

Analysis of Static Correlation using Atomic
Populations of Effectively Localized Electrons
(APELE)

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by

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Abstract

Static or nondynamic correlation is an effect where the single-reference approximation fails to adequately describe a molecular system [32]. Systems dominated by nondynamic correlation require multi-reference (MR) methods, such as full-configuration interaction (FCI) or multi-configurational self-consistent field theory (MCSCF), which are impractical for most systems due to their high computational complexity. Most functionals in Density Functional Theory (DFT) fail to describe such systems due to the ever-elusive exchange-correlation term (E_{XC}) [4, 43]. In order to avoid using MR methods a number of diagnostics have been proposed that allow the user to determine the quality of their single-reference solution [26, 16, 18, 34]. It has been shown through preliminary tests that some of these diagnostics prove not to be size-extensive, while simultaneously being computationally complex themselves. Using the Kong-Proynov '16 / Becke '13 (KP16/B13) functional, atomic populations of effectively localized electrons (APELE) are generated and compared against current diagnostics to estimate nondynamic correlation [32, 23]. It is also shown that the APELE method is size-extensive and correlates well with wave-function based diagnostics.

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List of Acronyms

HF - Hartree-Fock

RHF - Restricted Hartree-Fock

UHF - Unrestricted Hartree-Fock

WFT - Wave Function Theory

DFT - Density Functional Theory

KS-DFT - Kohn-Sham Density Functional Theory

STO - Slater Type Orbital

GTO - Gaussian Type Orbital

CI - Configuration Interaction

CC - Coupled Cluster

MRCC - Multi-reference Coupled Cluster

MRDFT - Multi-reference Density Functional Theory

QCI - Quadratic Configuration Interaction

CCSD(T) - Coupled Cluster Singles Doubles and Perturbative Triples Excitations

MCSCF - Multiconfigurational Self-Consistent Field Theory

CASSCF - Complete Active Space Self-Consistent Field Theory

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A Brief Description of Molecular Modeling

The production of molecular modeling and visualization programs is important to several scientific disciplines, Medicinal Chemistry, Materials Science, and Solid-State Physics to name a few [37, 20]. These tools allow scientists to probe various atomic and molecular systems which provides valuable insights into the problems they are attempting to address. The creation of a molecular modeling program involves extensive research into electronic structure theories or the physics behind atoms, as well as a good understanding of efficiently implementing theoretical/mathematical models into computational algorithms. Ultimately, it is the goal of computational chemist and theoreticians to produce a model(s) of these systems that can accurately and efficiently provide meaningful data. The aim of this research is to bring this goal just a bit closer to fruition.

1 Wave-Function Theory

1.1 Einstein, de Broglie, and the Shrödinger Equation

In his 1905 paper on the Photoelectric Effect, Einstein proposed the idea that light possesses wave and particle nature which came to be known as wave-particle duality [30, p. 8]. This idea lead Louis de Broglie in 1924, in his doctoral dissertation, to hypothesize and mathematically prove that matter too possesses this attribute. Not long after in 1925, Erwin Shrödinger presented his non-relativistic quantum wave equation. The Shrödinger equation, much like Newton's laws, is taken as a postulate, it is not formally derived. However, we can make certain steps in a "pseudo-derivation" of sorts to help us achieve a better understanding of how it was

formed [30, p. 98]. We start from the one-dimensional classical wave equation:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \quad (1)$$

It can be solved using a technique known as separation of variables, producing solutions of the form:

$$u(x, t) = \psi(x)\cos(\omega t) \quad (2)$$

where $\psi(x)$ is the spatial factor of the amplitude $u(x, t)$, and $\cos(\omega t)$ is the sinusoidal function of time. Substituting equation (2) in equation (1) we get:

$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = 0 \quad (3)$$

We can now use angular frequency ($\omega = 2\pi\nu$) and the equation associated with the velocity of a classical wave ($v = \lambda\nu$) to transform (3) into:

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0 \quad (4)$$

Defining kinetic energy in terms of momentum and mass, we can write the total energy expression:

$$E = \frac{p^2}{2m} + V(x) \quad (5)$$

Now we must rearrange the equation for the momentum. In doing so we can incorporate de Broglie matter waves and transform the classical treatment into a quantum model:

$$p = \sqrt{2m[E - V(x)]} \quad (6)$$

Setting the expression equal to the wavelength of de Broglie matter waves gives us

the following:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m[E - V(x)]}} \quad (7)$$

Taking equation (7) and inserting it into equation (4) and defining $\hbar = \frac{h}{2\pi}$ we obtain:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 \quad (8)$$

Rearranging the equation, we are left with the one-dimensional time-independent Schrödinger equation (TISE):

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (9)$$

There is a time-dependent alternative to the TISE which proves to be useful for systems that evolve with time. Similarly it is taken as a postulate of quantum mechanics and has a pseudo-derivation that happens to be quite a bit more involved [30, p. 99]. However, the TISE is adequate for most problems pursued in the realm of chemistry. Although, in this form the Schrödinger equation is still one-dimensional. In order to make it three-dimensional we define the *Laplacian* operator:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Substituting the *Laplacian* operator is substituted into equation (9) gives the three-dimensional form of the TISE:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad (10)$$

1.2 The Molecular Hamiltonian

The time-independent Schrödinger equation (10) is a second order differential equation that does not possess an analytical solution for multi-electron systems. Thus, we must resort to numerical approximations by refactoring the problem as a linear algebra problem, more specifically an eigenfunction/eigenvalue equation [30, p. 171]. In doing so, we are left with solving for the wave-function solutions that represent a superposition of the configuration states of the system:

$$\hat{H}\psi = E\psi \quad (11)$$

In quantum mechanics, eigenfunction/eigenvalue equations use a mathematical operator that characterizes a physical observable. The Hamiltonian (\hat{H}) is the operator representing the total energy of the system and possesses five terms:

$$\hat{H} = -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (12)$$

We can form a much more intuitive expression for the operator by breaking it down component by component where V is the potential energy, T is the kinetic energy, and the subscripts N and e represent nuclei and electrons:

$$\hat{H} = -T_N - T_e - V_{Ne} + V_{NN} + V_{ee} \quad (13)$$

Starting from the first term we have the nuclear kinetic energy (T_N), kinetic energy of the electrons (T_e), nuclear-electronic attraction (V_{Ne}), nuclear-nuclear repulsion (V_{NN}), and finally the electron-electron repulsion (V_{ee}).

1.3 The Born-Oppenheimer Approximation

The Hamiltonian operator (and therefore the entire problem) can be simplified by employing the Born-Oppenheimer (Frozen Nuclei) approximation which states that the nucleus is essentially frozen in space with respect to the movement of electrons [39, p. 43]. This is a good approximation because the mass of nuclei are approximately 1,800 times that of electrons [1, p. 258]. Doing so allows us to drop the nuclear kinetic energy (T_N) to zero and the nuclear-nuclear repulsion (V_{NN}) becomes a constant added on at the end of our calculations. By invoking this approximation the Hamiltonian operator is truncated to the electronic Hamiltonian used to solve the *electronic* Schrödinger equation:

$$\hat{H}_{elec} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (14)$$

This form of the Hamiltonian operator turns (11) into:

$$\hat{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \quad (15)$$

Solutions to (15) are known as electronic wave-functions (and eigenvalues) and are parametrically dependent on the nuclear coordinates as well as the overall charge of the system. The coordinates of the nuclei are described using three spatial components (ϕ) and one spin component (σ) brought together to form spin orbitals (χ). We represent the spin orbitals using mathematical functions known as basis functions.

1.4 Basis Functions

Basis functions are used to model atomic orbitals and when used in linear combination with each other form molecular orbitals. The MO LCAO approximation

represents molecular orbitals as a linear combination of atomic orbitals [6, p. 112]. It is used to create wave-function solutions for the Schrödinger equation. In Computational Chemistry there are two primary functions used. Slater type orbitals (STO) and Gaussian type orbitals (GTO) given respectively by Eq. (16) and Eq. (17) [6, p. 134, 167]:

$$\psi_{\alpha,n,l,m}(r, \theta, \phi) = N_{\alpha,n} Y_{l,m}(\theta, \phi) r^{n-1} e^{-\alpha r} \quad (16)$$

In Slater type orbitals, $N_{\alpha,n}$ is the normalization coefficient that depends on the principle quantum number n , $Y_{l,m}(\theta, \phi)$ represents the angular part of the function through spherical harmonics, $r^{n-1} e^{-\alpha r}$ is the radial part, and α is a parameter used in the radial part [21, p. 98].

$$\psi_{\alpha,n,l,m}(r, \theta, \phi) = N Y_{l,m}(\theta, \phi) r^{2n-2-1} e^{-\alpha r^2} \quad (17)$$

The variables in the radial part represent the same aspects of the function, however their form is different. The choice of basis function to characterize the atom and thus the molecule is quite important and highly dependent upon the system. Active research is being done using both types of basis functions [27, 14].

1.5 The Hartree-Fock Approximation

The Hartree-Fock (HF) approximation is the simplest approximation scheme that is physically sound. This is in large part due to the simplifications made in the model, such as treating electrons as independent particles. The general idea of the model is to represent the N -electron wave-function as an antisymmetrized product of N one-electron spin orbitals ($\chi_i(\vec{x}_i)$), where N is the number of electrons, and spin orbitals are comprised of a spatial component (ϕ_i) combined with a spin component ($\sigma = \alpha$ or β). An important principle to mention which is also postulated in quan-

tum mechanics, is the antisymmetry principle, which is a more general expression of the Pauli exclusion principle [39, p. 45]. It states that the wave-function must be antisymmetric with respect to the interchanging of any two electrons' coordinates:

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = -\Psi(\vec{x}_2, \vec{x}_1, \dots, \vec{x}_N) \quad (18)$$

Which is due to the fact that they are fermions. We can employ an $N \times N$ square matrix, known as a Slater determinant, to build the wave-function which conveniently enforces the antisymmetry principle:

$\chi_i = \phi_i \sigma_i$; where $\sigma = \alpha$ or β ; and N is the number of electrons

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} \quad (19)$$

From the determinant we can build the expectation value of the Hamiltonian operator [39, p. 50]:

$$E_{HF} = \langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) | \hat{H} | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \rangle = \sum_i^N (i | \hat{h} | i) + \frac{1}{2} \sum_i^N \sum_j^N (ii | jj) - (ij | ji) \quad (20)$$

We define $(i | \hat{h} | i)$, the one-electron kinetic and nuclear-electronic attraction energy, $(ii | jj)$, the coulomb energy, and $(ij | ji)$, the exchange energy, the later two of which represent two-electron interactions.

1.6 Electron Correlation

The HF approximation does a good job of capturing most of the physics involved in many-electron systems [17, p. 134]. However, due to the use of a single Slater determinant and the approximation to the V_{ee} term it does not provide the true ground state non-relativistic energy solution. The correlation energy is therefore defined as the difference of the energy in the Hartree-Fock limit (E_{HF}) and the exact non-relativistic energy of the system (E_{Exact}) [39, p. 233]:

$$E_C^{\text{HF}} = E_{\text{Exact}} - E_{\text{HF}} \quad (21)$$

Where E_{Exact} is defined as the Full Configuration Interaction solution (FCI) [1, 39].

1.7 Dynamic and Nondynamic Correlation

Correlation can be split into two types that are caused by two different phenomena [43, p. 67]. The first type is dynamic correlation and comes from the HF models approximation to the electron-electron repulsion [21, p. 15]. The HF scheme moves each of the electrons in an average field of charge created from all of the other electrons, and because the electrons get too close to each other, the repulsion energy ends up being larger than the true non-relativistic ground state energy. This is why the HF method is often referred to as a mean-field approximation [1, p. 299]. The second kind of correlation energy is known as nondynamic or near-degeneracy correlation which arises when a single Slater determinant is insufficient in the description of the system [17, p. 154]. This commonly occurs when there exist determinants that yield similar energies or degenerate electronic configuration states [17, p. 154].

The following example, as well as, the graphical representation of the Unrestricted Hartree-Fock (UHF) and Restricted Hartree-Fock (RHF) dissociation curves for H_2

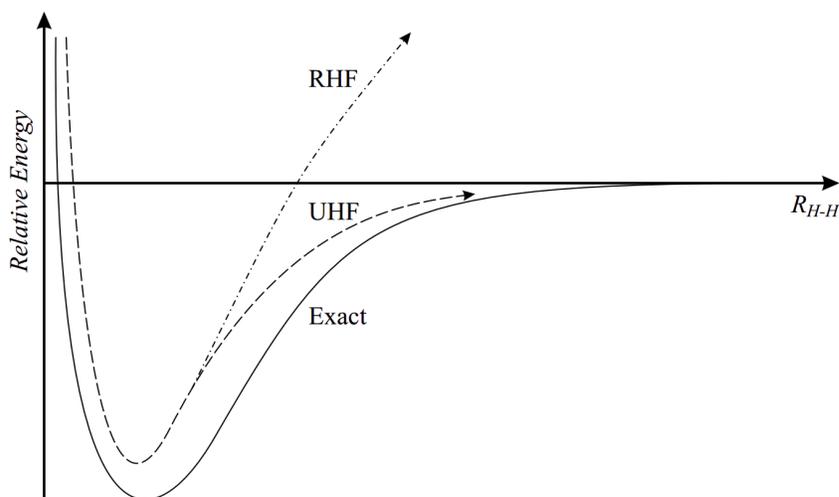


Figure 1: H₂ Bond Dissociation: Potential energy curves [21, p. 15]

come from reference [21, p. 15]. H₂ at an equilibrium bond length, gives an energy with an error of only $0.04E_h$ (hartrees). However, when the bond is stretched to infinity the error goes up to $0.25E_h$. Figure 1.7 shows the increase in error for the RHF model as the H₂ bond is stretched.

The RHF method fails to describe the dissociation properly due to the presence of ionic terms in its description of the wave-function. The ionic terms place both electrons on one hydrogen atom, while the neutral terms properly place a single electron on each of the hydrogen atoms. The ionic terms should contribute less as the distance between the atoms increase until they no longer contribute at all. The energy should approach that of two completely dissociated hydrogen atoms with an electron each (the neutral terms only):

$$E = \begin{cases} 2 * E(H_{atom}) & \text{if } r = \infty \\ 2h_{\sigma\sigma} + J_{\sigma\sigma} & \text{otherwise} \end{cases}$$

The proper dissociation can be described using a sum of two molecular orbital

(MO) configurations, or it can be modeled by an adequate occupation of the anti-bonding orbital [15]. The improper dissociation is due to the near-degeneracy that occurs between the bonding and anti-bonding orbitals as the molecule dissociates. There are many other examples where such left-right or static correlation manifests itself. Such as molecular transition states, geometries, metal-insulator transitions, and transition metal dimers to name a few [12, 41, 35, 48]. The dissociation of H_2 is properly described in the UHF scheme and other more advanced methods that address correlation such as configuration interaction (CI), complete active space self-consistent field theory (CASSCF), and multi-reference coupled cluster (MRCC) and density functional theory (MRDFT) [9, 11].

1.8 Configuration Interaction

The Configuration Interaction method treats both dynamic and nondynamic correlation by including more than one determinant when building the wave-function [39, p. 232]. Employing more than one determinant helps remedy dynamic correlation by using the spatial configuration of electrons with each and every different determinant, effectively allowing access to the correlated motion of the electrons. The treatment of nondynamic correlation is achieved through the use of a more descriptive wave-function solution built from multiple electronic configuration states (determinants). Put into mathematical terms, the CI wave-function takes the form:

$$\Psi_{\text{CI}} = c_0\Phi_{\text{HF}} + \sum_S c_S\Phi_S + \sum_D c_D\Phi_D + \dots \quad (22)$$

The first term represents the HF ground state determinant, the second term is the summation of all singly (S) excited determinants and each subsequent summation for the sum of the N^{th} excitation determinants. The number of excitations possible is

dependent upon the number of electrons in the system and the number of orbitals. By adding more excitation determinants to the CI calculation, we achieve convergence upon the true solution to the Schrödinger equation [17, p. 142]. This poses a problem however, the number of determinants required to produce the Full Configuration Interaction wave-function (using all possible determinants) is extremely large and scales out of practicality very quickly. For instance carrying out an FCI calculation on H₂O using a relatively small basis set, 6-31G*, produces over a 30*10⁶ different determinants that must be solved [17, p. 142].

At this point it is reasonable to think that truncating the number of determinants down to a more manageable quantity would help solve the issue while still providing more accurate solutions. However, truncating CI gives approximations that are no longer size-extensive, that is, the method does not scale with the system size properly [17, p. 153]. To solve the size-extensivity issues of CI, other methods such as, coupled cluster (CC) [17, p. 172] and quadratic configuration interaction (QCI) [6, p. 226] were designed.

1.9 Coupled Cluster

Coupled cluster theory as mentioned before was developed to remedy the size-extensivity issues with CI. CC is an extremely successful theory with its CCSD(T) method being deemed the “gold standard” for reproducing experimental results [6, p. 226]. The CC wave-function is built using the exponential of an excitation operator on the HF reference determinant [6, p. 225]:

$$\Psi_{CC} = e^{\mathbf{T}}\Phi_{HF} \quad (23)$$

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \dots + \mathbf{T}_n$$

n is the number of electrons and the excitation operator \mathbf{T}_i generates all determinants of excitation i . The single excitation operator takes the form:

$$\mathbf{T}_1\Phi_0 = \sum_{i,a} t_i^a \Phi_i^a$$

where the so-called \vec{t}_1 amplitudes represent weight coefficients for the excitation determinants. If we were to perform a CCD calculation only involving the double excitations, the wave-function would be built using a Taylor expansion of the excitations:

$$\Psi_{\text{CCD}} = (1 + \hat{T}_2 + \frac{\hat{T}_2^2}{2} + \frac{\hat{T}_2^3}{3!} + \dots)\Phi_{\text{HF}} \quad (24)$$

The Taylor expansion results in substitutions other than just doubles. For instance the square of the double excitations yields the quadruple excitations, and the cube results in the hextuple excitations [6, p. 225]. The inclusion of the higher order excitations is what makes the CC theory size-extensive [6, p. 225]. It is necessary to point out that although CC uses multiple determinants in its description of the wave-function, it is still considered a single-reference method because it only optimizes the wave-function using the HF determinant [29].

2 Density Functional Theory

2.1 The Thomas-Fermi model

It was understood that wave function theory (WFT), while providing excellent results, was too computationally complex [21, p. 29]. In 1927 Thomas and Fermi proposed that wave-functions are not the only route to solving the Schrödinger equation, but the electron density could be used as well [21, p. 29]. In order to define the Hamiltonian operator we need the number of electrons (N), the position of the nuclei (\vec{R}_A), and the charge of the nuclei (Z_A). All of which can be determined through the electron density. The number of electrons is found by integrating over the electron density:

$$\int \rho(\vec{r}) d\vec{r} = N \quad (25)$$

$\rho(\vec{r})$ has a maxima known as cusps that correspond to nuclear positions (\vec{R}_A) and contains information about the nuclear charge.

Although, the Thomas-Fermi (TF) model proved not to be accurate, it served as a proof of concept that the electron density could in fact be used to find the properties of a system [21, p. 31]:

$$E_{\text{TF}}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r} - Z \int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad (26)$$

It treats the nuclear-electronic attraction and electron-electron repulsion terms classically. The kinetic energy term has a very coarse approximation derived from the uniform electron gas model. The uniform electron gas is defined as an idealized system where the electron density is spread out in a uniform manner [28]. The uniformity of the gas makes handling the kinetic energy much more feasible, but results in loss of

accuracy.

Despite the giant step forward in achieving the Thomas-Fermi model, at this point there is no theoretical backing. While it serves as a proof the electron density can be used to find the energetics of a system, it is not understood if it is physically sound or variational in its parameters [21, 31].

2.2 Hohenberg-Kohn Theorems

In 1964, in order to lay a more rigorous foundation for density functional theory (DFT), Hohenberg and Kohn provided two theorems. The first theorem is an existence proof or a proof that the system is uniquely defined by its external potential (the expectation value of the nuclear-electronic attraction term ($\langle V_{Ne} \rangle$) in the Hamiltonian). The theorem is proven via *reductio ad absurdum* (or reduction to absurdity) [13]:

“ the external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes \hat{H} we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$ ”

It begins with the idea that there are two external potentials that have the same electron density (the opposite of the statement above). If we make a rather dangerous assumption that the wave function and the electron density have a one-to-one correspondence, it can be proven that the previous statement is false.

The second Hohenberg-Kohn theorem proves that the energy provided by the electron density, if we have the true ground state density, is a minimum energy solution of the system. This is the variational principle and it heavily relies on the first theorem to be true. That is if we have a trial density that meets the necessary boundary conditions [17, p. 232]:

- The integral of the density gives us the number of electrons.
- The density has maxima that correspond to nuclei.
- We can find nuclear charge from the maxima.

and is associated with an external potential, the energy from the functional represents an upper bound to the ground state energy.

2.3 Electron Density and Hole Functions

The probability density otherwise known as the electron density is a physical observable that can be measured using techniques such as X-ray diffraction and takes the form [21, 17]:

$$\rho(\vec{r}) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N \quad (27)$$

It tells us the probability of finding anyone of the N electrons in the same volume element $d\vec{r}_1$ while the other $N - 1$ electrons are in an arbitrary spatial/spin state. The electron density is the fundamental quantity used in density functional theory [21, p. 19], along with properties of the density such as, $\nabla\rho$ and $\nabla^2\rho$. Using the density, we can obtain the necessary information to solve the Schrödinger equation (number of electrons, location, and charge of the nucleus).

The concept of electron density can be extended further to the pair-density that takes into account more than one electron [21, 17]:

$$\rho(\vec{x}_1, \vec{x}_2) = N(N - 1) \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_3 \dots d\vec{x}_N \quad (28)$$

The pair density represents the probability of finding anyone of the N electrons at position $d\vec{r}_1$ while another one of the remaining $N - 1$ electrons is at $d\vec{r}_2$, while

the other $N - 2$ electrons are in arbitrary spatial/spin states. The pair-density is important because it contains all of the correlation information of the system [21, p. 21]. If we were dealing with non-charged, spin-less particles, the probability would simply be the product of the densities. However, we are dealing with charged fermions and we need to take Coulomb interactions and antisymmetry into account. Both of which will act to reduce the probability of find electrons close to each other. We can define the second-order reduced density matrix (2-RDM), a generalized form of the pair density, to account for antisymmetry [17, p. 237]:

$$\gamma(\vec{x}_1, \vec{x}_2; \vec{x}'_1, \vec{x}'_2) = N(N-1) \int \dots \int \Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \Psi^*(\vec{x}'_1, \vec{x}'_2, \vec{x}_3, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_N \quad (29)$$

The interchange of \vec{x}_1 and \vec{x}_2 or of \vec{x}'_1 and \vec{x}'_2 will result in a sign change for the 2-RDM. Using the diagonal elements of the 2-RDM, which corresponds to the pair density, and setting $\vec{x}_1 = \vec{x}_2$, we can show that the probability of finding two electrons with the same spin in the same space is equal to zero. That being the case we know the motion of same-spin electrons is correlated and we must account for this in the pair-density.

Similarly, the Coulombic interactions, more specifically, the electron-electron repulsion term produces a reduction in the probability of finding two electrons close to each other. The $\frac{1}{r_{12}}$ term as $r_{12} \rightarrow 0$, sends the repulsion energy to infinity. The reduced probability is modeled as a Coulomb or “correlation” hole [21, p. 27].

The reduction in probability of the pair density is modeled using so-called hole functions [21, p. 24]. There is a hole function for the exchange and correlation (Coulomb) terms which are combined to create the exchange-correlation hole [17, 21]:

$$h_{XC}(\vec{r}_1; \vec{r}_2) = h_X^{\sigma_1=\sigma_2}(\vec{r}_1; \vec{r}_2) + h_C^{\sigma_1, \sigma_2}(\vec{r}_1; \vec{r}_2) = \frac{\rho_2(\vec{r}_1, \vec{r}_2)}{\rho_1(\vec{r}_1)} - \rho_1(\vec{r}_2) \quad (30)$$

We can now define the electron-electron repulsion term using the exchange-correlation hole [17, 21]:

$$E_{ee} = \frac{1}{2} \int \int \frac{\rho_1(\vec{r}_1)\rho_1(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \int \int \frac{\rho_1(\vec{r}_1)h_{XC}(\vec{r}_1; \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad (31)$$

The first term is the classical electrostatic interaction of the charge distribution with itself, while the second term corrects the self-interaction energy of the first term. The use of hole functions makes correcting the electron-electron repulsion and kinetic energy more physically intuitive and easier to manipulate.

2.4 Kohn-Sham Density Functional Theory

Having the Hohenberg-Kohn theorems in place, proceeding with development of DFT can be done with far more confidence. The form of the expression in DFT for solving for the energy of a system is:

$$E_{DFT}[\rho] = T_s[\rho] + E_{ne}[\rho] + J[\rho] + E_{XC}[\rho] \quad (32)$$

Where $T_s[\rho]$ is the kinetic energy, $E_{ne}[\rho]$ is the nuclear-electron attraction, $J[\rho]$ is all of the classical Coulombic interactions, and $E_{XC}[\rho]$ is the notorious exchange-correlation term. The primary challenge in DFT is to determine the true form of the exchange-correlation functional which serves as a correction to the kinetic and correlation energy due to exchange and Coulomb interactions [4]:

$$E_{XC}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) \quad (33)$$

In Hohenberg-Kohn (HK) DFT, one must develop a form for the kinetic term, since it is not intuitive to go from a density to a kinetic energy, as well as, the

exchange-correlation term. Differently, in Kohn-Sham DFT (KS-DFT) [22], only the exchange-correlation energy needs to be derived. Kohn-Sham (KS) uses molecular orbitals much like the HF model to help it achieve more accurate kinetic energies than traditional HK DFT. Using this approach $\approx 99\%$ of the kinetic energy is obtained for most systems, while the missing $< 1\%$ is left for the exchange-correlation term.

Most DFT functionals aim to remedy the dynamical correlation left out in the HF scheme. It is a recent endeavor to try to tackle the nondynamic correlation using DFT. The Kong group has developed a KS-DFT functional, the KP16/B13 functional, that is capable of treating left-right correlation [33, 23, 24]. It use the adiabatic connection for the kinetic correlation energy and the correlation potential energy from the B13 model [23, 3].

3 Diagnostics of Nondynamic Correlation

3.1 Measuring Near-Degeneracy Correlation

We have discussed methods that can treat dynamic correlation, such as DFT and coupled cluster; and we have likewise mentioned methods that tackle both dynamic and nondynamic correlation, namely CI and MCSCF. While there are solutions to solving both types of correlation at our disposal, they are very costly and quickly out-scale our computational resources. Thus, currently there is a need for diagnostic tools that allow users to determine the quality of single-reference solutions (that only employ one Slater determinant) that do not address nondynamic correlation, e.g. most DFT functionals and coupled cluster.

There have been a number of techniques created for this very purpose [42, 26], however, they often involve the use of computationally complex methods themselves or require the help of other techniques to correct for their shortcomings [16]. Here we will dissect a few of the more common diagnostic methods and propose a technique of our own.

3.2 Current Diagnostics

Configuration Interaction and CASSCF

The configuration interaction wave function has coefficients for every determinant that represents contributions from each respective electronic state to the total wave function. Using this information we can deduce that systems with a large amount of nondynamic correlation would be those that have smaller contributions (to the total wave function) from the ground-state determinant or the HF determinant [17, p. 148]. This diagnostic is otherwise known as the leading wave function coefficient

(C_0), from the CI wave function expansion Eq. (22).

The CI version of this diagnostic is quite beneficial, although, it has been shown that it has an inherent bias to provide higher C_0 coefficients because the method uses HF orbitals [18]. Therefore, Complete Active Space SCF (CASSCF) [47] calculations are used to remedy CI’s shortcomings providing accurate C_0 coefficients. It is generally accepted that a system with a $C_0 < 0.95$ or a $C_0^2 < 0.90$ has multi-reference character and an MR method should be used in its description. The CASSCF solution however is a multi-reference solution and takes a considerable amount of time for all but small systems, thus in this research only figures provided by other sources were used.

Coupled Cluster

Coupled cluster employs *a priori* measures on \vec{t}_1 amplitudes and uses %TAE([T]) (percent total atomization energy (%TAE) of triple excitations ([T]) as indicators of near-degeneracy correlation. The Frobenius norm of the \vec{t}_1 amplitudes is taken and divided by the number of correlated electrons (n) to find the T_1 diagnostic [26]:

$$T_1 = \frac{\|\vec{t}_1\|}{\sqrt{n}} \quad (34)$$

The number of correlated electrons is only considered for valence electrons and not for the core electrons. There have been a few different thresholds suggested which are largely based on the types of systems observed [26, 18, 45]. Although, it is generally accepted that $T_1 > 0.02$ for organic molecules, $T_1 > 0.05$ for 3d transition metals, and $T_1 > 0.045$ for 4d transition metals indicates severe nondynamic correlation [18, 45].

The D_1 diagnostic is the matrix-norm of the \vec{t}_1 amplitudes. Instead of using the

sum of the \vec{t}_1 amplitudes, it uses the largest of the \vec{t}_1 amplitudes [16]:

$$D_1(\text{CCSD}) = \|\mathbf{T}\|_2 \quad (35)$$

D_1 was developed due to the realization that T_1 alone does not catch certain systems that are known to possess high degrees of static correlation [16]. Similar to T_1 , the D_1 diagnostic's threshold changes based on the system being observed [18, 45]. A threshold for organic molecules and the D_1 diagnostic was not found, but there are suggestions for $D_1 > 0.15$ for 3d- and $D_1 \geq 0.12$ for 4d-transition metals, indicating severe static correlation. Taking these two diagnostics a step further to analyze a system, one might also consider using the ratio between the $\frac{T_1}{D_1}$ diagnostics to determine the homogeneity of the system [25].

The final tool used from coupled cluster is %TAE([T]) [18]. It uses the total atomization energy of CCSD(T) (coupled cluster singles, doubles, and perturbative triple excitations) and CCSD to find the percentage of total atomization energy from triple excitations:

$$\%TAE([T]) = \frac{TAE(\text{CCSD}(T)) - TAE(\text{CCSD})}{TAE(\text{CCSD}(T))} * 100\% \quad (36)$$

The %TAE([T]) serves as the energy-based diagnostic for coupled cluster. It has been shown to correlate well with more comprehensive/expensive method based on the CCSDTQ and CCSDTQP methods, %TAE([T₄+T₅]) [18, 34]. %TAE([T]) indicated mild, moderate, and severe static correlation at less than 5%, greater than 5% and less than 10%, and greater than 10%, respectively [18].

Density Functional Theory

There have been a few methods developed for gauging static correlation in DFT,

however they have primarily been energy-based diagnostics. The promising B_1 method [36], developed by Truhlar, has shown to correlate with the T_1 diagnostic for systems such as BeO and MgO. Instead of this diagnostic however, another was chosen for this research that displayed similar qualities.

The A_λ diagnostic [34] was proposed, giving another energy-based measure of multi-reference character. It has been show to correlate very well with $\%TAE([T_4 + T_5])$ with certain functionals, such as PBE, boasting a correlation factor greater than 0.85:

$$A_\lambda = \frac{(1 - \frac{TAE[X_\lambda C]}{TAE})}{\lambda} \quad (37)$$

It uses the total atomization energy from a hybrid functional and its GGA complement. This measure gives indication of how much the hybrid functional deviates from the pure exchange functional, while the % Hartree-Fock exchange in the denominator acts to normalize the diagnostic. At $A_\lambda < 0.10$ the system is primarily dominated by dynamic correlation, $A_\lambda \approx 0.15$ indicates mild correlation, $A_\lambda \approx 0.30$ is moderate correlation, and $A_\lambda > 0.50$ is a severe correlation [34].

3.3 Atomic Populations of Effectively Localized Electrons

The concept of “odd electrons” originated from Takatsuka, Fueno, and Yamaguchi in 1978 and was further expanded upon by Staroverov and Davidson [40, 38]. Upon stretching the bond between two nuclei, the bonding electrons become partially decoupled and the electrons effectively localize on the nuclei. These electrons are referred to as odd electrons. Thus odd electrons are defined as electrons that exhibit radical character. Starting from the previously defined models in wave function theory, the Kong-group developed a KS-DFT model [33] that measures atomic populations of effectively localized electrons (APELE).

The APELE model is based on the deviation from idempotency of the first-order reduced density matrix (RDM-1 (γ_1)). Where idempotency is defined as the RDM-1 being equal to its square [31]:

$$\gamma_1 = \gamma_1^2 \quad (38)$$

The standard single-determinant KS RDM-1 is idempotent regardless of the exchange and correlation functionals that are used. The Kong group derived a non-idempotent correction to the RDM-1 based on the Becke '05 (B05) model exchange-correlation hole that takes left-right static correlation into account [32]:

$$D_\sigma(\mathbf{r}_1) = \rho_\sigma(\mathbf{r}_1) - \int \gamma_\sigma(\mathbf{r}_1; \mathbf{r}_2) \gamma_\sigma(\mathbf{r}_2; \mathbf{r}_1) d\mathbf{r}_2 \geq 0 \quad (39)$$

From Eq. (39) we get the number of effectively localized electrons of spin σ at position \mathbf{r}_1 . Summing over the spin gives us the total density of effectively localized electrons at position \mathbf{r}_1 :

$$D_u(\mathbf{r}) = 2 \sum_{\sigma} D_\sigma(\mathbf{r}) \quad (40)$$

The powerful aspect of this diagnostic is that it can decompose the total number of effectively localized electrons to give a local (or atom by atom) measure of static correlation:

$$F_r(A) = \int_{\Omega_A} D_u(\mathbf{r}) d\mathbf{r} \quad (41)$$

Where the atomic subregions are determined using Becke's grid integration scheme [32, 2].

4 Results and Discussion

4.1 Preliminary Diagnostics Tests

A small set of even numbered carbon chain molecules were taken to test the diagnostics’ ability to gauge static correlation. The two center carbon atoms were stretched out starting from an equilibrium bond length up to a maximum of 3.5Å. The stretching of the central C-C bond increases the left-right correlation in each of the molecules. The CCSD(T) calculations used to obtain the T_1 , D_1 , and %TAE([T]) diagnostics were performed with a 6-31G [7] basis set to ensure each diagnostic was computationally feasible. The APELE diagnostic used a cc-pVTZ [8] basis set to converge the measured APELE.

Table 1: Ethane: Left-Right Correlation Analysis

Diagnostic	$r_{eq}(1.53\text{\AA})$	2.0Å	2.5Å	3.0Å	3.5Å
APELE	0.1705	0.2141	0.2899	0.3669	0.4354
T_1	0.0036	0.0088	0.0185	0.0340	0.0312
D_1	0.0075	0.0324	0.0629	0.1304	0.1129
%TAE([T])	-0.0501	0.1946	1.3395	2.9680	4.7210
A_λ [M06]	-0.0088	-0.0086	0.0021	0.0174	0.0297
A_λ [M06-2X]	-0.0034	-0.0035	0.0090	0.0289	0.0493
A_λ [M06-HF]	-0.0059	-0.0077	0.0019	0.0204	0.0407

Table 2: Butane: Left-Right Correlation Analysis

Diagnostic	$r_{eq}(1.53\text{\AA})$	2.0Å	2.5Å	3.0Å	3.5Å
APELE	0.1708	0.2194	0.2987	0.3748	0.4399
T_1	0.0041	0.0074	0.0156	0.0350	0.0437
D_1	0.0104	0.0345	0.0653	0.1930	0.2074
%TAE([T])	0.0242	0.1819	1.0212	1.9267	2.2979
A_λ [M06]	-0.0079	-0.0043	0.0034	0.0118	0.0180
A_λ [M06-2X]	-0.0043	-0.0025	0.0050	0.0149	0.0245
A_λ [M06-HF]	-0.0060	-0.0050	0.0012	0.0104	0.0199

Psi4, an open-source quantum chemistry software package [44], was used to opti-

mize the structures at B3LYP/cc-pVQZ [46] using Gaussian’s [10] “very tight” convergence criteria (Max Forces: 2E-6 au, RMS Force: 1E-6 au, Max Displacement: 6E-6 au, RMS Displacement: 4E-6 au). Psi4 was also used to obtain the CCSD(T) diagnostics T_1 , D_1 , and %TAE([T]), as well as, the energies needed to obtain the A_λ diagnostic for M06, M06-2X, and M06-L. Instances in which the Psi4 package failed to deliver results were circumvented using the Gaussian09 software package for CCSD(T) calculations. The APELE results were obtained from KP16/B13 calculations with a 6-31G basis set (for the preliminary test) performed using the xTron code, an in-house computational program that allows users to run whole datasets with single commands in a cluster environment. The rest of the calculations done with the KP16 functional were performed with a cc-pVTZ basis set.

Table 3: Hexane: Left-Right Correlation Analysis

Diagnostic	$r_{eq}(1.53\text{\AA})$	2.0\AA	2.5\AA	3.0\AA	3.5\AA
APELE	0.1724	0.2209	0.3012	0.3785	0.4444
T_1	0.0043	0.0068	0.0152	0.0150	0.0188
D_1	0.0114	0.0355	0.0941	0.0847	0.1096
%TAE([T])	0.0567	0.1773	0.7456	1.0377	1.7525
A_λ [M06]	-0.0077	-0.0053	-0.0001	0.0054	0.0095
A_λ [M06-2X]	-0.0046	-0.0036	0.0013	0.0077	0.0141
A_λ [M06-HF]	-0.0058	-0.0056	-0.0018	0.0042	0.0105

Table 4: Octane: Left-Right Correlation Analysis

Diagnostic	$r_{eq}(1.53\text{\AA})$	2.0\AA	2.5\AA	3.0\AA	3.5\AA
APELE	0.1729	0.2209	0.3015	0.3788	0.4445
T_1	0.0044	0.0063	0.0131	0.0132	0.0151
D_1	0.0120	0.0353	0.0911	0.0840	0.0970
%TAE([T])	0.0743	0.1692	0.5989	0.8045	1.2862
A_λ [M06]	-0.0075	-0.0057	-0.0017	0.0025	0.0056
A_λ [M06-2X]	-0.0047	-0.0039	-0.0003	0.0046	0.0094
A_λ [M06-HF]	-0.0057	-0.0054	-0.0025	0.0020	0.0067

The preliminary test indicates that the APELE method properly displays an in-

Table 5: Correlation of diagnostics for ethane with increasing bond length.

	APELE	T_1	D_1	TAE([T])	A_λ [M06]	A_λ [M06-2X]
T_1	95.525					
D_1	94.028	99.777				
TAE([T])	98.513	91.496	89.762			
A_λ [M06]	98.362	92.901	91.256	99.784		
A_λ [M06-2X]	97.437	90.214	88.457	99.833	99.747	
A_λ [M06-HF]	95.779	87.519	85.713	99.287	99.119	99.781

crease in effectively localized electrons as the C-C bond distance increases. This trend holds steady, only varying slightly from ethane to octane. The data shows that the APELE method is size-extensive since it varies only slightly from ethane to octane and reflects the increase in left-right correlation through increasing measure of effectively localized electrons with increasing bond distance. Conversely, the total odd electron population, while showing the proper increase due to C-C bond distance, increases significantly as we add more atoms to the system. This is an issue worth looking into for the improvement of the model.

The T_1 diagnostic likewise shows the proper trend as the C-C bond distance is increased in each of the molecules. However, as we move from one molecule to the next the T_1 values slowly decline indicating that as the size of the system gets larger the ability of the diagnostic to accurately measure correlation decreases. Thus, the T_1 method lacks size-extensivity. The same trend is repeated in the other coupled cluster diagnostics as is reported in the literature [25]. The D_1 diagnostic does seem to be slightly more resilient to the increase in the size of the system, however, it inevitably displays size-extensivity issues as well.

The M06, M06-2X, and M06-HF functionals were chosen for the A_λ method in particular because they have increasing degrees of Hartree-Fock exchange, 27%, 54%, and 100% respectively. These functionals were used to determine if the amount

of Hartree-Fock exchange significantly affected the diagnostics ability to determine static correlation. The A_λ method, based on the thresholds suggested by the author, indicates no static correlation in any of the molecules at any bond length. However, it does display that static correlation increases with respect to the stretching of the bond. The A_λ , like the coupled cluster diagnostics, shows lack of size-extensivity. This seems to be particularly pathological in the energy-based methods.

Table 6: Correlation between the various diagnostics at the equilibrium bond length of the molecules.

	APELE	T_1	D_1	TAE([T])	A_λ [M06]	A_λ [M06-2X]
T_1	87.796					
D_1	86.671	99.963				
TAE([T])	88.670	99.982	99.899			
A_λ [M06]	82.595	99.477	99.703	99.269		
A_λ [M06-2X]	-83.679	-99.661	-99.836	-99.489	-99.980	
A_λ [M06-HF]	92.827	64.030	62.158	65.461	55.943	-57.567

A correlation analysis was done on the preliminary test between each method. The analysis done with respect to the increase in bond length for ethane in Table 5 shows great agreement with the lowest correlation being $\approx 85\%$. This trend shows that all diagnostics increase as the bond is stretched, indicating an increase in static correlation. A similar trend emerges from Table 6 where the correlation between the methods is done across each molecule at their respective equilibrium bond distances. The A_λ [M06-2X] method shows the exact opposite trend, while A_λ [M06-HF] only partially displays this trend. Thus, most methods do a good job of showing the proper lack of static correlation at the equilibrium bond length, however, the same analysis done at 3.5\AA further expands on the lack of size-extensivity with each method showing high negative correlations with the expected trend, given by the APELE method.

Table 7: Correlation between the diagnostics at the 3.5\AA stretched bond length of the molecules

	APELE	T_1	D_1	TAE([T])	A_λ [M06]	A_λ [M06-2X]
T_1	-66.114					
D_1	-26.425	89.755				
TAE([T])	-95.656	44.655	0.734			
A_λ [M06]	-98.997	64.709	24.589	97.107		
A_λ [M06-2X]	-98.088	53.475	10.777	99.458	98.974	
A_λ [M06-HF]	-98.333	54.429	11.891	99.319	99.103	99.992

4.2 W4-17

The W4-17 dataset was created by Karton *et. al.* for benchmarking purposes using the Weizmann-4 (W4) protocol [19]. It contains of 200 molecules comprised on first- and second-row atoms with geometry optimizations performed at the CCSD(T)/cc-pV(Q+d)Z level of theory. Using the W4 protocol, high confidence total atomization energies were generated for each of the 200 molecules. There are 17 molecules in the set that possess a high degree of multi-reference character, indicated by %TAE([T]) values provided in the supplementary material. A subset of singlet molecules

Table 8: Singlet Multi-reference: W4-17 subset

Molecule	Odd_{elec}	A_λ [M06]	A_λ [M06-2X]	A_λ [M06-HF]	T_1	D_1	%TAE([T])
BN	1.211	0.227	0.245	0.311	0.059	0.199	18.984
O ₃	1.541	0.223	0.210	0.270	0.023	0.077	17.840
F ₂ O ₂	1.863	0.328	0.274	0.289	0.022	0.087	16.877
ClF ₅	2.282	0.055	0.167	0.171			
F ₂ O	1.136	0.175	0.089	0.116	0.013	0.040	14.449
C ₂	1.397	0.194	0.594	0.271	0.032	0.086	13.144
ClF ₃	1.576	0.039	0.111	0.079	0.012	0.050	13.403
Cl ₂ O ₂	1.897	0.103	0.049	0.058	0.013	0.055	12.239
S ₄	2.553	0.169	0.184	0.153	0.014	0.088	12.663
Cl ₂ O	1.427	0.041	-0.001	-0.010	0.009	0.043	11.057
S ₃	1.867	0.148	0.143	0.101	0.014	0.054	10.594
F ₂	0.730	0.332	0.223	0.228	0.009	0.029	19.562

were chosen in specific, because singlet multi-reference systems are difficult to diag-

nose. In Table 8, the total odd electron populations are given instead of the APELE breakdown of each molecule. Only a few molecules will be analyzed to give the APELE, for practical purposes. In order to thoroughly investigate a given system one would need to use the APELE exclusively, not the total APELE. The total APELE analysis does not correlate well with the other methods, indicating that it is not a good measure of static correlation. It only shows a weak negative correlation with respect to the other diagnostics. The total APELE is not size-extensive and gets larger as the size of the system grows. A more accurate analysis, similar to the one done in the preliminary testing, would be to correlate the other diagnostics with the APELE of the local region suspected of having a large degree of static correlation.

There is excellent agreement between the A_λ method for M06 and M06-HF, showing a correlation factor of $\approx 77\%$. Interestingly, the higher the degree of Hartree-Fock exchange from the functionals the higher the correlation is between the A_λ and %TAE([T]), with A_λ [M06] and %TAE([T]) correlating at $\approx 78\%$ and A_λ [M06-HF] and %TAE([T]) correlating at $\approx 77\%$. The A_λ [M06-2X] method however shows very low correlation with %TAE([T]). Interestingly in the TM-11 dataset, the A_λ diagnostic for M06 and M06-HF show very low correlation with the %TAE([T]) diagnostic, $\approx 16\%$ for both, while M06-2X correlates very well with %TAE([T]) at $\approx 95\%$. The coupled cluster diagnostics show good agreement with T_1 and D_1 correlating at $\approx 95\%$, T_1 and %TAE([T]) at $\approx 47\%$, and D_1 and %TAE([T]) at $\approx 40\%$.

For a true comparison with the APELE method a set of molecules with similar composition were selected and built using ChemDraw [5]. Since the structures in Figure 4.2 have the same atomic composition we can make suggestions about the relative amount of static correlation in both structures. For instance, the carbon atoms in acetylene have more static correlation than either of the carbons in vinylidene. While the APELE of the hydrogen atoms in each only vary slightly. The static correlation

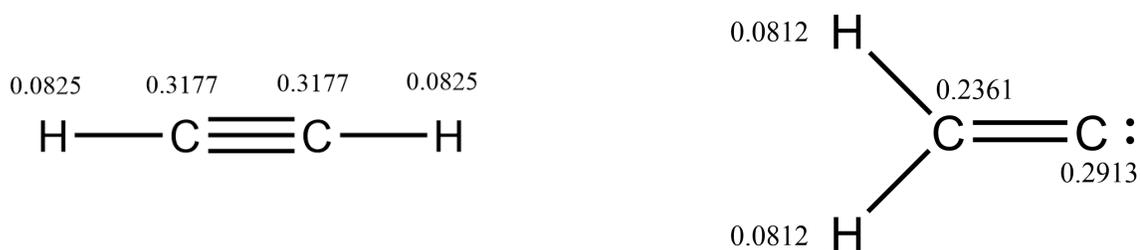


Figure 2: APELE: Acetylene and Vinylidene Comparison. The numbers represent the calculated atomic populations of effectively localized electrons

for acetylene provided by APELE is higher on all atoms, indicating a higher degree of static correlation on acetylene. The %TAE([T]) of acetylene and vinylidene backs this up with 1.97% and 1.82%, respectively. The T_1 and D_1 diagnostics show vinylidene as having more static correlation.

Similar to the acetylene and vinylidene comparison, we can evaluate the cis and trans conformations of nitrous acid. Based on wave-function diagnostics these two molecules have the same amount of static correlation. The APELE model shows that both have a very similar measure of effectively localized electrons with the trans conformation having slightly more. This is indicated once again by the %TAE([T]) with the cis- conformation having 5.14% and the trans- at 5.15%. The T_1 and D_1 show the opposite trend.

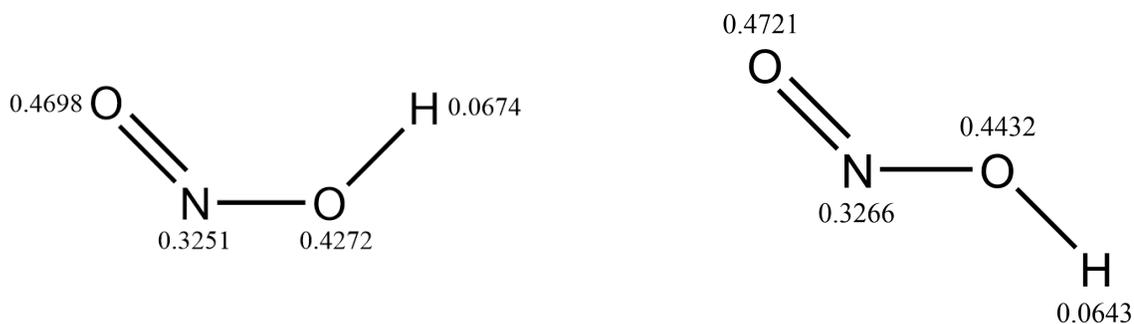


Figure 3: APELE: cis-Nitrous Acid and trans-Nitrous Acid Comparison. The numbers represent the calculated atomic populations of effectively localized electrons

4.3 TM-11

The TM-11 dataset contains 193 systems that span a variety of 3d transition metal molecules (i.e. metal hydrides, coordination complexes, etc.). DeYonker *et al.* provide geometries, thermochemical data, and coupled cluster as well as CASSCF-based measures of nondynamic correlation for most of the systems. A subset of the singlet multi-reference systems were hand-picked from the data to analyze. Those chosen for the subset were deemed statically correlated if any of the coupled cluster or CASSCF diagnostics indicated moderate to severe degrees of static correlation.

Table 9: Singlet Multi-reference: TM-11 subset

Molecule	Odd_{elec}	$A_\lambda[\text{M06}]$	$A_\lambda[\text{M06-2X}]$	$A_\lambda[\text{M06-HF}]$	T_1	D_1	%TAE([T])
ScH	0.984	0.043	0.355	0.302	0.023	0.044	1.300
ZnO	1.337	1.441	0.519	0.297	0.033	0.083	34.600
TiO ₂	1.970	0.192	0.285	0.219	0.042	0.096	10.400
CrO ₃	2.998	0.445	0.474	-4.170	0.051	0.190	20.000
CuF	0.737	0.258	0.148	0.124	0.041	0.163	3.400
Cr(CO) ₃	3.424	0.140	0.150	-1.812	0.054	0.179	6.500
Cr(CO) ₄	4.182	0.105	0.121	-1.334	0.036	0.137	5.800
Cr(CO) ₆	5.635	0.064	0.092	-0.869	0.028	0.090	5.300
NiCO	1.411	-0.057	0.298	0.294	0.046	0.133	11.100
Ni(CO) ₂	2.213	-0.006	0.187	0.188	0.037	0.097	7.500
Ni(CO) ₃	2.913	0.016	0.155	0.152	0.031	0.095	6.400
Ni(CO) ₄	3.664	0.024	0.140	0.134	0.031	0.089	6.100
Co(CO) ₄ H	4.045	0.003	0.003	0.002	0.052	0.253	5.500
Fe(CO) ₄ H ₂	4.231	0.002	0.002	0.002	0.056	0.191	5.100
Fe(C ₅ H ₅) ₂	2.926	0.017	0.042	0.038	0.047	0.188	2.800
Co(CO) ₂ H(PF ₃) ₂	4.994	-0.033	0.085	0.078	0.040	0.253	4.700
Co(CO) ₃ HPF ₃	4.544	0.002	0.003	0.003	0.046	0.255	5.100
V ₄ O ₁₀	9.165	0.062	0.247	0.256	0.042	0.122	10.700
Cr ₃ O ₉	8.820						17.500
VOCl ₃	3.201	0.100	0.306	0.311	0.034	0.110	11.100
CrOF ₂	2.166	0.288	0.212	-4.704	0.044	0.132	11.500
CrOCl ₂	2.388	0.392	0.283	-5.521	0.044	0.133	13.800
CrClFO ₂	3.338	0.358	0.399	-3.326	0.039	0.155	16.100
CrO ₂ F ₂	3.141	0.328	0.366	-3.137	0.039	0.148	15.000
CrO ₂ Cl ₂	3.537	0.392	0.436	-3.537	0.038	0.161	17.400
CrO ₂ (OH) ₂	3.329	0.004	0.004	-0.031	0.040	0.144	11.300
NiSi	1.601	-0.185	1.443	1.374	0.082	0.208	54.100
NiGe	2.080	-0.056	1.828	1.605	0.092	0.230	64.900

A correlation analysis including the C_0^2 values was skipped for the singlet multi-

reference subset in Table 9 since most of the singlet systems did not have it. The A_λ method characterizes only a few of these systems as having severe static correlation, despite the degree of multi-reference character indicated by the other methods. A good example of this is the results for ZnO, where each functional gives a significantly different result. Inconsistencies such as this make this method difficult to trust for diagnosing a system.

A correlation analysis done over the entire TM-11 dataset using C_0^2 showed a decent correlation between T_1 and C_0^2 at $\approx -60\%$ and an even better correlation between $\%TAE([T])$ and C_0^2 at $\approx -67\%$. The correlations are negative because as the C_0^2 decreases it indicates more static correlation, while the other methods increase as static correlation increases. The correlation found between C_0^2 and $\%TAE([T])$, although decent for this set of molecules, should decrease significantly as systems of greater size are taken into consideration. The leading wave-function coefficients are difficult to obtain and can only be done for small systems. This allows for the $\%TAE([T])$ method to correlate with C_0^2 , but if larger systems are introduced into the correlation analysis, $\%TAE([T])$'s lack of size-extensivity will cause their percent correlation to decrease. Analysis of the $A_\lambda[M06]$ and $[M06-2X]$ methods over the whole set show great agreement between each other, $\approx 99\%$, while the trends between M06 and M06-HF and M06-2X and M06-HF are $\approx -99\%$ and $\approx -87\%$, respectively. This data indicates that higher degrees of HF exchange might be detrimental to the diagnostic for 3d transition metals.

In Table 10 the metal center of a set of coordination complexes were analyzed using the APELE diagnostic. APELE estimates the strength of nondynamic correlation locally which is highest around the Ni center, despite the size of the ligands. The other diagnostics give a global system estimate, because of this their trend of increasing the global size of the system may be misleading. The $A_\lambda[M06]$ and APELE diagnostics

Table 10: APELE of Metal Center

Molecule	Odd_{elec}	$A_\lambda[\text{M06}]$	$A_\lambda[\text{M06-2X}]$	$A_\lambda[\text{M06-HF}]$	T_1	D_1	%TAE([T])
NiCO	0.63	-0.057	0.298	0.294	0.046	0.133	11.100
Ni(CO) ₂	0.67	-0.006	0.187	0.188	0.037	0.097	7.500
Ni(CO) ₃	0.66	0.016	0.155	0.152	0.031	0.095	6.400
Ni(CO) ₄	0.69	0.024	0.140	0.134	0.031	0.089	6.100
Ni(PF ₃) ₄	0.65	-0.105	0.034	0.032	0.020	0.086	4.600
Cr(CO) ₃	0.97	0.140	0.150	-1.812	0.054	0.179	6.500
Cr(CO) ₄	0.96	0.105	0.121	-1.334	0.036	0.137	5.800
Cr(CO) ₆	0.94	0.064	0.092	-0.869	0.028	0.090	5.300

have a trend indicating an increase in static correlation as the Ni complexes increase in size. The opposite trend is seen with the other diagnostics. The APELE of Cr in the Cr complexes show the opposite trend to that of Ni, following suite with the other diagnostics. Considering the inconsistency of these trends with APELE of the metal center, further investigation is needed.

4.4 Summary and Conclusion

While using multi-reference methods to determine whether or not a system possesses a high degree of static correlation is generally a more accurate approach, such as with the leading wave-function coefficient (C_0) from a CASSCF calculation, these methods are too computationally complex. They are also not necessarily foolproof either. The APELE method is size-extensive and efficient due to its implementation in the KS-DFT framework. More importantly the APELE method gives a local description of the nondynamic correlation on a local level, which is not seen from any other diagnostics thus far. The two energy-based diagnostics show the correct trend in a system with increasing static correlation, but using them to define a system as multi-reference should be done with caution seeing as size-extensivity is a big determining factor in their analysis. The T_1 diagnostic used in conjunction with D_1 is useful for small systems, but similarly succumbs to size-extensivity.

The APELE method ultimately has desirable benefits not seen in other methods. I believe the next step for this diagnostic involves determining a manner in which to compare the static correlation between a certain atom in one system with the same type of atom in a completely different system. This step will allow for a general qualitative definition of what is considered statically correlated, on a per atom basis, to form for the APELE method.

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Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
Acetaldehyde	1	1.0856	-0.0079	0.0013	0.0055	0.0125	0.0480	1.6136
Acetic	1	1.4048	-0.0237	-0.0081	0.0040	0.0126	0.0540	1.8834
AlCl ₃	1	1.6807	0.0967	0.0507	0.0470	0.0052	0.0235	2.1070
AlCl	1	0.9244	0.0034	0.0087	0.0146	0.0070	0.0256	2.2889
AlF ₃	1	1.2014	-0.0262	-0.0124	-0.0116	0.0098	0.0346	1.6633
AlF	1	0.7626	-0.0856	-0.0356	-0.0245	0.0105	0.0288	1.8662
AlH ₃	1	0.5172	0.0003	0.0555	0.0377	0.0056	0.0151	0.0718
AlH	1	0.5224	-0.1132	0.0073	0.0076	0.0076	0.0252	0.3099
Allene	1	1.1374	0.0172	0.0101	0.0065	0.0107	0.0298	1.6430
Allyl	2	0.9623	0.0097	0.0094	0.0055	0.0346	0.0000	1.2380
B ₂	3	0.5351	0.3002	0.0974	0.1061	0.0229	0.0000	7.4641
B ₂ H ₆	1	0.6635	0.0149	0.0152	0.0115	0.0086	0.0188	0.6813
Benzene	1	1.9992	0.0234	0.0099	0.0066	0.0088	0.0286	1.8500
Beta-Lactim	1	1.6961	-0.0023	-0.0015	0.0018	0.0124		2.0948
BF ₃	1	1.0637	-0.0718	-0.0300	-0.0072	0.0103	0.0436	1.6667
BF	1	0.5462	-0.0864	-0.0283	-0.0103	0.0135	0.0308	2.1305
BH ₃	1	0.2987	-0.0169	0.0062	-0.0010	0.0058	0.0094	0.2618
BH	1	0.2652	-0.1498	-0.0494	-0.0692	0.0110	0.0257	0.5744
BHF ₂	1	0.8244	-0.0588	-0.0212	-0.0083	0.0112	0.0435	1.4053
BN _T	3	0.4367	0.2079	0.6756	0.3708	0.0512	0.0000	5.8866
BN _S	1	1.2112	0.2272	0.2450	0.3113	0.0593	0.1987	18.9836
Borole	1	1.5769	0.0183	0.0104	0.0075	0.0100	0.0348	1.7342
C ₂	1	1.3969	0.1936	0.5945	0.2707	0.0315	0.0860	13.1443
C ₂ Cl ₂	1	1.7529	0.0614	0.0521	0.0442	0.0079	0.0261	3.9398
C ₂ Cl ₄	1	2.5479	0.0700	0.0452	0.0325	0.0071	0.0332	4.2055
C ₂ Cl ₆	1	3.2659	0.0397	0.0303	0.0178	0.0100		5.5089

Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
C ₂ ClH ₃	1	1.2062	0.0175	0.0087	0.0024	0.0080	0.0305	1.7958
C ₂ ClH ₅	1	1.1334	-0.0023	-0.0009	-0.0050	0.0065	0.0231	1.2233
C ₂ ClH	1	1.2770	0.0340	0.0290	0.0244	0.0088	0.0274	2.8590
C ₂ F ₄	1	1.7826	-0.0516	0.0029	0.0167	0.0107	0.0407	2.9825
C ₂ F ₆	1	2.2012	-0.0727	-0.0170	0.0043	0.0100	0.0355	2.6722
C ₂ H ₂	1	0.7956	0.0067	0.0070	0.0051	0.0114	0.0289	1.9568
C ₂ H ₃ F	1	1.0179	-0.0103	-0.0009	-0.0017	0.0105	0.0305	1.6708
C ₂ H ₄	1	0.7581	0.0013	-0.0003	-0.0047	0.0095	0.0325	1.2359
C ₂ H ₅ F	1	0.9687	-0.0209	-0.0082	-0.0091	0.0084	0.0236	1.1475
C ₂ H ₆	1	0.7113	-0.0089	-0.0035	-0.0060	0.0069	0.0134	0.8365
CCH	2	0.5838	0.0251	0.0322	0.0276	0.0163	0.0000	2.0480
CCl ₂	1	1.3479	0.0988	0.1015	0.0848	0.0138	0.0724	5.8638
CCl ₂ H ₂	1	1.2758	0.0150	0.0095	-0.0006	0.0060	0.0225	2.0803
CCl ₂ O	1	1.7227	0.0393	0.0474	0.0538	0.0103	0.0470	4.1737
CCl ₃ H	1	1.7197	0.0285	0.0202	0.0082	0.0063	0.0232	3.2162
CCl ₄	1	2.1583	0.0385	0.0340	0.0198	0.0065	0.0241	4.7594
CClH ₃	1	0.8338	-0.0002	0.0013	-0.0065	0.0059	0.0212	1.2377
CF ₂	1	0.8875	-0.0688	0.0034	0.0201	0.0146	0.0582	3.3747
CF ₂ Cl ₂	1	1.7772	-0.0239	0.0070	0.0147	0.0081	0.0309	3.5067
CF ₄	1	1.3913	-0.0882	-0.0222	0.0017	0.0094	0.0301	2.5929
CF	2	0.5192	-0.0592	0.0126	0.0210	0.0240	0.0000	3.6114
CH ₂ C	1	0.6885	-0.0036	0.0100	0.0084	0.0146	0.0405	1.8116
CH ₂ CH	2	0.6791	0.0184	0.0135	0.0098	0.0534	0.0000	1.3776
CH ₂ ClF	1	1.0971	-0.0188	-0.0044	-0.0081	0.0076	0.0264	1.8757
CH ₂ F ₂	1	0.9155	-0.0535	-0.0200	-0.0170	0.0093	0.0282	1.6745
CH ₂ NH ₂	2	0.6648	-0.0197	-0.0123	-0.0127	0.0200	0.0000	1.3023
CH ₂ NH	1	0.7997	-0.0041	-0.0036	-0.0073	0.0105	0.0352	1.8228

Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
CH ₂ _Sing	1	0.3236	-0.0678	-0.0001	-0.0072	0.0079	0.0189	0.9978
CH ₂ _Trip	3	0.2379	0.0021	-0.0030	0.0009	0.0135	0.0000	0.4406
CH ₃	2	0.3138	-0.0067	-0.0005	-0.0050	0.0104	0.0000	0.5504
CH ₃ F	1	0.6627	-0.0349	-0.0123	-0.0153	0.0081	0.0213	1.1446
CH ₃ NH ₂	1	0.7394	-0.0259	-0.0163	-0.0173	0.0067	0.0149	1.1563
CH ₃ NH	2	0.6337	-0.0017	0.1803	0.0947	0.0174	0.0000	1.3652
CH ₃ PH ₂	1	0.9471	-0.0284	-0.0137	-0.0178	0.0081	0.0223	1.0149
CH ₄	1	0.4066	-0.0134	-0.0041	-0.0072	0.0067	0.0121	0.6396
CH	2	0.2330	-0.0742	-0.0095	-0.0226	0.0133	0.0000	0.9755
cis-HCOH	1	0.7235	-0.0615	-0.0205	-0.0105	0.0159	0.0567	2.2037
CHF ₃	1	1.1600	-0.0703	-0.0222	-0.0092	0.0097	0.0298	2.1579
cis-HONO	1	1.2558	-0.0063	0.0056	0.0333	0.0181	0.0633	5.1369
cis-HOOO	2	1.2081	0.0707	0.0407	0.0800	0.0475		7.4351
cis-C ₂ F ₂ Cl ₂	1	2.1716	0.0090	0.0246	0.0257	0.0117		3.8444
Cl ₂	1	0.9922	0.0440	0.0598	0.0170	0.0052	0.0203	7.6554
Cl ₂ O	1	1.4272	0.0415	-0.0012	-0.0099	0.0094	0.0427	11.0573
ClCN	1	1.3257	0.0690	0.0480	0.0427	0.0101	0.0289	4.2468
ClCOF	1	1.4965	-0.0039	0.0262	0.0411	0.0112	0.0484	3.5694
ClF ₃	1	1.5765	0.0393	0.1114	0.0793	0.0123	0.0501	13.4025
ClF ₅	1	2.2824	0.0551	0.1673	0.1714	0.0152		26.1998
ClF	1	0.8217	-0.0561	-0.0279	-0.0607	0.0080	0.0305	8.3516
ClNO	1	1.5006	0.1303	0.1226	0.1344	0.0159	0.0614	8.7982
ClO ₃	2	1.7127	0.2362	0.2112	0.5626	0.0301	0.0000	24.3049
ClO	2	0.7947	0.1474	0.0823	0.0913	0.0384	0.0000	9.6169
ClOO	2	1.4502	0.2688	30.9165	0.2834	0.0473	0.0000	10.4035
ClOOC1	1	1.8967	0.1030	0.0486	0.0583	0.0129	0.0548	12.2393
cis-N ₂ H ₂	1	0.8500	-0.0007	-0.0075	-0.0078	0.0108	0.0340	3.3424

Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
CN	2	0.7819	-0.5587	-0.2481	0.0271	0.1056	0.0000	5.1937
CO ₂	1	1.1580	0.0021	0.0417	0.0689	0.0155	0.0472	3.4251
CO	1	0.7030	-0.0197	-0.0065	0.0095	0.0158	0.0394	2.9970
CS ₂	1	1.6638	0.1218	0.0912	0.0789	0.0131	0.0510	5.5756
CS	1	0.9698	0.0723	0.0459	0.0335	0.0170	0.0504	5.6723
Cyclobutadiene	1	1.4358	0.0222	0.0135	0.0090	0.0106	0.0408	2.1407
Cyclobutane	1	1.2536	-0.0001	0.0011	-0.0014	0.0071	0.0172	1.2004
Cyclobutene	1	1.3344	0.0126	0.0075	0.0038	0.0087	0.0305	1.5079
Cyclopentadiene	1	1.6675	0.0148	0.0071	0.0043	0.0096	0.0339	1.7075
Cyclopropane	1	0.9765	0.0016	0.0021	-0.0003	0.0067	0.0164	1.1873
Cyclopropene	1	1.0789	0.0127	0.0126	0.0098	0.0086	0.0300	1.6986
Cyclopropyl	2	0.9116	0.0129	0.0125	0.0107	0.0143	0.0000	1.2761
Dioxetan-2-one	1	1.7337	-0.0184	-0.0011	0.0157	0.0134	0.0569	2.7388
Dioxetane	1	1.3292	-0.0308	-0.0190	-0.0124	0.0091	0.0277	1.9197
Dioxirane	1	1.1672	0.0118	-0.0025	0.0112	0.0121	0.0360	3.3747
Dithiotane	1	1.6354	0.0087	0.0000	-0.0109	0.0078	0.0242	2.1065
Ethanol	1	1.0337	-0.0283	-0.0167	-0.0125	0.0078	0.0194	1.2018
F ₂	1	0.7299	0.3319	0.2233	0.2278	0.0093	0.0289	19.5618
F ₂ CO	1	1.2671	-0.0469	0.0074	0.0313	0.0120	0.0490	3.0529
F ₂ O	1	1.1365	0.1753	0.0888	0.1156	0.0130	0.0403	14.4494
FCCF	1	1.3182	-0.0531	0.0194	0.0359	0.0112	0.0298	3.4090
FNO	1	1.2309	0.0728	0.0740	0.0892	0.0182	0.0598	7.5113
FO ₂	2	1.3010	0.2998	0.2386	0.2613	0.0494	0.0000	19.3700
FOOF	1	1.8632	0.3283	0.2741	0.2889	0.0222	0.0866	16.8767
Formamide	1	1.1411	-0.0221	-0.0065	0.0003	0.0138	0.0540	2.1199
Formic-Anhydride	1	1.8357	-0.0166	0.0028	0.0183	0.0147	0.0492	2.7690
Formic	1	1.1166	-0.0377	-0.0124	0.0048	0.0141	0.0540	2.3582

Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
Furan	1	1.7277	0.0096	0.0037	0.0045	0.0134		2.1864
Glyoxal	1	1.4654	-0.0054	0.0068	0.0178	0.0138	0.0500	2.5604
H ₂	1	0.0955	-0.1441	-0.0844	-0.0751	0.0056	0.0080	0.0000
H ₂ CCN	2	1.0654	0.0355	0.0257	0.0238	0.0434	0.0000	2.1840
H ₂ CN	2	0.6814	0.0282	0.0199	0.0157	0.0552	0.0000	1.9660
H ₂ CO	1	0.7774	-0.0170	0.0014	0.0063	0.0135	0.0459	1.9966
H ₂ NO	2	0.6881	-0.0222	-0.0185	-0.0055	0.0297	0.0000	2.5864
H ₂ O	1	0.4010	-0.0993	-0.0575	-0.0350	0.0058	0.0106	1.3219
H ₂ S	1	0.6421	-0.0107	-0.0072	-0.0161	0.0062	0.0160	1.1766
HCCF	1	1.0556	-0.0185	0.0158	0.0234	0.0114	0.0274	2.6582
HCl	1	0.5499	0.0075	0.0110	0.0047	0.0038	0.0107	1.3120
HClO ₄	1	2.0523	0.0371	0.0566	0.1189	0.0144	0.0619	8.3154
HCN	1	0.8207	0.0199	0.0074	0.0061	0.0122	0.0294	2.8247
HCNH	2	0.7283	0.0179	0.0129	0.0120	0.0484	0.0000	2.3925
HCNO	1	1.3896	0.0327	0.0532	0.0634	0.0181	0.0539	4.6582
HCO	2	0.6962	0.0066	0.0183	0.0304	0.0273	0.0000	2.7875
HCOF	1	1.0378	-0.0292	0.0040	0.0170	0.0136	0.0484	2.5921
HF	1	0.3304	-0.1451	-0.0571	-0.0412	0.0059	0.0116	1.2698
HNC	1	0.7599	-0.0039	-0.0039	-0.0044	0.0141	0.0336	2.8315
HNCO	1	1.2172	0.0067	0.0305	0.0441	0.0156	0.0518	3.2315
HNNN	1	1.4415	0.0642	0.0588	0.0627	0.0169	0.0527	5.5113
HNO	1	0.8231	-0.0096	-0.0076	0.0070	0.0133	0.0432	4.7191
HOCl	1	0.8936	-0.0631	-0.0492	-0.0348	0.0072	0.0234	3.8293
HOCIO ₂	1	1.8097	0.0270	0.0569	0.1017	0.0228		9.9822
HOCIO	1	1.4033	0.0020	0.0158	0.0401	0.0180	0.0869	7.4488
HOCN	1	1.1664	-0.0127	0.0022	0.0171	0.0123	0.0337	3.1803
HOF	1	0.7534	-0.0357	-0.0288	-0.0023	0.0105	0.0355	4.7843

Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
HONC	1	1.1566	-0.0123	-0.0031	0.0100	0.0145	0.0393	3.8519
HOO	2	0.6712	-0.0151	-0.0234	0.0157	0.0407	0.0000	4.2403
HOOH	1	0.7986	-0.0774	-0.0582	-0.0263	0.0088	0.0224	3.0760
HS	2	0.5218	-0.0181	-0.0152	-0.0271	0.0097	0.0000	1.1421
Ketene	1	1.1514	0.0114	0.0210	0.0279	0.0144	0.0460	2.3290
Methanol	1	0.7278	-0.0425	-0.0245	-0.0190	0.0075	0.0173	1.2249
N ₂	1	0.7850	0.0328	-0.0125	-0.0091	0.0109	0.0269	4.0636
N ₂ H ₄	1	0.7659	-0.0489	-0.0340	-0.0305	0.0064	0.0137	1.7696
N ₂ H	2	0.7270	0.0371	0.0083	0.0082	0.0542	0.0000	3.9006
N ₂ O ₄	1	2.7983	0.0827	0.0999	0.1376	0.0179	0.0693	8.9220
N ₂ O	1	1.4003	0.0805	0.0868	0.1050	0.0171	0.0479	6.8453
n-Butane	1	1.3095	-0.0082	-0.0044	-0.0061	0.0072	0.0151	0.9968
NCCN	1	1.6287	0.0618	0.0407	0.0409	0.0127	0.0298	3.9554
NH ₂	2	0.3165	-0.0063	-0.0005	0.0025	0.0100	0.0000	1.2054
NH ₂ Cl	1	0.8921	-0.0220	-0.0176	-0.0209	0.0065	0.0231	2.5766
NH ₂ F	1	0.7167	-0.0439	-0.0257	-0.0219	0.0093	0.0312	2.6038
NH ₂ OH	1	0.7711	-0.0642	-0.0444	-0.0300	0.0077	0.0199	2.1622
NH ₃	1	0.4261	-0.0445	-0.0281	-0.0244	0.0055	0.0096	1.1704
NH	3	0.2197	0.0029	-0.0124	-0.0316	0.0118	0.0000	1.1987
NO ₂	2	1.2138	0.0996	0.0939	0.4427	0.0456	0.0000	8.5447
NO	2	0.6691	0.0413	0.0016	0.0221	0.0362	0.0000	5.7961
n-Pentane	1	1.6079	-0.0080	-0.0045	-0.0056	0.0081		1.0320
O ₂	3	0.6177	0.1211	0.0383	0.0950	0.0196	0.0000	6.5946
O ₃	1	1.5415	0.2235	0.2101	0.2697	0.0233	0.0767	17.8404
OCIO	2	1.3046	0.2167	0.1868	0.2261	0.0257	0.0000	14.3587
OCS	1	1.4049	0.0529	0.0603	0.0691	0.0141	0.0496	4.2201
OF	2	0.5996	0.1885	0.0881	0.1203	0.0611	0.0000	-6.6886

Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
OH	2	0.2629	-0.0608	-0.0432	-0.0096	0.0087	0.0000	1.3338
Oxadiazole	1	1.8954	0.0371	0.0178	0.0212	0.0150	0.0627	3.7674
Oxetane	1	1.3042	-0.0110	-0.0052	-0.0045	0.0099		1.5066
Oxirane	1	1.0423	-0.0056	-0.0019	0.0017	0.0092	0.0246	1.6906
Oxirene	1	1.1599	0.0055	0.0055	0.0120	0.0115	0.0325	2.9710
P ₂	1	1.2515	-0.1442	-0.0790	-0.0773	0.0102	0.0324	8.6986
P ₄	1	2.2461	0.0025	0.0123	0.0209	0.0105	0.0375	7.3279
PF ₃	1	1.3107	-0.1277	-0.0569	-0.0452	0.0103	0.0351	2.5526
PF ₅	1	1.7882	-0.0985	-0.0543	-0.0359	0.0109		2.5999
PH ₃	1	0.6780	-0.0623	-0.0204	-0.0254	0.0085	0.0203	0.7979
Propane	1	1.0105	-0.0085	-0.0041	-0.0057	0.0071	0.0145	0.9386
Propene	1	1.0653	0.0012	0.0001	-0.0028	0.0089	0.0318	1.2165
Propyne	1	1.1108	0.0079	0.0075	0.0057	0.0100	0.0283	1.5970
Pyrrole	1	1.7361	0.0122	0.0022	-0.0014	0.0096	0.0318	2.0063
S ₂	3	1.0063	0.1668	0.0937	0.0548	0.0151	0.0000	6.7101
S ₂ O	1	1.6614	0.0945	0.0983	0.0985	0.0151	0.0577	8.4165
S ₃	1	1.8671	0.1481	0.1434	0.1007	0.0135	0.0537	10.5937
S ₄	1	2.5532	0.1693	0.1840	0.1527	0.0137	0.0884	12.6629
SF ₆	1	2.1610	-0.0671	-0.0198	0.0024	0.0088	0.0276	4.1277
Si ₂ H ₆	1	1.1044	-0.0015	0.0334	0.0308	0.0082	0.0230	0.5228
SiF ₄	1	1.4596	-0.0556	-0.0436	-0.0318	0.0087	0.0281	1.6229
SiF	2	0.6578	-0.0996	-0.0433	-0.0374	0.0186	0.0000	2.3099
SiH ₃ F	1	0.8000	-0.0337	0.0061	0.0050	0.0078	0.0219	0.7442
SiH ₄	1	0.6022	-0.0165	0.0311	0.0280	0.0074	0.0166	0.2622
SiH	2	0.5005	-0.1178	-0.0175	0.0038	0.0159	0.0000	0.5352
Silole	1	1.8259	0.0188	0.0125	0.0073	0.0098	0.0331	1.7026
SiO	1	0.9490	-0.0533	-0.0244	-0.0018	0.0181	0.0563	4.3557

Appendix 1 - W4-17 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
SO ₂	1	1.4191	0.0297	0.0473	0.0793	0.0156	0.0548	6.2435
SO ₃	1	1.7355	0.0506	0.0659	0.1139	0.0138	0.0561	5.9864
SO	3	0.8056	0.1037	0.0404	0.0500	0.0191	0.0000	5.9131
SSH	2	1.0738	0.0495	0.0362	0.0096	0.0223	0.0000	3.5258
t-Butadiene	1	1.4497	0.0108	0.0047	0.0011	0.0099	0.0356	1.5205
Tetrahydrane	1	1.3414	0.0289	0.0213	0.0223	0.0075	0.0187	2.0044
trans-HCOH	1	0.7057	-0.0640	-0.0239	-0.0144	0.0155	0.0564	2.1386
Thiophene	1	1.8852	0.0302	0.0115	0.0057	0.0100	0.0375	2.2390
trans-HONO	1	1.2670	0.0009	0.0114	0.0379	0.0180	0.0603	5.1479
trans-HOOO	2	1.2774	0.0988	0.0668	0.1027	0.0502	0.0000	7.5512
trans-N ₂ H ₂	1	0.8291	-0.0054	-0.0115	-0.0117	0.0103	0.0339	3.2159
trans-C ₂ F ₂ Cl ₂	1	2.1725	0.0075	0.0239	0.0251	0.0116		3.8268

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
CoBr ₂	4	1.715	0.533	-0.047	0.604	0.990	0.034	0.098	3.100
CoCl ₂	4	1.358		0.940	0.036	0.988	0.031	0.088	3.000
CoCl ₃	5	1.921		0.238	0.246		0.062	0.180	6.800
CoCl	3	0.897	-0.206	0.014	0.099	0.511	0.073	0.284	9.100
Co(CO) ₂ H(PF ₃) ₂	1	4.994	-0.033	0.085	0.078		0.040	0.253	4.700
Co(CO) ₃ HPF ₃	1	4.544	0.002	0.003	0.003		0.046	0.255	5.100
CoCO ₄ H	1	4.045	0.003	0.003	0.002		0.052	0.253	5.500
CoCO ₄	2	3.728					0.036	0.110	5.800
CoCu	3	1.330	-0.050	0.671					
CoF ₂	4	1.037	-0.147	-0.046	0.006	0.976	0.031	0.088	3.100
CoGe	2	1.282				0.504	0.112	0.289	66.700
CoH	3	0.590	-0.153	0.293	0.425	0.653	0.070	0.205	12.400
CoO	4	0.998	0.096	0.510		0.751	0.097	0.225	20.800
CoSi	2	1.268	0.072	1.055	2.160	0.611	0.098	0.257	58.800
Cr ₂ Cl ₄	9	2.947	0.584	0.296	-7.407		0.031	0.110	8.600
Cr ₂	1	2.507	36.039	53.553	-697.202				
Cr ₃ O ₉	1	8.820							17.500
CrBr ₂	5	1.808	0.323	-0.056	-10.433	0.977	0.030	0.101	3.300
CrBr ₄	1	3.924					0.041	0.115	13.600
CrBr	6	1.118	0.310	-0.127	-20.201	0.989	0.152	0.539	1.800
CrC ₂	5	1.988	1.216	1.261		0.613	0.076	0.250	7.700
CrCl ₂	5	1.428		0.018	-8.559	0.977	0.028	0.086	3.100
CrCl ₃	4	2.112		1.852			0.049	0.120	6.600
CrCl ₄	1	3.031					0.037	0.101	10.900
CrClFO ₂	1	3.338	0.358	0.399	-3.326		0.039	0.155	16.100
CrCl	6	1.914	0.293	-0.011		0.992	0.134	0.474	2.600

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
Cr(CO) ₃	1	3.424	0.140	0.150	-1.812		0.054	0.179	6.500
Cr(CO) ₄	1	4.182	0.105	0.121	-1.334		0.036	0.137	5.800
Cr(CO) ₆	1	5.635	0.064	0.092	-0.869		0.028	0.090	5.300
CrCu	6	1.170		0.168	-35.573				
CrF ₂	5	1.037	0.144	-0.014	-6.930	0.983	0.029	0.074	3.100
CrF ₃	4	1.581	0.111	0.217	-4.625		0.030	0.087	4.500
CrF	6	0.944	0.170	0.558	-14.133	0.989	0.071	0.238	2.900
CrGe	5	1.563	1.864	0.315	-32.320	0.687	0.055	0.107	17.500
CrH	6	0.543		-0.074	-28.747	0.983	0.168	0.427	1.600
CrN	4	1.459	0.690	0.543		0.772	0.091	0.191	28.700
CrO ₂ Cl ₂	1	3.537	0.392	0.436	-3.537		0.038	0.161	17.400
CrO ₂ Cl	2	2.688		0.366			0.048	0.154	16.800
CrO ₂ F ₂	1	3.141	0.328	0.366	-3.137		0.039	0.148	15.000
CrO ₂ H ₂	5	1.851	0.003	0.001	-0.013		0.032	0.097	2.800
CrO ₂ (OH) ₂	1	3.329	0.004	0.004	-0.031		0.040	0.144	11.300
CrO ₂	3	1.899	0.360	0.321	-6.509	0.794	0.054	0.122	17.800
CrO ₃	1	2.998	0.445	0.474	-4.170		0.051	0.190	0.160
CrOCl ₂	1	2.388	0.392	0.283	-5.521		0.044	0.133	13.800
CrOF ₂	1	2.166	0.288	0.212	-4.704		0.044	0.132	11.500
CrOF	2	1.489				0.840	0.058	0.142	10.300
CrOH	6	0.940				0.978	0.073	0.242	2.800
CrO	5	1.103	1.844	0.778	-14.904	0.786	0.064	0.163	17.700
CrS	5	1.202	0.591	0.243	-18.986	0.622	0.098	0.278	17.200
Cu ₂	1	1.401	0.322	0.557	0.639				
Cu ₃ Br ₃	1	3.115	0.220	0.132	0.078		0.027	0.126	4.500
Cu ₃ Cl ₃	1	2.548	0.253	0.175	0.166		0.026	0.123	4.300
CuBr	1	1.136	0.258	0.094	0.015	0.993	0.028	0.107	2.900

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
CuCl	1	0.905	0.284	0.170	0.159	0.995	0.029	0.112	2.900
CuF ₂	2	1.075	0.359	0.093	0.037	0.995	0.027	0.100	0.500
CuF	1	0.737	0.258	0.148	0.124	0.810	0.041	0.163	3.400
CuGe	2	1.661				0.982	0.041	0.116	13.600
CuH	1	0.733	0.178	0.320	0.286	0.978	0.041	0.131	3.800
CuO	2	0.765	0.554	2.016	1.166	0.850	0.051	0.176	7.500
CuSe	2	1.261	0.376	0.399	0.264	0.994	0.035	0.117	6.400
CuS	2	1.004	0.408	0.370	0.303	0.990	0.036	0.120	6.800
Fe ₂ Br ₄	9	3.469	-0.179	0.092			0.046	0.222	25.800
Fe ₂ Cl ₄	9	2.601	-0.192	0.131	0.315		0.046	0.246	23.300
Fe ₂ Cl ₆	11	3.653	-0.120	0.088	0.228		0.045	0.123	4.300
Fe ₂ F ₆	7	2.954	-0.093	0.049	0.132		0.031	0.081	2.700
FeBr ₂	5	1.710	-0.286	-0.087	0.019	0.988	0.027	0.064	2.400
FeBr ₃	6	2.474					0.055	0.145	5.300
FeBr	6	1.306				0.997	0.024	0.047	1.600
Fe(C ₅ H ₅) ₂	1	2.926	0.017	0.042	0.038		0.047	0.188	2.800
FeCl ₂	5	1.322	-0.178	-0.061	0.820	0.988	0.025	0.058	2.300
FeCl ₃	6	1.906					0.045	0.118	4.300
FeCl	6	0.954				0.997	0.022	0.043	1.700
Fe(CO) ₂	3	2.203					0.042	0.129	7.100
Fe(CO) ₃	3	2.975	0.002	0.002	0.003		0.042	0.163	6.200
Fe(CO) ₄ (CH ₂) ₂	1	4.828	0.002	0.003	0.002		0.047	0.166	4.500
Fe(CO) ₄ H ₂	1	4.231	0.002	0.002	0.002		0.056	0.191	5.100
Fe(CO) ₄	3	3.861		27.553	14.880		0.040	0.121	5.700
Fe(CO) ₅	1	4.902	0.002	0.002	0.002		0.039	0.166	5.700
FeCO	5	1.490					0.046	0.125	7.600
FeF ₂	5	1.039	-0.268	-0.094	0.130	0.988	0.026	0.052	2.300

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
FeF ₃	6	1.433	-0.159	0.009	0.129		0.032	0.079	2.900
FeF	6	0.996				0.997	0.024	0.041	2.000
FeH	4	0.651	-0.746	0.165	0.179	0.517	0.097	0.289	10.600
Fe(OH) ₂	5	1.200					0.028	0.067	2.200
FeO	5	1.126	-0.606	0.091	0.441	0.783	0.090	0.206	16.000
FeS	5	1.168	-0.718	0.223	0.393	0.874	0.079	0.158	13.700
Mn ₂ Br ₄	11	3.311	0.238	0.043	-0.068		0.020	0.044	2.200
Mn ₂ Cl ₄	11	2.570	0.257	0.105	0.060		0.019	0.039	2.100
MnBr ₂	6	1.736	0.321	0.089	-0.034	0.985	0.021	0.042	2.100
MnBr	7	1.350				0.994	0.019	0.034	1.400
MnC ₅ H ₅ (CO) ₃	1	4.939	0.076	0.095	0.070		0.042	0.163	4.000
MnCl ₂	6	1.354		0.147	0.099	0.985	0.020	0.042	2.100
MnCl	7	1.018				0.994	0.018	0.031	1.400
MnCO ₅ Br	1	5.398	0.086	0.125	0.093		0.040	0.168	5.200
MnCO ₅ Cl	1	5.178	0.088	0.128	0.100		0.039	0.155	5.200
MnF ₂	6	1.077	0.183	0.090	0.053	0.984	0.024	0.050	2.400
MnF ₃	5	1.503		0.169	0.108		0.032	0.117	4.400
MnF	7	0.752	0.272	0.142	0.068	0.994	0.021	0.031	1.900
MnH	7	1.147	1.130	0.238	0.080		0.023	0.049	-1.600
MnOH	7	0.691	0.119	0.035	0.008	0.987	0.022	0.035	2.000
MnO	6	1.119	0.633	0.587	0.477	0.790	0.082	0.192	15.000
MnSe	6	1.490	0.905	0.680	0.331	0.858	0.055	0.093	12.000
MnS	6	0.978	0.770	0.565	0.384	0.850	0.059	0.095	11.900
Ni ₂	3	1.647	-1.842	1.195	1.050				
NiBr ₂	3	1.741		0.191	-0.079	0.894	0.038	0.145	2.900
NiBr	2	1.109		0.036	-0.006	0.994	0.039	0.138	8.300
NiCl ₂	3	1.385	0.051	0.091	0.052	0.903	0.038	0.120	3.900

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
NiCl	2	0.873	-0.385	0.103	0.140	0.991	0.041	0.150	7.800
Ni(CO) ₂	1	2.213	-0.006	0.187	0.188		0.037	0.097	7.500
Ni(CO) ₃	1	2.913	0.016	0.155	0.152		0.031	0.095	6.400
Ni(CO) ₄	1	3.664	0.024	0.140	0.134		0.031	0.089	6.100
NiCO	1	1.411	-0.057	0.298	0.294		0.046	0.133	11.100
NiCu	2	1.347							
NiF ₂	3	0.976	0.262	0.005	-0.018	0.925	0.032	0.088	3.600
NiF	2	0.748	-0.316	0.098	0.144	0.992	0.062	0.240	7.700
NiGe	1	2.080	-0.056	1.828	1.605		0.092	0.230	64.900
NiH	2	0.730	-0.965	0.214	0.183	0.777	0.055	0.174	10.600
Ni(OH) ₂	3	1.217	-0.063				0.058	0.197	2.900
NiO	3	1.198	0.028			0.717	0.118	0.309	23.800
Ni(PF ₃) ₄	1	5.652	-0.105	0.034	0.032		0.020	0.086	4.600
NiSi	1	1.601	-0.185	1.443	1.374		0.082	0.208	54.100
NiS	3	1.234		1.694	0.857	0.812	0.084	0.223	18.800
Sc ₂ Cl ₆	1	4.140	0.180	0.152	0.127		0.013	0.033	2.500
ScC ₂	1	1.643	0.326	0.153	0.120	0.865	0.046	0.101	5.900
ScC ₄	2	2.301			1.000		0.035	0.115	4.500
Sc(C ₅ H ₅) ₃	1	5.543	0.039	0.018	0.009		0.011	0.030	2.100
ScCl ₃	1	2.115	0.192	0.174	0.147		0.013	0.030	2.400
ScF ₂	2	1.332	0.077	0.106	0.066	0.975	0.020	0.046	2.500
ScF ₃	1	1.622	0.082	0.110	0.085		0.018	0.040	2.200
ScF	1	1.252	0.010	0.150	0.554	0.960	0.022	0.039	3.300
ScH	1	0.984	0.043	0.355	0.302	0.876	0.023	0.044	1.300
ScO	2	1.315	0.199	0.207		0.931	0.038	0.064	7.700
ScSe	2	1.788				0.914	0.054	0.111	11.300
ScS	2	1.468	0.386	0.324	0.254	0.916	0.047	0.094	9.700

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
Ti2Cl ₆	1	4.703	0.196	0.243	0.170		0.025	0.080	6.400
Ti ₂	3	1.709	1.046	2.054	1.227				
TiBr ₃	2	2.673		0.080			0.027	0.061	4.200
TiBr ₄	1	3.756	0.187	0.226	0.108		0.028	0.080	7.800
TiBr	4	1.139	0.992	0.220	-0.121	0.978	0.041	0.117	2.200
TiC ₂	3	1.575	0.224	0.188	0.084	0.864	0.056	0.131	6.100
TiC ₄	3	2.294		0.123	0.063		0.046	0.135	4.800
TiC ₅ H ₅ Cl ₃	1	3.945	0.066	0.069	0.048		0.020	0.070	3.200
TiCl ₂ Br ₂	1	3.339	0.185	0.230	0.146		0.026	0.075	6.900
TiCl ₂	3	1.546				0.984	0.022	0.052	2.400
TiCl ₃ Br	1	3.130	0.185	0.232	0.163		0.025	0.071	6.500
TiCl ₃	2	2.164					0.023	0.053	3.600
TiCl ₄	1	2.920	0.184	0.233	0.179		0.024	0.068	6.200
TiClBr ₃	1	3.549	0.186	0.228	0.128		0.027	0.077	7.400
TiCl	4	1.739		0.581		0.978	0.037	0.108	2.100
TiF ₄	1	2.166	0.081	0.135	0.091		0.023	0.063	3.800
TiF	4	0.808	-0.044	0.100	-0.070	0.978	0.034	0.080	2.700
TiH	4	1.036	0.840	0.909	0.352	0.989	0.058	0.115	0.800
TiN	2	1.276				0.884	0.049	0.096	16.600
TiO ₂	1	1.970	0.192	0.285	0.219	0.865	0.042	0.096	10.400
TiOCl ₂	1	2.372	0.173	0.222	0.170		0.028	0.079	6.800
TiOCl	2	1.680	0.202				0.042	0.096	8.400
TiOF ₂	1	2.014	0.107	0.171	0.123		0.029	0.077	5.700
TiOF	2	1.584	0.162	0.185	0.094		0.045	0.119	7.600
TiO	3	1.310		0.222	0.077	0.921	0.046	0.075	9.800
TiSe	3	1.590	0.578	0.725	0.066	0.866	0.088	0.199	11.500
TiS	3	1.445				0.888	0.065	0.110	11.700

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
V ₄ O ₁₀	1	9.165	0.062	0.247	0.256		0.042	0.122	10.700
VBr ₄	2	3.740	0.055	0.261	0.177		0.037	0.125	10.800
VBrCl ₃	2	3.096	0.073	0.260			0.033	0.111	9.000
VC ₂	4	1.564	0.006	0.159	0.185	0.856	0.063	0.147	6.700
VC ₄	4	2.244		0.102	0.230		0.043	0.102	4.900
VCl ₂	4	1.487				0.984	0.025	0.057	2.700
VCl ₃	3	2.145					0.036	0.111	4.700
VCl ₄	2	2.881					0.032	0.106	8.600
VCl	5	1.232	-0.398	0.146		0.992	0.053	0.170	1.900
VF ₅	1	2.863	0.062	0.238	0.230				
VH	5	3.008	0.017	0.551	0.215	0.988	0.092	0.207	0.200
VN	3	1.427	-0.048	0.452	0.980	0.852	0.063	0.129	19.400
VO ₂	2	2.049	0.014	0.301	0.292	0.062	0.159	0.175	
VOCl ₃	1	3.201	0.100	0.306	0.311				
VOOH ₃	1	2.889	0.001	1.837	0.993		0.033	0.108	6.200
VO	4	1.573	-0.266	0.248	0.249	0.899	0.054	0.097	12.600
VSe	4	1.697	-0.172	0.456	0.245	0.803	0.085	0.158	13.300
VS	4	1.395	-0.174	1.013	0.348	0.828	0.086	0.180	12.600
Zn ₂	1	1.826	-0.151	1.064	0.659				
ZnBr ₂	1	1.837	0.319	-0.059	-0.200	0.994	0.014	0.058	2.100
ZnBr	2	1.263		-0.283	-0.689		0.021	0.065	2.000
ZnCH ₂ CH ₂ (CH ₃) ₂	1	2.483	0.015	0.007	0.001		0.012	0.054	1.200
ZnCH ₂ (CH ₃) ₂	1	1.887	0.018	0.007	-0.001		0.012	0.054	1.200
Zn(CH ₃) ₂	1	1.267	0.030	0.003	-0.013		0.013	0.050	1.100
ZnCH ₃	2	1.010	0.054	-0.023	-0.056		0.024	0.076	1.100
ZnCl ₂	1	1.421	0.327	0.042	-0.012	0.995	0.014	0.055	2.100
ZnCl	2	1.025	0.682	-0.089	-0.293		0.019	0.055	1.800

Appendix 2 - TM-11 Data

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06]	A _λ [M06]	C ₀ ²	T1	D1	%TAE([T])
ZnF ₂	1	1.080	0.226	-0.007	-0.064	0.995	0.019	0.075	2.300
ZnH	2	0.677	0.991		-0.802		0.028	0.077	-1.700
ZnO	1	1.337	1.441	0.519	0.297	0.846	0.033	0.083	34.600
ZnSe	1	1.703	1.194	0.402	-0.220	0.944	0.022	0.067	20.400
ZnS	1	1.378	0.946	0.220	-0.051	0.939	0.024	0.075	19.700

Appendix 3 - G3-99

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
Acetaldehyde	1	1.0955	-0.0073	0.0016	0.0058	0.0129	0.0501	1.6432
Acetamide	1	1.4372	-0.0151	-0.0054	0.0004	0.0145		1.8321
Acetic Acid	1	1.4214	-0.0227	-0.0077	0.0045	0.0149		1.9580
Acetic Anhydride	1	2.4345	-0.0084	0.0007	0.0110	0.0138	0.0564	1.2157
Acetone	1	1.3886	-0.0058	0.0003	0.0043	0.0137		1.5151
Actetonitrile	1	1.1564	0.0182	0.0099	0.0085	0.0113	0.0312	2.0285
Acetylchloride	1	1.5628	0.0085	0.0147	0.0193	0.0147		2.2519
Acetylfluoride	1	1.3498	-0.0139	0.0032	0.0118	0.0146		2.0434
AlCl ₃	1	1.6798	0.0969	0.0508	0.0471	0.0052	0.0235	2.1052
AlF ₃	1	1.2093	-0.0252	-0.0117	-0.0118	0.0099	0.0351	1.6892
Allene	1	1.1412	0.0173	0.0102	0.0067	0.0108	0.0298	1.6487
Aniline	1	2.3529	0.0163	0.0056	0.0038	0.0111		1.9943
Aziridine	1	1.0393	-0.0026	-0.0006	-0.0013	0.0086		1.5901
Azulene	1	3.4160	0.1055	0.0547	0.0349			
BCl ₃	1	1.6321	0.0841	0.0488	0.0431	0.0074	0.0449	2.7739
BeH	2	0.3480	0.2136	0.1814		0.0148	0.0000	0.4535
Benzene	1	2.0038	0.0234	0.0099	0.0067	0.0102		1.8843
Benzoquinone	1	2.7714	0.0208	0.0152	0.0199	0.0160		2.5565
BF ₃	1	1.0721	-0.0706	-0.0300	-0.0078	0.0104	0.0445	1.6985
Bicyclobutane-110	1	1.3043	0.0132	0.0102	0.0092	0.0081		1.5384
C ₂ Cl ₄	1	2.5526	0.0702	0.0455	0.0328	0.0104		4.8271
C ₂ F ₄	1	1.8018	-0.0484	0.0032	0.0164	0.0109	0.0412	3.0447
C ₂ F ₆	1	2.2251	-0.0689	-0.0164	0.0042	0.0102	0.0365	2.7345
C ₂ H ₂	1	0.8058	0.0075	0.0074	0.0056	0.0116	0.0295	1.9969
C ₂ H ₃	2	0.6706	0.0175	0.0136	0.0099	0.0467	0.0000	1.3486
C ₂ H ₄	1	0.7602	0.0014	-0.0003	-0.0046	0.0095	0.0325	1.2397

Appendix 3 - G3-99

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
C ₂ H ₅	2	0.6340	-0.0006	0.0031	0.0010	0.0130	0.0000	0.8376
C ₂ H ₆	1	0.7129	-0.0090	-0.0035	-0.0060	0.0069	0.0134	0.8381
C ₃ H ₇	2	0.9472	-0.0003	0.0032	0.0022	0.0107		-1.923
C ₃ H ₈	1	1.0128	-0.0086	-0.0041	-0.0057	0.0071	0.0146	0.9401
C ₄ H ₁₀ O ₂	1	1.9983	-0.0266	-0.0168	-0.0132	0.0107		1.4526
C ₄ H ₄ N ₂	1	2.2057	0.0239	0.0104	0.0101	0.0115	0.0317	2.3731
C ₄ H ₄ O	1	1.8331	0.0111	0.0122	0.0164	0.0154		2.2131
C ₄ H ₆ O	1	1.7794	0.0047	0.0058	0.0072	0.0147		1.7705
C ₄ H ₆	1	1.4449	0.0118	0.0068	0.0039	0.0114		1.5307
C ₄ H ₇ N	1	1.7477	0.0058	0.0014	0.0003	0.0114		1.6522
C ₄ H ₈ O ₂	1	1.9148	-0.0248	-0.0165	-0.0122	0.0112		1.6343
C ₄ H ₈ O	1	1.6876	-0.0054	-0.0007	0.0021	0.0129		1.4463
CCH	2	0.5629	0.0209	0.0308	0.0255	0.0148	0.0000	1.9732
CCl ₄	1	2.1577	0.0391	0.0341	0.0198	0.0065	0.0241	4.7647
CF ₃ Cl	1	1.5951	-0.0532	-0.0075	0.0082	0.0089	0.0313	3.0586
CF ₃ CN	1	1.9399	-0.0179	0.0057	0.0196	0.0114	0.0342	3.2753
CF ₃	2	1.0991	-0.0550	-0.0056	0.0147	0.0176	0.0000	2.8768
CF ₄	1	1.4066	-0.0845	-0.0215	0.0016	0.0096	0.0308	2.6590
CH ₂ O	1	0.7864	-0.0157	0.0018	0.0069	0.0140	0.0479	2.0493
CH ₂ _sing	1	0.3236	-0.0679	-0.0001	0.5486	0.0148	0.0370	6.7942
CH ₂ _trip	3	0.2419	0.0047	-0.0022	0.0012	0.0134	0.0000	0.4390
CH ₃ CH ₂ O	2	0.9006	0.0063	0.0030	0.0029	0.0628	0.0000	2.6175
CH ₃ Cl	1	0.8349	-0.0002	0.0014	-0.0063	0.0058	0.0208	1.2383
CH ₃ CO	2	0.9972	0.0073	0.0103	0.0156	0.0249	0.0000	1.9458
CH ₃ OH	1	0.7342	-0.0422	-0.0245	-0.0188	0.0085		1.2465
CH ₃ O	2	0.6034	-0.0072	-0.0016	0.0023	0.0079		1.2473
CH ₃	2	0.3142	-0.0068	-0.0005	-0.0050			0.5380

Appendix 3 - G3-99

Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
CH ₃ SH	1	0.9216	-0.0064	-0.0061	-0.0131	0.0067	0.0202	1.2110
CH ₃ S	2	0.8128	-0.0118	-0.0088	-0.0132	0.0122	0.0000	1.2375
CH ₄	1	0.4076	-0.0136	-0.0041	-0.0072	0.0067	0.0121	0.6414
chlorobenzene	1	2.4392	0.0298	0.0137	0.0099	0.0102		2.1573
CH	2	0.2331	-0.0741	-0.0095	-0.0225	0.0133	0.0000	0.9758
Cl ₂ O ₂ S	1	2.3032	0.0742	0.0806	0.1052	0.0121	0.0590	6.7766
Cl ₂	1	0.9976	0.0383	0.0573	0.0151	0.0052	0.0207	7.7819
Cl ₂ S ₂	1	2.0772	0.0731	0.0866	0.0566	0.0164		10.956
ClF ₃	1	1.6207	0.0736	0.1343	0.0970	0.0129	0.0532	14.141
ClF	1	0.8361	-0.0384	-0.0153	-0.0507	0.0082	0.0319	8.7368
CINO	1	1.5528	0.1505	0.1373	0.1479	0.0164	0.0635	9.3729
ClO	2	0.8029	0.1577	0.0897	0.0979	0.0392	0.0000	9.8315
CN	2	1.5951	0.1076	0.0765	0.2095	0.0907	0.0000	4.8693
CO ₂	1	1.1861	0.0065	0.0437	0.0712	0.0163	0.0497	3.5850
COF ₂	1	1.2915	-0.0419	0.0090	0.0324	0.0125	0.0510	3.1758
CO	1	0.7189	-0.0156	-0.0035	0.0131	0.0167	0.0418	3.1499
CS ₂	1	1.6677	0.1218	0.0914	0.0792	0.0132	0.0515	5.6014
CS	1	0.9721	0.0726	0.0465	0.0342	0.0172	0.0508	5.7001
Cyanoethylene	1	1.5333	0.0276	0.0143	0.0120	0.0121	0.0401	2.3003
Cyclobutane	1	1.2544	-0.0001	0.0013	-0.0011	0.0080		1.2020
Cyclobutene	1	1.3365	0.0127	0.0078	0.0042	0.0100		1.5212
Cyclohexadiene-1,3	1	1.9495	0.0097	0.0038	0.0015	0.0107		1.6145
Cyclohexane	1	1.8070	-0.0062	-0.0038	-0.0052	0.0085		1.1852
Cyclooctatetraene	1	2.6631	0.0197	0.0087	0.0065	0.0116		1.9136
Cyclopentane_twist	1	1.5273	-0.0046	-0.0027	-0.0046	0.0084		1.1863
Cyclopentanone	1	1.8973	-0.0015	0.0010	0.0030	0.0129		1.5854
Cyclopropane	1	0.9772	0.0015	0.0023	-0.0001	0.0075		1.1880

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Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
Cyclopropene	1	1.0816	0.0127	0.0128	0.0101	0.0099		1.7245
diethyl-disulfide	1	2.2866	-0.0054	-0.0049	-0.0099	0.0106		1.4465
Diethylether	1	1.6680	-0.0177	-0.0105	-0.0088	0.0096		1.2201
Diethylketone	1	1.9860	-0.0053	-0.0013	0.0010	0.0124		1.4043
Difluorobenzene-13	1	2.5189	0.0143	0.0106	0.0112	0.0117		2.2852
Difluorobenzene-14	1	2.5224	0.0139	0.0105	0.0110	0.0115		2.2883
Dihydrothioepehe-25	1	1.7723	0.0085	0.0016	-0.0036	0.0109		1.7395
Diisopropylether	1	2.2549	-0.0153	-0.0091	-0.0077	0.0082		
Dimethylacetylene	1	1.4355	0.0078	0.0074	0.0057	0.0108		1.4891
Dimethylamine	1	1.0579	-0.0213	-0.0132	-0.0153	0.0083		1.1882
Dimethylether	1	1.0592	-0.0284	-0.0163	-0.0147	0.0096		1.2456
Dimethyl_sulfone	1	1.9075	0.0015	0.0020	0.0101	0.0158		2.1283
Dimethylsulfoxide	1	1.5896	-0.0041	-0.0035	-0.0033	0.0153		1.7903
Dimethylthioether	1	1.1969	-0.0064	-0.0066	-0.0124	0.0090		1.2125
Dipyridine-14	1	2.1083	0.0245	0.0087	0.0050	0.0114		2.6319
Divinylether	1	1.8047	-0.0009	-0.0021	-0.0014	0.0132		1.8001
Ethanol	1	1.0407	-0.0282	-0.0166	-0.0123	0.0088		1.2177
Ethylchloride	1	1.1340	-0.0023	-0.0008	-0.0049			1.1955
F ₂ O	1	1.1654	0.2074	0.1083	0.1311	0.0134	0.0416	15.053
F ₂	1	0.7362	0.3517	0.2389	0.2414	0.0094	0.0294	19.933
Fluorobenzene	1	2.2626	0.0188	0.0102	0.0088	0.0111		2.0850
Furan	1	1.7371	0.0100	0.0040	0.0049	0.0134		2.2045
Glyoxal	1	1.4874	-0.0032	0.0078	0.0190	0.0143	0.0522	2.6361
H ₂ CCl ₂	1	1.2772	0.0151	0.0097	-0.0004	0.0060	0.0224	2.0813
H ₂ CF ₂	1	0.9221	-0.0521	-0.0198	-0.0171	0.0094	0.0286	1.7010
H ₂ COH	2	0.6456	-0.0387	-0.0221	-0.0125	0.0205	0.0000	1.4497
H ₂ O ₂	1	0.8168	-0.0736	-0.0561	-0.0242	0.0091	0.0234	3.1780

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Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
H ₂ O	1	0.4069	-0.0991	-0.0577	-0.0350	0.0067		1.3636
H ₂	1	0.0948	-0.1439	-0.0846	-0.0753	0.0055	0.0078	0.0000
H ₂ S	1	0.6422	-0.0110	-0.0072	-0.0162	0.0062	0.0159	1.1749
HCCl ₃	1	1.7214	0.0286	0.0203	0.0083	0.0093		3.5151
HCF ₃	1	1.1707	-0.0676	-0.0218	-0.0094	0.0099	0.0304	2.2027
HCl	1	0.5507	0.0069	0.0109	0.0047	0.0038	0.0107	1.3179
HCN	1	0.8437	0.0238	0.0103	0.0095	0.0128	0.0308	2.9623
HCOOCH ₃	1	1.4519	-0.0205	-0.0073	0.0005	0.0158		2.0364
HCOOH	1	1.1327	-0.0361	-0.0117	0.0057	0.0145	0.0560	2.4178
HCO	2	0.7039	0.0091	0.0195	0.0318	0.0283	0.0000	2.8683
HF	1	0.3352	-0.1434	-0.0573	-0.0418	0.0061	0.0121	1.3112
HOCl	1	0.9089	-0.0588	-0.0465	-0.0322	0.0074	0.0241	3.9566
Isobutane	1	1.3065	-0.0099	-0.0051	-0.0065	0.0080		1.0094
Isobutene	1	1.3686	-0.0005	-0.0005	-0.0023	0.0098		1.2276
Isoprene	1	1.7514	0.0075	0.0032	0.0005	0.0145		0.1423
Isopropylacetate	1	2.3401	-0.0117	-0.0048	-0.0001			
Isopropyl_alcohol	1	1.3397	-0.0236	-0.0140	-0.0103	0.0092		1.2280
Ketene	1	1.1670	0.0129	0.0218	0.0288	0.0149	0.0483	2.3892
Li ₂	1	0.3216	-0.1978	-0.0725	0.3276	0.0159		-0.292
LiF	1	0.4236	-0.0292	0.0139	0.0660	0.0127	0.0281	1.9549
LiH	1	0.2844	0.0547	0.0625	0.1474	0.0076	0.0150	0.0563
Methylamine	1	0.7434	-0.0259	-0.0163	-0.0173	0.0067	0.0151	1.1631
Methylenecyclopropane	1	1.3522	0.0127	0.0085	0.0060	0.0100		1.5098
Methylethylether	1	1.3636	-0.0216	-0.0126	-0.0113	0.0096		1.2286
Methylethylketone	1	1.6876	-0.0054	-0.0007	0.0021	0.0129		1.4463
Methylnitrite	1	1.6192	0.0092	0.0090	0.0188	0.0210		3.5610
Methylpentane-3	1	1.9018	-0.0088	-0.0046	-0.0059			

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Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
Methylsilane	1	0.8848	-0.0064	0.0103	0.0073	0.0096		0.6130
Methylthiophene-2	1	2.1865	0.0231	0.0088	0.0040			
N ₂ H ₄	1	0.7719	-0.0489	-0.0339	-0.0303	0.0065	0.0138	1.7838
N ₂ O	1	1.4734	0.0980	0.1016	0.1218	0.0179	0.0491	7.5372
N ₂	1	0.8237	0.0445	-0.0036	0.0013	0.0117	0.0288	4.4253
Na ₂	1	1.1093	0.0375	-0.0236	0.2016	0.0065	0.0267	1.7054
NaCl	1	0.6541	0.2434	0.1965	0.1811	0.0041	0.0146	1.8074
Naphthalene	1	3.2665	0.0287	0.0131	0.0103			
n-Butylchloride	1	1.7211	-0.0040	-0.0029	-0.0054			
NCCN	1	1.6923	0.0699	0.0468	0.0474	0.0133	0.0315	4.2149
Neopentane	1	1.5902	-0.0122	-0.0059	-0.0072			
NF ₃	1	1.3379	0.0201	0.0328	0.0499	0.0133	0.0397	7.6428
NH ₂	2	0.3168	-0.0065	-0.0007	0.0024	0.0100	0.0000	1.2102
NH ₃	1	0.4288	-0.0449	-0.0283	-0.0246	0.0056	0.0097	1.1785
n-Heptane	1	2.2094	-0.0080	-0.0047	-0.0056			
n-Hexane	1	1.9109	-0.0080	-0.0046	-0.0058			
NH	3	0.2204	0.0033	-0.0120	-0.0313	0.0119	0.0000	1.2039
Nitromethane	1	1.6541	0.0116	0.0128	0.0225			
Nitro-s-butane	1	2.5435	0.0006	0.0019	0.0058			
n-Methylpyrrole	1	2.0590	0.0088	0.0008	-0.0033			
NO ₂	2	1.2494	0.1133	0.1028	0.4243	0.0485	0.0000	8.5186
n-Octane	1	2.5095	-0.0079	-0.0047	-0.0057			
NO	2	0.6603	0.0360	-0.0021	0.0179	0.0299	0.0000	5.6874
n-Pentane	1	1.6111	-0.0082	-0.0045	-0.0056			
O ₂	3	0.6489	0.1486	0.0590	0.1185	0.0210	0.0000	7.3583
O ₃	1	1.6177	0.2663	0.2424	0.3012	0.0258	0.0853	19.442
OCS	1	1.4251	0.0564	0.0627	0.0719	0.0146	0.0515	4.3700

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Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
OH	2	0.2649	-0.0606	-0.0433	-0.0096	0.0088	0.0000	1.3546
Oxirane	1	1.0492	-0.0051	-0.0017	0.0018			
P ₂	1	1.2775	-0.1436	-0.0719	-0.0695	0.0105	0.0338	9.1015
P ₄	1	2.2406	0.0024	0.0121	0.0208	0.0104	0.0374	7.3024
Para-cyclohexadiene	1	1.9271	0.0101	0.0038	0.0018			
PCl ₃	1	1.9225	0.0045	0.0395	0.0334	0.0077	0.0335	4.6629
PCl ₅	1	2.7372	0.0561	0.0616	0.0472	0.0105		8.7154
Perhydropyridine	1	1.8528	-0.0123	-0.0087	-0.0097			
PF ₃	1	1.3378	-0.1214	-0.0541	-0.0443	0.0135		2.8691
PF ₅	1	1.7460	-0.1239	-0.0575	-0.0335	0.0113		3.1003
PH ₂	2	0.5823	-0.0844	-0.0407	-0.0445	0.0137	0.0000	0.7606
PH ₃	1	0.6757	-0.0629	-0.0208	-0.0260	0.0085	0.0201	0.7889
Phenol	1	2.3385	0.0132	0.0045	0.0055			
Phenyl.radical	2	1.8689	0.0317	0.0172	0.0139			
POCl ₃	1	2.2329	0.0299	0.0362	0.0458	0.0137		5.4246
Propene	1	1.0683	-0.0720	-0.0544	-0.0513			
Propylchloride	1	1.4316	-0.0037	-0.0023	-0.0056			
Propyne	1	1.1226	0.0084	0.0078	0.0061			
Pyridine	1	2.0507	0.0236	0.0093	0.0058			
Pyrimidine	1	2.0831	0.0228	0.0077	0.0040			
Pyrrole	1	1.7428	0.0123	0.0023	-0.0013			
S ₂	3	1.0163	0.1652	0.0964	0.0582	0.0154	0.0000	6.9207
SCl ₂	1	1.5131	0.0409	0.0658	0.0358	0.0074	0.0312	6.6995
SF ₆	1	2.2371	-0.0534	-0.0136	0.0055	0.0093	0.0296	4.4679
SH	2	0.5256	-0.0183	-0.0152	-0.0270	0.0097	0.0000	1.1449
Si ₂ H ₆	1	1.1091	-0.0014	0.0335	0.0310	0.0083	0.0231	0.5258
Si ₂	3	1.1577	-0.1771	-0.0497	-0.0070	0.0147	0.0000	5.7257

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Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
SiCl ₂	1	1.4266	0.0163	0.0366	0.0394	0.0080	0.0361	3.1804
SiCl ₄	1	2.1654	0.0800	0.0519	0.0457	0.0056	0.0220	2.6931
SiF ₄	1	1.4810	-0.0527	-0.0426	-0.0322			
SiH ₂ _sing	1	0.5887	-0.0845	0.0036	0.0134	0.0087	0.0272	0.5674
SiH ₂ _trip	3	0.5086	0.0398	0.0014	-0.0030	0.0159	0.0000	0.2842
SiH ₃	2	0.5557	-0.0050	0.0195	0.0160	0.0134	0.0000	0.2757
SiH ₄	1	0.6054	-0.0166	0.0310	0.0281	0.0074	0.0166	0.2647
SiO	1	0.9692	-0.0472	-0.0205	0.0019	0.0190	0.0595	4.5778
SiO ₂	1	1.4193	0.0159	0.0265	0.0622	0.0194	0.0762	6.2490
SO ₃	1	1.8295	0.0657	0.0732	0.1203	0.0152	0.0628	6.6190
SO	3	0.8281	0.1148	0.0490	0.0590	0.0201	0.0000	6.3810
Spiropentane	1	1.5508	0.0090	0.0062	0.0044	0.0080		1.4147
t-Butanethiol	1	1.7907	-0.0121	-0.0072	-0.0099			
t-Butanol	1	1.6274	-0.0223	-0.0127	-0.0095			
t-Butylamine	1	1.6300	-0.0185	-0.0109	-0.0107			
t-Butylchloride	1	1.7061	-0.0084	-0.0036	-0.0057	0.0087		1.2482
t-Butylmethylether	1	1.9403	-0.0179	-0.0100	-0.0089	0.0097		1.2627
t-Butyl _{rad}	2	1.2570	-0.0013	0.0024	0.0019	0.0108		1.0215
Tetrahydrofuran	1	1.5730	-0.0142	-0.0091	-0.0082	0.0099		1.4175
Tetrahydropyran	1	1.8613	-0.0142	-0.0093	-0.0082	0.0099		1.3793
Tetrahydropyrrole	1	1.5768	-0.0114	-0.0077	-0.0093	0.0090		1.3757
Tetrahydrothiophene	1	1.7079	-0.0026	-0.0038	-0.0080	0.0097		1.4342
Tetrahydrothiopyran	1	1.9888	-0.0045	-0.0050	-0.0082	0.0095		1.3891
Tetramethylsilane	1	1.7269	-0.0008	-0.0044	-0.0073	0.0089		0.9686
Thioethanol	1	1.2191	-0.0069	-0.0061	-0.0105	0.0089		1.1830
Thiooxirane	1	1.1966	0.0130	0.0083	0.0024	0.0096		1.7176
Thiophene	1	1.8907	0.0304	0.0117	0.0059			

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Molecule	Mult	Odd _{elec}	A _λ [M06]	A _λ [M06-2X]	A _λ [M06-HF]	T1	D1	%TAE([T])
Toluene	1	2.3049	0.0187	0.0080	0.0053	0.0100		1.7775
1,3-trans-Butadiene	1	1.4538	0.0109	0.0048	0.0013	0.0113		1.5387
trans-Butane	1	1.3125	-0.0082	-0.0044	-0.0061	0.0080		0.9955
trans-Ethylamine	1	1.0487	-0.0198	-0.0129	-0.0130	0.0082		1.1808
Trimethylamine	1	1.3703	-0.0212	-0.0127	-0.0152	0.0089		0.0093
Vinylchloride	1	1.2088	0.0176	0.0088	0.0025	0.0105		1.8047
Vinylfluoride	1	1.0232	-0.0097	-0.0009	-0.0018			
z-Methylacetate	1	1.7404	-0.0152	-0.0057	0.0008	0.0144		1.7805