1-bk		10.3	10.2	10.9	6.7	7.9
3N2-as		10.3	10.6	11.3	6.7	7.5
3N6-bq		10.3	10.5	11.5	6.3	7.3
3N6-br		10.3	10.5	11.4	6.6	7.5
3N2-at		10.4	8.9	8.7	5.9	5.7
3N8-bs		10.4	11.4	11.1	4.8	4.9
3N6-bs		10.5	11.1	10.9	8.3	8.7
3N4-e		10.5	11.1	11.1	5.4	5.8
3N8-bt		10.5	11.2	11.2	7.0	7.2
3N4-f		10.7	11.4	10.7	5.9	6.0
3N4-g		10.8	10.7	9.6	8.5	7.9
3N8-bu		10.8	11.4	11.3	8.0	8.3
3N3-t		10.9	10.8	10.5	6.7	7.1
3N4-h		10.9	11.0	10.9	7.4	7.7
3N4-i		11.0	10.9	10.8	7.3	7.6
3N6-bt		11.0	11.5	11.8	8.4	9.3
3N7-n		11.2	12.2	10.1	6.9	6.0
3N8-bv		11.2	11.5	12.0	7.8	8.5
3N2-au		11.3	11.5	11.6	6.5	7.0
3N4-j		11.3	12.0	11.3	6.9	7.2
3N6-bu		11.4	12.1	12.3	8.7	9.0
3N8-bw		11.4	11.5	12.0	8.4	8.8
3N8-bx		11.4	11.5	11.9	8.5	8.7
3N8-by		11.4	11.5	11.9	5.2	8.7
3N2-av		11.5	11.6	12.2	7.4	8.0
3N8-bz		11.6	12.8	11.2	8.5	7.4
3N7-o		11.6	12.7	10.2	8.4	6.8
3N7-p		11.7	12.7	10.6	7.2	6.2

TABLE 3: (continued)

Structure	Refs	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3N7-q		11.7	12.8	9.9	9.9	7.9
3N5-f		11.7	11.9	10.2	8.0	7.0
3N6-bv		11.8	12.2	11.8	7.8	8.0
3N8-ca		11.8	12.1	12.4	8.3	9.0
3N5-g		11.9	12.8	12.1	7.7	8.0
3N8-cb		11.9	11.4	11.0	8.6	8.5
3N6-bw		11.9	11.7	12.4	7.9	9.3
3N5-h		12.0	13.3	12.2	8.1	8.0
3N2-aw		12.1	13.0	12.3	7.1	7.1
3N7-r		12.1	13.3	11.2	7.2	6.2
3N4-k		12.1	12.4	12.1	7.7	8.1
3N4-l		12.2	13.2	11.9	10.1	9.0
3N7-s		12.4	14.0	13.2	7.3	7.3
3N7-t		12.4	12.7	12.1	8.7	8.7
3N5-i		12.5	13.7	11.3	11.1	9.5
3N8-cc		12.5	13.5	13.6	8.7	8.8
3N7-u		12.5	13.1	12.9	7.9	8.5
3N7-v		12.6	13.3	11.9	6.9	6.6
3N7-w		12.7	13.8	13.1	7.4	7.6
3N5-j		12.7	13.0	12.7	8.7	8.9
3N7-x		12.7	13.7	12.7	9.8	9.7
3N3-u		12.8	13.5	11.7	9.0	8.3
3N5-k		12.9	13.9	12.4	7.7	7.3
3N5-l		13.0	14.1	13.0	9.8	9.2
3N7-y		13.0	13.5	13.4	6.5	7.2
3N4-m		13.0	14.0	13.3	8.1	8.3
3N7-z		13.0	13.6	13.7	6.6	7.4
3N7-aa		13.1	14.7	13.5	6.9	6.9
3N4-n		13.2	14.1	12.7	8.7	8.2
3N6-bx		13.2	13.7	14.8	7.5	9.1
3N5-m		13.2	13.9	12.6	10.5	9.9
3N4-o		13.4	13.0	12.6	10.7	10.4
3N7-ab		13.5	13.7	12.7	8.3	8.2
3N7-ac		13.8	14.1	13.9	7.9	8.2
3N7-ad		15.7	16.0	16.5	7.9	8.9
3N7-ae		17.9	18.0	18.1	13.5	14.1
3N7-af		18.5	18.9	20.1	9.2	11.2
3Z-a	b,c	14.7	15.6	5.2	1.9	-6.9
3Z-b		15.7	17.2	6.8	3.4	-5.3
3Z-c		15.8	15.9	6.1	1.7	-6.4
3Z-d		16.3	15.5	6.0	1.2	-6.6
3Z-e		16.3	16.6	7.1	3.7	-4.5
3Z-f		16.4	15.5	6.0	1.5	-6.4
3Z-g		16.5	16.3	6.0	2.4	-6.2
3Z-h		16.6	16.7	7.4	3.7	-4.2

TABLE 3: (continued)

Structure	Refs	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
3Z-i		17.0	17.4	7.4	3.3	-4.8
3Z-j		17.2	16.3	7.1	1.2	-6.2
3Z-k		17.4	17.7	8.1	1.8	-5.9
3Z-l		19.1	18.6	10.0	2.3	-4.8
3Z-m		19.5	19.5	11.2	2.2	-4.2
3Z-n		19.5	19.6	10.2	4.1	-3.5
3Z-o		19.6	19.2	10.6	3.4	-3.2
3Z-p		19.6	19.6	11.3	2.2	-4.1
3Z-q		19.7	17.0	7.1	1.9	-5.9
3Z-r		20.0	20.3	11.6	2.7	-4.1
3Z-s		20.0	19.1	9.8	7.0	-0.9
3Z-t		22.2	21.6	12.3	6.1	-1.6
3Z-u		22.7	21.5	12.4	6.0	-1.6
3Z-v		23.0	22.0	14.6	4.5	-1.4
3Z-w		23.6	22.5	15.8	3.7	-1.3
3Z-x		25.0	24.2	17.3	5.7	0.3

TABLE 4: Structures and relative energies for glycine(H₂O)₄

Structure	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
4N1-a	0.0	0.0	0.0	0.0	0.0
4N1-b	0.3	0.4	0.5	0.0	0.1
4N1-c	0.7	1.0	0.8	0.4	0.3
4N1-d	0.9	0.3	0.4	0.3	0.5
4N1-e	1.2	1.4	1.3	0.5	0.5
4N1-f	1.5	1.0	1.2	0.4	0.7
4N1-g	1.6	1.8	1.8	2.6	2.7
4N1-h	1.7	1.6	1.2	2.1	1.7
4N1-i	1.7	1.4	1.1	0.7	0.5
4N1-j	1.8	2.4	2.3	2.1	1.8
4N1-k	1.8	1.4	2.1	1.4	2.1
4N1-l	1.9	1.4	2.3	1.4	2.3
4N1-m	2.0	1.8	1.6	0.7	0.7
4N1-n	2.1	2.1	2.0	0.9	1.1
4N1-o	2.2	2.3	2.3	2.1	2.0
4N1-p	2.2	2.8	2.7	2.5	2.3
4N1-q	2.2	1.9	2.1	1.0	1.3
4N1-r	2.2	2.1	2.2	0.9	1.2
4N1-s	2.3	0.9	2.3	0.3	1.8
4N1-t	2.3	1.7	2.7	1.6	2.6
4N1-u	2.4	2.2	2.4	1.0	1.3
4N1-v	2.4	2.1	2.4	1.2	1.5
4N1-w	2.4	2.2	2.3	1.1	1.4
4N1-x	2.7	2.5	2.8	1.5	1.7
4N1-y	2.9	3.5	2.8	4.2	3.3
4N1-z	2.9	2.8	2.4	1.2	1.1
4N6-a	0.3	0.8	-1.0	0.4	-1.0
4Z-a	12.1	11.7	1.6	1.2	-7.7
4Z-b	12.2	13.4	2.7	1.9	-7.4
4Z-c	12.3	13.3	3.0	0.9	-7.8
4Z-d	12.3	13.1	2.6	0.9	-8.0
4Z-e	12.5	13.6	3.2	1.2	-7.5
4Z-f	12.8	14.9	3.2	4.9	-5.3
4Z-g	13.1	13.2	3.9	0.2	-7.6
4Z-h	13.3	13.1	3.1	1.0	-7.4
4Z-i	13.5	12.0	2.9	0.6	-7.1
4Z-j	13.5	14.0	3.6	1.8	-7.0
4Z-k	13.6	13.3	3.3	2.8	-5.8
4Z-l	13.6	14.8	4.8	3.2	-5.3
4Z-m	13.7	14.6	4.8	1.8	-6.2
4Z-n	13.7	12.5	3.4	-0.5	-8.0
4Z-o	13.7	13.0	3.3	1.6	-6.7
4Z-p	13.8	14.5	4.2	2.1	-6.4
4Z-q	13.9	12.8	3.2	1.5	-6.6
4Z-r	14.0	13.0	3.4	0.1	-7.9

TABLE 4: (continued)

Structure	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
4Z-s	14.1	14.1	4.9	0.9	-6.6
4Z-t	14.1	13.7	4.8	2.3	-5.3
4Z-u	14.1	14.5	4.8	1.6	-6.5
4Z-v	14.2	12.9	3.9	-0.5	-7.8
4Z-w	14.3	13.4	3.7	1.4	-6.7
4Z-x	14.5	12.9	4.0	2.7	-4.7
4Z-y	14.6	14.9	4.9	1.9	-6.4
4Z-z	14.6	13.7	5.0	1.6	-5.8
4Z-aa	14.6	13.7	4.5	-0.2	-7.5
4Z-ab	14.6	14.0	5.2	2.4	-5.1
4Z-ac	14.6	13.9	4.6	0.2	-7.4
4Z-ad	14.6	14.2	4.8	3.3	-4.7
4Z-ae	14.7	13.9	4.2	1.6	-6.4
4Z-af	14.7	14.7	4.3	3.8	-5.0
4Z-ag	14.7	13.1	4.6	3.0	-4.2
4Z-ah	14.8	15.0	5.5	0.9	-6.8
4Z-ai	14.8	14.2	4.8	0.6	-7.2
4Z-aj	14.9	15.5	6.1	3.2	-4.8
4Z-ak	15.0	14.8	4.9	2.5	-5.8
4Z-al	15.0	14.1	5.5	1.6	-5.7
4Z-am	15.1	14.1	4.9	0.0	-7.3
4Z-an	15.1	13.6	4.5	1.2	-6.3
4Z-ao	15.1	14.9	5.4	0.8	-6.8
4Z-ap	15.1	13.8	4.9	1.8	-5.6
4Z-aq	15.1	16.2	5.8	1.5	-7.1

TABLE 5: Structures and relative energies for glycine(H_2O)₅

Structure	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
5N6-a	0.0	0.0	0.0	0.0	0.0
5N6-b	0.1	0.2	0.3	0.2	0.3
5N6-c	0.3	0.3	0.5	0.1	0.4
5N8-a	0.3	1.0	0.3	1.5	0.8
5N6-d	0.4	0.8	0.8	0.3	0.4
5N1-a	0.4	0.2	2.2	-0.1	1.7
5Z-a	8.6	9.5	0.4	0.8	-7.3
5Z-b	8.7	9.9	1.0	0.6	-7.1

TABLE 6: Structures and relative energies for glycine(H_2O)₆

Structure	EFP1/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
6N6-a	0.0	0.0	0.0	0.0	0.0
6N8-a	0.1	0.3	0.7	-0.7	-0.2
6N8-b	0.2	1.5	1.4	0.4	0.3
6N8-c	0.3	1.3	1.3	0.3	0.3
6N6-b	0.6	1.7	1.3	1.1	0.2
6N1-a	0.6	0.3	1.5	0.1	1.0
6N6-c	0.7	0.6	1.2	-0.7	-0.1
6N8-d	0.8	0.7	1.1	-0.5	0.1
6N1-b	1.0	0.7	2.1	0.5	1.5
6N1-c	1.1	0.6	0.7	-0.1	0.1
6N1-d	1.1	0.8	2.3	0.2	1.4
6N1-e	1.2	0.3	3.4	-1.2	1.9
6N8-e	1.4	1.7	1.7	0.7	0.6
6N1-f	1.5	0.5	3.2	-1.0	1.4
6N1-g	1.6	0.8	2.1	0.5	1.5
6Z-a	7.4	8.4	0.8	-0.2	-6.9

TABLE 7: Structures and relative energies for glycine(H₂O),

Structure	EFPI/HF and RHF/6-31++G(d,p)	Full RHF/ 6-31++G(d,p)	MP2//RHF/ 6-31++G(d,p)	PCM+RHF//RHF/ 6-31++G(d,p)	PCM+MP2//RHF/ 6-31++G(d,p)
7N1-a	0.0	0.0	0.0	0.0	0.0
7N1-b	0.2	0.1	0.2	0.1	0.2
7N8-a	0.5	1.2	-1.0	1.6	0.0
7N8-b	0.6	1.3	-0.7	1.7	0.3
7N6-a	0.7	1.3	-0.7	2.1	0.6
7N6-b	0.7	1.3	-0.6	2.0	0.4
7N8-c	0.9	1.5	-0.6	1.7	0.3
7Z-a	7.3	9.0	-0.7	0.7	-7.8
7Z-b	7.4	8.5	-1.3	-0.5	-8.8
7Z-c	8.0	9.5	0.1	1.4	-6.7
7Z-d	8.6	9.9	0.9	1.5	-6.4
7Z-e	8.7	9.5	0.3	1.0	-7.0
7Z-f	8.9	8.4	-0.5	2.5	-5.4
7Z-g	8.9	9.0	0.1	0.4	-7.4

TABLE 8: Nonionized-Zwitterion Energy Difference (kcal/mol)

Number		EFP1/HF and		Full RHF/	MP2//RHF/	PCM+RHF//RHF/	PCM+MP2//RHF/
of waters	N Structure	Z Structure	RHF/6-31++G(d,p)	6-31++G(d,p)	6-31++G(d,p)	6-31++G(d,p)	6-31++G(d,p)
1	1N1-a	1Z-a	24.2	23.5	15.3	2.4	-3.6
2	2N1-a	2Z-a	20.2	19.8	10.8	2.4	-4.7
3	3N1-a	3Z-a	14.7	15.6	5.2	1.9	-6.9
4	4N1-a	4Z-a	12.1	11.7	1.6	1.2	-7.7
	4N6-a	4Z-a	11.8	10.5	2.6	0.8	-6.7
5	5N6-a	5Z-a	8.6	9.5	0.4	0.8	-7.3
6	6N6-a	6Z-a	7.4	8.4	0.8	-0.2	-6.9
7	7N1-a	7Z-a	7.3	9.0	-0.7	0.7	-7.8
	7N8-a	7Z-b	6.9	7.4	-0.3	-2.1	-8.8

Figure 1. Neutral glycine conformer structures and relative energies (kcal/mol) at the RHF/6-31G(d,p) and MP2/6-31++G(d,p)//RHF/6-31G(d,p) levels of theory.

Figure 2. Six lowest energy conformers and relative energies (kcal/mol) of nonionized glycine(H_2O).

Figure 3. Five lowest energy conformers and relative energies (kcal/mol) of zwitterionic glycine(H_2O).

Figure 4. Six lowest energy conformers and relative energies (kcal/mol) of nonionized glycine(H_2O)₂.

EFP1/HF waters and RHF/6-31++G(d,p) glycine (kcal/mol)
(RHF/6-31++G(d,p))
[MP2//RHF/6-31++G(d,p)]
PCM+RHF//RHF/6-31++G(d,p)
[PCM+MP2// RHF/6-31++G(d,p)]

Figure 5. Five lowest energy conformers and relative energies (kcal/mol) of zwitterionic glycine(H_2O)₂.

Figure 6. Conformers and relative energies (kcal/mol) of nonionized glycine(H_2O)₃.

Figure 7. Conformers and relative energies (kcal/mol) of zwitterionic glycine(H_2O)₃.

EFP1/HF waters and RHF/6-31++G(d,p) glycine (kcal/mol)

(RHF/6-31++G(d,p))

[MP2//RHF/6-31++G(d,p)]

PCM+RHF//RHF/6-31++G(d,p)

[PCM+MP2// RHF/6-31++G(d,p)]

Figure 8. Conformers and relative energies (kcal/mol) of glycine(H_2O)₄.

EFP1/HF waters and RHF/6-31++G(d,p) glycine (kcal/mol)

(RHF/6-31++G(d,p))

[MP2//RHF/6-31++G(d,p)]

PCM+RHF//RHF/6-31++G(d,p)

[PCM+MP2// RHF/6-31++G(d,p)]

Figure 9. Conformers and relative energies (kcal/mol) of glycine(H_2O)₅. **Figure 10.** Conformers and relative energies (kcal/mol) of glycine(H_2O)₆.

Figure 11. Conformers and relative energies (kcal/mol) of glycine(H_2O)₇.

EFP1/HF waters and RHF/6-31++G(d,p) glycine (kcal/mol)
 (RHF/6-31++G(d,p))
 [MP2//RHF/6-31++G(d,p)]
 PCM+RHF//RHF/6-31++G(d,p)
 [PCM+MP2// RHF/6-31++G(d,p)]

CHAPTER 5. PARALLEL UNRESTRICTED MP2 ANALYTIC GRADIENTS USING THE DISTRIBUTED DATA INTERFACE

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A scalable distributed data parallel analytic gradient algorithm for unrestricted second-order Møller-Plesset perturbation theory is presented. Features of the implementation using the Distributed Data Interface are discussed in detail. Benchmark timing calculations on a parallel cluster system are presented for a variety of gold cluster molecules. The speedups, parallel efficiencies, and percentage parallelism for these calculations are reported.

I. Introduction

Professor Schaefer has made many contributions in the field of electronic structure theory, including early efforts at parallelization.¹ We are pleased to be able to present this contribution in honor of his 60th birthday.

Second-order Møller-Plesset (MP2) perturbation theory² is a correlated electronic structure method that is widely used to calculate molecular energies and geometries, since it provides a balance between the amount of electron correlation recovered and the computational cost of the calculation. The first derivation of the MP2 gradient was presented in 1979 by Pople et al.³ Subsequent formulations by Handy et al.⁴ and Pulay and Saebø⁵ eliminated the storage of derivative integrals and three-virtual molecular orbital integrals, used the Z-vector method of Handy and Schaefer⁶ to reduce the number of unknown response vectors in the coupled-perturbed Hartree-Fock (CPHF) equations from $3N$ (where N is the number of nuclei) to 1, and eliminated the need to solve the CPHF equations in the

occupied-occupied and virtual-virtual blocks. Frozen orbitals were introduced to reduce the computational requirements of the calculations, and an explicit derivation of the MP2 gradient using frozen orbitals was presented by Lee et al.⁷ The implementation of the first direct MP2 gradient algorithm,⁸ in which the two-electron repulsion integrals are recomputed as needed instead of stored on disk or in memory, allowed much larger calculations than were previously possible, although this came at a greater computational cost. Semi-direct algorithms were also developed in order to minimize computation depending on available memory and disk space.⁹ Recently, Head-Gordon developed an improved semi-direct MP2 gradient algorithm, which reduces the required memory and disk storage to that of a semi-direct MP2 energy calculation, eliminates disk-based sorting and transposition steps, and accounts for frozen orbitals.¹⁰

For the MP2 methods, the time requirements for a calculation grow as $O(n^5)$ with the number of basis functions n , while the memory requirements can increase by as much as $O(n^3)$, depending on the algorithm. As these methods are applied to increasingly larger molecules with reliable basis sets, the requirements of the calculation quickly outgrow the capabilities of a single-processor computer. Replicated-data parallel schemes are relatively easy to implement and reduce the time requirements of a calculation, but the size of systems that can be treated with them is limited by the memory on a single node. Distributed-data implementations are preferred, as these reduce both the single-node memory requirement and the wall clock time for a calculation.

The computer architecture must also be considered when designing an algorithm. Currently, clusters of workstations or PC's are an attractive alternative to large massively parallel processor (MPP) platforms due to a good performance/price ratio. Individual

research groups and departments do not normally have enough resources to purchase large computer systems. Cluster computing also has the advantages that commodity parts can be used, installation is relatively easy, scalability can be attained in principle, and the computational resources are controlled locally. However, cluster computing also has some disadvantages that must be addressed. In particular, the slow speed interconnection between nodes in clusters can be a source of poor performance and scalability of algorithms designed for MPP systems. In addition, not all parallel programming tools are available or optimized for cluster computing.

Fletcher et al. developed the Distributed Data Interface (DDI)^{11,12} to provide a set of tools for distributed memory programming that is useful on both large parallel machines and clusters. It allows storage of large data arrays over the aggregate memory of distributed memory architectures. Like the Global Array (GA) tools,¹³ DDI represents a global memory access model that is based on a data-passing model. It includes a set of basic network communication functions (Table 1) such as point-to-point operations like send and receive and collective operations like broadcast and global sum. It also includes features for using distributed and globally addressed arrays and one-sided communication. These functions are implemented using TCP/IP socket code or MPI-1 or SHMEM libraries, so DDI is available for a variety of architectures. The advantages of one-sided communication include reduced programming difficulty and increased efficiency due to asynchronous communication. The presence of remote memory adds a new level to the memory access time hierarchy:

registers < cache(s) < main memory < remote memory < disk

Most systems have significantly slower access time to remote memory than to local memory, so data locality must be considered in the design of an algorithm. Information on data locality is also available within DDI.

To date, DDI has been used to implement distributed storage versions of SCF energies,¹⁴ analytic SCF Hessians,¹⁵ multireference self-consistent field energies and gradients,¹⁶ closed shell MP2 energies and gradients,¹¹ Z-averaged perturbation theory energies,¹⁷ multireference perturbation theory energies,¹⁸ singles CI energies and gradients,¹⁹ and Full CI energies.²⁰ Other distributed data tools have been used to generate distributed memory versions of SCF energies,²¹⁻²⁷ analytic SCF Hessians,²⁸ CPHF equations,²⁹ perturbation theory energies³⁰⁻³⁶ and gradients,^{37,38} CI energies,^{39,40} and coupled cluster energies.^{41,42}

In this paper, the parallel implementation of unrestricted MP2 (UMP2) energies and gradients into the quantum chemistry package GAMESS¹⁷ through the use of DDI is discussed. An assessment of the speedup and parallel efficiency is reported for a series of gold clusters using a cluster architecture.

II. Parallel UMP2 Gradient Algorithm

A distributed-data UMP2 gradient algorithm is discussed in this section. The details of the gradient derivation and serial implementation may be found elsewhere.⁴³ In general, the analytic derivative of the UMP2 electronic energy may be expressed as:

$$E^x = \sum_{\mu\nu}^{AO} P_{\mu\nu}^{MP2} H_{\mu\nu}^x + \sum_{\mu\nu}^{AO} W_{\mu\nu}^{MP2} S_{\mu\nu}^x + \sum_{\mu\nu\lambda\sigma}^{AO} \Gamma_{\mu\nu\lambda\sigma}^{MP2} (\mu\nu|\lambda\sigma)^x \quad (1)$$

where $H_{\mu\nu}^x$ are the core-Hamiltonian derivative integrals, $S_{\mu\nu}^x$ are the overlap derivative integrals, $(\mu\nu|\lambda\sigma)^x$ are the derivatives of the electron repulsion integrals (ERI's), and $\mu, \nu, \lambda,$

and σ index atomic orbitals. The MP2 density matrix $P_{\mu\nu}^{MP2}$, “energy-weighted” density matrix $W_{\mu\nu}^{MP2}$, and two-particle density matrix $\Gamma_{\mu\nu\lambda\sigma}^{MP2}$ in Eq. (1) are sums of their corresponding SCF and second-order correction terms:

$$P_{\mu\nu}^{MP2} = P_{\mu\nu}^{\alpha SCF} + P_{\mu\nu}^{\beta SCF} + P_{\mu\nu}^{(2)}(\alpha\alpha) + P_{\mu\nu}^{(2)}(\beta\beta) \quad (2)$$

$$W_{\mu\nu}^{MP2} = W_{\mu\nu}^{\alpha SCF} + W_{\mu\nu}^{\beta SCF} + W_{\mu\nu}^{(2)}(\alpha\alpha) + W_{\mu\nu}^{(2)}(\beta\beta) \quad (3)$$

$$\Gamma_{\mu\nu\lambda\sigma}^{MP2} = \Gamma_{\mu\nu\lambda\sigma}^{SCF} + \Gamma_{\mu\nu\lambda\sigma}^{(2)} \quad (4)$$

The second-order correction to the two-particle density matrix is normally divided into the sum of so-called separable (Γ^S) and non-separable (Γ^{NS}) terms:

$$\Gamma_{\mu\nu\lambda\sigma}^{(2)} = \Gamma_{\mu\nu\lambda\sigma}^{NS} + \Gamma_{\mu\nu\lambda\sigma}^S \quad (5)$$

In practice, Eq. (1) is usually evaluated by forming the density matrices $\mathbf{P}^{(2)}$, $\mathbf{W}^{(2)}$, and $\mathbf{\Gamma}^{(2)}$ in the MO basis and back-transforming these matrices to the AO basis. The expressions for these matrix elements are shown in the appendix.

A. Implementation Considerations. In the MO basis, the expressions for the density matrix elements require 18 different types of integrals, which may be divided into five classes. Using “v” to denote a virtual MO and “o” to denote an occupied MO, these integral types may be expressed as:

1. $(o^\alpha o^\alpha | o^\alpha o^\alpha) (o^\alpha o^\alpha | o^\beta o^\beta) (o^\beta o^\beta | o^\beta o^\beta)$
2. $(v^\alpha o^\alpha | o^\alpha o^\alpha) (v^\alpha o^\alpha | o^\beta o^\beta) (v^\beta o^\beta | o^\alpha o^\alpha) (v^\beta o^\beta | o^\beta o^\beta)$
3. $(v^\alpha v^\alpha | o^\alpha o^\alpha) (v^\alpha v^\alpha | o^\beta o^\beta) (v^\beta v^\beta | o^\alpha o^\alpha) (v^\beta v^\beta | o^\beta o^\beta)$
4. $(v^\alpha o^\alpha | v^\alpha o^\alpha) (v^\alpha o^\alpha | v^\beta o^\beta) (v^\beta o^\beta | v^\beta o^\beta)$
5. $(v^\alpha v^\alpha | v^\alpha o^\alpha) (v^\alpha v^\alpha | v^\beta o^\beta) (v^\beta v^\beta | v^\alpha o^\alpha) (v^\beta v^\beta | v^\beta o^\beta)$

Parallel processor systems with global memories in the terabyte range are now common, so it is feasible that the smaller integral classes may be stored in memory even for larger problems. Thus, global memory on the order of $n_o^2 n^2$ is assumed, where n_o is the number of occupied orbitals and n is the number of basis functions, and it is assumed that n_o is much smaller than n . A different algorithm setup that trades additional computation for reduced memory requirements could also be envisioned, but will not be discussed here. The first four integral classes fall within the assumption of $O(n_o^2 n^2)$ global memory, so these integrals may be stored in a distributed fashion across the nodes. The fifth class is closer in size to $O(n_o n^3)$. However, this class is only used in the construction of the Lagrangian, so the terms involving these integrals will be calculated separately and in a direct fashion to avoid storage of this larger integral class. In addition, since n^4 memory is not assumed, the AO integrals will be calculated in a direct fashion. The density matrices, MO coefficients, orbital energies, and other data of order n^2 or less are replicated across the nodes.

The implementation of the following parallel UMP2 gradient scheme will be discussed in more detail in the subsequent sections:

1. Parallel direct transformation to yield MO integrals that contain at most two virtual orbital indices (stored in global memory)
2. Evaluation of UMP2 energy and construction of immediately obtainable terms of $\mathbf{P}^{(2)}$, $\mathbf{W}^{(2)}$, and the Lagrangian $\mathbf{L}$
3. Computation of the Lagrangian terms involving (vv|vo) class integrals directly from AO integrals
4. Solution of the Z-vector equations⁶ in the MO basis

5. Completion of one-particle density matrices and the one-particle contribution to the gradient
6. Back transformation of integrals to generate Γ^{NS} and completion of the two-particle contribution to the gradient

B. Integral Transformation and Storage. First, the fourteen distributed arrays that hold the first four classes of transformed integrals must be created. These are depicted in Figure 1. Triangular pairings of two occupied or virtual indices are used wherever possible to reduce the number of integrals stored. Integral type $(v^\alpha o^\alpha | v^\beta o^\beta)$ has no available triangular pairings, so the full range of each index must be used for this array. Overall, the limiting storage requirement for the seven two-virtual integral types (and thus for the algorithm) is $(n_o^{\alpha 2} + n_o^{\beta 2} + n_o^\alpha n_o^\beta) n^2$. The “supermatrix” symmetry of integral types $(o^\alpha o^\alpha | o^\alpha o^\alpha)$ and $(o^\beta o^\beta | o^\beta o^\beta)$ is not used so that the arrays have a regular rectangular structure. The excess storage cost for this is not large, since this is the smallest integral class. For all integral types, all pairs of occupied indices are divided among the available nodes, with the full range of the other indices located on a given node. The integrals are distributed in this manner so that the long summations over virtual indices will be local.

Next, the fourteen integral types that correspond to the first four classes must be generated and stored in the distributed arrays. The general parallel transformation fourfold loop procedure has been described previously,¹¹ so the details will not be presented here. The appropriate alpha and beta MO coefficients are used in the transformation of each index to generate the required integral types. The replicated data requirement for this procedure is $l^2 n(n_o^\alpha + n_o^\beta)$, where l is the length of a shell (1 for s , 3 for p , 6 for Cartesian d , etc.). After

the integrals are generated, they are stored in the appropriate distributed arrays through the use of the DDI_PUT operation.

C. Density Matrix Creation. Most of the terms in the one-particle density matrices and the Lagrangian (Eqs. A1-A6, A13) may be evaluated from the integrals discussed in section B. The amplitudes for the virtual-virtual blocks of $\mathbf{P}^{(2)}$ (Eq. A3) and $\mathbf{W}^{(2)}$ (terms 1 and 2 of Eq. A5) are calculated from (volvo) integrals on the local node and multiplied by (volvo) integrals that are also locally held. Thus, these blocks do not require remote memory access. The occupied-occupied blocks of $\mathbf{P}^{(2)}$ (Eqs. A1 and A2) and $\mathbf{W}^{(2)}$ (terms 1 and 2 of Eq. A4) require remote DDI_GET operations to obtain a set of (volvo) integrals for a given vv pair. Then, the amplitude generation and integral multiplication steps may proceed locally. A global sum of $\mathbf{P}^{(2)}$ is performed so that each node holds the complete occupied-occupied and virtual-virtual blocks.

The fourth and fifth terms of Eq. A4 use the (ooloo) integrals when p and q are both occupied indices. Since this is the only matrix block that requires these integrals, the memory for these is released after the terms are computed. The (vvloo) class of integrals contributes to terms 4 and 5 of Eq. A4 when p and q are both virtual indices. This class is also used to compute the orbital Hessian in Eqs. A7 and A8, so it is retained in memory. The (voloo) class of integrals is used in the calculation of terms 1 and 2 of Eq. A6 and terms 1, 2, 5, and 6 of Eq. A13. It will also contribute to the fourth and fifth terms of Eq. A4 after the virtual-occupied block of $\mathbf{P}^{(2)}$ is determined, so these integrals are retained in memory.

D. Three-Virtual Terms for Lagrangian. Terms 3,4,7, and 8 of Eq. A13 require the (vv|vo) integrals. These terms in the Lagrangian may be rearranged to form terms in a mixed MO/AO basis as discussed previously.^{11,37,38} For the UMP2 gradient, modified integrals

instead of amplitudes will be transformed. For example, term 8 of Eq. A13 may be rearranged as:

$$\begin{aligned} L_{a^{\alpha} i^{\alpha}}^8 &= \sum_{j^{\beta}} \sum_{b^{\alpha}}^{act^{\beta}} \sum_{c^{\beta}}^{virt^{\alpha}} \frac{(i^{\alpha} b^{\alpha} | j^{\beta} c^{\beta})}{D_{i^{\alpha} j^{\beta}}^{b^{\alpha} c^{\beta}}} (a^{\alpha} b^{\alpha} | j^{\beta} c^{\beta}) \\ &= \sum_{v\lambda\sigma} \sum_{j^{\beta}} \sum_{b^{\alpha}}^{act^{\beta}} \sum_{c^{\beta}}^{virt^{\alpha}} C_{\lambda a}^{\alpha} C_{ob}^{\alpha} C_{vc}^{\beta} (j^{\beta} v | \lambda \sigma) \frac{(i^{\alpha} b^{\alpha} | j^{\beta} c^{\beta})}{D_{i^{\alpha} j^{\beta}}^{b^{\alpha} c^{\beta}}} \end{aligned} \quad (6)$$

where i and j index occupied orbitals, a , b , and c index virtual orbitals, and λ , v , σ index atomic orbitals. A mixed MO/AO Lagrangian is introduced on the left-hand side of Eq. 6 as

$$L_{a^{\alpha} i^{\alpha}}^8 = \sum_{\lambda} C_{\lambda a}^{\alpha} L_{\lambda i^{\alpha}}^8 \quad (7)$$

and further rearrangement of Eq. 6 yields

$$\sum_{\lambda} C_{\lambda a}^{\alpha} L_{\lambda i^{\alpha}}^8 = \sum_{v\lambda\sigma} \sum_{j^{\beta}}^{act^{\beta}} C_{\lambda a}^{\alpha} (j^{\beta} v | \lambda \sigma) \left(\sum_{b^{\alpha}}^{virt^{\alpha}} \sum_{c^{\beta}} C_{ob}^{\alpha} C_{vc}^{\beta} \frac{(i^{\alpha} b^{\alpha} | j^{\beta} c^{\beta})}{D_{i^{\alpha} j^{\beta}}^{b^{\alpha} c^{\beta}}} \right) \quad (8)$$

Thus,

$$L_{\lambda i^{\alpha}}^8 = \sum_{v\sigma} \sum_{j^{\beta}}^{act^{\beta}} (j^{\beta} v | \lambda \sigma) I_{i^{\alpha} j^{\beta}}^{\sigma v} \quad (9)$$

where the half-transformed integral is:

$$I_{i^{\alpha} j^{\beta}}^{\sigma v} = \sum_{b^{\alpha}}^{virt^{\alpha}} \sum_{c^{\beta}} C_{ob}^{\alpha} C_{vc}^{\beta} \frac{(i^{\alpha} b^{\alpha} | j^{\beta} c^{\beta})}{D_{i^{\alpha} j^{\beta}}^{b^{\alpha} c^{\beta}}} \quad (10)$$

Term 7 of Eq. A13 can be represented as a difference of half-transformed integrals:

$$L_{\lambda i^{\alpha}}^7 = \sum_{v\sigma} \sum_{j^{\alpha}}^{act^{\alpha}} (j^{\alpha} v | \lambda \sigma) (I_{i^{\alpha} j^{\alpha}}^{\sigma v} - I_{i^{\alpha} j^{\alpha}}^{\omega \sigma}) \quad (11)$$

The half-transformed integrals may be generated from locally held (volvo) integrals without communication since all gets and puts are done locally (Figure 2). To save memory at the

cost of extra computation later, the half-transformed integrals replace the (volvo) integrals in memory.

In a similar manner, terms 3 and 4 of Eq. A13 may be rearranged to the form

$$L_{v\alpha}^3 = \sum_{\lambda\sigma} (i^\alpha v|\lambda\sigma) P_{\lambda\sigma}^{(2)}(\alpha\alpha) \quad (12)$$

$$L_{v\alpha}^4 = \sum_{\lambda\sigma} (i^\alpha v|\lambda\sigma) P_{\lambda\sigma}^{(2)}(\beta\beta) \quad (13)$$

where the virtual-virtual density matrix has been back-transformed to the AO basis. Since the required storage for the AO density matrix is $O(n^2)$ and the time required for the back-transformation is trivial, this back-transformation is not distributed.

Representation of these Lagrangian terms in the mixed MO/AO basis has the benefit that the quarter-transformed ERI's with one MO and three AO indices may be used as soon as they are generated. A second fourfold loop over shells is used to calculate and quarter-transform the ERI's as described previously.¹¹ After the inner two loops, a DDI_GET operation must be performed to read in half-transformed integrals such as $I_{\mu\alpha}^{\sigma\nu}{}_{j\beta}$ for a given σ, ν pair. This requires communication among the processors. Once the quarter-transformed ERI's are contracted with the respective half-transformed integrals or AO density matrix elements and the mixed MO/AO Lagrangian terms are formed, these terms are transformed to the MO basis and combined with the other four terms of the Lagrangian. The Lagrangian is summed globally so each node holds the full matrix.

Once the Lagrangian has been calculated, the (volvo) integrals must be restored. The half-transformed integrals are transformed with the inverse MO coefficient matrix $C^{-1}(=C^TS$, where S is the overlap matrix over AOs), which restores the virtual MO indices, and are

then multiplied by the appropriate orbital-energy factor (such as $D_{i\alpha j\beta}^{b^a c^b}$) to recreate the original (volvo) integrals. Since the entire set of indices for a given occupied-occupied pair is on the local processor, this step requires no communication.

E. Solution of Z-vector Equations. A reduced Lagrangian and alpha and beta trial vectors containing only symmetry-allowed elements are used in the solution of the Z-vector equations. In each step of the iterations, blocks of the orbital Hessian are constructed from (volvo) and (vvloo) integrals. If the integrals for a given pair of occupied indices are held locally, the (volvo) and (vvloo) integrals for the alpha, beta, and mixed spin terms are used to form blocks of the orbital Hessian in Eqs. A7 and A8 (Figure 3). These blocks are multiplied by appropriate sections of the trial vectors, and the products are globally summed to generate the alpha and beta product vectors. In this way, storage of the full orbital Hessian is avoided. Alpha and beta error vectors are calculated. A Direct Inversion in the Iterative Subspace (DIIS)^{44,45} interpolation method is used to determine the trial vectors for the next iteration. Since previous trial and error vectors are needed for DIIS, these are stored in a distributed manner across the nodes. At convergence, the trial vectors are the virtual-occupied block of the alpha and beta one-particle density matrices. The (vvloo) integrals are not needed further, so the memory for these is released.

F. Completion of One-Particle Gradient. After solution of the Z-vector equations, the one-particle density matrix is complete. The third term in the virtual-occupied block of the one-particle energy-weighted density matrix (Eq. A6) may now be calculated. In addition, the final contribution to the fourth and fifth terms of Eq. A4 can be evaluated using the (voloo) integrals. This contribution may be computed in a distributed fashion and

globally summed to complete the energy-weighted density matrix. This concludes the use of the (voloo) integrals, so memory for these is released. Finally, the completed alpha and beta one-particle density matrices and energy-weighted density matrices are back-transformed to the AO basis, added to their SCF counterparts (Eqs. 2 and 3), and contracted with the core Hamiltonian and overlap derivatives (Eq. 1) to yield the one-electron portion of the gradient

G. Two-Particle Gradient. The four-index back-transformation of the amplitudes in the non-separable two-particle density (Eq. A14) is similar in essence to the procedure described in section D. The process begins with the half-back-transformation described earlier to generate half-transformed integrals (Figure 2). A third fourfold loop algorithm is required to generate the derivative ERI's. Inside the outer two loops, a DDI_GET operation necessitating communication between the processors is required to read in the half-transformed integrals with a given σ, ν pair (Figure 4). These half-transformed integrals are used to form the half-transformed amplitudes. Inside the third loop over shells, the half-transformed amplitudes are further back-transformed to all AO indices in one range and to AO indices over the third-loop shell in the other range. This step is done locally to avoid further communication. However, since the non-separable density is not symmetrized, the derivative ERI's must be calculated four times more than the minimal list. After the non-separable density is calculated, it is combined with the separable density (Eq. A15), added to its SCF analog, and contracted with the derivative ERI's.

III. Timings/Benchmarks

The parallel UMP2 gradient code described above has been implemented in GAMESS and has been benchmarked on a cluster system. The cluster under consideration is comprised of IBM p640 nodes connected by dual Gigabit Ethernet. Each p640 node has 4

Power3-II processors running at 375 MHz and contains 16 GB of memory. On 8 nodes, global memory of 128 GB is available.

The smallest molecule under consideration in the benchmarks is Au_3H_4 . Two basis sets have been used with this molecule. The smaller of the two consists of the 6-31++G**⁴⁶⁻⁴⁸ basis set on H and the Stevens-Basch-Krauss-Jasien-Cundari (SBKJC)⁴⁹⁻⁵¹ effective core potential basis set with f polarization functions and one diffuse sp function on Au, for a total of 170 spherical harmonic basis functions. The larger basis set consists of the aug-cc-pVTZ⁵² basis set on H and the uncontracted SBKJC basis set with 3f2g polarization functions and one sp diffuse function on Au, for a total of 380 spherical harmonic basis functions. For both basis sets, there are 31 alpha occupied orbitals and 30 beta occupied orbitals for Au_3H_4 . A UMP2 gradient calculation with the smaller basis set requires 4 Mwords of replicated memory and 116 Mwords of distributed memory, so it fits in the memory of a single processor on the IBM cluster. The calculation using the larger basis set requires 18 Mwords of replicated memory and 647 Mwords of distributed memory. This calculation requires the memory allotted to two processors on the IBM cluster.

A larger test case is Au_3O_4 . The basis set used with this molecule consists of the aug-cc-pVTZ^{52,53} basis set on O and the uncontracted SBKJC basis set with 3f2g polarization functions and one sp diffuse function on Au, for a total of 472 spherical harmonic basis functions. For this molecule, there are 45 alpha occupied orbitals and 44 beta occupied orbitals. A UMP2 gradient calculation on this molecule requires 41 Mwords of replicated memory and 2166 Mwords of distributed memory. This calculation requires the memory allotted to six processors on the IBM cluster.

Table 2 lists the average CPU time in seconds and the associated speedups and parallel efficiencies for a UMP2 gradient calculation on 1, 2, 4, 8, 16, and 32 processors for the three gold clusters benchmarked in this study. Since the second and third test cases require more than one processor on the IBM cluster, the single-processor time required for these calculations is determined from runs on two and eight processors, respectively, assuming ideal speedup. The speedups may be visualized graphically in Figure 5. A superlinear speedup is exhibited for the smallest test case running on two processors. This may be due to the increased cache capacity available on two processors. As the number of processors increases, the observed speedup is less than the ideal speedup. This may be due to serial portions of the code, load balancing issues, or the communication and synchronization costs. On larger numbers of processors, the larger test cases exhibit greater parallel efficiencies than the smaller test cases. This is expected, since the amount of parallel computation relative to communication and other costs is higher for larger runs.

Table 3 lists an assessment of the "percentage parallelism" in each calculation. These values are determined by assuming Amdahl scaling and fitting an equation of the form $T(P) = T_s + T_p/P$ to the series of wall clock times $T(P)$ on P processors for a given calculation, as discussed in Ref 3. This yields T_s , the amount of time spent on serial portions of the calculation, and T_p , the total amount of time spent on parallel sections. The parallel percentage represents the percentage of the calculation that is scalable. Unlike parallel efficiencies, which only compare two calculations, this model provides a way to assess the scalability over a range of processors. It does not consider effects due to load balancing or communication latencies, but these effects are usually small. Given the small number of data points in the analysis, it is not meaningful to quantitatively distinguish the three parallel%

values in the table. However, the R^2 values suggest that the parallel percentage of the UMP2 gradient calculation is over 90%.

IV. Conclusions

A scalable parallel gradient algorithm for UMP2 using the Distributed Data Interface is presented. The purpose of this algorithm is to increase the speed for a given UMP2 gradient calculation as well as to permit the evaluation of larger jobs. The transformed molecular orbital integrals with two virtual indices or fewer are distributed across the nodes. Data of order n^2 or less is replicated across the nodes. The algorithm has been designed to use locally held data wherever possible, and sections where communication is required have been identified. Redundant computation of two-electron integrals and derivative integrals is used in order to reduce communication and required memory costs.

Benchmark calculations have been run on a series of three gold cluster molecules using an IBM cluster, and the calculations scale well. The percentage parallelism for the UMP2 gradient calculation is above 90%.

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Appendix. Density Matrix Expressions

In general, indices p, q, r, and s represent any molecular orbital. Occupied orbitals are indexed by i, j, and k; virtual orbitals are indexed by a, b, and c; core orbitals are indexed by K. The one-particle alpha-alpha density matrix expressions for the core-active, active-active, and virtual-virtual blocks of $\mathbf{P}^{(2)}$ in the MO basis are

$$P_{K^\alpha i^\alpha}^{(2)} = P_{i^\alpha K^\alpha}^{(2)} = \frac{1}{(\epsilon_i^\alpha - \epsilon_{K^\alpha}^\alpha)} \left[\sum_{j^\alpha} \sum_{a^\alpha b^\alpha} \frac{[(i^\alpha a^\alpha | j^\alpha b^\alpha) - (i^\alpha b^\alpha | j^\alpha a^\alpha)]}{D_{i^\alpha j^\alpha}^{a^\alpha b^\alpha}} (K^\alpha a^\alpha | j^\alpha b^\alpha) \right. \\ \left. + \sum_{j^\beta} \sum_{a^\alpha} \sum_{b^\beta} \frac{(i^\alpha a^\alpha | j^\beta b^\beta)}{D_{i^\alpha j^\beta}^{a^\alpha b^\beta}} (K^\alpha a^\alpha | j^\beta b^\beta) \right] \quad (\text{A1})$$

$$P_{i^\alpha j^\alpha}^{(2)} = - \sum_{k^\alpha} \sum_{a^\alpha} \sum_{b^\alpha} \frac{[(i^\alpha a^\alpha | k^\alpha b^\alpha) - (i^\alpha b^\alpha | k^\alpha a^\alpha)]}{D_{i^\alpha k^\alpha}^{a^\alpha b^\alpha}} \frac{(j^\alpha a^\alpha | k^\alpha b^\alpha)}{D_{j^\alpha k^\alpha}^{a^\alpha b^\alpha}} \\ - \sum_{k^\beta} \sum_{a^\alpha} \sum_{b^\beta} \frac{[(i^\alpha a^\alpha | k^\beta b^\beta)]}{D_{i^\alpha k^\beta}^{a^\alpha b^\beta}} \frac{[(j^\alpha a^\alpha | k^\beta b^\beta)]}{D_{j^\alpha k^\beta}^{a^\alpha b^\beta}} \quad (\text{A2})$$

$$P_{a^\alpha b^\alpha}^{(2)} = \sum_{i^\alpha} \sum_{j^\alpha} \sum_{c^\alpha} \frac{[(i^\alpha a^\alpha | j^\alpha c^\alpha) - (i^\alpha c^\alpha | j^\alpha a^\alpha)]}{D_{i^\alpha j^\alpha}^{a^\alpha c^\alpha}} \frac{(i^\alpha b^\alpha | j^\alpha c^\alpha)}{D_{i^\alpha j^\alpha}^{b^\alpha c^\alpha}} \\ + \sum_{i^\alpha} \sum_{j^\beta} \sum_{c^\beta} \frac{(i^\alpha a^\alpha | j^\beta c^\beta)}{D_{i^\alpha j^\beta}^{a^\alpha c^\beta}} \frac{(i^\alpha b^\alpha | j^\beta c^\beta)}{D_{i^\alpha j^\beta}^{b^\alpha c^\beta}} \quad (\text{A3})$$

The one-particle alpha-alpha energy-weighted density matrix expressions for the occupied-occupied, virtual-virtual, and virtual-occupied blocks of $\mathbf{W}^{(2)}$ are

$$\begin{aligned}
W_{i^\alpha j^\alpha}^{(2)} = & -N_{i^\alpha j^\alpha} \sum_{k^\alpha}^{act^\alpha} \sum_{a^\alpha b^\alpha}^{virt^\alpha} \frac{[(i^\alpha a^\alpha | k^\alpha b^\alpha) - (i^\alpha b^\alpha | k^\alpha a^\alpha)]}{D_{i^\alpha k^\alpha}^{a^\alpha b^\alpha}} (j^\alpha a^\alpha | k^\alpha b^\alpha) \\
& - N_{i^\alpha j^\alpha} \sum_{k^\beta}^{act^\beta} \sum_{a^\alpha}^{virt^\alpha} \sum_{b^\beta}^{virt^\beta} \frac{(i^\alpha a^\alpha | k^\beta b^\beta)}{D_{i^\alpha k^\beta}^{a^\alpha b^\beta}} (j^\alpha a^\alpha | k^\beta b^\beta) - \frac{1}{2} P_{i^\alpha j^\alpha}^{(2)} (\epsilon_i^\alpha + \epsilon_j^\alpha) \\
& - \sum_{p^\alpha q^\alpha}^{all^\alpha} P_{p^\alpha q^\alpha}^{(2)} [(p^\alpha q^\alpha | i^\alpha j^\alpha) - (p^\alpha i^\alpha | q^\alpha j^\alpha)] - \sum_{p^\beta q^\beta}^{all^\beta} P_{p^\beta q^\beta}^{(2)} (p^\beta q^\beta | i^\alpha j^\alpha)
\end{aligned} \tag{A4}$$

$$\text{where } N_{i^\alpha j^\alpha} \equiv \begin{cases} 0, & \text{for both } i, j \in \text{core} \\ 1, & \text{otherwise} \end{cases}$$

$$\begin{aligned}
W_{a^\alpha b^\alpha}^{(2)} = & - \sum_{i^\alpha j^\alpha}^{act^\alpha} \sum_{c^\alpha}^{virt^\alpha} \frac{[(i^\alpha a^\alpha | j^\alpha c^\alpha) - (i^\alpha c^\alpha | j^\alpha a^\alpha)]}{D_{i^\alpha j^\alpha}^{a^\alpha c^\alpha}} (i^\alpha b^\alpha | j^\alpha c^\alpha) \\
& - \sum_{i^\alpha}^{act^\alpha} \sum_{j^\beta}^{act^\beta} \sum_{c^\beta}^{virt^\beta} \frac{(i^\alpha a^\alpha | j^\beta c^\beta)}{D_{i^\alpha j^\beta}^{a^\alpha c^\beta}} (i^\alpha b^\alpha | j^\beta c^\beta) - \frac{1}{2} P_{a^\alpha b^\alpha}^{(2)} (\epsilon_a^\alpha + \epsilon_b^\alpha)
\end{aligned} \tag{A5}$$

$$\begin{aligned}
W_{a^\alpha i^\alpha}^{(2)} = & -2 \sum_{j^\alpha k^\alpha}^{act^\alpha} \sum_{b^\alpha}^{virt^\alpha} \frac{[(j^\alpha a^\alpha | k^\alpha b^\alpha) - (j^\alpha b^\alpha | k^\alpha a^\alpha)]}{D_{j^\alpha k^\alpha}^{a^\alpha b^\alpha}} (i^\alpha j^\alpha | b^\alpha k^\alpha) \\
& - 2 \sum_{j^\alpha}^{act^\alpha} \sum_{k^\beta}^{act^\beta} \sum_{b^\beta}^{virt^\beta} \frac{(j^\alpha a^\alpha | k^\beta b^\beta)}{D_{j^\alpha k^\beta}^{a^\alpha b^\beta}} (i^\alpha j^\alpha | b^\beta k^\beta) - P_{a^\alpha i^\alpha}^{(2)} \epsilon_i^\alpha
\end{aligned} \tag{A6}$$

The virtual-occupied block of $\mathbf{P}^{(2)}$ is obtained from the iterative solution of the Z-vector equations due to Handy and Schaefer⁶

$$\sum_{b^\alpha}^{virt^\alpha} \sum_{j^\alpha}^{occ^\alpha} \{A_{a^\alpha i^\alpha b^\alpha j^\alpha} + \delta_{ab} \delta_{ij} (\epsilon_b^\alpha - \epsilon_j^\alpha)\} P_{b^\alpha j^\alpha}^{(2)} + \sum_{b^\beta}^{virt^\beta} \sum_{j^\beta}^{occ^\beta} \{A_{a^\alpha i^\alpha b^\beta j^\beta}\} P_{b^\beta j^\beta}^{(2)} = -L_{a^\alpha i^\alpha} \tag{A7}$$

$$\sum_{b^\beta}^{virt^\beta} \sum_{j^\beta}^{occ^\beta} \{A_{a^\beta i^\beta b^\beta j^\beta} + \delta_{ab} \delta_{ij} (\epsilon_b^\beta - \epsilon_j^\beta)\} P_{b^\beta j^\beta}^{(2)} + \sum_{b^\alpha}^{virt^\alpha} \sum_{j^\alpha}^{occ^\alpha} \{A_{a^\beta i^\beta b^\alpha j^\alpha}\} P_{b^\alpha j^\alpha}^{(2)} = -L_{a^\beta i^\beta} \tag{A8}$$

where the orbital Hessian is found by

$$A_{p^\alpha q^\alpha r^\alpha s^\alpha} = 2(p^\alpha q^\alpha | r^\alpha s^\alpha) - (p^\alpha r^\alpha | q^\alpha s^\alpha) - (p^\alpha s^\alpha | q^\alpha r^\alpha), \tag{A9}$$

$$A_{p^\alpha q^\alpha r^\beta s^\beta} = 2(p^\alpha q^\alpha | r^\beta s^\beta), \quad (\text{A10})$$

$$A_{p^\beta q^\beta r^\alpha s^\alpha} = 2(p^\beta q^\beta | r^\alpha s^\alpha), \quad (\text{A11})$$

$$A_{p^\beta q^\beta r^\beta s^\beta} = 2(p^\beta q^\beta | r^\beta s^\beta) - (p^\beta r^\beta | q^\beta s^\beta) - (p^\beta s^\beta | q^\beta r^\beta), \quad (\text{A12})$$

and the alpha-alpha Lagrangian is given by

$$\begin{aligned} L_{a^\alpha i^\alpha} = & \sum_{j^\alpha k^\alpha}^{occ^\alpha} P_{j^\alpha k^\alpha}^{(2)} A_{a^\alpha i^\alpha j^\alpha k^\alpha} + \sum_{j^\beta k^\beta}^{occ^\beta} P_{j^\beta k^\beta}^{(2)} A_{a^\alpha i^\alpha j^\beta k^\beta} \\ & + \sum_{b^\alpha c^\alpha}^{virt^\alpha} P_{b^\alpha c^\alpha}^{(2)} A_{a^\alpha i^\alpha b^\alpha c^\alpha} + \sum_{b^\beta c^\beta}^{virt^\beta} P_{b^\beta c^\beta}^{(2)} A_{a^\alpha i^\alpha b^\beta c^\beta} \\ & - 2N_{a^\alpha} \sum_{j^\alpha k^\alpha}^{act^\alpha} \sum_{b^\alpha}^{virt^\alpha} \frac{[(j^\alpha a^\alpha | k^\alpha b^\alpha) - (j^\alpha b^\alpha | k^\alpha a^\alpha)]}{D_{j^\alpha k^\alpha}^{a^\alpha b^\alpha}} (i^\alpha j^\alpha | b^\alpha k^\alpha) \\ & - 2N_{a^\alpha} \sum_{j^\alpha}^{act^\alpha} \sum_{k^\beta}^{act^\beta} \sum_{b^\beta}^{virt^\beta} \frac{(j^\alpha a^\alpha | k^\beta b^\beta)}{D_{j^\alpha k^\beta}^{a^\alpha b^\beta}} (i^\alpha j^\alpha | b^\beta k^\beta) \\ & + 2N_{i^\alpha} \sum_{j^\alpha}^{act^\alpha} \sum_{b^\alpha c^\alpha}^{virt^\alpha} \frac{[(i^\alpha b^\alpha | j^\alpha c^\alpha) - (i^\alpha c^\alpha | j^\alpha b^\alpha)]}{D_{i^\alpha j^\alpha}^{b^\alpha c^\alpha}} (a^\alpha b^\alpha | j^\alpha c^\alpha) \\ & + 2N_{i^\alpha} \sum_{j^\beta}^{act^\beta} \sum_{b^\alpha}^{virt^\alpha} \sum_{c^\beta}^{virt^\beta} \frac{(i^\alpha b^\alpha | j^\beta c^\beta)}{D_{i^\alpha j^\beta}^{b^\alpha c^\beta}} (a^\alpha b^\alpha | j^\beta c^\beta) \end{aligned} \quad (\text{A13})$$

$$\text{where } N_{i^\alpha} \equiv \begin{cases} 0, & \text{for } i = \text{core} \\ 1, & \text{for } i = \text{active} \end{cases}$$

Expressions for the beta-beta matrices are direct analogs of the alpha-alpha expressions. The two-particle density matrices are given by

$$\begin{aligned}
\Gamma_{\mu\nu\lambda\sigma}^{NS} = & \sum_{i^\alpha j^\alpha}^{act^\alpha} \sum_{a^\alpha b^\alpha}^{vir^\alpha} \frac{[(i^\alpha a^\alpha | j^\alpha b^\alpha) - (i^\alpha b^\alpha | j^\alpha a^\alpha)]}{\epsilon_i^\alpha + \epsilon_j^\alpha - \epsilon_a^\alpha - \epsilon_b^\alpha} C_{\mu i}^\alpha C_{\nu a}^\alpha C_{\lambda j}^\alpha C_{\sigma b}^\alpha \\
& + 2 \sum_{i^\alpha j^\beta}^{act^\alpha} \sum_{a^\alpha b^\beta}^{vir^\alpha} \sum_{a^\beta b^\beta}^{vir^\beta} \frac{(i^\alpha a^\alpha | j^\beta b^\beta)}{\epsilon_i^\alpha + \epsilon_j^\beta - \epsilon_a^\alpha - \epsilon_b^\beta} C_{\mu i}^\alpha C_{\nu a}^\alpha C_{\lambda j}^\beta C_{\sigma b}^\beta \\
& + \sum_{i^\beta j^\beta}^{act^\beta} \sum_{a^\beta b^\beta}^{vir^\beta} \frac{[(i^\beta a^\beta | j^\beta b^\beta) - (i^\beta b^\beta | j^\beta a^\beta)]}{\epsilon_i^\beta + \epsilon_j^\beta - \epsilon_a^\beta - \epsilon_b^\beta} C_{\mu i}^\beta C_{\nu a}^\beta C_{\lambda j}^\beta C_{\sigma b}^\beta
\end{aligned} \tag{A14}$$

and

$$\begin{aligned}
\Gamma_{\mu\nu\lambda\sigma}^S = & P_{\mu\nu}^{(2)}(\alpha\alpha)P_{\lambda\sigma}^{\alpha SCF} - P_{\mu\lambda}^{(2)}(\alpha\alpha)P_{\nu\sigma}^{\alpha SCF} + P_{\mu\nu}^{(2)}(\alpha\alpha)P_{\lambda\sigma}^{\beta SCF} \\
& + P_{\mu\nu}^{(2)}(\beta\beta)P_{\lambda\sigma}^{\beta SCF} - P_{\mu\lambda}^{(2)}(\beta\beta)P_{\nu\sigma}^{\beta SCF} + P_{\mu\nu}^{(2)}(\beta\beta)P_{\lambda\sigma}^{\alpha SCF}
\end{aligned} \tag{A15}$$

References

- (1) Whiteside, R. A.; Binkley, J. S.; Colvin, M. E.; Schaefer III, H. F. *J. Chem. Phys.* **1987**, *86*, 2185-2193.
- (2) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618-622.
- (3) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225.
- (4) Handy, N. C.; Amos, R. D.; Gaw, J. F.; Rice, J. E.; Simandiras, E. D. *Chem. Phys. Lett.* **1985**, *120*, 151.
- (5) Pulay, P.; Saebø, S. *Theor. Chim. Acta* **1986**, *69*, 357.
- (6) Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* **1984**, *81*.
- (7) Lee, T. J.; Racine, S. C.; Rice, J. E.; Rendell, A. P. *Mol. Phys.* **1995**, *85*, 561.
- (8) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275.
- (9) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281.

- (10) Head-Gordon, M. *Mol. Phys.* **1999**, *96*, 673.
- (11) Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons, Inc., 1999; Vol. 110, pp 267-294.
- (12) Fletcher, G. D.; Schmidt, M. W.; Bode, B. M.; Gordon, M. S. *Comput. Phys. Commun.* **2000**, *128*, 190-200.
- (13) Nieplocha, J.; Harrison, R. J.; Littlefield, R. J. In *Proceedings of Supercomputing 1994*; IEEE Computer Society Press: Washington DC, 1994, pp 340-349.
- (14) Alexeev, Y.; Kendall, R. A.; Gordon, M. S. *Comput. Phys. Commun.* **2002**, *143*, 69-82.
- (15) Alexeev, Y.; Schmidt, M. W.; Windus, T. L.; Gordon, M. S., *manuscript in preparation*.
- (16) Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S., *manuscript in preparation*.
- (17) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery Jr., J. A. *J. Comput. Chem* **1993**, *14*, 1347-1363.
- (18) Umeda, H.; Koseki, S.; Nagashima, U.; Schmidt, M. W. *J. Comput. Chem* **2001**, *22*, 1243-1251.
- (19) Webb, S. P.; Petrich, J. W.; Gordon, M. S., *manuscript in preparation*.
- (20) Gan, Z.; Alexeev, Y.; Kendall, R. A.; Gordon, M. S. *J. Chem. Phys.* **2003**, *119*, 47-59.
- (21) Colvin, M. E.; Janssen, C. L.; Whiteside, R. A.; Tong, C. H. *Theor. Chim. Acta* **1993**, *84*, 301-314.

- (22) Furlani, T. R.; King, H. F. *J. Comput. Chem* **1995**, *16*, 91-104.
- (23) Foster, I. T.; Tilson, J. L.; Wagner, A. F.; Shepard, R. L.; Harrison, R. J.; Kendall, R. A.; Littlefield, R. J. *J. Comput. Chem* **1996**, *17*, 109-123.
- (24) Harrison, R. J.; Guest, M. F.; Kendall, R. A.; Bernholdt, D. E.; Wong, A. T.; Stave, M.; Anchell, J. L.; Hess, A. C.; Littlefield, R. J.; Fann, G. L.; Wagner, A. F.; Foster, I. T.; Lusk, E.; Stevens, R. *J. Comput. Chem* **1996**, *17*, 124-132.
- (25) Fruchtl, H.; Kendall, R. A.; Harrison, R. J.; Dyll, K. G. *Int. J. Quantum Chem.* **1997**, *64*, 63-69.
- (26) Furlani, T. R.; King, H. F. In *Quantum Mechanical Simulation Methods for Studying Biological Systems*; Spencer, France, 1996.
- (27) Furlani, T. R.; Kong, J.; Gill, P. M. W. *Comput. Phys. Commun.* **2000**, *128*, 170-177.
- (28) Marquez, A. M.; Oviedo, J.; Sanz, J. F.; Dupuis, M. *J. Comput. Chem* **1997**, *18*, 159-168.
- (29) Korambath, P. P.; Kong, J.; Furlani, T. R.; Head-Gordon, M. *Mol. Phys.* **2002**, *100*, 1755-1761.
- (30) Limaye, A. C.; Gadre, S. R. *J. Chem. Phys.* **1994**, *100*, 1303.
- (31) Marquez, A. M.; Dupuis, M. *J. Comput. Chem* **1995**, *16*, 395-404.
- (32) Nielsen, I. M. B.; Seidl, E. T. *J. Comput. Chem* **1995**, *16*, 1301-1313.
- (33) Wong, A. T.; Harrison, R. J.; Rendell, A. P. *Theor. Chim. Acta* **1996**, *93*, 317-321.
- (34) Bernholdt, D. E.; Harrison, R. J. *J. Chem. Phys.* **1995**, *102*, 9582-9589.
- (35) Bernholdt, D. E. *Chem. Phys. Lett.* **1996**, *250*, 477-484.

- (36) Schütz, M.; Lindh, R. *Theor. Chim. Acta* **1997**, *95*, 13-34.
- (37) Nielsen, I. M. B. *Chem. Phys. Lett.* **1996**, *255*, 210-216.
- (38) Fletcher, G. D.; Rendell, A. P.; Sherwood, P. *Mol. Phys.* **1997**, *91*, 431-438.
- (39) Daschel, H.; Lishka, H.; Shepard, R.; Nieplocha, J.; Harrison, R. J. *J. Comput. Chem* **1997**, *18*, 430-448.
- (40) Dobbyn, A. J.; Knowles, P. J.; Harrison, R. J. *J. Comput. Chem* **1998**, *19*, 1215-1228.
- (41) Rendell, A. P.; Guest, M. F.; Kendall, R. A. *J. Comput. Chem* **1993**, *14*, 1429-1439.
- (42) Kobayashi, R.; Rendell, A. P. *Chem. Phys. Lett.* **1997**, *265*, 1-11.
- (43) Aikens, C. M.; Webb, S. P.; Bell, R. L.; Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S. *Theor. Chem. Acc.* **2003**, *110*, 233.
- (44) Pulay, P. *Chem. Phys. Lett.* **1980**, *73*, 393-398.
- (45) Pulay, P. *J. Comput. Chem* **1982**, *3*, 556-560.
- (46) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724-728.
- (47) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.
- (48) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem* **1983**, *4*, 294-301.
- (49) Stevens, W. J.; Basch, H.; Krauss, M. J. *Chem. Phys.* **1984**, *81*, 6026.
- (50) Stevens, W. J.; Basch, H.; Krauss, M.; Jaisan, P. *Can. J. Chem.* **1992**, *70*, 612.
- (51) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.
- (52) Dunning Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

- (53) Kendall, R. A.; Dunning Jr., T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769.

TABLE 1: Distributed Memory Operations

DDI_SEND	Synchronous send
DDI_RECV	Synchronous receive
DDI_GET	Get block of distributed array
DDI_PUT	Put block of distributed array
DDI_ACC	Accumulate data into block
DDI_BCAST	Broadcast data to all nodes
DDI_GSUMF	Floating point global sum
DDI_GSUMI	Integer global sum
DDI_CREATE	Create distributed array
DDI_DESTROY	Destroy distributed array
DDI_DISTRIB	Obtain distributed matrix distribution

TABLE 2: Wall Clock Time (Seconds), Speedup, and Parallel Efficiency for UMP2 Gradient Step on IBM Cluster

Molecule n (basis)	Au_3H_4				Au_3H_4				Au_3O_4			
	170		380		472							
P (number of processors)	wall time	speedup	efficiency	wall time	speedup	efficiency	wall time	speedup	efficiency	wall time	speedup	efficiency
1	2867	1.0	100.0	166482 ^a	1.0	100.0	665392 ^b	1.0	100.0	665392 ^b	1.0	100.0
2	1412	2.0	101.5	83241	2.0	100.0	332696 ^b	2.0	100.0	332696 ^b	2.0	100.0
4	771	3.7	93.0	42555	3.9	97.8	166348 ^b	4.0	100.0	166348 ^b	4.0	100.0
8	596	4.8	60.1	22602	7.4	92.1	83174	8.0	100.0	83174	8.0	100.0
16	295	9.7	60.7	11980	13.9	86.9	45138	14.7	92.1	45138	14.7	92.1
32	231	12.4	38.8	7509	22.2	69.3	25205	26.4	82.5	25205	26.4	82.5

^aValue calculated from run using two processors, assuming ideal speedup.

^bValues calculated from run using eight processors, assuming ideal speedup.

TABLE 3: Serial Time, Parallel Time, and Parallel Percentage for UMP2 Gradient Calculation

	Au_3H_4 (170)	Au_3H_4 (380)	Au_3O_4 (472)
Ts (seconds)	150	3270	6187
Tp (seconds)	2679	159396	616942
parallel %	93.5	95.7	92.7
R^2	0.99542	0.99994	0.99986

Figure 1. Indices used for integral arrays. Triangular indices used wherever possible to reduce amount of memory required.

Figure 2. First half-back-transformation of the (volvo) integrals. This procedure is used in the creation of (vv|vo) integrals and the non-separable two-particle density matrix. No communication is required in this step.

Figure 3. Solution of the Z-vector equations. Locally held integrals are used to construct a block of the orbital Hessian. Storage of the full orbital Hessian is avoided. Interprocessor communication is needed only for the global sum.

Figure 4. Second half-back-transformation of the (volvo) integrals. This procedure is used in the creation of the non-separable two-particle density matrix. Communication across the processors is required to retrieve the half-back-transformed integrals.

Figure 5. Speedup curves for three gold cluster molecules. The size of the basis set is listed in parentheses.

CHAPTER 6. SCALABLE IMPLEMENTATION OF ANALYTIC GRADIENTS FOR SECOND-ORDER Z-AVERAGED PERTURBATION THEORY USING THE DISTRIBUTED DATA INTERFACE

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Abstract

The analytic gradient expression for second-order Z-averaged perturbation theory is revised and its parallel implementation into GAMESS is described in detail. The Distributed Data Interface is used to access molecular orbital integral arrays stored in distributed memory. The algorithm is designed to maximize the use of local data and reduce communication costs. The iterative solution and the preconditioner used to induce convergence of the coupled perturbed Hartree-Fock equations are presented. Several illustrative timing examples are discussed.

I. Introduction

Second-order Møller-Plesset (MP2) perturbation theory¹ is extensively employed to calculate molecular energies and geometries since it provides a balance between the amount of electron correlation recovered and the computational requirements of a calculation. For closed-shell systems, perturbation theory based on a restricted Hartree-Fock (RHF) wave function is well defined. However, open-shell systems are much more challenging. Although perturbation theory based on an unrestricted Hartree-Fock (UHF) wave function follows directly from the MP2 spin-orbital equations, the wave function is not an eigenfunction of the $\hat{S}^2$ operator, and this results in spin contamination problems. In

addition, since different spatial orbitals are used for the α and β electrons, the method requires 3-4 times as much memory, disk space, etc. as a comparable closed-shell calculation. Spin-projected methods may alleviate some of the spin-contamination, but this can introduce size-consistency problems.²

As a result, many open-shell perturbation theory methods based on RHF wave functions have been proposed.³⁻⁹ These methods may be divided into two classes: those that have a configuration state function (CSF) basis (which are $\hat{S}^2$ eigenfunctions), and those that have a spin-orbital determinant basis. Methods with a CSF basis include the method of Hubac and Carsky (HCPT),³ the OPT1 and OPT2 methods,⁴ and the IOPT method.⁹ Methods using a spin-orbital basis include the ROMP,⁵ RMP⁶/ROHF-MBPT,⁷ and Z-averaged perturbation theory⁸ methods. The convergence of the perturbation series for HCPT and OPT1 is expected to be poor.^{5,10} OPT2 is not invariant with respect to rotations between degenerate singly-occupied orbitals.¹¹ IOPT is not size-consistent,¹² although the effects of this on its results have been debated.¹³ ROMP and RMP use different α and β spatial orbitals, so the cost of these two methods will be similar to unrestricted perturbation theory.

Z-averaged perturbation theory (ZAPT)⁸ is based on a set of "symmetric spin orbitals"¹⁴, and the symmetry of these orbitals leads to significant computational savings over ROMP and RMP. The spatial parts of the spin orbitals come from an open-shell ROHF calculation. The standard α and β spin functions are assigned to doubly occupied and unoccupied orbitals in the reference function. The spin parts of the singly occupied orbitals are assigned to be σ^+ and σ^- , where

$$\sigma^+ = \frac{1}{\sqrt{2}}(\alpha + \beta),$$

$$\sigma^- = \frac{1}{\sqrt{2}}(\alpha - \beta).$$

So, the reference function is symmetric with respect to the interchange of α and β spin indices. The single determinant based on these orbitals is an eigenfunction of $\hat{S}^2$, although the n th order perturbed wavefunctions generally are not. There are no $\hat{S}^2$ contaminants in the second-order (ZAPT2) energies. The reference function is a linear combination of $\hat{S}_z$ eigenfunctions, but suitable use of the raising and lowering operators $\hat{S}_+$ and $\hat{S}_-$ can be used to recover eigenfunctions of $\hat{S}_z$.¹⁴ The canonicalization chosen for the molecular orbitals (MO's) is equivalent to using $\frac{1}{2}(\hat{F}^\alpha + \hat{F}^\beta)$ to canonicalize the three shells (doubly occupied, singly occupied, and unoccupied (virtual)).¹⁵ The zeroth-order Hamiltonian is defined as the diagonal part of the spin orbital Fock matrix.

In order to effectively use this method, it is desirable to calculate analytic derivatives of the second-order energy. Equations for the ZAPT2 gradient have been previously derived by Fletcher et al.¹⁶ A few revisions to these equations are made in section 2 of this work, and the subsequent implementation is described in section 3.

The efficient implementation of gradients for post-Hartree-Fock methods has been of interest for many years. The first closed-shell MP2 gradient derivation was presented by Pople et al. in 1979.¹⁷ Later, the storage of derivative integrals and three-virtual MO integrals was eliminated,¹⁸ the number of unknown response vectors was reduced to one,¹⁹ and the need to solve the coupled perturbed Hartree-Fock equations in the occupied-occupied and virtual-virtual blocks was removed.²⁰ Frozen orbitals further reduced the computational cost.²¹ Direct and semi-direct algorithms reduced the required memory and disk storage

requirements and permitted larger calculations, although this came at the cost of increased integral computation.²²⁻²⁴

Even with these improvements, the computational requirements for large molecules with reasonable basis sets quickly outgrow the capabilities of a single-processor computer. For second-order perturbation theory, the time requirements for a calculation increase as $O(n^5)$ with the number of basis functions n , and the memory needs can grow as $O(n^3)$, depending on the algorithm. Distributed data parallel schemes are desirable, as these alleviate both the single-node memory and time requirements of a calculation.

The Distributed Data Interface (DDI) was developed by Fletcher et al. to provide a set of tools for distributed memory programming.^{25,26} Like Global Arrays (GA),²⁷ DDI provides a programming environment that mimics the ease of a shared-memory environment yet permits the scalability of a distributed memory architecture. Large data arrays can be stored over the collective memory of the system. These arrays can be easily accessed by any of the nodes, although the programmer must be aware of the increased time required for remote memory access and should design algorithms that maximize the use of local memory. In order to maximize scalability, the programmer must also limit the replicated memory requirements. To date, distributed storage algorithms for self-consistent field (SCF) energies,²⁸ analytic SCF Hessians, closed-shell²⁵ and unrestricted²⁹ MP2 energies and gradients, ZAPT2 energies, multireference self-consistent field energies,³⁰ gradients,³⁰ and Hessians,³¹ multireference perturbation theory energies,³² single excitation configuration interaction (CI) energies,³⁰ gradients,³³ and full CI energies³⁴ have been implemented using DDI into the electronic structure code GAMESS,³⁵ which is freely available from Iowa State

University at www.msg.ameslab.gov. Recently, DDI has been extended to take optimal advantage of shared memory processor (SMP) computers.³⁶

II. Theory

A. Notation and Energy Expression

The notation used here is as similar as possible to a recent overview of MP2 gradient equations.³⁷ The ZAPT2 energy is the sum of the SCF and second-order correction energies. The frozen-core ZAPT second-order energy correction may be expressed in the MO basis as

$$\begin{aligned}
 E_{ZAPT}^{(2)} = & \frac{1}{2} \sum_{ij} \sum_{pq}^{s.v.} (ip | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \\
 & + \frac{1}{2} \sum_{ab} \sum_{pq}^{d.s.} (pa | qb) [C_{pq}(pa | qb) - (pb | qa)] / D_{pq}^{ab} \\
 & + \sum_{ixya} (ix | ya)(ix | ya) / D_{iy}^{xa} + \frac{1}{2} \sum_{ixya} (ix | xa)(iy | ya) / D_i^a
 \end{aligned} \quad (1)$$

General MO's are indexed by p, q, r, s . Doubly occupied active MO's (referred to as DOCC) are indexed by i, j, k . Singly occupied MO's (SOCC) are indexed by w, x, y, z . Virtual (unoccupied) MO's (VIRT) are indexed by a, b, c . Doubly occupied frozen-core MO's (CORE) are indexed by m, n . The summation range denoted $s.v.$ extends over the SOCC and VIRT spaces; likewise, $d.s.$ extends over the DOCC and SOCC spaces and $c.d.$ extends over the CORE and DOCC spaces. The four-index symbol $(pq | rs)$ is a two-electron repulsion integral (ERI) over MO's in Mulliken notation. These integrals are transformed into the MO basis from the atomic orbital (AO) basis by

$$(pq | rs) = \sum_{\mu\nu\lambda\sigma} C_{\mu p} C_{\nu q} C_{\lambda r} C_{\sigma s} (\mu\nu | \lambda\sigma) \quad (2)$$

where $\mu, \nu, \lambda, \sigma$ index AO's, $C_{\mu p}$ is a MO coefficient, and $(\mu\nu | \lambda\sigma)$ is an ERI in the AO basis. The MO coefficient $C_{\mu p}$ must be distinguished from the coefficient in the ZAPT2 energy expression in Eqn. 1, where the coefficient C_{pq} is

$$\begin{aligned} C_{pq} &= 1, \text{ for both } p \in \text{SOCC and } q \in \text{SOCC} \\ C_{pq} &= 2, \text{ otherwise.} \end{aligned} \quad (3)$$

The four-index denominator is expressed as

$$D_{pq}^{rs} = \varepsilon_p + \varepsilon_q - \varepsilon_r' - \varepsilon_s' \quad (4)$$

and the two-index denominator is written as

$$D_p^q = \varepsilon_p - \varepsilon_q' \quad (5)$$

The orbital energies in Eqns. 4 and 5 are defined as

$$\begin{aligned} \varepsilon_p &= \varepsilon_p' = \varepsilon_{pp}, \text{ for } p \notin \text{SOCC} \\ \varepsilon_p &= \varepsilon_{pp} - \frac{1}{2} \sum_y (py | py), \text{ for } p \in \text{SOCC} \\ \varepsilon_p' &= \varepsilon_{pp} + \frac{1}{2} \sum_y (py | py), \text{ for } p \in \text{SOCC} \end{aligned} \quad (6)$$

with

$$\varepsilon_{pp} = h_{pp} + \sum_q^{all} f_q [2(pp | qq) - (pq | pq)] \quad (7)$$

where h_{pq} is a core Hamiltonian element and f_p is the occupation number of the p th shell (1 for DOCC; $\frac{1}{2}$ for SOCC). The SOCC orbital energies in Eqn. 6 have an additional "integral component" that comes from the choice of canonicalization of the Fock matrix. The abbreviations IP and DP will be used to denote independent and dependent pairs of molecular orbitals, respectively. A rotation between two doubly occupied, between two singly

occupied, or between two virtual orbitals does not change the SCF energy, so these pairs are called dependent pairs. The other orbital pairs are uniquely determined, so these are called independent pairs.

B. General gradient expression

The derivative of the ZAPT2 energy is the sum of the derivatives of the SCF and second-order correction contributions to the energy. The general form of this derivative with respect to a nuclear displacement γ has the following form:

$$E^\gamma = \sum_{\mu\nu}^{AO} P_{\mu\nu} h_{\mu\nu}^\gamma + \sum_{\mu\nu}^{AO} W_{\mu\nu} S_{\mu\nu}^\gamma + \sum_{\mu\nu\lambda\sigma}^{AO} \Gamma_{\mu\nu\lambda\sigma} (\mu\nu|\lambda\sigma)^\gamma. \quad (8)$$

In Eqn. 7, $h_{\mu\nu}^\gamma$ are the core Hamiltonian derivative integrals, $S_{\mu\nu}^\gamma$ are the overlap derivative integrals, and $(\mu\nu|\lambda\sigma)^\gamma$ are the derivatives of the ERI's in the AO basis. The one-particle density matrix $P_{\mu\nu}$, energy-weighted density matrix $W_{\mu\nu}$, and two-particle density matrix $\Gamma_{\mu\nu\lambda\sigma}$ are sums of their SCF analogues and a second-order correction:

$$P_{\mu\nu} = P_{\mu\nu}^{SCF} + P_{\mu\nu}^{(2)} \quad (9)$$

$$W_{\mu\nu} = W_{\mu\nu}^{SCF} + W_{\mu\nu}^{(2)} \quad (10)$$

$$\Gamma_{\mu\nu\lambda\sigma} = \Gamma_{\mu\nu\lambda\sigma}^{SCF} + \Gamma_{\mu\nu\lambda\sigma}^{(2)}. \quad (11)$$

The second-order two-particle density correction is expressed as the sum of separable (S) and non-separable (NS) terms:

$$\Gamma_{\mu\nu\lambda\sigma}^{(2)} = \Gamma_{\mu\nu\lambda\sigma}^S + \Gamma_{\mu\nu\lambda\sigma}^{NS}. \quad (12)$$

The equations for the SCF terms may be written as follows:

$$P_{\mu\nu}^{SCF} = 2 \sum_P^{c,d,s} f_P C_{\mu P} C_{\nu P} \quad (13)$$

$$W_{\mu\nu}^{SCF} = 2 \sum_{pq}^{all} C_{\mu p} C_{\nu q} \zeta_{pq} \quad (14)$$

$$\Gamma_{\mu\nu\lambda\sigma}^{SCF} = \frac{1}{2} P_{\mu\nu}^{SCF} P_{\lambda\sigma}^{SCF} - \frac{1}{4} P_{\mu\lambda}^{SCF} P_{\nu\sigma}^{SCF} - \frac{1}{4} P_{\mu\lambda}^S P_{\nu\sigma}^S \quad (15)$$

where

$$P_{\mu\nu}^S = \sum_x C_{\mu x} C_{\nu x} \quad (16)$$

and ζ_{pq} is defined in Eqn. 41 below.

C. Gradient of the ZAPT2 energy

The usual derivative techniques are employed; these are described in detail in Ref. 16.

A few modifications to the previous procedure are presented in this section.

The derivative of the fourth term in the second-order energy expression (Eqn. 1) may be written

$$\begin{aligned} & \left(\frac{1}{2} \sum_{ixya} (ix | xa)(iy | ya) / D_i^a \right)^{(\gamma)} \\ &= \frac{1}{2} \sum_{ixya} \left\{ 2(ix | xa)^{(\gamma)}(iy | ya) / D_i^a - [D_i^a]^\gamma (ix | xa)(iy | ya) / (D_i^a)^2 \right\} \end{aligned} \quad (17)$$

where (γ) indicates the derivative over MO's. The derivative of an ERI in the MO basis is well known³⁸ to be

$$\begin{aligned} (pq | rs)^{(\gamma)} &= (pq | rs)^\gamma + \sum_i U_{ip}^\gamma (iq | rs) + \sum_i U_{iq}^\gamma (pi | rs) \\ &\quad + \sum_i U_{ir}^\gamma (pq | is) + \sum_i U_{is}^\gamma (pq | ri) \end{aligned} \quad (18)$$

where the U^γ matrix describes the response of the MO coefficients to the perturbation γ .

Upon substitution of Eqn. 18 into Eqn. 17, the first term in the resulting equation has the form

$$\sum_{ixya} (ix | xa)^{\gamma} (iy | ya) / D_i^a, \quad (19)$$

where

$$(ix | xa)^{\gamma} = \sum_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu x} C_{\lambda x} C_{\sigma a} (\mu\nu | \lambda\sigma)^{\gamma}. \quad (20)$$

Eqn. (19) can be rearranged as follows:

$$\begin{aligned} \sum_{ixya} (ix | xa)^{\gamma} (iy | ya) / D_i^a &= \sum_{\mu\nu\lambda\sigma} \sum_{ixya} C_{\mu i} C_{\nu x} C_{\lambda x} C_{\sigma a} (\mu\nu | \lambda\sigma)^{\gamma} (iy | ya) / D_i^a \\ &= \sum_{\mu\nu\lambda\sigma} (\mu\nu | \lambda\sigma)^{\gamma} \sum_x \frac{1}{2} C_{\nu x} C_{\lambda x} \sum_{ia} 2 C_{\mu i} C_{\sigma a} \sum_y (iy | ya) / D_i^a \\ &= \sum_{\mu\nu\lambda\sigma} (\mu\nu | \lambda\sigma)^{\gamma} P_{\nu\lambda}^S \sum_{ia} 2 C_{\mu i} C_{\sigma a} T_{ia}^{(4)} \\ &= \sum_{\mu\nu\lambda\sigma} (\mu\nu | \lambda\sigma)^{\gamma} P_{\nu\lambda}^S T_{\mu\sigma}^{(4)} \end{aligned} \quad (21)$$

where

$$T_{ia}^{(4)} = \sum_y (iy | ya) / D_i^a \quad (22)$$

$$T_{\mu\sigma}^{(4)} = 2 \sum_{ia} C_{\mu i} C_{\sigma a} T_{ia}^{(4)}. \quad (23)$$

This yields a separable density term $T_{\mu\sigma}^{(4)} P_{\nu\lambda}^S$.

During the derivation, terms such as

$$2 \sum_{y>x} U_{yx}^{\gamma} {}^1P_{yx}^{(2)} (\varepsilon'_x - \varepsilon'_y) \quad (24)$$

are formed, where ${}^1P_{yx}^{(2)}$ indicates the first term of $P_{yx}^{(2)}$. Using Eqn. 6, Eqn. 24 can be

rewritten as

$$2 \sum_{y>x} U_{yx}^{\gamma} {}^1P_{yx}^{(2)} \left\{ \varepsilon_{xx} - \varepsilon_{yy} + \frac{1}{2} \sum_z [(xz | xz) - (yz | yz)] \right\}. \quad (25)$$

Eqn. 25 may be divided into an orbital energy part

$$2 \sum_{y>x} U_{yx}^{\gamma} {}^1P_{yx}^{(2)} \{ \varepsilon_{xx} - \varepsilon_{yy} \} \quad (26)$$

and an integral component part

$$2 \sum_{y>x} U_{yx}^{\gamma} {}^1P_{yx}^{(2)} F_{yx} \quad (27)$$

where

$$F_{yx} = \frac{1}{2} \sum_z [(xz | xz) - (yz | yz)]. \quad (28)$$

The orbital energy part in Eqn. 26 is treated with the usual procedure.¹⁶ Eqn. 27 is divided into two pieces, and the x and y indices are swapped in the first term as follows:

$$\sum_{x>y} U_{xy}^{\gamma} {}^1P_{xy}^{(2)} F_{xy} + \sum_{y>x} U_{yx}^{\gamma} {}^1P_{yx}^{(2)} F_{yx}. \quad (29)$$

The derivative of the orthogonality condition,

$$U_{pq}^{\gamma} + U_{qp}^{\gamma} + S_{pq}^{\gamma} = 0, \quad (30)$$

may be used to rearrange the second half of Eqn. 29 to yield:

$$\sum_{x>y} U_{xy}^{\gamma} {}^1P_{xy}^{(2)} F_{xy} - \sum_{y>x} U_{xy}^{\gamma} {}^1P_{yx}^{(2)} F_{yx} - \sum_{y>x} S_{xy}^{\gamma} {}^1P_{yx}^{(2)} F_{yx}. \quad (31)$$

Since ${}^1P_{yx}^{(2)} = {}^1P_{xy}^{(2)}$ and $F_{xy} = -F_{yx}$, the first two terms can be combined and the third term can be modified slightly, giving:

$$\sum_{x \neq y} U_{xy}^{\gamma} {}^1P_{xy}^{(2)} F_{xy} + \sum_{y>x} S_{xy}^{\gamma} {}^1P_{xy}^{(2)} F_{xy}. \quad (32)$$

The second term in Eqn. 32 produces a contribution to the one-particle energy-weighted density matrix. Given that

$$U_{pq}^{\gamma} = \frac{Q_{pq}^{\gamma}}{(\varepsilon_{qq} - \varepsilon_{pp})}, \quad (33)$$

the first term of Eqn. 32 becomes

$$\sum_{xy} Q_{xy}^{\gamma} \left[\frac{1 - \delta_{xy}}{(\epsilon_{yy} - \epsilon_{xx})} P_{xy}^{(2)} F_{xy} \right], \quad (34)$$

which yields a contribution to the one-particle density matrix. Due to Eqn. 34, a potential singularity exists when singly occupied orbitals are degenerate and $\epsilon_{yy} = \epsilon_{xx}$. Assuming F_{xy} goes to zero faster than the orbital energy difference, this term can be neglected for degenerate SOCC orbitals.

Also during the derivation, terms such as

$$2 \sum_{ij} \sum_{pq} \sum_{m}^{s.v.} U_{mi}^{\gamma}(mp | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \quad (35)$$

are produced. This term may be divided into two parts, and Eqn. 30 may be used to rearrange Eqn. 35 as:

$$\begin{aligned} & \sum_{ij} \sum_{pq} \sum_{m}^{s.v.} U_{mi}^{\gamma}(mp | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \\ & - \sum_{ij} \sum_{pq} \sum_{m}^{s.v.} U_{im}^{\gamma}(mp | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \\ & - \sum_{ij} \sum_{pq} \sum_{m}^{s.v.} S_{mi}^{\gamma}(mp | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \end{aligned} \quad (36)$$

The third term in Eqn. 36 includes an overlap derivative integral, so the expression multiplying the integral is a contribution to the energy-weighted density matrix:

$$W_{im}^{(2)} = - \sum_j \sum_{pq}^{s.v.} (mp | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq}. \quad (37)$$

A similar procedure is used to determine the other three amplitude terms of $W_{im}^{(2)}$.

For implementation purposes, the energy-weighted density matrix is symmetrized.

Thus,

$$W_{im}^{(2)} = -P_{im}^{(2)} \epsilon_{mm} \quad (38)$$

and

$$W_{mi}^{(2)} = -P_{mi}^{(2)} \epsilon_{ii} \quad (39)$$

become

$$W_{im}^{(2)} = W_{mi}^{(2)} = \frac{1}{2}(W_{im}^{(2)} + W_{mi}^{(2)}) = -\frac{1}{2}P_{mi}^{(2)}(\epsilon_{mm} + \epsilon_{ii}), \quad (40)$$

since the one-particle density is also symmetrized.

In the general restricted open-shell CPHF equations, the Lagrangian matrices ζ_{pq} , the generalized Lagrangian matrices ξ_{pq}^r , and the τ matrices can be defined by

$$\zeta_{pq} = f_p h_{pq} + \sum_s^{c.d.s.} [\alpha_{rs}(pq|ss) + \beta_{rs}(ps|qs)], \quad (41)$$

$$\xi_{pq}^r = f_r h_{pq} + \sum_s^{c.d.s.} [\alpha_{rs}(pq|ss) + \beta_{rs}(ps|qs)], \quad (42)$$

and

$$\tau_{rs}^{pq} = 2(\alpha_{rp} - \alpha_{sp})(pq|rs) + (\beta_{rp} - \beta_{sp})[(pr|qs) + (ps|qr)], \quad (43)$$

where α_{pq} and β_{pq} are the Coulomb and exchange coupling constants, respectively. These constants have the values

α_{pq}	D	S	V	β_{pq}	D	S	V
D	2	1	0	D	-1	$-\frac{1}{2}$	0
S	1	$\frac{1}{2}$	0	S	$-\frac{1}{2}$	$-\frac{1}{2}$	0
V	0	0	0	V	0	0	0

(44)

where p and q index DOCC (D), SOCC (S), or VIRT (V) MO's. From the variational conditions, $\zeta_{pq} = \zeta_{qp}$. In addition, $\xi_{pq}^r = \xi_{qp}^r$. If r and p belong to the same shell, $\xi_{pq}^r = \zeta_{pq}$. For virtual orbital a , $\zeta_{pa} = \zeta_{ap} = 0$, $\xi_{pq}^a = \xi_{qp}^a = 0$, and $\tau_{rs}^{aq} = 0$. As a result, the ζ_{pq} and ξ_{pq}^r terms do not contribute to the diagonal blocks of the $\mathbf{W}^{(2)}$ matrix. The expressions for the off-diagonal blocks are also simpler (see section IID).

Formally, $\tau_{rs}^{pq} \neq \tau_{rs}^{qp}$, but $\tau_{rs}^{pq} = \tau_{rs}^{qp}$ if p and q belong to the same shell. Diagonal blocks of $\mathbf{W}^{(2)}$ contain terms with the form

$$W_{rs}^{(2)} = -\frac{\delta_{rs}}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rr} - \delta'_{rs} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rs} \quad (45)$$

where Z_{pq} is the solution to the Z-vector equations (see section IIID) and a modified

Kronecker delta is defined as

$$\begin{aligned} \delta'_{pq} &= 1, \quad p > q \\ \delta'_{pq} &= 0, \quad p \leq q \end{aligned} \quad (46)$$

By symmetrizing the terms, Eqn. 45 can subsequently be simplified to:

$$\begin{aligned} \frac{W_{rs}^{(2)} + W_{sr}^{(2)}}{2} &= -\frac{\delta_{rs}}{4} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rr} - \frac{\delta_{sr}}{4} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{ss} - \frac{\delta'_{rs}}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rs} - \frac{\delta'_{sr}}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{sr} \\ &= -\frac{\delta_{rs}}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rr} - \frac{\delta'_{rs}}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rs} - \frac{\delta'_{sr}}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rs} \\ &= -\frac{\delta_{rs}}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rr} - \frac{(1-\delta_{rs})}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rs} \\ &= -\frac{1}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{rs} \end{aligned} \quad (47)$$

D. Density matrix expressions

In this section, the density-like quantities, χ , $P^{(2)}$, $W^{(2)}$, Γ^S , and Γ^{NS} , and the Lagrangian, L , are summarized in terms of the matrix elements of their various shell-shell blocks. G_{pqrs} is defined to be $G_{pqrs} = 4(pq | rs) - (pr | qs) - (ps | qr)$.

- χ :

$$\begin{aligned} \chi_x = & \sum_{ij} \sum_p^{s.v.} (ix | jp) [C_{xp}(ix | jp) - (ip | jx)] / D_{ij}^{xp} D_{ij}^{xp} \\ & + \sum_{ab} \sum_p^{d.s.} (xa | pb) [C_{xp}(xa | pb) - (xb | pa)] / D_{xp}^{ab} D_{xp}^{ab} \\ & + \sum_{iza} \left[(ix | za)^2 / (D_{iz}^{xa})^2 + (iz | xa)^2 / (D_{ix}^{za})^2 \right] \end{aligned} \quad (48)$$

- CORE-CORE response density: $P_{mm}^{(2)} = 0$. (49)

- DOCC-CORE response density:

$$\begin{aligned} P_{im}^{(2)} = & \frac{1}{(\epsilon_i - \epsilon_m)} \left[2 \sum_j \sum_{p,q}^{s.v.} (mp | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \right. \\ & + 2 \sum_{a,b} \sum_p^{d.s.} (ma | pb) [2(ia | pb) - (ib | pa)] / D_{ip}^{ab} \\ & \left. + 2 \sum_{x,y} \sum_a (mx | ya)(ix | ya) / D_{iy}^{xa} + \sum_{x,y,a} (mx | xa)(iy | ya) / D_i^a \right] \end{aligned} \quad (50)$$

- DOCC-DOCC response density:

$$\begin{aligned} P_{ij}^{(2)} = & - \sum_k \sum_{p,q}^{s.v.} (ip | kq) [C_{pq}(jp | kq) - (jq | kp)] / D_{ik}^{pq} D_{jk}^{pq} \\ & - \sum_{a,b} \sum_p^{d.s.} (ia | pb) [2(ja | pb) - (jb | pa)] / D_{ip}^{ab} D_{jp}^{ab} \\ & - \sum_{x,y} \sum_a (ix | ya)(jx | ya) / D_{iy}^{xa} D_{jy}^{xa} - \frac{1}{2} \sum_{x,y,a} (ix | xa)(jy | ya) / D_i^a D_j^a \end{aligned} \quad (51)$$

- SOCC-SOCC response density:

$$\begin{aligned}
P_{xy}^{(2)} = & \sum_{i,j} \sum_p^{s.v.} (ix | jp) [C_{yp}(iy | jp) - (ip | jy)] / D_{ij}^{xp} D_{ij}^{yp} \\
& - \sum_{a,b} \sum_p^{d.s.} (xa | pb) [C_{yp}(ya | pb) - (yb | pa)] / D_{xp}^{ab} D_{yp}^{ab} \\
& + \sum_{i,z} \sum_a [(ix | za)(iy | za) / D_{iz}^{xa} D_{iz}^{ya} - (iz | xa)(iz | ya) / D_{ix}^{za} D_{iy}^{za}] \\
& + \frac{(1 - \delta_{xy})}{2(\epsilon_y - \epsilon_x)} \sum_w [(yw | yw) - (xw | xw)] \times \\
& \left[\sum_{i,j} \sum_p^{s.v.} (ix | jp) [C_{yp}(iy | jp) - (ip | jy)] / D_{ij}^{xp} D_{ij}^{yp} \right. \\
& + \sum_{a,b} \sum_p^{d.s.} (xa | pb) [C_{yp}(ya | pb) - (yb | pa)] / D_{xp}^{ab} D_{yp}^{ab} \\
& + \sum_{i,z} \sum_a [(ix | za)(iy | za) / D_{iz}^{xa} D_{iz}^{ya} + (iz | xa)(iz | ya) / D_{ix}^{za} D_{iy}^{za}] \left. \right] \\
& + \frac{(1 - \delta_{xy})}{(\epsilon_y - \epsilon_x)} \sum_z (xz | yz) [\chi_y - \chi_x]
\end{aligned} \tag{52}$$

- VIRT-VIRT response density:

$$\begin{aligned}
P_{ab}^{(2)} = & \sum_{i,j} \sum_p^{s.v.} (ia | jp) [2(ib | jp) - (ip | jb)] / D_{ij}^{ap} D_{ij}^{bp} \\
& + \sum_c \sum_{p,q}^{d.s.} (pa | qc) [C_{pq}(pb | qc) - (pc | qb)] / D_{pq}^{ac} D_{pq}^{bc} \\
& + \sum_{x,y} \sum_i (ix | ya)(ix | yb) / D_{iy}^{xa} D_{iy}^{xb} + \frac{1}{2} \sum_{i,x,y} (ix | xa)(iy | yb) / D_i^a D_i^b
\end{aligned} \tag{53}$$

- The off-diagonal IP response density for $p > q$ is given by:

$$P_{pq}^{(2)} = (f_p - f_q) Z_{pq}. \tag{54}$$

- CORE-CORE energy-weighted response density:

$$W_{mn}^{(2)} = -\frac{1}{2} \sum_{p,q}^{d.p.} P_{pq}^{(2)} G_{pqmn} - \frac{1}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{mn}. \tag{55}$$

- DOCC-CORE energy-weighted response density:

$$\begin{aligned}
W_{im}^{(2)} = & - \sum_j \sum_{p,q}^{s.v.} (mp | jq) [C_{pq} (ip | jq) - (iq | jp)] / D_{ij}^{pq} \\
& - \sum_{a,b} \sum_p^{d.s.} (ma | pb) [2(ia | pb) - (ib | pa)] / D_{ip}^{ab} \\
& - \sum_{x,y} \sum_a (mx | ya) (ix | ya) / D_{iy}^{xa} - \frac{1}{2} \sum_{x,y,a} (mx | xa) (iy | ya) / D_i^a \\
& - \sum_{p,q}^{d.p.} P_{pq}^{(2)} G_{pqim} - P_{im}^{(2)} \frac{\epsilon_m + \epsilon_i}{2} - \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{im}
\end{aligned} \tag{56}$$

- DOCC-DOCC energy-weighted response density:

$$\begin{aligned}
W_{ij}^{(2)} = & - \sum_k \sum_{p,q}^{s.v.} (ip | kq) [C_{pq} (jp | kq) - (jq | kp)] / D_{jk}^{pq} \\
& - \sum_{a,b} \sum_p^{d.s.} (ia | pb) [2(ja | pb) - (jb | pa)] / D_{jp}^{ab} \\
& - \sum_{x,y} \sum_a (ix | ya) (jx | ya) / D_{jy}^{xa} - \frac{1}{2} \sum_{x,y,a} (ix | xa) (jy | ya) / D_j^a \\
& - \frac{1}{2} \sum_{p,q}^{d.p.} P_{pq}^{(2)} G_{pqij} - P_{ij}^{(2)} \epsilon_j - \frac{1}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{ij}
\end{aligned} \tag{57}$$

- SOCC-SOCC energy-weighted response density:

$$\begin{aligned}
W_{xy}^{(2)} = & -\sum_{i,j} \sum_p^{s.v.} (ix | jp) [C_{yp}(iy | jp) - (ip | jy)] / D_{ij}^{yp} \\
& -\sum_{a,b} \sum_p^{d.s.} (xa | pb) [C_{yp}(ya | pb) - (yb | pa)] / D_{yp}^{ab} \\
& -\sum_{z,a} \sum_i \left[(ix | za)(iy | za) / D_{iz}^{ya} + (iz | xa)(iz | ya) / D_{iy}^{za} \right] \\
& -\sum_{i,z,a} (ix | ya)(iz | za) / D_i^a - \frac{1}{4} \sum_{p,q}^{d.p.} P_{pq}^{(2)} G_{pq,xy} - P_{xy}^{(2)} \epsilon_y \\
& -\frac{1}{2} \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{xy} - \frac{\delta_{xy}}{2} \sum_z (xz | xz) [\chi_x + \chi_z] \\
& + \frac{\delta'_{yx}}{2} \sum_w [(yw | yw) - (xw | xw)] \times \\
& \left[\sum_{i,j} \sum_p^{s.v.} (ix | jp) [C_{yp}(iy | jp) - (ip | jy)] / D_{ij}^{yp} D_{ij}^{yp} \right. \\
& + \sum_{a,b} \sum_p^{d.s.} (xa | pb) [C_{yp}(ya | pb) - (yb | pa)] / D_{yp}^{ab} D_{yp}^{ab} \\
& \left. + \sum_{z,a} \sum_i \left[(ix | za)(iy | za) / D_{iz}^{xa} D_{iz}^{ya} + (iz | xa)(iz | ya) / D_{ix}^{za} D_{iy}^{za} \right] \right]
\end{aligned} \tag{58}$$

- VIRT-VIRT energy-weighted response density:

$$\begin{aligned}
W_{ab}^{(2)} = & -\sum_{i,j} \sum_p^{s.v.} (ia | jp) [2(ib | jp) - (ip | jb)] / D_{ij}^{pb} \\
& -\sum_c \sum_{p,q}^{d.s.} (pa | qc) [C_{pq}(pb | qc) - (pc | qb)] / D_{pq}^{bc} \\
& -\sum_{x,y} \sum_i (ix | ya)(ix | yb) / D_{iy}^{xb} - \frac{1}{2} \sum_{i,x,y} (ix | xa)(iy | yb) / D_i^b - P_{ab}^{(2)} \epsilon_b
\end{aligned} \tag{59}$$

- SOCC-CORE and SOCC-DOCC energy-weighted response density:

$$\begin{aligned}
W_{xr}^{(2)} = & -2 \sum_{i,j} \sum_p^{s.v.} (ir | jp) [C_{xp}(ix | jp) - (ip | jx)] / D_{ij}^{xp} \\
& -2 \sum_{a,b} \sum_p^{d.s.} (ra | pb) [C_{xp}(xa | pb) - (xb | pa)] / D_{xp}^{ab} \\
& -2 \sum_{y,a} \sum_i [(ir | ya)(ix | ya) / D_{iy}^{xa} + (iy | ra)(iy | xa) / D_{ix}^{ya}] \\
& - \sum_{i,y,a} [(ix | ra) + (ir | xa)](iy | ya) / D_i^a \\
& - \frac{1}{2} \sum_{p,q}^{d.p.} P_{pq}^{(2)} G_{pqxr} - 2 \sum_y P_{xy}^{(2)} \epsilon_{yr} - \sum_{p>q}^{i.p.} Z_{pq} \tau_{pq}^{xr} \\
& - \sum_i^{c.d.} Z_{xi} (\xi_{ri}^x - \zeta_{ir}) + \sum_a Z_{ax} \xi_{ra}^x - \sum_z (rz | xz) [\chi_x + \chi_z]
\end{aligned} \tag{60}$$

where r indexes a CORE or a DOCC MO.

- VIRT-CORE, VIRT-DOCC, and VIRT-SOCC energy-weighted response density:

$$\begin{aligned}
W_{ar}^{(2)} = & -2 \sum_{i,j} \sum_p^{s.v.} (ir | jp) [2(ia | jp) - (ip | ja)] / D_{ij}^{ap} \\
& -2 \sum_b \sum_{p,q}^{d.s.} (pr | qb) [C_{pq}(pa | qb) - (pb | qa)] / D_{pq}^{ab} \\
& -2 \sum_{x,y} \sum_i (ix | yr)(ix | ya) / D_{iy}^{xa} \\
& - \sum_{i,x,y} (ix | xr)(iy | ya) / D_i^a - 2 \sum_b P_{ab}^{(2)} \epsilon_{br} \\
& + \sum_i^{c.d.} Z_{ai} \zeta_{ir} + \sum_x Z_{ax} \zeta_{xr}
\end{aligned} \tag{61}$$

where r indexes a CORE, DOCC, or SOCC MO.

- SOCC-CORE Lagrangian elements:

$$\begin{aligned}
L_{xm} = & -2 \sum_{i,j}^{s.v.} \sum_p (im | jp) [C_{xp}(ix | jp) - (ip | jx)] / D_{ij}^{xp} \\
& -2 \sum_{a,b}^{d.s.} \sum_p (ma | pb) [C_{xp}(xa | pb) - (xb | pa)] / D_{xp}^{ab} \\
& -2 \sum_{y,a} \sum_i [(im | ya)(ix | ya) / D_{iy}^{xa} + (iy | ma)(iy | xa) / D_{ix}^{ya}] \\
& - \sum_{i,y,a} [(ix | ma) + (im | xa)](iy | ya) / D_i^a - \sum_y (my | xy) [\chi_x + \chi_y] \\
& + \frac{1}{2} \sum_{pq}^{d.p.} P_{pq}^{(2)} G_{pqxm} + 2 \sum_i^{c.d.} P_{im}^{(2)} \epsilon_{xi} - 2 \sum_y P_{xy}^{(2)} \epsilon_{ym}
\end{aligned} \tag{62}$$

- VIRT-CORE Lagrangian elements:

$$\begin{aligned}
L_{am} = & -2 \sum_{i,j}^{s.v.} \sum_p (im | jp) [2(ia | jp) - (ip | ja)] / D_{ij}^{ap} \\
& -2 \sum_b \sum_{p,q}^{d.s.} (pm | qb) [C_{pq}(pa | qb) - (pb | qa)] / D_{pq}^{ab} \\
& -2 \sum_{x,y} \sum_i (ix | ym)(ix | ya) / D_{iy}^{xa} - \sum_{i,x,y} (ix | xm)(iy | ya) / D_i^a \\
& + \sum_{pq}^{d.p.} P_{pq}^{(2)} G_{pqam} + 2 \sum_i^{c.d.} P_{im}^{(2)} \epsilon_{ai} - 2 \sum_b P_{ab}^{(2)} \epsilon_{bm}
\end{aligned} \tag{63}$$

- SOCC-DOCC Lagrangian elements:

$$\begin{aligned}
L_{xi} = & 2 \sum_j \sum_{p,q}^{s.v.} (xp | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \\
& -2 \sum_{j,k} \sum_p^{s.v.} (ik | jp) [C_{xp}(kx | jp) - (kp | jx)] / D_{jk}^{xp} \\
& +2 \sum_{a,b} \sum_p^{d.s.} (xa | pb) [2(ia | pb) - (ib | pa)] / D_{ip}^{ab} \\
& -2 \sum_{a,b} \sum_p^{d.s.} (ia | pb) [C_{xp}(xa | pb) - (xb | pa)] / D_{xp}^{ab} \\
& +2 \sum_{y,z} \sum_a (xy | za)(iy | za) / D_{iz}^{ya} \\
& -2 \sum_{y,a} \sum_j [(ij | ya)(jx | ya) / D_{jy}^{xa} + (jy | ia)(jy | xa) / D_{jx}^{ya}] \\
& + \sum_{y,z,a} (xy | ya)(iz | za) / D_i^a - \sum_{j,y,a} [(jx | ia) + (ij | xa)](jy | ya) / D_j^a \\
& - \sum_z (iz | xz) [\chi_x + \chi_z] + \frac{1}{2} \sum_{pq}^{d.p.} P_{pq}^{(2)} G_{pqxi} + 2 \sum_j^{c.d.} P_{ij}^{(2)} \epsilon_{xj} - 2 \sum_y P_{xy}^{(2)} \epsilon_{yi}
\end{aligned} \tag{64}$$

- VIRT-DOCC Lagrangian elements:

$$\begin{aligned}
L_{ai} = & 2 \sum_j \sum_{p,q}^{s.v.} (pa | jq) [C_{pq}(ip | jq) - (iq | jp)] / D_{ij}^{pq} \\
& - 2 \sum_{j,k} \sum_p^{s.v.} (ik | jp) [2(ka | jp) - (kp | ja)] / D_{jk}^{ap} \\
& + 2 \sum_{b,c} \sum_p^{d.s.} (ab | pc) [2(ib | pc) - (ic | pb)] / D_{ip}^{bc} \\
& - 2 \sum_b \sum_{p,q}^{d.s.} (ip | qb) [C_{pq}(pa | qb) - (pb | qa)] / D_{pq}^{ab} \\
& + 2 \sum_{x,y} \sum_b (xa | yb)(ix | yb) / D_{iy}^{xb} - 2 \sum_{x,y} \sum_j (iy | jx)(jx | ya) / D_{jy}^{xa} \\
& + \sum_{x,y,b} (xa | xb)(iy | yb) / D_i^b - \sum_{j,x,y} (ix | jx)(jy | ya) / D_j^a \\
& + \sum_{pq}^{d.p.} P_{pq}^{(2)} G_{pqai} + 2 \sum_j^{c.d.} P_{ij}^{(2)} \varepsilon_{aj} - 2 \sum_b P_{ab}^{(2)} \varepsilon_{bi}
\end{aligned} \tag{65}$$

- VIRT-SOCC Lagrangian elements:

$$\begin{aligned}
L_{ax} = & 2 \sum_{i,j} \sum_p^{s.v.} (ia | jp) [C_{xp}(ix | jp) - (ip | jx)] / D_{ij}^{xp} \\
& - 2 \sum_{i,j} \sum_p^{s.v.} (ix | jp) [2(ia | jp) - (ip | ja)] / D_{ij}^{ap} \\
& + 2 \sum_{b,c} \sum_p^{d.s.} (ab | pc) [C_{xp}(xb | pc) - (xc | pb)] / D_{xp}^{bc} \\
& - 2 \sum_b \sum_{p,q}^{d.s.} (xp | qb) [C_{pq}(pa | qb) - (pb | qa)] / D_{pq}^{ab} \\
& + 2 \sum_{i,y} \sum_b (ia | yb)(ix | yb) / D_{iy}^{yb} + (iy | ab)(iy | xb) / D_{ix}^{yb} \\
& - 2 \sum_{y,z} \sum_i (iz | xy)(iz | ya) / D_{iy}^{za} \\
& + \sum_{i,y,b} [(ix | ab) + (ia | xb)](iy | yb) / D_i^b - \sum_{i,y,z} (iy | xy)(iz | za) / D_i^a \\
& + \frac{1}{2} \sum_{pq}^{d.p.} P_{pq}^{(2)} G_{pqax} + 2 \sum_y P_{xy}^{(2)} \varepsilon_{ay} - 2 \sum_b P_{ab}^{(2)} \varepsilon_{bx} + \sum_y (xy | ya) [\chi_x + \chi_y]
\end{aligned} \tag{66}$$

- Separable two-particle density:

$$\Gamma_{\mu\nu\lambda\sigma}^S = P_{\mu\nu}^{(2)} P_{\lambda\sigma}^{SCF} - \frac{1}{2} P_{\mu\lambda}^{(2)} P_{\nu\sigma}^{SCF} + \frac{1}{2} T_{\mu\sigma}^{(4)} P_{\nu\lambda}^S + \frac{1}{4} \chi_{\nu\sigma} P_{\mu\lambda}^S + \frac{1}{4} \chi_{\mu\lambda} P_{\nu\sigma}^S + \frac{1}{4} (Z_{\mu\lambda}^{VS} - Z_{\mu\lambda}^{SD}) P_{\nu\sigma}^S \tag{67}$$

where,

$$T_{\mu\nu}^{(4)} = 2 \sum_{ia} C_{\mu i} C_{\nu a} T_{ia}^{(4)}, \quad T_{ia}^{(4)} = \sum_y (iy | ya) / D_i^a \quad (68)$$

$$\chi_{\mu\nu} = \sum_x C_{\mu x} C_{\nu x} \chi_x \quad (69)$$

$$Z_{\mu\nu}^{VS} = \sum_{ax} C_{\mu a} C_{\nu x} Z_{ax}, \quad Z_{\mu\nu}^{SD} = \sum_{xi} C_{\mu x} C_{\nu i} Z_{xi} \quad (70)$$

- Non-separable two-particle density:

$$\Gamma_{\mu\nu\lambda\sigma}^{NS} = \sum_{p,q}^{d.s.} \sum_{r,s}^{s.v.} C_{\mu p} C_{\nu r} C_{\lambda q} C_{\sigma s} T_{pq}^{rs}, \quad (71)$$

where,

$$T_{ij}^{ab} = 2[2(ia | jb) - (ib | ja)] / D_{ij}^{ab},$$

$$T_{ij}^{ax} = [2(ia | jx) - (ix | ja)] / D_{ij}^{ax}, \quad T_{ij}^{xa} = [2(ix | ja) - (ia | jx)] / D_{ij}^{xa},$$

$$T_{ij}^{xy} = [(ix | jy) - (iy | jx)] / D_{ij}^{xy},$$

$$T_{iy}^{xa} = 2(ix | ya) / D_{iy}^{xa},$$

$$T_{ix}^{ab} = [2(ia | xb) - (ib | xa)] / D_{ix}^{ab}, \quad T_{xi}^{ab} = [2(xa | ib) - (xb | ia)] / D_{xi}^{ab},$$

$$T_{xy}^{ab} = [(xa | yb) - (xb | ya)] / D_{xy}^{ab},$$

$$T_{ix}^{yz} = T_{xi}^{yz} = T_{xy}^{za} = T_{xy}^{az} = T_{wx}^{yz} = 0 \quad (72)$$

III. Parallel ZAPT2 Gradient Algorithm

The implementation of the following parallel ZAPT2 gradient algorithm is organized below into the following subsections:

1. Creation of distributed integral arrays
2. Construction of immediately obtainable terms of $\mathbf{P}^{(2)}$, $\mathbf{W}^{(2)}$, and $\mathbf{L}$
3. Three-virtual integrals and the completion of $\mathbf{L}$

4. Solution of the Z-vector equations
5. Completion of the one-particle density matrices and computation of the one-particle gradient
6. Back-transformation of amplitudes to generate the nonseparable density matrix and calculation of the two-particle gradient

A. Distributed Integral Arrays

The equations for the density matrices in section IID require five classes of integrals. Using “v” to denote a virtual MO (VIRT) and “o” to denote an occupied MO (CORE, DOCC, or SOCC), these classes are:

1. (ooloo)
2. (voloo)
3. (vvloo)
4. (volvo)
5. (vvlvo)

The first four integral classes are created and stored in distributed memory as described previously.²⁵ The fifth class is the largest and is only used in the construction of the Lagrangian, so the terms involving these integrals are calculated in a direct fashion as described in section IIIC.

In addition to the integral arrays, the trial vectors of the Z-vector equation are distributed across the nodes. The density matrices ($\mathbf{P}^{(2)}$ and $\mathbf{W}^{(2)}$) and other data of order n^2 or less are stored in a replicated fashion.

B. Density Matrix Creation

The “integral component” $\frac{1}{2} \sum_y (py | py)$ in Eqn. 6 distinguishes ZAPT2 from other related methods. Since these values will be used often in the creation of the density matrices, an array of integral components is stored in replicated memory. These terms require $(xy|xy)$ integrals, which are also used in the multiplicative factor in term 4 of P_{xy} and term 9 of W_{xy} . This factor is stored in an intermediate matrix:

$$F_{xy} = \frac{1}{2} \sum_w [(yw | yw) - (xw | xw)] \quad (73)$$

Each processor reads local integrals and computes a contribution to both arrays. These contributions are then globally summed.

The algorithm for density matrix term creation is structured so as to reduce communication needs as much as possible. In general, a set of integrals is read from local or remote processors, amplitudes are formed by subtracting appropriate integrals and dividing by an orbital energy denominator, and suitable integrals and amplitudes are contracted (multiplied) in order to create each term of the density matrix blocks. More details about the structure of this algorithm are discussed in the Appendix. During the density matrix creation, the ZAPT2 energy can be calculated according to

$$E_{ZAPT}^{(2)} = -\frac{1}{4} \sum_p^{d.s.v.} W_{pp}^{(2)} \quad (74)$$

where $W_{pp}^{(2)}$ includes terms 1-4 of $W_{ii}^{(2)}$, $W_{xx}^{(2)}$, and $W_{aa}^{(2)}$ (Eqns. 57, 58, and 59).

C. Three-Virtual Terms

The (vv|vo) orbitals are required for terms 1-VV (1-VV refers to $p \in \text{VIRT}$ and $q \in \text{VIRT}$ in term 1), 3, and 9 of L_{ai} (Eqn. 65) and terms 3 and 9 of L_{ax} (Eqn. 66). As discussed previously,^{25,29,39,40} these terms can be written in a mixed MO/AO basis and consequently use quarter-transformed ERI's with one occupied MO index and three AO indices that are computed in a direct fashion. Terms 1-VV and 3 of L_{ai} and term 3 of L_{ax} may be rearranged as:

$$\begin{aligned}
 L_{ar} &= 2 \sum_{b,c} \sum_{p \in \text{d.s.}} (ab|pc) [C_{rp}(rb|pc) - (rc|pb)] / D_{rp}^{bc} \\
 &= 2 \sum_{b,c} \sum_{p \in \text{d.s.}} \sum_{v\lambda\sigma} C_{vc} C_{\lambda a} C_{ob} (pv|\lambda\sigma) [C_{rp}(rb|pc) - (rc|pb)] / D_{rp}^{bc} \\
 &= 2 \sum_{p \in \text{d.s.}} \sum_{v\lambda\sigma} C_{\lambda a} (pv|\lambda\sigma) [C_{rp} I_{rp}^{\sigma v} - I_{rp}^{v\sigma}] / D_{rp}^{\sigma v}
 \end{aligned} \tag{75}$$

where the half-transformed integral is

$$I_{rp}^{\sigma v} = \sum_{b,c} C_{vc} C_{ob} (rb|pc) / D_{rp}^{bc}. \tag{76}$$

Then, a mixed MO/AO Lagrangian may be formed as follows:

$$L_{ar} = \sum_{\lambda} C_{\lambda a} L_{\lambda r} = 2 \sum_{p \in \text{d.s.}} \sum_{v\lambda\sigma} C_{\lambda a} (pv|\lambda\sigma) [C_{rp} I_{rp}^{\sigma v} - I_{rp}^{v\sigma}] / D_{rp}^{\sigma v} \tag{77}$$

$$L_{\lambda r} = 2 \sum_{p \in \text{d.s.}} \sum_{v\sigma} (pv|\lambda\sigma) [C_{rp} I_{rp}^{\sigma v} - I_{rp}^{v\sigma}] / D_{rp}^{\sigma v}. \tag{78}$$

Term 9 of L_{ai} and L_{ax} may be similarly rearranged to yield

$$L_{vr} = \sum_{\lambda\sigma} (rv|\lambda\sigma) P_{\lambda\sigma}^{(2)}. \tag{79}$$

Half-transformed integrals are generated from (vo|vo) integrals. The transformation is done locally, so no communication is required (Figure 1). In order to save memory, the half-

transformed integrals overwrite the (volvo) integrals. The quarter-transformed integrals are generated as described previously.²⁵ After the inner two loops, half-transformed integrals for a given v, σ pair are read, which requires communication among the processors (Figure 2). Once the mixed MO/AO Lagrangian terms are created, these terms are transformed to the MO basis. The complete Lagrangian is globally summed so that each processor holds the full matrix. Then, the (volvo) integrals are restored by transforming with the inverse MO coefficient matrix $C^{-1} = C^T S$, where S is the overlap matrix over AOs. Multiplication by the appropriate orbital-energy factor (D_{rp}^{bc}) recreates the original (volvo) integrals. This step requires no communication.

D. Solution of the CPHF Equations

The General Restricted Open-Shell Coupled-Perturbed Hartree-Fock (CPHF) equations must be solved for the response vectors. The Z-vector substitution is used,¹⁹ where $\mathbf{Z}$ is the solution to the linear equation

$$\sum_{p,q}^{IP} A'_{pqrs} Z_{pq} = L_{rs}. \quad (80)$$

A reduced Lagrangian L_{rs} containing only symmetry-allowed elements is used in the solution of (80). The ZAPT2 orbital Hessian A'_{pqrs} has more terms than the closed-shell form; this may be visualized in Figure 3. The equations governing the six unique matrix blocks may be written as:

$$\begin{aligned}
A'_{xij} &= (xi | yj) - \frac{1}{2}(xj | yi) - \frac{1}{2}(xy | ij) + \delta_{xy}(\xi_{ij}^x - \zeta_{ji}) + \delta_{ij}(\xi_{xy}^i - \zeta_{yx}) \\
A'_{aij} &= 2(ai | yj) - \frac{1}{2}(aj | yi) - \frac{1}{2}(ay | ij) + \delta_{ij}\xi_{ay}^i \\
A'_{axyj} &= (ax | yj) - \delta_{xy}\xi_{aj}^x \\
A'_{aibj} &= 4(ai | bj) - (aj | bi) - (ab | ij) - \delta_{ab}\zeta_{ji} + \delta_{ij}\xi_{ab}^i \\
A'_{axbj} &= 2(ax | bj) - \frac{1}{2}(aj | bx) - \frac{1}{2}(ab | xj) - \delta_{ab}\zeta_{jx} \\
A'_{axby} &= (ax | by) - \frac{1}{2}(ay | bx) - \frac{1}{2}(ab | xy) - \delta_{ab}\zeta_{yx} + \delta_{xy}\xi_{ab}^x
\end{aligned} \tag{81}$$

The notation A_{pqrs} (without a prime) will be used to indicate the integral-only part of the orbital Hessian (no ξ_{pq}^r or ζ_{pq} contributions). Portions of the ξ_{pq}^r and ζ_{pq} values are formed from locally held integrals and then summed onto all processors. Explicit storage of the orbital Hessian is impractical for systems with a large number of orbitals, so the CPHF equations are solved iteratively. In each step of the iterations, blocks of the orbital Hessian are created from locally held integrals. For A_{aibj} (the closed-shell-like block), A_{axbj} , and A_{axby} , the (volvo) and (vvloo) integrals reside on the same processor for a given oo pair. A local contribution to the orbital Hessian is constructed and subsequently multiplied by the appropriate section of the trial vector in order to yield a segment of the new vector. For A_{xij} , a similar procedure is followed for the (xy|ij) integrals and for the (xi|yj) integrals.

Contributions to the orbital Hessian are formed from local (voloo) integrals for the A_{aij} and A_{axyj} blocks.

For closed-shell systems, the linear equations are

$$\sum_b \sum_j \{A_{aibj} + \delta_{ab}\delta_{ij}(\epsilon_b - \epsilon_j)\} Z_{bj} = L_{ai} \tag{82}$$

Normally, the orbital energy term is taken outside the summation to yield:

$$(\epsilon_a - \epsilon_i)Z_{ai} + \sum_b \sum_j A_{aibj} Z_{bj} = L_{ai}. \tag{83}$$

This equation is divided by the orbital energy terms to yield a “preconditioned” equation

$$Z_{ai} + \sum_b \sum_j A_{aibj} \frac{Z_{bj}}{(\epsilon_a - \epsilon_i)} = \frac{L_{ai}}{(\epsilon_a - \epsilon_i)} \quad (84)$$

whose diagonal element ($A_{aiai}/(\epsilon_a - \epsilon_i)$) are of the order of unity, and then this is solved iteratively for Z_{ai} . In order to restructure the ZAPT2 equations and generate a similar form, a quantity m_{pq} is added and subtracted in diagonal elements of Eqn. 80:

$$\sum_{p,q}^{IP} \{ A_{pqrs} + \delta_{pr} (\xi_{qs}^p - \zeta_{sq}) + \delta_{qs} (\xi_{pr}^q - \zeta_{rp}) - m_{pq} * \delta_{pr} \delta_{qs} + m_{pq} * \delta_{pr} \delta_{qs} \} Z_{pq} = L_{rs} \quad (85)$$

where

$$\begin{aligned} m_{xi} &= \xi_{ii}^x + \xi_{xx}^i - \zeta_{ii} - \zeta_{xx} \\ m_{ai} &= \xi_{aa}^i - \zeta_{ii} = \epsilon_a - \epsilon_i \\ m_{ax} &= \xi_{aa}^x - \zeta_{xx} \end{aligned} \quad (86)$$

The last term in Eqn. 85 is separated out:

$$\sum_{p,q}^{IP} Z_{pq} m_{pq} \delta_{pr} \delta_{qs} + \sum_{p,q}^{IP} \{ A_{pqrs} + \delta_{pr} (\xi_{qs}^p - \zeta_{sq}) + \delta_{qs} (\xi_{pr}^q - \zeta_{rp}) - m_{pq} * \delta_{pr} \delta_{qs} \} Z_{pq} = L_{rs}, \quad (87)$$

and all terms are divided by m_{rs} to yield:

$$Z_{rs} + \sum_{p,q}^{IP} \{ A_{pqrs} + \delta_{pr} (\xi_{qs}^p - \zeta_{sq}) + \delta_{qs} (\xi_{pr}^q - \zeta_{rp}) - m_{pq} * \delta_{pr} \delta_{qs} \} \frac{Z_{pq}}{m_{rs}} = \frac{L_{rs}}{m_{rs}}. \quad (88)$$

This can be solved iteratively for Z_{rs} . The subtraction of and division by m_{rs} is a necessary preconditioning in order to keep the diagonal elements close to one and induce convergence of the iterative equations.

E. Completion of the One-Particle Density Matrices

Once Z_{rs} is known, the remaining terms in the one-particle density matrices may be finished. The off-diagonal blocks of $\mathbf{P}^{(2)}$ are determined by Eqn. 54. Terms 8 and 9 of W_{sr}

and terms 6 and 7 of W_{or} are computed from the ξ and ζ values. Contributions to terms 1 and 2 of W_{mm} , and terms 5 and 7 of W_{im} , W_{ij} , W_{xr} , and W_{xy} are created from local integrals and then globally summed. The (vvoo) integrals are no longer required, so the memory for these is released. The remaining integrals are needed in the two-particle nonseparable density matrix, so these are retained in memory. The completed $\mathbf{P}^{(2)}$ and $\mathbf{W}^{(2)}$ matrices are back-transformed to the AO basis, combined with their SCF analogs, and contracted with the appropriate derivative integrals.

F. Two-Particle Gradient

The four-index back-transformation of the amplitude terms in Γ^{NS} is similar to the procedure described previously.²⁵ For the closed-shell case, T_{ij}^{ab} amplitudes formed from (volvo) integrals that are locally held for a given oo pair are half-back-transformed to yield amplitudes with the form $T_{ij}^{\sigma\nu}$, which overwrite the (volvo) integrals in storage. For ZAPT2, an analogous procedure is employed for the closed-shell-like terms T_{ij}^{ab} , T_{ix}^{ab} , T_{xi}^{ab} , and T_{xy}^{ab} to yield amplitudes with the form $T_{pq}^{\sigma\nu}$, where p and q are occupied (DOCC and SOCC) indices. This part of the half-back-transformation requires no communication. The T_{ij}^{ax} , T_{ij}^{xa} , T_{ij}^{xy} , and T_{iy}^{xa} amplitudes can also be transformed to yield $T_{pq}^{\sigma\nu}$ amplitudes, which can be added to the half-back-transformed closed-shell-like amplitudes in the (volvo) storage. Since the two occupied indices that have not been back-transformed do not constitute a local pair in either the (voloo) or (ooloo) integral storage, communication between processors must occur. The number of amplitudes that must be transmitted will likely be small compared to the number of closed-shell-like amplitudes since these amplitudes involve at least one singly occupied

index. Once these amplitudes have been created, the memory for the (voloo) and (ooloo) integrals is released.

The separable two-particle density matrix for ZAPT2 includes terms that come from the back-transformation of Z_{xi} , Z_{av} , χ_{av} , and $\mathbf{P}^{\text{SCF-S}}$. These two-index transformations are not done in parallel since they are fairly trivial. A fourfold loop over shells is used to calculate the derivative ERI's. Inside the outer two loops, a set of $T_{pq}^{\sigma\nu}$ amplitudes is read in for a given σ, ν pair, which requires communication between the processors (Figure 4). Inside the third and fourth loops, the p and q indices are back-transformed to the AO basis. These steps are done locally. Inside the loops, the nonseparable and separable second-order two-particle density matrices are created, added to their SCF analog, and contracted with the appropriate derivative integrals. Since Γ^{NS} is not symmetrized, the derivative ERI's are computed four times more than the minimal list. This increased n^4 computation eliminates the need for n^4 storage and n^5 effort in the symmetrization.

IV. Timings

In this section, the scalability of the ZAPT2 gradient algorithm described in Section III is examined. All calculations were performed on a cluster system comprised of IBM p640 nodes connected by dual Gigabit Ethernet. Each p640 node has four 375 MHz Power3-II processors and 16 GB of memory.

Five molecular systems are considered in the benchmark calculations: three small gold clusters (Au_3H_4 , Au_3O_4 , and Au_5H_4), a dimeric dicyclopentadienyltitanium(III) chloride system, and a Fe-porphyrin:imidazole system. The smallest molecule under consideration is Au_3H_4 (Figure 5). The basis set used on this molecule consists of the aug-cc-pVTZ⁴¹ basis

set on H and the uncontracted Stevens-Basch-Krauss-Jasien-Cundari (SBKJC)⁴²⁻⁴⁴ effective core potential basis set, augmented with a set of 3f2g polarization functions and one set of sp diffuse functions on Au, for a total of 380 spherical harmonic basis functions. This molecule has 31 doubly occupied orbitals and one singly occupied orbital. A ZAPT2 gradient calculation requires 9.5 MWords of replicated memory and 170 MWords of distributed memory, so it fits in the memory of a single processor on the IBM cluster. For Au_3O_4 (Figure 6), the aug-cc-pVTZ^{41,45} basis set is used on O and the uncontracted SBKJC basis set with 3f2g polarization functions and one sp diffuse function is used on Au, for a total of 472 spherical harmonic basis functions. Calculations on this molecule involve 44 doubly occupied orbitals and one singly occupied orbital. 20.7 MWords of replicated memory and 562 MWords of distributed memory are required for a ZAPT2 gradient calculation, so the memory allotted to two nodes of the IBM cluster is necessary. Calculations on Au_5H_4 (Figure 7) employ the same basis set as that used for Au_3H_4 . 572 spherical harmonic basis functions are used in the ZAPT2 gradient calculations. This molecule has 49 doubly occupied orbitals and one singly occupied orbital. Each calculation requires 30.1 MWords of replicated memory and 1011 MWords of distributed memory. The memory allotted to three processors of the IBM cluster is sufficient to run a calculation on this system. For the $\text{Ti}_2\text{Cl}_2\text{Cp}_4$ system (Figure 8), the TZV basis set as defined in GAMESS³⁵ was employed, yielding 486 basis functions. A ZAPT2 gradient calculation on the lowest energy triplet state of this system involves 108 doubly occupied orbitals and two singly occupied orbitals, and requires 30.5 MWords of replicated memory and 2470 MWords of distributed memory. Six processors of the IBM cluster are required in order to run a calculation on this system. For the iron-porphyrin:imidazole system (Figure 9), two basis sets were used. The smaller basis

set consists of the MIDI basis set⁴⁶ with d polarization functions, and a calculation with this basis set has 493 basis functions. The larger basis set consists of the TZV basis set with d and p polarization functions, and a calculation with this basis set has 728 basis functions. For the triplet state, 110 orbitals are doubly occupied and two orbitals are singly occupied. A ZAPT2 gradient calculation with the smaller basis set requires 32.1 MWords of replicated memory and 2635 MWords of distributed memory, which corresponds to the memory allotted to seven processors on the IBM system. A similar calculation with the larger basis set requires 52.1 MWords of replicated memory and 5536 MWords of distributed memory, which corresponds to memory allotted to 15 processors on the IBM system.

Table 1 lists the wall clock time in seconds for a ZAPT2 gradient calculation on 1, 2, 4, 8, 16, 32, and 64 processors for the molecules benchmarked in this study. Tables 2 and 3 list the associated speedups and parallel efficiencies, respectively. The speedups may be visualized in Figure 10. Some superlinear speedup is noted for $\text{Ti}_2\text{Cl}_2\text{Cp}_4$ with the TZV basis set and Fe-porphyrin:imidazole with the MIDI(d) basis set with 16 processors and for the Fe-porphyrin:imidazole with the TZV(d,p) basis set with 32 and 64 processors. Most likely, this is due to an unusually long time for the run with 16 processors. Calculations investigating this hypothesis are in progress. The parallel efficiency for the ZAPT2 gradients is at least 85% on 32 processors and at least 73% on 64 processors for the systems examined in this analysis. As the size of the system increases, the parallel efficiency tends to increase as the time required for computation grows faster than the time required for communication.

ZAPT2 gradients require much less memory and computational time than similar UMP2 gradient calculations. A UMP2 gradient calculation on the Au_3H_4 system requires 18 MWords of replicated memory and 647 MWords of distributed memory, so it requires two

processors on the IBM cluster. This UMP2 calculation takes 79828 seconds, which is approximately a factor of three times the time required for a ZAPT2 gradient calculation (28292 seconds). For Au_5H_4 , a UMP2 gradient calculation requires 59.2 MWords of replicated memory and 3911 MWords of distributed memory. This would require the use of 11 processors on the IBM system. For a calculation with 16 processors on this system, the UMP2 gradient step takes 98418 seconds in contrast to a ZAPT2 gradient step that takes 26690 seconds.

V. Conclusion

The ZAPT2 gradient equations have been revised and subsequently implemented in GAMESS. Features of the scalable implementation using DDI have been discussed in detail. Data of order n^2 or less is replicated across the nodes, while molecular orbital integrals with two virtual indices or fewer are distributed across the nodes. Gradient terms involving molecular orbital integrals with three virtual indices have been adapted to utilize quarter-transformed integrals in a direct fashion. The algorithm has been designed to use locally held data as much as possible in order to reduce communication costs.

Benchmark calculations have been run on an IBM cluster for five molecular systems. The parallel efficiency for 32 processors is over 85%, and the parallel efficiency for 64 processors is over 73%. As the number of basis functions increases, the parallel efficiencies tend to increase. ZAPT2 gradient calculations require approximately one fourth of the memory and one third of the computational time necessary for a UMP2 gradient calculation.

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Appendix. Density Matrix Term Creation

In order to reduce communication needs, the algorithm for density matrix term creation is organized to take advantage of local integrals as much as possible. The following paragraphs outline the construction of each term, with emphasis on the integrals required.

For the P_{ab} block (Eqn. 53), the four terms that must be computed are:

$$\text{Term 1: } \sum_{i,j} \sum_{p \in \text{S.O.}} (ia | jp) [2(ib | jp) - (ip | jb)] / D_{ij}^{ap} D_{ij}^{bp}$$

$$\text{Term 2: } \sum_c \sum_{p,q \in \text{D.S.}} (pa | qc) [C_{pq}(pb | qc) - (pc | qb)] / D_{pq}^{ac} D_{pq}^{bc}$$

$$\text{Term 3: } \sum_{x,y} \sum_i (ix | ya)(ix | yb) / D_{iy}^{xa} D_{iy}^{xb}$$

$$\text{Term 4: } \frac{1}{2} \sum_{i,x,y} (ix | xa)(iy | yb) / D_i^a D_i^b$$

In order to further classify terms 1 and 2, the notation 1-P and 2-PQ will be used, where P and Q denote summations over V(IRT), S(OCC), or D(OCC) orbitals. For example, 1-V refers to $p \in \text{VIRT}$ in term 1 and 2-DS refers to $p \in \text{DOCC}$ and $q \in \text{SOCC}$ in term 2.

Similar notation is used for each density matrix block.

For terms 1-V and 2 of W_{ab} and P_{ab} , (volvo) integrals for a given oo pair are read from the local processor, amplitudes are formed, and the integrals and amplitudes are contracted without the need for communication between processors. However, most terms can not be completed in this manner. In order to create terms 1-VV and 2 of W_{im} and P_{im} , terms 1-VV and 2 of W_{ij} and P_{ij} , term 2 of W_{xy} and P_{xy} , term 2 of W_{xr} , and terms 1-VV and 3 of L_{xi} , a single

DDI_GET command^{25,26} is used in order to read a set of (volvo) integrals for a given vv pair. No further communication is required, since the essential amplitudes for these terms are created and contracted with these integrals. As each P_{xy} term is calculated, its contribution to χ_x and to term 4 of P_{xy} and term 9 of W_{xy} is determined. Term 9 of W_{xy} is held in a separate matrix until after the energy is calculated. Locally held (volvo) integrals are used to form amplitudes for contraction with remote (voloo) integrals to form terms 1-VV and 2 of W_{ar} .

Local (ooloo) integrals are used in the creation of term 1-SS of W_{im} and P_{im} , term 1-SS of W_{ij} and P_{ij} , term 1-S of W_{xy} and P_{xy} , term 1-SS of L_{xi} , and term 1-S of W_{xr} . Some communication is required to read in (voloo) integrals for term 1-SS of L_{ai} and 1-S of L_{ax} for use with the (ooloo) amplitudes. Local (voloo) integrals are used to form amplitudes, which are contracted with two sets of remote (voloo) integrals in order to form terms 1-S of W_{ab} and P_{ab} and terms 1-SV and 1-VS of W_{im} , P_{im} , W_{ij} , and P_{ij} . These amplitudes are also contracted with remote integrals to create term 1-S of W_{ar} and terms 1-SV and 1-VS of L_{xi} and L_{ar} . Next, local integrals are used to form term 1-V of W_{xy} and P_{xy} , and the amplitudes created are also used with remote integrals to form term 1-V of W_{xr} and L_{ax} .

For terms involving amplitudes of the form $(ix | ya)/D_{iy}^{xa}$, contributions to the amplitudes are produced from local integrals on each processor. These contributions are summed globally so that each processor has the full set of amplitudes in its local replicated memory. Then, they are contracted with locally held integrals to form term 3 of W_{ab} , P_{ab} , W_{ij} , P_{ij} , W_{im} , P_{im} , W_{xy} , P_{xy} , W_{xr} , and W_{ar} and term 5 of L_{xi} , L_{ai} , and L_{ax} . At this point, χ_x is complete so it is globally summed onto all processors. The amplitudes described in this paragraph may then be adjusted to form amplitudes of the type $\frac{1}{2}(ix | xa)/D_i^a$. Finally, term 4 of W_{im} , P_{im} ,

W_{ij} , P_{ij} , W_{xy} , W_{ab} , P_{ab} , W_{xr} , and W_{ar} and term 7 of L_{ax} , L_{ai} , and L_{xi} are created from contraction with locally held integrals.

At this point, the ZAPT2 energy can be calculated according to Eqn. 74. Then, χ_x and local integrals are used to form term 5 of P_{xy} , term 8 of W_{xy} , term 10 of W_{xr} , and term 12 of L_{ax} . This completes $\mathbf{P}^{(2)}$, so it is globally summed onto all processors.

Orbital energies are multiplied by appropriate elements of $\mathbf{P}^{(2)}$ in order to form term 6 of W_{im} , W_{ij} , and W_{xy} and term 5 of W_{ab} . Likewise, locally held integrals are multiplied by elements of $\mathbf{P}^{(2)}$ in order to create term 9 of L_{ai} and L_{ax} and term 10 of L_{xi} . The ϵ matrix is calculated from the α and β Fock matrices. Term 6 of W_{xr} , term 5 of W_{ar} , term 11 of L_{xi} , and term 10 of L_{ax} are formed by multiplying appropriate ϵ and $\mathbf{P}^{(2)}$ values.

References

- (1) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (2) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.
- (3) Hubac, I.; Carsky, P. *Phys. Rev. A* **1980**, *22*, 2392.
- (4) Murray, C.; Davidson, E. R. *Chem. Phys. Lett.* **1991**, *187*, 451.
- (5) Amos, R. D.; Andrews, J. S.; Handy, N. C.; Knowles, P. J. *Chem. Phys. Lett.* **1991**, *185*, 256.
- (6) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130.
- (7) Lauderdale, W. J.; Stanton, J. F.; Gauss, J.; Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1991**, *187*, 21.
- (8) Lee, T. J.; Jayatilaka, D. *Chem. Phys. Lett.* **1993**, *201*, 1.

- (9) Kozlowski, P. M.; Davidson, E. R. *Chem. Phys. Lett.* **1994**, 226, 440.
- (10) Murray, C.; Handy, N. C. *J. Chem. Phys.* **1992**, 97, 6509.
- (11) Lee, T. J.; Rendell, A. P.; Dyllal, K. G.; Jayatilaka, D. J. *Chem. Phys.* **1994**, 100, 7400.
- (12) Malmqvist, P.-Å. *Chem. Phys. Lett.* **1995**, 241, 429.
- (13) Davidson, E. R. *Chem. Phys. Lett.* **1995**, 241, 432.
- (14) Jayatilaka, D.; Lee, T. J. *Chem. Phys. Lett.* **1992**, 199, 211.
- (15) Guest, M. F.; Saunders, V. *Mol. Phys.* **1974**, 28, 819.
- (16) Fletcher, G. D.; Gordon, M. S.; Bell, R. L. *Theor. Chem. Acc.* **2002**, 107, 57.
- (17) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, 13, 225.
- (18) Pulay, P.; Saebø, S. *Theor. Chim. Acta* **1986**, 69, 357.
- (19) Handy, N. C.; Schaefer, H. F. J. *Chem. Phys.* **1984**, 81.
- (20) Handy, N. C.; Amos, R. D.; Gaw, J. F.; Rice, J. E.; Simandiras, E. D. *Chem. Phys. Lett.* **1985**, 120, 151.
- (21) Lee, T. J.; Racine, S. C.; Rice, J. E.; Rendell, A. P. *Mol. Phys.* **1995**, 85, 561.
- (22) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, 166, 275.
- (23) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, 166, 281.
- (24) Head-Gordon, M. *Mol. Phys.* **1999**, 96, 673.

- (25) Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S. Developments in Parallel Electronic Structure Theory. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons, Inc., 1999; Vol. 110; pp 267.
- (26) Fletcher, G. D.; Schmidt, M. W.; Bode, B. M.; Gordon, M. S. *Comput. Phys. Commun.* **2000**, 128, 190.
- (27) Nieplocha, J.; Harrison, R. J.; Littlefield, R. J. Global Arrays: A Portable "Shared-Memory" Programming Model for Distributed Memory Computers. In *Proceedings of Supercomputing 1994*; IEEE Computer Society Press: Washington DC, 1994; pp 340.
- (28) Alexeev, Y.; Kendall, R. A.; Gordon, M. S. *Comput. Phys. Commun.* **2002**, 143, 69.
- (29) Aikens, C. M.; Gordon, M. S. *J. Phys. Chem. A* **2004**, 108, 3103.
- (30) Fletcher, G. D., manuscript in preparation.
- (31) Dudley, T. J.; Olson, R. M.; Schmidt, M. W.; Gordon, M. S. *J. Comput. Chem.*, submitted.
- (32) Umeda, H.; Koseki, S.; Nagashima, U.; Schmidt, M. W. *J. Comput. Chem* **2001**, 22, 1243.
- (33) Krishnamoorthy, G.; Webb, S. P.; Nguyen, T.; Chowdhury, P. K.; Halder, M.; Wills, N. J.; Carpenter, S.; Kraus, G. A.; Gordon, M. S.; Petrich, J. W. *Photochem. Photobio.*, in press.
- (34) Gan, Z.; Alexeev, Y.; Kendall, R. A.; Gordon, M. S. *J. Chem. Phys.* **2003**, 119, 47.

- (35) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery Jr., J. A. *J. Comput. Chem* **1993**, *14*, 1347.
- (36) Olson, R. M.; Schmidt, M. W.; Gordon, M. S.; Rendell, A. P. *Proc. Supercomputing* **2003**.
- (37) Aikens, C. M.; Webb, S. P.; Bell, R. L.; Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S. *Theor. Chem. Acc.* **2003**, *110*, 233.
- (38) Yamaguchi, Y.; Osamura, Y.; Goddard, J. D.; Schaefer III, H. F. *A New Dimension to Quantum Chemistry. Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*; Oxford University Press: New York, 1994.
- (39) Nielsen, I. M. B. *Chem. Phys. Lett.* **1996**, *255*, 210.
- (40) Fletcher, G. D.; Rendell, A. P.; Sherwood, P. *Mol. Phys.* **1997**, *91*, 431.
- (41) Dunning Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (42) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.
- (43) Stevens, W. J.; Basch, H.; Krauss, M.; Jaisan, P. *Can. J. Chem.* **1992**, *70*, 612.
- (44) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.
- (45) Kendall, R. A.; Dunning Jr., T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769.
- (46) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

TABLE 1: Wall Clock Time (Seconds) for ZAPT2 Gradient Step on IBM Cluster

n	Au_3H_4 380	Au_3O_4 472	Au_5H_4 570	$\text{Ti}_2\text{Cl}_2\text{Cp}_4$ 486	Fe-porphyrin 493	Fe-porphyrin 728
P						
1	54943					
2	28292	68645				
4	13904	35181	105567			
8	6975	18324	53171	24852	65042	
16	3596	9422	26690	12205	31866	232551
32	1895	4965	13858	6859	16671	96404
64	1087	2843	7453	4214	9437	55019

TABLE 2: Speedup for ZAPT2 Gradient Step on IBM Cluster

n	Au_3H_4 380	Au_3O_4 472	Au_5H_4 570	$\text{Ti}_2\text{Cl}_2\text{Cp}_4$ 486	Fe-porphyrin 493	Fe-porphyrin 728
P						
1	1.0					
2	1.9	1.0				
4	4.0	2.0	1.0			
8	7.9	3.7	2.0	1.0	1.0	
16	15.3	7.3	4.0	2.0	2.0	1.0
32	29.0	13.8	7.6	3.6	3.9	2.4
64	50.5	24.1	14.2	5.9	6.9	4.2

TABLE 3: Parallel Efficiencies for ZAPT2 Gradient Step on IBM Cluster

n	Au_3H_4 380	Au_3O_4 472	Au_5H_4 570	$\text{Ti}_2\text{Cl}_2\text{Cp}_4$ 486	Fe-porphyrin 493	Fe-porphyrin 728
P						
1	100.0					
2	97.1	100.0				
4	98.8	97.6	100.0			
8	98.5	93.7	99.3	100.0	100.0	
16	95.5	91.1	98.9	101.8	102.1	100.0
32	90.6	86.4	95.2	90.6	97.5	120.6
64	79.0	75.5	88.5	73.7	86.2	105.7

Figure 1. First half-back-transformation of the (vo|vo) integrals. This procedure is used to form half-back-transformed integrals in the creation of (vv|vo) integrals. An analogous procedure yields half-back-transformed amplitudes for the creation of the non-separable two-particle density matrix. No communication is required in this step.

Figure 2. Algorithm for the creation of the Lagrangian (vv|vo) terms. This step requires communication across the processors in order to read in the half-back-transformed integrals.

	<i>yj</i>	<i>bj</i>	<i>by</i>
<i>xi</i>	A_{xiyj} (ooloo)	A_{xibj} (voloo)	A_{xiby} (voloo)
<i>ai</i>	A_{aiyj} (voloo)	A_{aibj} (vvloo) (volvo)	A_{aiby} (vvloo) (volvo)
<i>ax</i>	A_{axyj} (voloo)	A_{aiby} (vvloo) (volvo)	A_{axby} (vvloo) (volvo)

 $\times$

<i>yj</i>	Z_{yj}
<i>bj</i>	Z_{bj}
<i>by</i>	Z_{by}

 $=$

<i>xi</i>	L_{xi}
<i>ai</i>	L_{ai}
<i>ax</i>	L_{ax}

Figure 3. Pictorial representation of the Z-vector equations.

Figure 4. Second half-back-transformation of the amplitudes for the creation of the non-separable two-particle density matrix. This step requires communication across the processors in order to retrieve the half-back-transformed amplitudes.

Figure 5. Structure of Au_3H_4 .

Figure 6. Structure of Au_3O_4 .

Figure 7. Structure of Au_5H_4 .

Figure 8. Structure of $\text{Ti}_2\text{Cl}_2\text{Cp}_4$.

Figure 9. Structure of iron-porphyrin:imidazole.

Figure 10. Speedup curves for benchmark systems. The size of the basis set is listed in parentheses.