ELECTRONIC STRUCTURE CALCULATIONS OF OPEN-SHELL MOLECULES

by

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Abstract

Equation-of-motion coupled-cluster (EOM-CC) approach is a powerful tool for accurate calculations of electronically excited and open-shell molecules. The spin-flip (SF) variant of EOM-CC, EOM-SF-CC, extends the applicability of EOM to diradicals, triradicals, and bond-breaking. This work presents applications of the SF approach to challenging diradicals such as methylene, ortho-, meta-, and para-benzynes, and trimethylenemethane, and triradicals (1,3,5-tridehydrobenzene and dehydro-meta-xylylene). In addition to accurate excitation energies, spectroscopic and thermochemical properties of these molecules, as well as ionization potentials are calculated. Modelling of photoelectron spectra is also discussed. To improve the accuracy of EOM-CC with single and double excitations [EOM-CCSD], I implemented the EOM-CC(2,3) method, in which triple excitations are included in the EOM part. Performance of both the spin-conserving and spin-flipping variants of EOM-CC(2,3), as well as their
active space counterparts, EOM-EE-CC(2,3) and EOM-SF-CC(2,3), with semi-
internal triples is benchmarked on a number of radical, diradical, and triradical
systems.
Chapter 1

Electronic structure methods for open-shell and electronically excited species

1.1 Introduction

The focus of this work is on the electronic structure, spectroscopic and thermochemical properties of open-shell molecules, i.e., radicals, diradicals, and triradicals. As a main tool, I employed the equation-of-motion (EOM) coupled-cluster (CC) approach, which describes many multi-configurational wave functions within a single-reference formalism. The spin-flip (SF) variant of EOM-CC, EOM-SF-CC, which was introduced in our group [1], extends the applicability of EOM to diradicals, triradicals, and bond-breaking.

This Chapter discusses the electronic structure of open-shell species, i.e., diradicals and triradicals, and gives a brief overview of the EOM approach and its SF variant. Chapter 2 presents benchmarks of the SF method on a number
of diradicals, such as methylene, ortho-, meta-, and para-benzynes, trimethylenemethane (TMM), and others. Spectroscopic and structural properties of the lowest electronic states of TMM are investigated in details in Chapter 3. The SF study of the 1,3,5-tridehydrobenzene triradical is summarized in Chapter 4. Electronic structure and thermochemical properties of dehydro-meta-xyylene (DMX) triradical, an organic molecule with a genuine open-shell doublet ground state, are discussed in Chapter 5. The negative ion of DMX, with 4-electron-in-3-orbital pattern, presents a major challenge for any \textit{ab initio} method. Accurate calculations of its electronic excitation and ionization energies are discussed in Chapter 6.

A powerful experimental technique for studying diradicals is photoelectron spectroscopy. Some comments on computational modelling photoelectron spectra are given in Chapter 7 and Appendices A and B.

The important methodological development, the implementation of the EOM-CC(2,3) method and its active space counterpart, EOM-CC(2,\overline{3}), is reported in Chapter 8. Finally, concluding remarks are given in Chapter 9.

1.2 Hierarchy of theoretical model chemistries

High-level calculations of closed-shell molecules can now be carried out almost routinely due to the availability of efficient and user friendly electronic structure
packages featuring a hierarchy of "theoretical model chemistries" [2]. The well-defined nature of these approximate methods of solving electronic Schrödinger equation enables their calibration [3] thus providing error bars for each model. By using these error bars as criteria for balancing accuracy versus computational cost, a chemist can choose just right tool for a particular problem at hand, and use it in a "black box" fashion.

As defined by Pople, "theoretical model chemistry" consists of a pair of well-defined approximations to the exact wave function correlation treatment and one-electron basis set [2]. Fig. 1.1 summarizes a hierarchy of approximate methods for correlation treatment [3, 4] in the ground and excited states. Both the ground state’s (left panel) and excited states’ (right panel) series converge to the exact solution, and the accuracy of the description improves with each additional step of sophistication (at the price of increased computational cost, of course). Fortunately, chemically and spectroscopically relevant answers can be obtained within computationally tractable (for moderate size molecules) models. For example, the coupled-cluster model with single and double excitations [5] augmented by triple excitations treated perturbatively [CCSD(T)] [6] yields highly accurate structural (errors in bond lengths of 0.002-0.003 Å) and thermochemical (errors of less than 1 kcal/mol in reaction enthalpies) data [3].
Ground state models:

- SCF: \( \Psi = \Phi_0 = |\phi_1...\phi_n> \)
- MP2: SCF + \( T_2 \) by PT
- CCSD: \( \Psi = \exp(T_1 + T_2) \Phi_0 \)
- CCSD(T): CCSD + \( T_3 \) by PT
- CCSDT: \( \Psi = \exp(T_1 + T_2 + T_3) \Phi_0 \)

Excited state models:

- CIS: \( \Psi_{ex} = R_1 \Psi_0 \)
- CIS(D): CIS + \( R_2 \) by PT
- EOM-CCSD: \( \Psi_{ex} = (R_1 + R_2) \Psi_0 \)
- EOM-CCSDT: \( \Psi_{ex} = (R_1 + R_2 + R_3) \Psi_0 \)

\[ \text{FCI: } \Psi = (1 + T_1 + T_2 + ... + T_n) \Phi_0 \text{ - exact!} \]

Figure 1.1. The hierarchy of approximations to an N-electron wave function. The left panel presents models of increasing complexity for ground state wave functions. The emerging hierarchy of excited states’ methods is summarized on the right panel. The simplest possible description of an N-electron wave function is given by a single Slater determinant composed of spin-orbitals, i.e., states of pseudo-independent electrons moving in the field of nuclei and a mean field of other electrons [self-consistent field (SCF), or Hartree-Fock (HF) model]. The effects of electron interaction, i.e., correlation, can gradually be turned on by including single, double, and higher excitations (\( T_1, T_2 \), etc.). This can be done perturbatively, e.g., as in the Møller-Plesset theory (MP), or explicitly, e.g., as in coupled-cluster (CC) methods. The corresponding excited states’ models can be derived within the linear response (LR) or equation-of-motion (EOM) formalisms. The resulting wave functions have a physically appealing form: excited states are described as electronic excitations from approximate ground state wave functions (the operator \( R_m \) generates all possible \( m \)-electron excitations out of the reference determinant \( \Phi_0 \)). For example, the SCF analog for excited states, the configuration interaction singles (CIS) model, describes excited states as a linear combination of all singly excited determinants. Similarly to the ground state models, accuracy can be systematically improved by including higher excitations. Both series converge to the exact solution of the Schrödinger equation (in a given one-electron basis set) — full configuration interaction (FCI), which, in turn, becomes exact in the limit of the complete one-electron basis set.

Excitation energies of the single-reference closed-shell molecules can be calculated with 0.1-0.3 eV accuracy (for the states dominated by single electron excitations) [7] by the excited states’ counterpart of CCSD, equation-of-motion for excitation energies (EOM-EE) CCSD method [8–10]. However, many chemically
important situations, such as diradicals and triradicals, cannot be described by these methods due to multiconfigurational character of their wave function, as described below. Sections 1.5 and 1.6 discuss how to extend the single reference EOM approach to treat diradicals and triradicals.

1.3 Electronic structure of diradicals

\[
\begin{array}{ccccccc}
(a) & (b) & (c) & (d) & (e) & (f) \\
\phi_2 & & & & & \\
\phi_1 & & & & & \\
M_s = 0 & M_s = 0 & M_s = 0 & M_s = 0 & M_s = -1 & M_s = -1 \\
\end{array}
\]

**Figure 1.2.** Slater determinants that can be generated by distributing two electrons in two molecular orbitals. The projection of the total spin, \( M_s \), is shown. Determinants (a)-(d) have \( M_s = 0 \). Determinants (a) and (b) are also eigenfunctions of the \( \hat{S}^2 \) operator with expectation value zero (singlet). Note that these determinants always belong to the fully symmetric irreducible representation as they are of the closed-shell type. Therefore, they both can be present in fully symmetric singlet diradical’s wave functions, i.e., Eqns. (1.1) and (1.2). \( \langle \hat{S}^2 \rangle \) for the determinants (c) and (d) equals one. Their linear combinations are eigenfunctions of \( \hat{S}^2 \): (c)-(d) yields a singlet wave function [Eq. (1.4)], whereas (c)+(d) yields the \( M_s = 0 \) component of the triplet [Eq. (1.4)]. Determinants (e) and (f) are high-spin \( M_s = \pm 1 \) components of the triplet state [Eqns. (1.5) and (1.6), respectively].

Following Salem [11], one can define diradicals as molecules with two electrons occupying two (near)-degenerate molecular orbitals. More loosely, Salem considers molecules with a broken bond as diradicals. Since chemical reactions
involve bond breaking, diradicals as reaction intermediates or transition states are essential in interpreting mechanisms [12–15].

Fig. 1.2 shows the six Slater determinants which can be generated by distributing two electrons in two molecular orbitals. From these, three singlet, $\{\Psi_s^i\}_{i=1}^3$, and three triplet, $\{\Psi_t^i\}_{i=1}^3$, wave functions can be composed as follows:

\begin{align*}
\Psi_s^1 &= \frac{1}{2} \left[ \sqrt{1 - \lambda^2} (\phi_1)^2 - \lambda (\phi_2)^2 \right] \cdot (\alpha\beta - \beta\alpha) \quad (1.1) \\
\Psi_s^2 &= \frac{1}{2} \left[ \lambda (\phi_1)^2 + \sqrt{1 - \lambda^2} (\phi_2)^2 \right] \cdot (\alpha\beta - \beta\alpha) \quad (1.2) \\
\Psi_s^3 &= \frac{1}{2} (\phi_1\phi_2 + \phi_2\phi_1) \cdot (\alpha\beta - \beta\alpha) \quad (1.3) \\
\Psi_t^1 &= \frac{1}{2} (\phi_1\phi_2 - \phi_2\phi_1) \cdot (\alpha\beta + \beta\alpha) \quad (1.4) \\
\Psi_t^2 &= \frac{1}{\sqrt{2}} (\phi_1\phi_2 - \phi_2\phi_1) \cdot (\alpha\alpha) \quad (1.5) \\
\Psi_t^3 &= \frac{1}{\sqrt{2}} (\phi_1\phi_2 - \phi_2\phi_1) \cdot (\beta\beta) \quad (1.6)
\end{align*}

Here $\phi_i\phi_j$ is a shorthand notation for the $\phi_i(1)\phi_j(2)$, and $\alpha\beta$ stands for the $\alpha(1)\beta(2)$. As dictated by the Pauli principle, the spatial parts of singlets are symmetric with respect to the interchange of two electrons, whereas the spatial parts of triplets are anti-symmetric.

Much insight concerning the properties of diradicals has been derived from a simple analysis of these wave functions and their interactions [11, 13, 14]. For example, all two-electron triplet states are purely covalent, regardless of
the nature of $\phi_1$ and $\phi_2$. This is consistent with the Pauli principle that does not allow two electrons with the same spin to coexist in the same volume of space, as required in ionic (or zwitter-ionic) configurations. When the orbitals $\phi_1$ and $\phi_2$ are non-bonding (heterosymmetric diradical [11], e.g., the two p-orbitals in methylene), the singlet $\Psi_3^s$ is also covalent, whereas $\Psi_1^s$ and $\Psi_2^s$ are purely ionic wave functions. However, when the orbitals $\phi_1$ and $\phi_2$ constitute a bonding-antibonding pair (homosymmetric diradical [11], e.g. $\pi$ and $\pi^*$ in twisted ethylene), the singlet $\Psi_3^s$ state becomes purely ionic, while $\Psi_1^s$ and $\Psi_2^s$ can vary from purely ionic to purely covalent configurations\textsuperscript{1}.

From a methodological point of view, however, it is important that all three singlet wave functions are two-determinantal. When $\phi_1$ and $\phi_2$ are exactly degenerate, each singlet wave function consists of two equally important configurations. Therefore, the Hartree-Fock wave function, i.e., the single Slater determinant, is a qualitatively incorrect approximation for $\Psi_1^s$ and $\Psi_2^s$. Only a multi-configurational model that treats the important determinants on an equal

\textsuperscript{1}For example, when orbitals $\phi_1$ and $\phi_2$ are exactly degenerate (as are $\pi$ and $\pi^*$ in 90\textdegree twisted ethylene), the determinants (a) and (b) from Fig. 1.2 contribute equally to $\Psi_1^t$ and $\Psi_2^t$, i.e., $\lambda = \frac{1}{\sqrt{2}}$. By substituting $\pi = \frac{1}{\sqrt{2}}(p_A + p_B)$ and $\pi^* = \frac{1}{\sqrt{2}}(p_A - p_B)$ in Eqs. (1.1) and (1.2), the spatial parts of $\Psi_1^t$ and $\Psi_2^t$ become:

$$\Psi_1^t = \frac{1}{\sqrt{2}}(p_A p_B + p_B p_A) \quad (1.7)$$

$$\Psi_2^t = \frac{1}{\sqrt{2}}(p_A p_A + p_B p_B), \quad (1.8)$$

where $p_{A,B}$ denote p-orbitals centered on the two carbons of ethylene. Thus, the wave function $\Psi_1^t$ is purely covalent, whereas $\Psi_2^t$ is ionic.
footing, such as multi-configurational self-consistent field (MCSCF) [16–18], provides an appropriate zero-order wave function for a diradical. To achieve quantitative accuracy, an appropriate zero-order wave function should be augmented by dynamical correlation, e.g., by configuration interaction (MRCI) or perturbation theory (MRPT). Multi-reference CI with single and double excitations (MR-CISD) [19], also known as second order CI (SOCI), complete active space SCF with second order perturbation corrections (CASPT2) [20, 21], or multi-configurational quasi-degenerate perturbation theory (MCQDPT2) [22] are the most commonly used methods of this type (see Ref. [23] for a comprehensive review of multi-reference methods). Recently, variants of MRCC and EOM-CC models targeting diradicals have been introduced by Nooijen [24, 25].

The inclusion of dynamical correlation is crucial for a correct quantitative (and sometimes even qualitative) description of the electronic structure of diradicals [26–29]. Besides the well-known tendency of bare MCSCF wave functions to overestimate bond lengths and underestimate frequencies, the stationary points of the PES corresponding to diradicals can disappear at higher level of theory [29]. Moreover, the balanced description of non-dynamical and dynamical correlations requires active spaces much larger than the simple two-orbital one.²

²Ideally, one would like to always employ a full valence active space (bonding, anti-bonding, and lone pair orbitals). Such active space is uniquely defined, and the corresponding CASSCF wave function is flexible enough to describe all the major interactions of the valence electrons,
To summarize, the theoretical description of singlet diradicals [Eqns. (1.1)-(1.4)] is difficult due to their multi-reference character. The triplet diradical wave functions, however, are much simpler. While the $M_s=0$ triplet wave function (1.4) is also two-configurational, the corresponding high-spin components (1.5) and (1.6) are single-determinantal. Therefore, these states can be described by any single-reference method, the accuracy being systematically improved as one proceeds from the Hartree-Fock model towards correlated approaches (as described in the section 1.2). With respect to the high-spin [Eqns. (1.5,1.6)] triplet states, all singlet states [Eqns. (1.1)-(1.4)] as well as the $M_s=0$ component of the triplet [Eq. (1.4)] are formally single electron excitations involving spin-flip. This suggests that one can employ excited state technique including spin flip to target these states. This is an essence of the spin-flip (SF) approach described in Section 1.6.

e.g., the polarization of $\sigma$ electrons for the $\pi\pi^*$ ionic configurations, as in the V-state of ethylene [26, 28], etc. Unfortunately, the computational cost, which grows factorially with molecular size, rapidly makes this approach unfeasible for systems of more than two or three heavy atoms. The most common approximation involves reduction of the active space guided by physical considerations, which are specific for each particular species or reaction. In addition to the certain arbitrariness of such an approach, the small active space can seriously affect the quality of the resulting wave function, even when dynamical correlation is included in MRCI or MRPT fashion. For example, a recent study of tetramethylene [29] has demonstrated that the selection of the active space for the CASSCF wave function strongly influences the shape of the PES even at the CASPT2 level (the existence of some stationary points calculated at the lower level of theory was not confirmed by more accurate calculations). Recently, alternative approximations to the full valence space CASSCF have been introduced [30, 31]
1.4 Electronic structure of triradicals

In a triradical, three electrons are distributed in three nearly degenerate orbitals. All the relevant Slater determinants with a positive projection of the total spin are shown in Fig. 1.3.

\begin{figure}[h]
\centering
\begin{tabular}{cccc}
\phi_3 & \phi_2 & \phi_1 \\
\hline
(1) & (2) & (3) & (4) \\
\hline
(5) & (6) & (7) & (8) & (9) & (10) \\
\end{tabular}
\caption{Slater determinants that can be generated by distributing three electrons over three orbitals. Only determinants with a positive projection of the total spin are shown. Determinant (1) has \( M_s = \frac{3}{2} \), determinants (2)-(10) have \( M_s = \frac{1}{2} \). With respect to high-spin determinant (1), all low-spin determinants (2)-(10) are formally singly excited configurations including the spin-flip of one electron. By reversing the spins of all the electrons, a set of determinants with \( M_s = -\frac{3}{2}; -\frac{1}{2} \) can be generated. Since spin is not present in the non-relativistic Hamiltonian, determinants with different \( M_s \) do not interact across the Hamiltonian and, therefore, do not mix in the triradical wave functions. Determinants (1), (5)-(10) are eigenfunctions of \( \hat{S}^2 \), whereas (2)-(4) are not (however, their proper linear combinations are).}
\end{figure}

The high-spin determinant (1) has \( M_s = \frac{3}{2} \). Nine determinants have \( M_s = \frac{1}{2} \), six of them [(5)-(10)] being of a closed-shell type (these are the eigenfunctions of \( \hat{S}^2 \)), and three [(2)-(4)] — of an open-shell type (these are not the eigenfunctions of \( \hat{S}^2 \)). Fig. 1.4 shows valid wave functions which can be
Figure 1.4. Triradical wave functions that are eigenstates of $\hat{S}_z$ and $\hat{S}^2$. Symmetry of the orbitals determines if these configurations can interact and further mix with each other. All doublets (c)-(j) and the low-spin component of quartet (b) are multiconfigurational, while the high-spin component of quartet state (a) is singly-determinantal.
constructed from the determinants from Fig. 1.3. From the open-shell determinants (2)-(4), one can construct one quartet (b) and two doublet states (c)-(d). These wave functions are eigenstates of both $\hat{S}_z$ and $\hat{S}^2$. Regardless of the spatial symmetry of the orbitals $\phi_1 - \phi_3$, the closed-shell determinants can form several doublet wave functions (e)-(j), as shown in Fig. 1.4. The values of $\lambda$ depend upon the energy separation between the orbitals, i.e., large $\lambda$ values correspond to nearly degenerate orbitals. For example, when $\phi_2$ and $\phi_3$ are exactly degenerate, two different doublet states, (i) and (j), are obtained by taking the sum and the difference of determinants (7) and (8). Similarly to the closed-shell diradicals’ singlets, these doublet determinants interact regardless of the orbitals’ symmetries. The symmetries and nodal structure of the MOs define which of the configurations shown in Fig. 1.4 can interact and mix further in the triradical wave functions.

From the methodological perspective, it is important that all the doublets and the low-spin quartet state are multi-determinantal. Therefore, a multiconfigurational method should be employed when the triradical orbitals are nearly degenerate. However, if the triradical orbitals are well separated in energy, some of the states [for example, (g) and, perhaps, (e)] can be described by a single-reference method.

Unlike the $M_s = 1/2$ triradical states, the high-spin component ($M_s = 3/2$) of the quartet state is single-determinantal. Moreover, all the low-spin
determinants are formally single spin-flipping excitations from the high-spin $M_s = 3/2$ determinant. Therefore, similarly to diradicals, the SF approach can be employed to describe triradicals, as explained below.

1.5 Equation-of-motion coupled-cluster approach

In equation-of-motion approach or closely related to it linear response (LR) theory [8–10], the target states are found by diagonalizing the so-called similarity transformed Hamiltonian $\bar{H} = e^{-T}He^{T}$:

$$\bar{H}R(k) = E_k R(k), \quad (1.9)$$

where $T$ and $R(k)$ are general excitation operators with respect to the reference determinant $|\Phi_0\rangle$. Regardless of the choice of $T$, the spectrum of $\bar{H}$ is exactly the same as that of the original Hamiltonian $H$ — thus, in the limit of the complete many-electron basis set, EOM is identical to full configuration interaction (FCI). However, in the case of truncated bases, EOM is superior to CI, in virtue of correlation effects being folded in through the similarity transformation. The amplitudes $T$ are determined from the CC equations for the reference state $|\Phi_0\rangle$:

$$\langle \Phi_{\mu} | \bar{H} | \Phi_0 \rangle, \quad (1.10)$$
where $\Phi_\mu$ denotes $\mu$-tuple excited determinants, e.g., \{\Phi_i^a, \Phi_{ij}^{ab}\} in the case of coupled-cluster singles and doubles (CCSD). Here and below $a, b, c$ indexes label virtual spin-orbitals, and $i, j, k$ denote occupied spin-orbitals.

Whereas the cluster operator $T$ describes correlation in the reference wave function, the excitation operator $R(k)$ treats differential correlation effects between the reference and the target state wave functions. In practical applications, both $T$ and $R(k)$ operators are truncated at some order and, therefore, an approximate EOM-CC method is characterized by two parameters, $m$ and $n$, i.e., the orders of $T$ and $R(k)$, respectively, with each model being denoted by EOM-CC($m, n$) [32]:

\[ T = T_1 + T_2 + \ldots + T_m \]  (1.11)

\[ R(k) = R_0(k) + R_1(k) + R_2(k) + \ldots + R_n(k) \]  (1.12)

For example, EOM-CC with truncation of $R$ and $T$ at the second order is called EOM-CC(2,2), or EOM-CCSD. With increase of the truncation order, the accuracy of the EOM-CC model would systematically approach the accuracy of FCI.

In principle, $T$ and $R(k)$ operators can be truncated at different levels. For example, more accurate description of target states can be achieved by including
triple excitations in the EOM part only. Our implementation of the EOM-CC(2,3) method [32], i.e., the EOM-CC model with:

\[
T = T_1 + T_2; \quad R(k) = R_0(k) + R_1(k) + R_2(k) + R_3(k),
\]

(1.13)
is discussed in details in Section 1.7 and Chapter 8.

By combining different types of excitation operators and references \(|\Phi_0\rangle\), different groups of target states can be accessed (see Fig. 1.5). For example, electronically excited states can be described when the reference \(|\Phi_0\rangle\) corresponds to the ground state wave function, and operators \(R\) conserve the number of electrons and a total spin, i.e., EOM-EE-CC [8–10]:

\[
R_0 = r_0, \quad R_1 = \sum_{ia} r_i^a a^+ i, \quad R_2 = \frac{1}{4} \sum_{ijab} r_{ij}^{ab} a^+ b^+ j i, \ldots,
\]

(1.14)
The EOM-EE-CC method accurately describes the singly excited states of closed-shell systems but breaks down if applied to doubly excited states and to molecules with degenerate electronic states (such as diradicals) since the single-reference description of the reference wave function becomes inappropriate.
Figure 1.5. The reference wave functions $\Psi_0$ and determinants that can be obtained as single and double excitations are shown for a variety of EOM-CC models.
In the EOM-SF-CC (or, simply SF-CC) method, the excitation operators $R(k)$ include spin-flip of one electron [1, 33]. This method accurately describes diradicals, triradicals, and bond-breaking, as described in Section 1.6.

In the ionized/electron attached EOM models, the excitation operators are not electron conserving:

\[
R = \sum_i r_i + \frac{1}{4} \sum_{iya} r_{ija}^{a+i} + \cdots , \tag{1.15}
\]

\[
R = \sum_a r^a_i + \frac{1}{4} \sum_{iab} r_{iab}^{a+b} + \cdots . \tag{1.16}
\]

These EOM-CC models are called equation-of-motion coupled-cluster methods for ionized potentials (EOM-IP-CC) and for electron affinities (EOM-EA-CC), respectively. The application of the EOM-IP-CC and EOM-EA-CC operators to a closed-shell reference creates properly spin-adapted wave functions for open-shell systems, which makes EOM-IP-CC and EOM-EA-CC effective tools for describing ground and excited states of radicals [34, 35].

The EOM-IP-CC and EOM-EA-CC methods can be extended to describe diradical states. For this purpose, one needs to consider the doubly ionized or doubly electron affinity operator $R$:

\[
R = \sum_{ij} r_{ij} + \frac{1}{4} \sum_{ijk} r_{ijk}^{a+k} + \cdots , \tag{1.17}
\]
\[ R = \sum_{ab} r^{ab} a^+ b^+ + \frac{1}{4} \sum_{abc} r^{abc} a^+ b^+ c^+ + \cdots. \] 

(1.18)

These operators change the number of electrons between the reference and the target states:

\[ \Psi(N) = R(N - 2) \Psi_0(N + 2), \] 

(1.19)

\[ \Psi(N) = R(N + 2) \Psi_0(N - 2), \] 

(1.20)

where \( N \) is the number of electrons. The corresponding methods are referred to as EOM-DIP-CC and EOM-DEA-CC [25].

### 1.6 The Spin-Flip approach

In the SF approach, one describes low-spin states within a single reference formalism as spin-flipping, e.g., \( \alpha \rightarrow \beta \), excitations from a high-spin reference state for which both dynamical and non-dynamical correlation effects are much smaller than for the corresponding low-spin states [1, 33, 36–39].

In traditional (non-SF) single-reference based excited states models, the excited state wave functions are parameterized as follows:

\[ \Psi_{M_s=0}^{\sigma \tau} = \tilde{R}_{M_s=0} \Psi_{M_s=0}^{\sigma \tau}, \] 

(1.21)
where $\hat{\Psi}_{M_s=0}^*$ is a closed-shell reference wave function, and the operator $\hat{R}$ is an excitation operator truncated at a certain level of excitation (which should be consistent with the theoretical model employed to describe the reference $\hat{\Psi}^*$). Note that only excitation operators that do not change the total number of $\alpha$ and $\beta$ electrons, i.e. $M_s=0$, need to be considered in Eq. (1.21).

When the closed-shell reference $\hat{\Psi}^*$ is well described by a single-reference wave function, the excited singlet and triplet states [including open-shell configurations, such as (1.4) and (1.4)] are also well described by Eq. (1.21). However, the quality of the excited states $\Psi_{s,t}^{s,t}$ deteriorates when a single-reference description of $\hat{\Psi}^*$ becomes inappropriate, as in the case of diradicals whose singlet states are two-configurational wave functions of type (1.1).

To overcome this problem, the SF model employs a high-spin triplet reference state, which is accurately described by a single-reference wave function. The target states, closed and open shell singlets and triplets, are described as spin-flipping excitations:

$$ \Psi_{M_s=0}^{s,t} = \hat{R}_{M_s=-1} \hat{\Psi}_{M_s=+1}^t, $$

where $\hat{\Psi}_{M_s=+1}^t$ is the $\alpha\alpha$ component of the triplet reference state, $\Psi_{M_s=0}^{s,t}$ stands for the final ($M_s=0$) singlet and triplet states, respectively, and the operator $\hat{R}_{M_s=-1}$ is an excitation operator that flips the spin of an electron. As can be seen from Fig. 1.2, all the configurations used to describe diradical wave
functions (1.1)-(1.4) are formally single excitations with respect to configuration (1.5). Therefore, the SF ansatz (1.23) is sufficiently flexible to describe both closed-shell and open-shell diradical states in a balanced fashion, i.e., without overemphasizing the importance of one of the configurations.

In the case of triradicals, we choose the high-spin \((M_s = 3/2)\) component of the quartet state as a reference. This state is accurately described by single-reference methods. The target states, the low-spin component of the quartet and the open- and closed-shell doublets [(b) and (c)-(j), respectively], are described as single electron excitations including the spin-flip of an electron:

\[
\Psi^{d,q}_{M_s=1/2} = \hat{R}_{M_s=-1}\Psi^{q}_{M_s=3/2},
\]  

(1.23)

where \(\Psi^{q}_{M_s=3/2}\) is the \(\alpha\alpha\alpha\) component of the quartet reference state [(a) from Fig. 1.4], \(\Psi^{d,q}_{M_s=1/2}\) stands for the final \((M_s=1/2)\) doublet and quartet states [(b)-(j)], and the operator \(\hat{R}_{M_s=-1}\) is an excitation operator that flips the spin of an electron.

By employing theoretical models of increasing complexity for the reference wave function, the description of the final states can be systematically improved. For example, the simplest SF model employs a Hartree-Fock wave function, and the operator \(\hat{R}\) is then truncated at single excitations (SF-CIS or SF-SCF) [1]. The spin-complete version of SF-CIS was also developed [39]. SF-CIS can be
further augmented by perturbative corrections [SF-CIS(D) or SF-MP2] [36].

A more accurate description can be achieved by describing the reference wave function by a coupled-cluster model, e.g., CCSD or optimized orbitals coupled-cluster doubles (OO-CCD). In this case, the excitation operator $\hat{R}$ consists of single and double excitation operators involving a flip of the spin of an electron (SF-CCSD and SF-OD models) [1, 33]. Moreover, the SF idea can be used to extend density functional theory to multireference situations [38].

Corresponding SF equations in spin-orbital form are identical to those of traditional excited state theories, i.e., CIS, CIS(D), or EOM-EE-CCSD, however, they are solved in a different subspace of determinants: non-SF theories consider only $M_s=0$ excitation operators, whereas SF operates in the $M_s=-1$ subspace. The computational cost and scaling of SF models is identical to that of the corresponding non-SF excited state theories.

To summarize, the EOM approach enables one to describe many multi-configurational wave functions within a single-reference formalism. The EOM models are rigorously size-extensive, and their accuracy can be systematically improved (up to exact FCI results) by including higher excitations explicitly or perturbatively. Moreover, the EOM methods are multi-state schemes — several target states are obtained in the single diagonalization step. The built-in error cancellation significantly improves the accuracy of EOM.
1.7 Equation-of-motion coupled-cluster method with triple excitations [EOM-CC(2,3)]

1.7.1 Introduction

As discussed above, EOM-CCSD describes electronic states with predominantly single-excitation character with accuracy of 0.1-0.2 eV [7]. Unfortunately, the EOM-CCSD accuracy deteriorates for electronic states with large contributions of double excitations as, for example, dark states of polyenes, or some valence states of radicals. Moreover, the EOM-CCSD accuracy degrades when the reference wave function is spin-contaminated. Inclusion of triple excitations solves these problems, which originate from incomplete treatment of non-dynamical correlation, and also provides overall more accurate treatment of well-behaved excited states by more complete accounting of dynamic correlation. For example, the error bars of EOM-CCSDT are 0.1 eV for the states with doubly excited character, and 0.01 eV for singly excited states [32].

An overview of the high-level CC and EOM-CC model can be found, e.g., in Ref. [40]. Several approaches that incorporate triple excitations in EOM-CC were reported [41–53]. Implementations of full EOM-CCSDT, EOM-CCSDTQ, and even EOM-CCSDTQP were reported [47, 49–51], as well a variety of approximations of the full EOM-CCSDT. For example, Watts and Bartlett implemented an approximate EOM-CCSDT model, in which only two-body
elements in the triple blocks of the similarity transformed Hamiltonian were included [41], iterative EOM-CCSDT-1 and EOM-CCSDT-3 models, and their non-iterative counterparts EOM-CCSD(T) and EOM-CCSD($\tilde{T}$) [42, 43]. The iterative CC3 and the non-iterative CCSDR(3) models were introduced by Christiansen, Koch, Jørgenson and co-workers [44–46]. Active-space EOM-CC models were introduced by Kowalski and Piecuch [48, 49], and by Krylov et.al. [54]. The initial benchmarks for these models included singlet and triplet excited states of closed-shell molecules, e.g., CH$^+$, C$_2$, N$_2$, and focused on accurate description of the excited states with a dominant doubly excited character.

Another scope of problems when inclusion of triples in EOM-CC is important is excited states of radicals, especially, when the reference and, consequently, the excited state wave functions of are strongly spin-contaminated. To this end, several methods were developed [52, 53]. Szalay and Gauss introduced spin-restricted (SR) version of LRT with inclusion of so-called pseudotriple (psT) excitations (SR-CCSD-LRT and CCSD-psT-LRT) and tested it on the series of small radicals, i.e., OH, CN, CO$^+$, and CH [52]. Crawford and co-workers implemented the open-shell variant of the CC3 method and applied it to low-lying electronic states of allyl and nitromethyl radicals [53].

The SF variant of EOM-CCSD, which employs a high-spin (triplet or quartet) Hartree-Fock determinant as a reference [33], may also be sensitive to spin-contamination of the reference. For example, in $\sigma - \pi$ benzene-derivatives, the
high-spin UHF determinant may be spin-contaminated, which results in severe
spin-contamination of EOM excited states [55]. Similarly to radicals, inclusion
of triples (or a subset of triples) in this case would reduce spin-contamination
and improve accuracy.

Inclusion of triple excitations for the excited states usually results in the
computational scaling of $N^7 - N^8$, where $N$ is the size of the system, and is
therefore computationally demanding. As a result, a model with full triple
excitations can be applied only to small molecules in a moderate basis set.
However, several approaches exist to extend a scope of models with triple exci-
tations to larger systems. These are energy separability schemes [56], basis
set extrapolations [3, 57, 58], and restricting triple excitations by choosing the
most important ones, e.g., models with active-space triples [48, 49, 52, 54]. By
employing these schemes, one can evaluate effects of triple and even quadrupole
excitations in much larger systems.

We implemented the EOM-CC(2,3) method, i.e., the EOM-CC model with
inclusion of triples in the EOM part only, for excitation-energies and spin-flip
variants. As shown by Hirata, Nooijen, and Bartlett [32], the accuracy of EOM-
CC(2,3) closely follows that of full EOM-CCSDT for singly and doubly excited
states of closed-shell molecules. Our benchmark demonstrates that this method
performs very well for open-shell systems as well. As a less computa-
tionally demanding alternative to EOM-CC(2,3), the active-space EOM-CC(2,3)
model, EOM-CC(2,3), in which only semi-internal triples are included, is also implemented. We benchmarked full and active-space EOM-CC(2,3) on a number of small open-shell molecules, trimethylenemethane (TMM) diradical, and dehydro-meta-xyylene (DMX) triradical (see Chapter 8).

A desired property of a correlated model is its insensitivity to the reference determinant. For example, FCI is invariant with respect to the reference choice, CCSD is less sensitive than lower level MP2, etc. In general, CCSD is moderately sensitive to a choice of the reference, e.g., UHF and ROHF based CCSD or CCSD(T) results are usually rather similar\(^3\). However, this is less so for the EOM-CCSD target states. For example, if the reference UHF determinant is spin-contaminated, the EOM-CCSD states are very likely to be spin-contaminated, even though the CC almost completely recovers the spin-symmetry of the reference. As a result, the UHF and ROHF based EOM excitations energies can differ by several tenths of eV. This unsatisfactory behavior was observed in EOM-EE-CCSD calculations of radicals \(^{52}\), and also in the EOM-SF-CCSD applications to \(\sigma - \pi\) diradicals and triradicals \(^{55}\).

As shown in Chapter 8, contrarily to EOM-CCSD, EOM-CC(2,3) is much less sensitive to the choice of a reference determinant. For example, for the

\(^3\)This may be not so for the high-spin (triplet or quartet) states, when the results of ROHF and UHF based CCSD and CCSD(T) differ quite considerably, as in Ref. \(^{59}\).
electronic states of CH radical, the EOM-CC(2,3) energies differ only by thousandths of eV, whereas the corresponding differences in UHF and ROHF based EOM-EE-CCSD energies are up to 0.4 eV.

1.7.2 EOM-CC(2,3)

As discussed in Section 1.5, in EOM approach, the cluster operator $T$ describes correlation in the reference wave function, whereas the excitation operator $R(k)$ treats differential correlation effects between the reference and the target state wave functions. In practical applications, both $T$ and $R(k)$ operators are truncated at some order and, therefore, an approximate method EOM-CC is characterized by two parameters, $m$ and $n$, i.e., the orders of $T$ and $R(k)$, respectively, with each model being denoted by EOM-CC$(m, n)$ [32].

In principle, $T$ and $R(k)$ operators can be truncated at different levels. As demonstrated in Ref. [32], truncation of $T$ and $R(k)$ at the same order, e.g., $m = n = 2$, as in EOM-CCSD, or $m = n = 3$, as in full EOM-CCSDT, results in the most accurate and balanced description of the excited states. However, the leading effect in capturing accuracy of the description of the excited states is in the EOM rather than the CC part:

$$ EOM − CC(2, 2)[≡ EOM − CCSD] ≃ EOM − CC(3, 2) \ll $$

$$ EOM − CC(2, 3) ≃ EOM − CC(3, 3)[≡ EOM − CCSDT] $$
i.e., accuracy of the EOM-CC(2,3) method closely follows that of full EOM-CCSDT [or EOM-CC(3,3)], whereas the computational cost of the former is less.

We implemented the EE and SF variants of EOM-CC(2,3), i.e., the EOM-CC model with:

\[ T = T_1 + T_2; \quad R(k) = R_0(k) + R_1(k) + R_2(k) + R_3(k), \quad (1.24) \]

as a less computationally demanding substitute of full EOM-CCSDT. The scaling of the EOM-CC(2,3) model is \( N^8 \), the same as of CISDT and EOM-CCSDT.

Amplitudes \( T \) satisfy the CCSD equations for the reference state:

\[ E_{CC} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle, \quad (1.25) \]

\[ \langle \Phi^a_i | \hat{H} - E | \Phi_0 \rangle = 0, \quad \langle \Phi^{ab}_{ij} | \hat{H} - E | \Phi_0 \rangle = 0. \quad (1.26) \]
\( \tilde{H} \) assumes the following form in the basis of the reference and the singly, doubly, and triply excited determinants:

\[
\tilde{H} = \begin{pmatrix}
E_{CC} & \tilde{H}_{OS} & \tilde{H}_{OD} & 0 \\
0 & \tilde{H}_{SS} & \tilde{H}_{SD} & \tilde{H}_{ST} \\
0 & \tilde{H}_{DS} & \tilde{H}_{DD} & \tilde{H}_{DT} \\
\tilde{H}_{TO} & \tilde{H}_{TS} & \tilde{H}_{TD} & \tilde{H}_{TT}
\end{pmatrix}, \quad (1.27)
\]

where \( E_{CC} \) is the reference CC energy, and \( \tilde{H}_{SO} = \tilde{H}_{DO} = 0 \) in virtue of the CC equations (1.25) and (1.26). Due to different truncation levels of \( T \) and \( R(k) \), the effective Hamiltonian matrix element \( \tilde{H}_{TO} \) associated with triply excited determinant \( |\Phi_{abc}^{ijk}\rangle \) is non-vanishing, and, consequently, the reference determinant \( |\Phi_0\rangle \) is no longer an eigenstate of \( \tilde{H} \) in the subspace of singly, doubly, and triply excited determinants. The \( \tilde{H}_{OT} \) matrix element is zero because the maximum excitation level of Hamiltonian is two.

Since in EOM-CC(2,3) the order of truncation of the cluster operator \( T \) is 2, as in EOM-CCSD, common to these two models elements of Hamiltonian (up to \( \tilde{H}_{DD} \) block) are identical. Therefore, the implementation of EOM-CC(2,3) only requires inclusion of matrix elements involving triple excitations. Unlike EOM-CCSD, \( \tilde{H} \) of the EOM-CC(2,3) should be diagonalized in the basis of
zero, single, double, and triple excitations. However, in the SF variant of EOM-
CC(2,3), the reference is not present in final EOM states (i.e., \( R_0 = 0 \) for all
the EOM-SF states), and \( \tilde{H} \) is diagonalized in the basis of single, double, and
triple excitations only.

After subtracting the reference energy from \( \tilde{H} \), the EOM-CC(2,3) right
eigenproblem reads as follows:

\[
\begin{pmatrix}
0 & \tilde{H}_{OS} & \tilde{H}_{OD} & 0 \\
0 & \tilde{H}_{SS} - E_{CC} & \tilde{H}_{SD} & \tilde{H}_{ST} \\
0 & \tilde{H}_{DS} & \tilde{H}_{DD} - E_{CC} & \tilde{H}_{DT} \\
\tilde{H}_{TO} & \tilde{H}_{TS} & \tilde{H}_{TD} & \tilde{H}_{TT} - E_{CC}
\end{pmatrix}
\begin{pmatrix}
R_0(k) \\
R_1(k) \\
R_2(k) \\
R_3(k)
\end{pmatrix}
= \omega_k
\begin{pmatrix}
R_0(k) \\
R_1(k) \\
R_2(k) \\
R_3(k)
\end{pmatrix},
\]

(1.28)

where \( \omega_k \) is the energy difference between the coupled-cluster reference energy
and the energy of \( k \)-th excited state: \( \omega_k = E_k - E_{CC} \). For energy calculations,
it is sufficient to solve only the right eigenvalue problem. However, both right
and left eigenvectors are required for properties or gradient calculations.
1.7.3 Programmable EOM-CC(2,3) equations

We solve Eq. (1.28) by using a generalized Davidson’s iterative diagonalization procedure [60–62], which requires calculation of the products of the transformed Hamiltonian acting on trial vectors:

\[ \sigma_0 = \tilde{H}_{OS}R_0 + \tilde{H}_{OD}R_0 \] (1.29)

\[ \sigma_i^a = ([\tilde{H}_{SS} - E_{CC}]R_1)_i^a + (\tilde{H}_{SD}R_2)_i^a + (\tilde{H}_{ST}R_3)_i^a \] (1.30)

\[ \sigma_{ij}^{ab} = (\tilde{H}_{DS}R_1)_{ij}^{ab} + ([\tilde{H}_{DD} - E_{CC}]R_2)_{ij}^{ab} + (\tilde{H}_{DT}R_3)_{ij}^{ab} \] (1.31)

\[ \sigma_{ijk}^{abc} = (\tilde{H}_{TO}R_0)_{ijk}^{abc} + (\tilde{H}_{TS}R_1)_{ijk}^{abc} + (\tilde{H}_{TD}R_2)_{ijk}^{abc} \] (1.32)

Programmable expressions for \( \sigma \) including only single and double terms can be found in Ref. [33]. The terms which are specific to EOM-CC(2,3) are:

\[ (\tilde{H}_{ST}R_3)_i^a = \langle \Phi_i^a | \tilde{H} | R_3 \Phi_0 \rangle = \frac{1}{4} \sum_{j k b c} \langle j k || b c \rangle r_{j k i}^{b c a} \] (1.33)

\[ (\tilde{H}_{DT}R_3)_{ij}^{ab} = \langle \Phi_{ij}^{ab} | \tilde{H} | R_3 \Phi_0 \rangle = \] (1.34)

\[ + \sum_{k c} F_{k c} r_{k i j}^{c a b} + 1/2 P(ij) \sum_{k l c} r_{k l c}^{a b c} r_{k l j}^{a b c} + 1/2 P(ab) \sum_{k l d} I_{k a c d}^{l} r_{k l i j}^{c d b} \]
\[
(|\tilde{H}_{TT} - E_{CC}| R_3)_{ij}^{abc} = \langle \Phi_{ijk}^{abc} | \tilde{H} | R_3 \Phi_0 \rangle = \\
+ P(ij|k) \left[ - \sum_l F_{klr}^{abc} + \sum_{lm} I^4_{ijlmr}^{abc} \right] \\
+ P(ab|c) \left[ \sum_d F_{cdr}^{abd} + \sum_{de} I^5_{abcdr}^{dec} \right] \\
- P(a|bc) P(i|jk) \sum_{dl} I^1_{idlar}^{dbc} \\
+ P(a|bc) P(ij|k) \left[ - \sum_d H^7_{kdbc} t_{ad}^{ijla} + \sum_l H^6_{ijla} t_{bc}^{kl} \right]
\]

\[
(|\tilde{H}_{TO} R_0)_{ij}^{abc} = \langle \Phi_{ijk}^{abc} | \tilde{H} | R_0 \Phi_0 \rangle = \\
+ P(a|bc) P(ij|k) R_0 \left[ \sum_l t_{ijk}^{abc} (- r^2_{ijla} + \sum_d t_{ij}^{adv} F_{lde} + \sum_d r^3_{ij} t_{kdbc} \right]
\]

\[
(|\tilde{H}_{TS} R_1)_{ij}^{abc} = \langle \Phi_{ijk}^{abc} | \tilde{H} | R_1 \Phi_0 \rangle = \\
+ P(a|bc) P(ij|k) \left[ \sum_l t_{klr}^{bc} H^2_{ijla} + \sum_d t_{ij}^{adv} H^3_{kdbc} \right]
\]

\[
(|\tilde{H}_{TD} R_2)_{ij}^{abc} = \langle \Phi_{ijk}^{abc} | \tilde{H} | R_2 \Phi_0 \rangle = \\
+ P(a|bc) P(ij|k) \left[ \sum_l r_{klr}^{abc} r^2_{ijla} + \sum_d r^3_{ij} t_{kdbc} + \sum_l t_{klr}^{bc} H^4_{ijla} + \sum_d t_{ij}^{adv} H^5_{kdbc} \right]
\]
Table 1.1. H-intermediates used in Eqs. (1.33)-(1.38)

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{ia}^{1}$</td>
<td>$\sum_{jb} r_{j}^{b} \langle ij</td>
</tr>
<tr>
<td>$H_{jklc}^{2}$</td>
<td>$2 \sum_{m} r_{m}^{e} I_{jkm}^{1} + P(jk) \sum_{d} r_{d}^{d} I_{jklc}^{1}$</td>
</tr>
<tr>
<td>$H_{kbdc}^{3}$</td>
<td>$-2 \sum_{e} r_{e}^{b} I_{kecd}^{1} + P(bc) \sum_{i} r_{i}^{b} I_{kbdc}^{1} + \sum_{t} H_{idt}^{1}$</td>
</tr>
<tr>
<td>$H_{jklc}^{4}$</td>
<td>$-1/2 \sum_{ab} r_{jk}^{ab} I_{jklc}^{1} + P(jk) \sum_{i} r_{ki}^{ab} I_{jklc}^{1}$</td>
</tr>
<tr>
<td>$H_{kbdc}^{5}$</td>
<td>$-1/2 \sum_{ij} r_{ij}^{bc} r_{ijkd}^{6} - P(bc) \sum_{ia} r_{ia}^{bc} I_{kbdc}^{1}$</td>
</tr>
<tr>
<td>$H_{jklc}^{6}$</td>
<td>$-1/2 \sum_{ab} r_{jk}^{ab} \langle li</td>
</tr>
<tr>
<td>$H_{kbdc}^{7}$</td>
<td>$-1/2 \sum_{aij} r_{ij}^{bc} \langle ij</td>
</tr>
</tbody>
</table>

$I$ and $T$ intermediates used in these equations are given in Table V of Ref. [33]. To avoid storage of large 7-index quantities, we introduced additional intermediates that should be updated at each iteration of Davidson’s diagonalization procedure. They are given in Table 1.1.

1.7.4 Active space EOM-CC(2,3) model

To reduce cost of the calculations and to extent the scope of the problems amenable to the EOM-CC(2,3) model, we also implemented the active-space variant of EOM-CC(2,3), EOM-CC(2,3). We start by dividing all spin-orbitals into $O$ core (restricted occupied) spin-orbitals ($i,j,k$), $O$ active occupied spin-orbitals ($I,J,K$), $V$ active unoccupied spin-orbitals ($A,B,C$), and $V$ restricted
virtual spin-orbitals \((a,b,c)\), all relative to \(|\Phi_0\rangle\). Our implementation of the active space model is defined as follows:

\[
T = T_1 + T_2, \quad (1.39)
\]

\[
R'(k) = R_0(k) + R_1(k) + R_2(k) + r_3(k), \quad (1.40)
\]

where all excitation operators are defined as usual, except for \(r_3(k)\), which is defined as:

\[
r_3(k) = r_{ijk}^{abc}(k), \quad (1.41)
\]

that is, in the EOM-CC(2,3) model, all \(T\)-amplitudes and \(R_{1,2}(k)\) are determined in the full space, whereas only internal and semi-internal triple excitations are present in \(R'(k)\). The excitation energies are defined by solving the set of equations (1.28), in which the active space \(R'(k)\) operator and triexcited determinant \(|\Psi_{ijk}^{abc}\rangle\) substitute the full space \(R(k)\) and \(|\Psi_{ijk}^{abc}\rangle\). The number of these semi-internal triples is \(O\) \(V^2\), i.e., the prefactor times the number of doubles.

As for any active space method, the thoughtful choice of the active space for the EOM-CC(2,3) is crucial for obtaining accurate excitation energies. For valence states, the most straightforward but prohibitively expensive choice is to include all valence orbitals. Fortunately, as shown in Chapter 8, using much
smaller active spaces can be sufficient. In general, the active space should include: (i) orbitals that describe the leading character of a target state (later referred to as the minimal active space); and (ii) orbitals which contribute to the spin-contamination, symmetry-breaking, or other problems of the reference or the target state. Selecting orbitals of type (i) is straightforward, e.g., these are a singly occupied orbitals in radicals, (nearly)-degenerate diradical or triradical orbitals, and so on. However, choosing orbitals of type (ii) is more ambiguous. Analysis of the $T$ and $R$ amplitudes obtained from a separate EOM-CCSD calculation is often needed to select orbitals of the type (ii). Usually, the problematic orbitals are those appearing in $R(k)$ or $T$ amplitudes with considerable weight, i.e., the orbitals that contribute to the multiconfigurational nature of the reference or excited states. In some cases, there is no need in orbitals of type (ii), e.g., see methylene example from Section 8.2, whereas in others, e.g., see Section 8.4, omitting important orbitals of type (ii) can significantly affect the results.

Overall, the active space with semi-internal triples results in significant improvements when non-dynamical correlation is important, e.g., when there is a degeneracy between orbitals. However, to accurately recover dynamical correlation, inclusion of full triples is needed. Overall, the accuracy of EOM-CC(2,3) will differ from that of full EOM-CC(2,3) by the value of dynamical
correlation correction recovered by triple excitations. Based on our benchmarks, this value is usually less than 0.1 eV for excited states.

There are different approaches of constructing an active space model. In our implementation, the active space model is similar to that implemented in Refs. [30, 31, 48, 49]. Alternative approach for inclusion triple excitations was investigated by Szalay and Gauss, who augmented single and double excitations by a selection of triples recovering the spin-symmetry of the excited state, i.e., so called pseudo-triple excitations.

1.7.5 Size-extensivity of EOM-CC(2,3)

In this Section, we discuss the size-extensivity of the EOM-EE-CC(2,3) and EOM-SF-CC(2,3) models, closely following the presentation from Ref. [37] and [39]. We adhere to the terminology used in Refs. [37] and [63] and use the term size-extensivity to refer to the additive separability of the energy in the limit of non-interacting fragments:

\[
E_{AB} = E_A + E_B,
\]  

(1.42)

where \(E_{AB}\) is the energy of a system composed of two non-interacting fragments, \(A\) and \(B\), at infinite separation; and \(E_A, E_B\) are energies of the corresponding fragments. Here, we restrict ourselves to the case when either \(A\) and/or \(B\) are
closed-shell systems. For the EOM-CC(2,3) models, the total energy of a target state consists of the reference energy and the corresponding transition energy. Thus, Eq. (1.42) is satisfied if: (i) the reference energy of the composite system is the sum of the reference energies for fragments; and (ii) the transition energy is additive. The condition (i) is satisfied by any EOM-CC model due to size-extensivity of the coupled-cluster model for cases when either both fragments are closed-shell molecules or, for a closed-shell and an open-shell fragment, provided that the UHF orbitals are employed.

Below we show that for EOM-SF-CC(2,3), the transition energy for the “excitation” localized on fragment $\mathbf{A}$ in the super-molecule is the same as the transition energy for the isolated fragment $\mathbf{A}$, i.e., that energies of target states on the fragment $\mathbf{A}$ are not affected by the presence (at infinite distance) of the fragment $\mathbf{B}$. Thus, the quality of EOM-SF-CC(2,3) description would not degrade with the increase of molecular size. The EOM-EE-CC(2,3) model, however, is not fully size-extensive, because the transition energy between the reference and the excited state in EOM-EE-CC(2,3) is not additive. However, the transition energies between the EOM-EE-CC(2,3) excited states are additive. Thus, EOM-EE-CC(2,3) exhibits limited size-extensivity.

We start by dividing all the determinants into four groups; (i) the reference determinant, $|0_A \cdot 0_B\rangle$ or simply $|0\rangle$; (ii) determinants involving excitations localized on fragment $\mathbf{A}$, $|\Phi_A \cdot 0_B\rangle$ or $|A\rangle$; (iii) determinants involving excitations
localized on fragment $B$, $|0_A \cdot \Phi_B\rangle$ or $|B\rangle$; (iv) determinants that involve excitations of electrons on both fragments, $|\Phi_A \cdot \Phi_B\rangle$ or $|AB\rangle$ (i.e., those which describe simultaneous excitation of both subsystems or electron transfer between them).

In the SF implementation employing a triplet reference, the reference determinant is the CC solution describing the $\alpha\alpha$ component of the reference triplet state. Without loss of generality, we assume that the two unpaired $\alpha$-electrons are localized on fragment $A$. Thus, for EOM-SF, $|0_A\rangle$ is the CC wave function for fragment $A$ in the triplet state, and $|0_B\rangle$ is the CC wave function for fragment $B$ in the singlet state. Later in the discussion, we use $|0\rangle$ and $|p\rangle$ to refer to (i) and (ii)-(iv) determinants, respectively. While $|0\rangle$ is the $M_s=1$ determinant, all $|p\rangle$ have $M_s=0$, since they are generated by spin-flipping excitations from $|0\rangle$.

In the separated limit, the Hamiltonian operator (and the similarity transformed Hamiltonian as well) of the composite system is the sum of those for the individual fragments$^4$:

$$\bar{H} = \bar{H}_A + \bar{H}_B$$  \hspace{1cm} (1.43)

$^4$This follows from the fact that similarity transformation does not change the spectrum of the Hamiltonian.
As pointed out by Koch et al. [64], the sufficient condition for size-extensivity is an upper-triangle structure of the matrix of the Hamiltonian (1.43) in the many-electron basis described above, which ensures that eigenvalues of the composite Hamiltonian \( \tilde{H}_{AB} \) include eigenvalues of \( \tilde{H}_A \) and \( \tilde{H}_B \).

For EOM-CC(2,3), the matrix of the Hamiltonian (1.43) has the following form in the above basis:

\[
H = \begin{pmatrix}
\tilde{H}_{00} & \tilde{H}_{0A} & \tilde{H}_{0B} & \tilde{0} \\
\tilde{H}_{A0} & \tilde{H}_{AA} & \tilde{0} & \tilde{H}_{A,AB} \\
\tilde{H}_{B0} & \tilde{0} & \tilde{H}_{BB} & \tilde{H}_{B,AB} \\
\tilde{0} & \tilde{0} & \tilde{0} & \tilde{H}_{AB,AB}
\end{pmatrix}
\] (1.44)

where the shorthand notation \( \tilde{H}_{PQ} \equiv \langle P | \tilde{H} | Q \rangle \) has been used. The \( \tilde{H}_{AB}, \tilde{H}_{BA}, \tilde{H}_{0,AB}, \) and \( \tilde{H}_{AB,0} \) blocks, i.e., tilded zeros \( \tilde{0} \) from Eq. (1.44), involve only matrix elements of the Hamiltonian that couple subsystems A and B and vanish in the separated limit [63]:

\[
\tilde{H}_{AB} = \langle \Phi_A | 0_B | \tilde{H}_A + \tilde{H}_B | 0_A \cdot \Phi_B \rangle = \\
\langle 0_B | \Phi_B \rangle \cdot \langle \Phi_A | \tilde{H}_A | 0_A \rangle + \langle 0_A | \Phi_A \rangle \cdot \langle \Phi_B | \tilde{H}_B | 0_B \rangle = \\
0 \cdot \langle \Phi_A | \tilde{H}_A | 0_A \rangle + 0 \cdot \langle \Phi_B | \tilde{H}_B | 0_B \rangle = 0
\] (1.45)
The boldface zeros in the Eq. (1.44) vanish as a result of the coupled-cluster condition $\langle \mathbf{p} | \vec{H} | 0 \rangle = 0$, where $| \mathbf{p} \rangle$ includes single and double excitations only (i.e., the $H_{OS}$ and $H_{OD}$ blocks in Eq. 1.27 are zeros). For example, for the $\vec{H}_{AB,A}$ element:

$$
\vec{H}_{AB,A} = \langle \Phi'_A \cdot \Phi_B | \vec{H}_A + \vec{H}_B | \Phi_A \cdot 0_B \rangle = \\
\langle \Phi_B | 0_B \rangle \cdot \langle \Phi'_A | \vec{H}_A | \Phi_A \rangle + \langle \Phi'_A | \vec{H}_A | \Phi_A \rangle \cdot \langle \Phi_B | 0_B \rangle = \\
\langle \Phi'_A | \Phi_A \rangle \cdot \langle \Phi_B | \vec{H}_B | 0_B \rangle = 0 \quad (1.46)
$$

The last statement is true because in the $| \Phi'_A \cdot \Phi_B \rangle$ determinant, $\Phi_A$ includes at least one electron excitation, and the excitation level in the determinant $\Phi_B$ does not exceed doubly excited substitutions.

Thus, the only elements that prevent the Hamiltonian (1.44) to have the upper-triangle form, and affect the size-extensivity of the method, are $\vec{H}_{A0}$ and $\vec{H}_{B0}$. Moreover, the presence of $\vec{H}_{A0}$ does not break the size-extensivity of the model, because this matrix element couples only $|0\rangle$ and $|A\rangle$ determinants, which are already coupled in EOM-CC(2,3). $\vec{H}_{B0}$ is zero for the SF variant of EOM-CC(2,3) because, as discussed in Sec. 1.7.2, the $\vec{H}_{TO}$ matrix element of Hamiltonian is zero for EOM-SF-CC(2,3), see Eq. (1.27). Thus, the EOM-SF-CC(2,3) model is size-extensive. However, this is true only if one employs unrestricted Hartree-Fock triplet or quartet orbitals for the reference
determinant. In case, when restricted triplet or quartet orbitals are used, the EOM-SF-CC(2,3) model, as well as any ground state ROHF based CC model, includes terms violating size-extensivity.

Contrarily to EOM-SF-CC(2,3), in EOM-EE-CC(2,3) the $\tilde{H}_{B0}$ in Eq. (1.44) is not zero due to the non-vanishing $\langle \Phi_{ijk} | \tilde{H} | \Phi_0 \rangle$ matrix element of Hamiltonian, see Eq. (1.27). Thus, the EOM-EE-CC(2,3) model is not size-extensive. However, the $\tilde{H}_{TO}$ element is not zero only for the EOM amplitudes of the reference state and the excited states of the same spin- and spatial symmetry as the reference state; in all other excited states $R_0$, and, consequently, $\tilde{H}_{TO}$ is zero. For the excited states of the same spin and spatial symmetry as the reference state, the $\tilde{H}_{TO}$ matrix element is not zero, however, its contribution to excitation energy is tiny (excluding cases when the excited state is degenerate with the reference). As a result, the transition energies between almost any two excited states except of the reference state are size-extensive or nearly size-extensive.

Interestingly, both EE and SF variants of the active space EOM-CC(2,3) model are size-extensive. Whereas the size-extensivity of EOM-SF-CC(2,3) is not surprising, additional comment is required on size-extensivity of EOM-EE-CC(2,3). Indeed,
Table 1.2. EOM-EE-CC(2,3) and EOM-SF-CC(2,3) ground state reference energies (hartree) and excitation energies (eV) for Be atom with and without a Ne atom 100 Å away\(^a,\)\(^b\)

<table>
<thead>
<tr>
<th>Method</th>
<th>system</th>
<th>reference(^c)</th>
<th>(1S) ((1s^22s^2))</th>
<th>(3P) ((1s^22s2p))</th>
<th>(1P) ((1s^22s2p))</th>
<th>(3P) ((1s^22p_x2p_{x,y}))</th>
<th>(1D) ((1s^22p^2))</th>
<th>(1S) ((1s^22p^2))</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-0.0006</td>
<td>2.8608</td>
<td>6.5767</td>
<td></td>
<td></td>
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<td>10.9514</td>
</tr>
<tr>
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<td>10.9514</td>
</tr>
<tr>
<td>EOM-EE-CC(2,3)(^e) Be</td>
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<td>-0.0006</td>
<td>2.8609</td>
<td>6.5767</td>
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<td></td>
<td>8.6241</td>
<td>10.9515</td>
</tr>
<tr>
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<td>6.5767</td>
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<td>8.6241</td>
<td>10.9515</td>
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<tr>
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<td>3.7158</td>
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<td>-2.8615</td>
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<td>4.8074</td>
<td></td>
<td>5.7630</td>
<td>8.0900</td>
</tr>
</tbody>
</table>

\(^a\) 6-31G basis set.

\(^b\) The excitation energies are given with respect to the energy of the reference state, i.e., for example, the real excitation energies of Be by EOM-SF-CC(2,3) are: \(E[3P(1s^22s2p)] = 2.8616 \text{ eV}; \ E[1P(1s^22s2p)] = 6.5774 \text{ eV}; \ E[3P(1s^22p_x2p_{x,y})] = 7.6689 \text{ eV}; \ E[1D(1s^22p^2)] = 8.6245 \text{ eV}.\)

\(^c\) The CCSD energy of the \(1S\) state for EOM-EE-CC(2,3) and of the \(3P\) state for EOM-SF-CC(2,3).

\(^d\) At the EOM-SF-CC(2,3) level, these states regained the degeneracy.

\(^e\) The active space consists of the valence \(2s\) and \(2p_x, 2p_y, 2p_z\) orbitals of Be.
the problematic element of full space EOM-EE-CC(2,3), $H_{B0}$, becomes zero for EOM-SF-CC(2,3) since, with active space being localized on the fragment $A$, there are no triple excitations on the fragment $B$.

Table 1.2 presents a numerical example, which demonstrates the size-extensivity issues for EOM-SF-CC(2,3) and EOM-EE-CC(2,3) for a Be atom with a Ne atom located 100 Å away. For a size-extensive method, the excitation energies of Be would not be affected by the presence of Ne. This is indeed the case for EOM-SF-CC(2,3), EOM-SF-CC(2,3), and EOM-EE-CC(2,3). However, for EOM-EE-CC(2,3), the EOM energy of the target $^1S(1s^22s^2)$ state is affected by Ne. This is because the EOM energy of the reference state is dominantly affected by the $\bar{H}_{TO}$ matrix element of Hamiltonian, which breaks the size-extensivity of EOM-EE-CC(2,3). $\bar{H}_{TO}$ is also non-zero for the second $^1S$ state. However, as expected, the violation of size-extensivity for this state is much smaller than for the reference state, e.g., for Be-Ne example, it is less than 0.0001 eV. For all other excited states from Table 1.2, the excitation energies with respect to the reference state are size-extensive.

1.7.6 Conclusions

We implemented the EE and SF variants of the EOM-CC(2,3) method for computing accurate excitation energies for closed-shell systems, radicals, diradicals, and triradicals. In our implementation, both ROHF and UHF determinants
can be used as a reference. Scaling of the model is $N^8$. The active-space EOM-CC(2,3) method with semi-internal triples was also implemented; in this approach, only a small subset of triples (number of doubles times a prefactor) is included.

The full and active-space EOM-SF-CC(2,3) and active space EOM-EE-CC(2,3) are rigorously size-extensive, whereas the full EOM-EE-CC(2,3) model is only partially size-extensive.

### 1.8 Accurate electronic excitation and ionization energies of the electronic states

Accurate *ab initio* calculation of energy differences, such as electronic excitation and ionization energies, and heats of formation is a challenging task, which can be fulfilled by different strategies depending on the electronic structure of species involved.

In the most straightforward ”brute force” approach one attempts to calculate *total energies* of the relevant states as accurately as possible, and then computes energy differences. This is often performed using multi-reference (MR) state-specific techniques such as MCSCF, or, more appropriately, MR methods that include dynamical correlation, e.g., MRCI, MRPT, or MR-CC [65, 66]. Along with obvious advantages of this approach, such as flexibility and potentially
high accuracy, there are obvious disadvantages, e.g., the ambiguity of choosing the active space, the factorial scaling, and its reliance on having almost exact total energies\textsuperscript{5}. In some situations, an accurate single-reference (SR) approach such as CCSD(T) \cite{67} can be used.

Alternatively, a multi-state method, such as a single-reference EOM-CC, can be employed to directly calculate energy differences. As discussed in Section 1.5, EOM can describe many multi-configurational wave functions within a single-reference formalism. The built-in error cancellation and ability to systematically improve the EOM accuracy by including higher excitations makes this approach very promising for calculating energy differences.

Yet another approach employs energy additivity schemes in which effects of one and many electron basis sets are extrapolated from series of lower level calculations. Of this type are the G3 energy additivity scheme \cite{68, 69}, the W3 scheme for accurate thermochemistry \cite{56}, and basis set extrapolations \cite{3, 57, 58}. Furthermore, for calculating accurate thermochemistry, one can employ isodesmic or isogyric reactions, and high-low spin pathways \cite{59, 70}. In general, this approach is not a "black-box" method, as it requires thorough understanding of

\textsuperscript{5}Indeed, tiny errors in total energies may result in very large errors in energy differences. For example, one percent of the ethylene total energy is about 21 eV, which exceeds even the ionization potential of the molecule! 0.01% of the total energy of ethylene is 0.21 eV, which is the typical error bar of excitation energies calculated by EOM-CCSD, one of the approaches formulated for energy differences.
electronic structure of species involved, and it can be rather ambiguous. How-
ever, its potential accuracy is very high.

We investigate the performance of ”brute force” approaches and that of schemes based on a combination of ground state single-reference and EOM methods on the example of the electronic excitation and ionization energies of the dehydro-meta-xylylene (DMX) anion (see Chapter 6).

1.9 Computational details

Most of the calculations reported in this work are performed using the Q-
CHEM [71] ab initio package, to which our SF and EOM-CC(2,3) codes are interfaced. Additional results are obtained using the ACES II [72] and PSI 3 [73] electronic structure programs. Multi-reference calculations are performed using the GAMESS electronic structure package [74]. Some basis sets are obtained from the EMSL database [75]. All electrons are active in our calculations unless stated otherwise.
Reference List


www.qtp.ufl.edu/Aces2.


[75] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version , as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.
Chapter 2

Singlet-Triplet Gaps in Diradicals by the
Spin-Flip Approach: A Benchmark Study

2.1 Introduction

In this Chapter, the accuracy of the SF models for evaluating energy differences, e.g., singlet-triplet (ST) gaps in diradicals, is investigated.

Since the diradical wave functions (1.1)-(1.4) differ in their character (i.e., triplets are covalent while singlets may vary from purely covalent to purely ionic), it is not surprising that the chemical properties of diradicals in different electronic states are also considerably different [1]. The small energy separation between these states makes them easily accessible in experiments thereby allowing to fine-tune the chemical properties of diradicals.\(^1\) Determining the energy

\(^1\)This can have far reaching consequences: for example, unlike triplet species, singlet p-benzynes have been shown to selectively cleave DNA [2–5], thus suggesting their use as anti-tumor agents [6, 7].
Separation between triplet and low-lying singlet states of diradicals is the first step in understanding their chemical properties.

Most of the previously reported calculations of ST gaps have used MRCI or MRPT methods [8–29]. Due to the difficulties inherent in multi-reference techniques, the capability of highly correlated single reference models to describe some of the diradical states has raised considerable enthusiasm: Schreiner and coworkers have reported applications [30, 31] of Brueckner CCD [32] with perturbative account of the triples, B-CCD(T) method [33] (spin-symmetry broken solutions have been employed to describe $\Psi_3^s$, while $\Psi_1^s$ has been modeled within a spin-restricted formalism). Moreover, a number of attempts have been made to generalize DFT to treat multi-reference situations [34–36].

2.2 Computational details

Several considerations should be taken into account when calibrating electronic structure models [37]. A direct comparison to experiment is not always possible, in particular when short-lived transient species such as diradicals are concerned. For example, even for methylene, arguably the most studied diradical, the experimental data are very scarce for states other than the ground triplet and the lowest singlet states. Moreover, often it is not the vertical but the adiabatic ($T_e$) excitation energies which are reported. The dependence of $T_e$ on equilibrium
geometries of both states introduces additional uncertainties (vertical excitation energies are more useful for benchmark purposes, because they are calculated at the ground state equilibrium geometry). In addition, most of the experimentally measured energy separations are between the lowest vibrational states (\(T_{00}\)) and thus include changes in zero-point energies (ZPE). Lastly, it is important to separate the method from one electron basis set effects. Unlike molecular geometries and frequencies, the convergence of energy differences with respect to the latter is rather slow \([37]\). That is why it is advantageous to benchmark a new theory against FCI or other accurate models, e.g. MRCI or MRPT. In addition to addressing the basis set issue, this strategy enables the elimination of uncertainties due to equilibrium geometries and ZPEs.

With the above considerations in mind, we start our benchmark study by calculating singlet-triplet gaps in atoms, i.e., carbon, oxygen, and silicon. Since for atoms there is no uncertainty associated with equilibrium geometries and vibrational frequencies, the comparison with experiment is straightforward. Thus, these simple systems allow us to investigate the convergence of the SF models with respect to the one-particle basis set. We then proceed to a set of isovalent molecules with a varying diradical character, i.e., \(\text{CH}_2\), \(\text{NH}_2^+\), \(\text{SiH}_2\), and \(\text{PH}_2^+\). These diradicals are popular as benchmark systems \([11–17, 19, 38]\), because of their small size (but rich electronic structure), and the availability of experimental data \([39–44]\). For these systems, we compare the performance of the SF
models against a variety of single and multi-reference methods, and investigate
the convergence of different methods with respect to the one-particle basis set.
Next we consider a set of diatomic molecules with a diradical singlet state (NH,
NF, OH\textsuperscript{+}, and O\textsubscript{2}) for which accurate experimental data are available [45].
After thorough investigation of the performance of the SF method for these
semi-model systems, we proceed to two important prototype diradicals: the
benzyne isomers and trimethylenemethane. These systems, which are impor-
tant in organic and bio-organic chemistry, have attracted the attention of both
experimentalists and theoreticians [9, 20–26, 30, 46–50].

In order to minimize uncertainties due to equilibrium structures, we follow
a commonly used strategy: adiabatic energies are estimated by using the best
available structures, the same geometries being used for all the benchmarked
methods. The choice of structures is specific for each system, and is discussed
in the corresponding sections. For TMM, we also report vertical excitation
energies, which are more suitable for benchmarking because they do not depend
on excited states geometries.

To investigate one-particle basis set effects, we complement the calculations
in relatively large basis sets by estimating the complete basis set (CBS) limiting
values. Several procedures are employed: (i) two-point extrapolation (CBS-
2p), which is based on cc-pVTZ and cc-pVQZ energies; (ii) two three-point
extrapolations based on cc-pVDZ, cc-pVTZ, and cc-pVQZ energies: CBS-3pa
and CBS-3pb; (iii) an energy separability scheme where basis set effects for a highly correlated model are evaluated by performing calculations with a less computationally expensive method.

The two-point procedure (i) extrapolates the asymptotic values of the total energies in the CBS limit \( E_{CBS} \) as follows [37]:

\[
E_{CBS} = E_X + A \cdot X^{-3},
\]

where \( X \) is the basis set cardinal number (i.e., \( X=3 \) for the cc-pVTZ basis, \( X=4 \) for the cc-pVQZ basis, etc.), \( E_X \) is the corresponding total energy\(^2\), and \( A \) is a fitting parameter defined such that Eq. (2.1) is satisfied for two bases (e.g., for \( X=3 \) and for \( X=4 \)).

The three-point extrapolation, CBS-3pa, employs the following formula for the asymptotic behavior of the total energy [51, 52]:

\[
E_{CBS} = E_X + B \cdot \exp(-C \cdot X)
\]

\(^2\)This formula has been proposed for the extrapolation of correlation energy. However, it is unclear how to define correlation energy in the EOM methods. One possibility is to define correlation energy as a difference between the total energy of the final state and the Hartree-Fock energy of the (triplet) reference state. We have found that in this case the resulting \( \Delta E_{ST} \) values differ from the ones obtained by extrapolating the total energies by no more than 0.001 eV.
CBS-3ph three-point extrapolation suggested by Peterson and coworkers [53, 54] is defined as:

\[
E_{CBS} = E_X + B \cdot \exp[-(X-1)] + C \cdot \exp[-(X-1)^2]
\] (2.3)

In Eqns. (2.2) and (2.3), parameters \(B\) and \(C\) are defined such that the corresponding equations are satisfied for the three basis sets (e.g., \(X=2\), \(X=3\), and \(X=4\)).

In addition, we have also used an extrapolation technique based on an energy separability scheme:

\[
E_{SF-OD}^{\text{large}} = E_{SF-OD}^{\text{small}} + (E_{SF-CIS(D)}^{\text{large}} - E_{SF-CIS(D)}^{\text{small}}),
\] (2.4)

where \(E_{\text{large}}\) and \(E_{\text{small}}\) refer to the total energies calculated in large (e.g., cc-pVTZ) and small (e.g., 6-31G*) basis sets. This procedure assumes that changes in the total energy due to the basis set increase are similar for the less and more correlated models [e.g., MP2 and CCSD, or SF-CIS(D) and SF-OD].

For all extrapolation procedures, the CBS values of singlet-triplet splittings are obtained by taking the differences between the extrapolated total energies of triplet and singlet states.
2.3 Results and discussion

When benchmarking *ab initio* methods, two aspects should be addressed: (i) the relative performance of methods with similar computational scaling and cost; and (ii) the absolute performance, e.g., the accuracy of a given method as compared against more computationally expensive but more accurate models. With this in mind, we compare: the performance of the SF methods with (i) the corresponding non-SF approaches whose computational cost and scaling are identical [e.g., SF-CIS vs. CIS, SF-CIS(D) vs. CIS(D), SF-OD vs. EOM-OD or EOM-CCSD]; and (ii) potentially more accurate methods which have higher computational cost [e.g., SF-OD vs. CCSD(T)/B-CCD(T), or vs. MRPT/MRCI]. Our results demonstrate that the performance of the SF models is systematically better than that of non-SF methods. On an absolute scale, it is comparable to that of the more computationally expensive multi-reference models.

The errors in ST energy gaps calculated by SF and single-reference non-SF methods are systematic. For example, in systems with a triplet ground state, the energy splittings between the triplet and the closed-shell singlet are overestimated; whereas for systems whose ground state is a closed-shell singlet the corresponding energy gaps are underestimated. The errors in the SF are systematically smaller in both cases, with the differences between the SF and
non-SF models getting smaller as more correlated wave functions are employed for the reference. These trends can be easily rationalized by considering the two electrons in two orbitals model described in Sec. 1.3.

Consider first the most straightforward approach, in which the energy separation between the lowest singlet and the lowest triplet states is computed as a difference between the total energies of the corresponding states calculated by a ground state method. For a molecule with a significant diradical character, the closed-shell singlet state $\Psi_1^s$ is poorly described by a single-reference wave function which fails to treat determinants (a) and (b) from Fig. 1.2 on an equal footing. Therefore, the resulting total energy of this state is too high. In contrast, the high-spin triplet states ($\Psi_2^t$ or $\Psi_3^t$) are better described by a single-reference method. That is why the triplet’s total energy is too low relative to the singlet’s, and the corresponding energy gap is too small for molecules with a singlet ground state, and too large for molecules with a triplet ground state. Sometimes even the ordering of states can be reversed. For example, Hartree-Fock calculations predict that the ground state of ozone is a triplet. The imbalance decreases as more correlated wave functions are employed (e.g., CCSD yields the correct multiplicity of the ground state; however, the energy gap is still grossly underestimated).
A more balanced description can be achieved by employing the corresponding excited state theory [see Eq. (1.21)], e.g., CIS in case of a Hartree-Fock reference wave function. However, since traditional (i.e., non SF) single-reference methods employ a (poorly described) closed-shell singlet wave function $\Psi_s^1$ as the reference in excited state calculations, the ST gaps are still underestimated (for molecules with a singlet ground state). An additional advantage of using excited state theory to calculate ST gaps (as opposed to a direct energy differences approach) is that it can also describe other singlet states, e.g., the open-shell singlet $\Psi_s^3$ and the second closed-shell singlet $\Psi_s^2$. Note that a single-reference excited state theory will describe $\Psi_s^3$ and $\Psi_s^t$ in a more or less balanced fashion, since both states are formally single excitations from $\Psi_s^1$. Thus, the energy difference between $\Psi_s^1$ and $\Psi_s^3$ will also be underestimated. The second closed-shell singlet, $\Psi_s^2$, is formally a doubly excited state from the $\Psi_s^1$ reference. Therefore, it can only be described by methods that explicitly include double excitations (e.g., EOM-OD or EOM-CCSD). Moreover, the energy of this state will be too high relative to the singly excited states. To summarize, for a diradical with a triplet ground state (e.g., methylene), single-reference methods will: (i) overestimate the ST energy separation between the triplet and the first closed-shell singlet; (ii) dramatically overestimate the energy gap between the triplet and the second closed-shell singlet; and (iii) underestimate the energy separation between the first closed-shell singlet and open-shell singlet, the relative ST gap
between \( \Psi_1^t \) and \( \Psi_3^t \) being reproduced relatively well. When heavily correlated methods (e.g., EOM-OD) are employed, the description of all states is improved, however the inherent imbalance in the non-SF single-reference wave functions would result in rather large errors in the relative energies.

The SF models use a triplet high-spin state, e.g., \( \Psi_2^t \), as a reference. Since this reference is accurately described by single-reference wave functions, and since all \( M_s = 0 \) electronic configurations from \( \Psi_{1-3}^s \) and \( \Psi_1^t \) are formally single electron excitations from \( \Psi_2^t \), all these states are described with similar accuracy. Thus, even though the ST gaps will still be overestimated (in a methylene-type diradical), the errors will be systematically smaller than those obtained in the corresponding non-SF methods.

### 2.3.1 \( ^3P-^1D \) energy gaps in carbon, oxygen, and silicon atoms

In atoms, there is no ambiguity due to geometries and ZPEs, and therefore the comparison between the calculated and experimental ST gaps is straightforward. In the following three examples, we compare the accuracy of the traditional excited state methods with that of the SF models. In order to elucidate basis
set effects on the ST energy differences, we employ nine basis sets\(^3\) and perform CBS extrapolations [37, 51–54].

For all three atoms, the ground state is a triplet \(^3\)P state, and the lowest singlet is a \(^1\)D state. Table 2.1 summarizes the ST energy gaps calculated by the traditional, i.e., non-SF, and the SF methods. The convergence of \(\Delta E_{ST}\) with respect to the basis set is illustrated in Figures 2.1-2.3. Clearly, the SF results are consistently more accurate than those of the corresponding non-SF models. For example, the ST gaps calculated by the SF-CIS model are approximately 0.2 eV closer to the experimental values than those obtained by the CIS method. The difference between the SF-OD and the EOM-OD results is about 0.06-0.09 eV, with the SF results being more accurate. The CIS(D) and SF-CIS(D) methods give similar values of ST gaps (in most basis sets, the differences are about 0.03 eV, 0.04 eV, less than 0.01 eV for oxygen, silicon, and carbon, respectively).

\(^3\)The DZP basis for carbon and oxygen is defined by Dunning's double-\(\zeta\) contraction [55] of Huzinaga's primitive Gaussian functions [56] and a single set of polarization functions \([\alpha_d(C)=0.75, \alpha_d(O)=0.85]\), the contraction scheme being (9s5p1d/4s2p1d). The triple-\(\zeta\) (TZ) Huzinaga-Dunning bases [56, 57] [contraction schemes are (10s6p/5s3p) for carbon and oxygen, and (12s9p/6s5p) for silicon] are augmented by: (i) two sets of polarization functions (TZ2P) \([\alpha_d(C)=1.50, 0.375; \alpha_d(O)=1.70, 0.4250; \alpha_d(Si)=1.00, 0.25]\); (ii) three sets of polarization functions (TZ3P) \([\alpha_d(C)=3.00, 0.75, 0.1875; \alpha_d(O)=3.40, 0.85, 0.2125]\). Then additional sets of f-functions are added: (i) one set of f-functions for TZ2P (TZ2PF) \([\alpha_f(C)=0.80; \alpha_f(O)=1.40]\); (ii) two sets of f-functions for TZ3P (TZ3PF) \([\alpha_f(C)=1.60, 0.40; \alpha_f(O)=2.80, 0.70]\). In addition, TZ2P and TZ2PF bases augmented by one set of diffuse functions (TZ2P+diff and TZ2PF+diff, respectively) are considered \([\alpha_s(C)=0.04812, \alpha_p(C)=0.03389; \alpha_s(O)=0.08993, \alpha_p(O)=0.0584; \alpha_s(Si)=0.02567, \alpha_p(Si)=0.02354]\). Cartesian d- and f-functions are used for carbon and oxygen, and pure angular momentum — for silicon. In addition, series of correlation consistent basis sets (cc-pVDZ, cc-pVTZ, and cc-pVQZ [58, 59]) are used (these employ pure angular momentum d-, f-, and g- functions).

61
Table 2.1. The energy separation between $^1$D and $^3$P states (eV) in carbon, oxygen, and silicon atoms$^a$

<table>
<thead>
<tr>
<th>Basis</th>
<th>CIS</th>
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<th>EOM-OD</th>
<th>SF-CIS</th>
<th>SF-CIS(D)</th>
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<tr>
<td>DZP$^b$</td>
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<td>1.472</td>
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<td>DZP$^b$</td>
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<td>2.087</td>
<td>2.126</td>
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<td>2.119</td>
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<td>CBS-3pb</td>
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<td>0.834</td>
<td>0.845</td>
<td>0.787</td>
<td>0.747</td>
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$^a$ Experimental values are: 1.26 eV, 1.97 eV, and 0.75 eV for C, O, and Si, respectively [60].

$^b$ FCI/DZP values are 1.471 eV for carbon and 2.166 eV for oxygen.
Figure 2.1. Singlet-triplet energy separations in carbon. The SF-OD/cc-pVQZ values are very close to the experimental ones. The SF models consistently yield more accurate results than the non-SF ones.

Figures 2.1-2.3 demonstrates that the accurate description of the ground triplet state and the first excited singlet state (and the energy difference between them) requires basis sets with extensive polarization (e.g., f-functions are very important), while diffuse functions do not affect the quality of the description. In the case of the less correlated methods (CIS and SF-CIS), the basis set convergence is fast. For the more correlated EOM-OD and SF-OD methods, large basis sets are crucial for obtaining converged results. In the largest basis set used, cc-pVQZ, the SF-OD results are within 0.01 eV of the experimental
Figure 2.2. Singlet-triplet energy separations in oxygen. The SF-OD/cc-pVQZ values are very close to the experimental ones. The SF models consistently yield more accurate results than the non-SF ones values. The SF-CIS(D) limiting values deviate from the experiment by no more than 0.04 eV (1 kcal/mol). For carbon and oxygen, we also estimate the CBS values of the ST energy differences by two-point and three-point extrapolations (see Sec. 2.2). For oxygen, all the approximations give similar results: the CBS values of $E_{ST}$ for the SF-OD method are about 0.02 eV lower than the experimental value. However, the discrepancy between the different models is much larger in the case of carbon: while the CBS-2p and CBS-3pb values are reasonable, the CBS-3pa extrapolation fails. This is because our CBS-3pa
Figure 2.3. Singlet-triplet energy separations in silicon. The SF-OD/cc-pVQZ values are very close to the experimental ones. The SF models consistently yield more accurate results than the non-SF ones.

procedure uses cc-pVDZ total energies which are apparently too far from the CBS limit, in order for the extrapolation formula (2.2) to be justified. Note that whereas the values of the ST gaps calculated in cc-pVDZ basis are reasonable, CBS-3pa which uses cc-pVDZ total energies, yields inconsistent results. The CBS-3pb extrapolation appears to be more robust: even though it also uses the cc-pVDZ total energies, it yields consistent results which agree well with the CBS-2p ones. As in case for oxygen, the CBS-3pb extrapolated SF-OD value of $E_{ST}$ in carbon is 0.02 eV lower than the experimental value.
2.3.2 Methylene and other isovalent molecules

The electronic structure of the isovalent CH$_2$, NH$_2^+$, SiH$_2$, and PH$_2^+$ molecules is qualitatively described in Fig. 1.2. The orbitals $\phi_1$ and $\phi_2$ (see Fig. 1.2) are derived from a p-orbital and a $s^{1-x}p^x$-hybridized orbital of the heavy atom, respectively. Thus, in Salem classification, these species are heterosymmetric diradicals (except for the linear geometry) [61]. The symmetries of the (nearly) degenerate $\phi_1$ and $\phi_2$ are: (i) 3$a_1$ and 1$b_1$ in CH$_2$ and NH$_2^+$; and (ii) 5$a_1$ and 2$b_1$ in SiH$_2$ and PH$_2^+$. The energy gap between $\phi_1$ and $\phi_2$ gradually changes in these series. This tunable diradical character along with the small size of these species makes them very attractive model systems for both experimental [39–44] and theoretical [11–17, 19, 38] studies.

The ground state of methylene (CH$_2$) and the nitrenium ion (NH$_2^+$) is the triplet state $\tilde{X}^3B_1$ whose electronic configuration is described by Eqns. (1.4)-(1.6):

$$\tilde{X}^3B_1 \approx (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1)$$ (2.5)

The first excited state is a closed shell singlet $\tilde{a}^1A_1$ state, i.e., $\Psi^t_1$ of Eq. (1.1):

$$\tilde{a}^1A_1 \approx \sqrt{1 - \lambda^2(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 - \lambda(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2}$$ (2.6)
The second excited singlet state is an open-shell singlet $\tilde{b}^1B_1$, i.e. $\Psi_3^*$ of Eq. (1.4), whose the electronic configuration is similar to that of the triplet state of Eq. (2.5). The third excited state is a closed-shell singlet $\tilde{c}^1A_1$ of $\Psi_2^*$ type [Eq. (1.2)];

$$\tilde{c}^1A_1 \approx \sqrt{1 - \lambda^2(4a_1)^2(2b_2)^2(5a_1)^2} - \lambda[core](4a_1)^2(2b_2)^2(2b_1)^2, \quad (2.7)$$

This state has the same symmetry as the lowest singlet and is formally a double excitation from the $\tilde{a}^1A_1$ state.

At linear geometries, the $\phi_1$ and $\phi_2$ orbitals become exactly degenerate, and the coefficient $\lambda$ reaches the value of $1/\sqrt{2}$. In this case, the proper labels are $\tilde{c}^1\Sigma_g^+$ for the second closed-shell singlet [Eq. (2.7)], and $^1\Delta_g$ for the first closed-shell and the open-shell singlet states, which then become exactly degenerate. (For example, the equilibrium geometry of the second closed-shell singlet state of NH$_2^+$ is linear, and therefore the $\tilde{c}^1\Sigma_g^+$ label is used).

As explained by the Walsh correlation diagrams [62], SiH$_2$ and PH$_2^+$ favor a closed-shell $\Psi_1^*$ singlet as their ground state:

$$\tilde{X}^1A_1 \approx \sqrt{1 - \lambda^2[core](4a_1)^2(2b_2)^2(5a_1)^2} - \lambda[core](4a_1)^2(2b_2)^2(2b_1)^2, \quad (2.8)$$
where:

\[
[\text{core}] = (1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2 \tag{2.9}
\]

The first excited state in SiH$_2$ and PH$_2^+$ is the triplet $\tilde{a}^3B_1$ state, whose electronic configuration is:

\[
\tilde{a}^3B_1 \approx [\text{core}] (4a_1)^2 (2b_2)^2 (5a_1)(2b_1) \tag{2.10}
\]

The next state is an open-shell singlet $\tilde{A}^1B_1$, whose electronic configuration is similar to that of the $\tilde{a}^3B_1$ triplet from Eq. (2.10). Finally, the $\tilde{B}^1A_1$ state has the following electronic configuration:

\[
\tilde{B}^1A_1 \approx \sqrt{1-\lambda^2}[\text{core}] (4a_1)^2 (2b_2)^2 (2b_1)^2 + \lambda[\text{core}] (4a_1)^2 (2b_2)^2 (5a_1)^2 \tag{2.11}
\]

The systematic changes in the diradical character of these species, their ground state multiplicities, and equilibrium geometries can be rationalized by using the Walsh diagrams and Hund rules. By using hybridization theory, Walsh correlates the energy of the four valence orbitals with the HXH angle. The two bonding ($\sigma_{XH}$) and two non-bonding ($\phi_1$ and $\phi_2$) orbitals derive from the s and three p orbitals of the heavy atom. At linear geometry, the bonding orbitals are $sp$ hybrids, whereas the non-bonding ones are the exactly degenerate non-hybridized p-orbitals. Since the energy of the valence s-orbital is lower than that of the p-orbitals, the increased s-character lowers the energy of a
hybridized orbital. At 90°, the two $\sigma_{XH}$ orbitals are unhybridized p-orbitals, whereas the non-bonding orbitals $\phi_1$ and $\phi_2$ become the unhybridized s and p orbitals, respectively. In the diradicals’ states discussed in this section, the $\sigma_{XH}$ orbitals are always doubly occupied and therefore can be excluded from further discussion. The $\Psi_1^s$ state is dominated by a configuration in which the two remaining electrons are placed on the $\phi_1$ orbital, which is stabilized at small HXH angles. The open-shell $\Psi_3^s$ and $\Psi_{1-3}^t$ states favor larger angles, since both $\phi_1$ and $\phi_2$ host one electron. Finally, the second closed shell singlet in which $\phi_2$ is doubly occupied favors the largest HXH angles (up to 180°, as in NH$_2^+$).

In order to explain the changes in the diradical character, and the relative ordering of the first closed shell singlet and lowest triplet states, the molecular geometries and charge distributions must be considered. As dictated by electronegativity considerations and covalent atomic radii, the XH bondlength increases in the following order: NH$_2^+$ → CH$_2$ → PH$_2^+$ → SiH$_2$. The de-stabilization of small HXH angles decreases in the same order, because the repulsion between hydrogen atoms is larger for short bond lengths. At large angles, when $\phi_1$ and $\phi_2$ are almost degenerate, Hund rule favors a triplet coupling, and this is why the ground state of NH$_2^+$ and CH$_2$ is a triplet. At small angles, when the energy gap between $\phi_1$ and $\phi_2$ is large, one-electron energetic considerations prevail, and a closed shell singlet becomes the ground state (PH$_2^+$ and SiH$_2$). To summarize, the degeneracy between the non-bonding orbitals
decreases in the above sequence, and therefore the diradical character increases in the reverse order: \( \text{SiH}_2 \rightarrow \text{PH}_2^+ \rightarrow \text{CH}_2 \rightarrow \text{NH}_2^+ \).

Calculations are performed using eight basis sets\(^4\). The geometries used to calculate adiabatic energy separations are summarized in the footnote\(^5\).

\(^{4}\)The TZ bases for carbon and hydrogen are from Refs. [11, 38], for nitrogen — from Ref. [12]. The TZ bases for silicon and phosphorus are from Refs. [13] and [14], respectively. All carbon bases are the same as in the previous section. However, some labels are slightly different: i.e., TZ2P(f,d) and TZ3P(2f,2d) are equivalent to TZ2PF and TZ3P2F from Sec. 2.3.1. The TZ-quality basis sets for hydrogen and nitrogen are derived from the Huzinaga-Dunning basis [56, 57], the contraction scheme being \((10s6p/5s3p)\) for \(N\), and \((5s/3s)\) for \(H\). The TZ-quality bases for silicon and phosphorus are defined by the McLean and Chandler's TZ contraction [63] of the Huzinaga's primitive Gaussian functions [64]: the contraction scheme is \((12s9p/6s5p)\) for \(Si\) and \(P\). We augment these basis sets by: (i) two sets of polarization functions (TZ2P) \(\alpha_p(H)=1.50, 0.375; \alpha_d(N)=1.60, 0.40; \alpha_d(Si)=1.00, 0.25\) and \(\alpha_d(P)=1.20, 0.30\); (ii) three sets of polarization function, TZ3P(2f,2d) \(\alpha_p(H)=3.00, 0.75, 0.1875\). The orbital exponents of higher angular momentum functions are: (i) \(\alpha_d(H)=1.00, \alpha_f(N)=1.00, \alpha_f(Si)=0.32\) and \(\alpha_f(P)=0.45\) for a single set of higher angular momentum functions [TZ2P(f,d) bases]; and (ii) \(\alpha_d(H)=2.00, 0.50\) for a double set of higher angular momentum functions [TZ3P(2f,2d)]. In addition, the TZ2P and TZ2P(f,d) bases are augmented by one set of diffuse functions [TZ2P+diff and TZ2P(f,d)+diff respectively], with the exponent \(\alpha_s(H)=0.03016\) (diffuse functions on heavy atoms are the same as in the previous section). Lastly, correlation-consistent basis sets have been employed, i.e., cc-pVDZ, cc-pVTZ and cc-pVQZ [58, 59]. Pure angular momentum d-, f-, and g-functions are used in all the calculations reported in this section.

\(^{5}\)To calculate adiabatic energy separations in methylene, FCI/TZ2P optimized geometries [38] are used (\(r_c, \Theta_c, \text{degree}\)): 1.0775/133.29, 1.1089/101.89, 1.0748/141.56, and 1.0678/170.08 for the \(\tilde{X}^1A_1, \tilde{a}^1A_1, \tilde{b}^1B_1, \) and \(\tilde{c}^1A_1\) states, respectively. The equilibrium geometries for \(\text{NH}_2^+\) are CISD/TZ2P(f,d) optimized geometries [12]: 1.0295/150.88, 1.0459/107.96, 1.0293/161.47, and 1.0315/180.00 for the \(\tilde{X}^1B_1, \tilde{a}^1A_1, \tilde{b}^1B_1, \) and \(\tilde{c}^1A_1\) states, respectively. For \(\text{SiH}_2\) and \(\text{PH}_2^+\)\(^d\), we employ the CISD/TZ2P(f,d) optimized geometries from the Refs. [13] and [14], respectively. The equilibrium structures of the \(\tilde{X}^1A_1, \tilde{a}^3B_1, \tilde{A}^1B_1, \) and \(\tilde{B}^1A_1\) states of \(\text{SiH}_2\) are: 1.5145/92.68, 1.4770/118.26, 1.4830/122.65, and 1.4573/162.34, respectively. For \(\text{PH}_2^+\), geometries of these states are: 1.4178/93.06, 1.4056/121.77, 1.4194/124.84, and 1.4118/159.62.
Since experimental geometries [39, 65, 66] are not available for all four diradical states of CH$_2$, we calculate adiabatic excitation energies at the FCI/TZ2P optimized geometries [38] (see footnote 5). The SF models accurately describe the equilibrium properties of all these states, with the SF-OD geometries and frequencies being very close to those of FCI [67].

Table 2.2 compares the adiabatic ST energy gaps calculated by the SF models and by CASSCF SOCI [11]. As explained above, the SF models systematically overestimate $\Delta E_{ST}$, the errors being smallest for the $\tilde{X}^3B_1-\tilde{b}^1B_1$ splittings. The absolute errors of the SF models against CASSCF SOCI are rather small: SF-CIS overestimates the adiabatic excitation energy for the $\tilde{b}^1B_1$ state by 0.37 eV, and for both $^1A_1$ states — by 1.00 eV. As more correlated SF models are used, these errors become smaller: 0.10-0.25 eV for SF-CIS(D), and 0.01-0.04 eV for SF-OD. Thus, for methylene the SF-OD results are within 1 kcal/mol of those of CASSCF SOCI.

Fig. 2.4 presents the calculated $\Delta E_{\tilde{X}^3B_1-\tilde{a}^1A_1}$ as a function of the one-particle basis set. The convergence of the SF-CIS model is rather fast. However, for correlated wave functions very large bases are needed for the converged results. As Fig. 2.4 and Table 2.2 demonstrate, heavy polarization (e.g., three sets of d-functions and two sets of f-functions) is necessary for accurate results. On
Table 2.2. Total energies (hartree) for the ground $\tilde{X}^3B_1$ state of CH$_2$, and adiabatic excitation energies (eV) for the three singlet states$^a$

<table>
<thead>
<tr>
<th>Method</th>
<th>$\tilde{X}^3B_1$</th>
<th>$\tilde{a}^1A_1$</th>
<th>$\tilde{b}^1B_1$</th>
<th>$\tilde{c}^1A_1$</th>
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</thead>
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<tr>
<td>SF-CIS/TZ2P</td>
<td>-38.93254</td>
<td>0.883</td>
<td>1.875</td>
<td>3.599</td>
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<td>SF-CIS(D)/TZ2P</td>
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<td>0.613</td>
<td>1.646</td>
<td>2.953</td>
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<td>SF-OD/TZ2P</td>
<td>-39.08045</td>
<td>0.514</td>
<td>1.564</td>
<td>2.715</td>
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<tr>
<td>FCI/TZ2P [38]</td>
<td>39.066738</td>
<td>0.483</td>
<td>1.542</td>
<td>2.674</td>
</tr>
<tr>
<td>SF-CIS/TZ2P(f,d)</td>
<td>-38.93301</td>
<td>0.875</td>
<td>1.829</td>
<td>3.590</td>
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<td>2.647</td>
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<td>CASSCF SOCI/TZ3P(2f,2d) [11]</td>
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<td>0.861</td>
<td>1.821</td>
<td>3.593</td>
</tr>
<tr>
<td>SF-CIS(D)/CBS-3pa</td>
<td>-39.11162</td>
<td>0.464</td>
<td>1.535</td>
<td>2.829</td>
</tr>
<tr>
<td>SF-OD/CBS-3pa</td>
<td>-39.13335</td>
<td>0.395</td>
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<td>2.647</td>
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<tr>
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<td>0.861</td>
<td>1.816</td>
<td>3.588</td>
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<tr>
<td>SF-CIS(D)/CBS-3pb</td>
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<td>1.498</td>
<td>2.780</td>
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<td>2.579</td>
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$^a$ FCI/TZ2P optimized geometries [38], see footnote 5.

The other hand, diffuse functions, an increase in n-ζ beyond TZ, and polarization beyond f-functions are less important. For example, the SF-OD results in
Figure 2.4. Basis set dependence of the energy gap between the $a^1A_1$ and $X^3B_1$ states in methylene. $E_{ST}$ values calculated by the single-reference (SF and non-SF) and multi-reference (CASSCF SOCI) methods are compared against the experimental value. For the DZP and TZ2P bases, the FCI results are also shown. The convergence of the $E_{ST}$ values with respect to the basis set is rather slow for the highly correlated models, e.g., EOM-OD, SF-OD, and the CASSCF SOCI. SF results are consistently closer to the experimental value (and that of the CASSCF SOCI) than those of the corresponding single-reference non-SF methods.

The TZ3P(2f,2d) basis are within 0.02 eV of the SF-OD/cc-pVQZ values [cc-pVQZ basis has the same number of $f$- and $d$- functions as TZ3P(2f,2d), but it also contains one set of $g$-functions on carbon and one set of $f$-functions of hydrogen]. The less extensive cc-pVTZ basis, which contains two sets of $d$-functions and one set of $f$-functions on carbon, yields results within 0.06 eV of
our largest basis set, cc-pVQZ. We have also estimated the CBS limiting values of the ST gaps (see Sec. 2.2 for details). As in the case of carbon (Sec. 2.3.1), the three-point extrapolation CBS-3pa breaks down for the $\tilde{X}^3B_1 - \tilde{b}^1B_1$ and the $\tilde{X}^3B_1 - \tilde{c}^1A_1$ transitions. The $\Delta E_{ST}$ estimated by the two-point procedure CBS-2p are suspiciously low. The three-point extrapolation CBS-3pb gives reasonable values for $\Delta E_{ST}$ for all transitions. Thus, the methylene results confirm the conclusions based on the results from Sec. 2.2: (i) the CBS extrapolation procedures should be used carefully in bases smaller than quintuple-ζ quality; (ii) CBS-3pb [Eq. (2.3)] is more robust than CBS-3pa [Eq. (2.2)] when using the cc-pVDZ/cc-pVTZ/cc-pvQZ results.

The assessment of the accuracy of the SF models against the experiment is less straightforward. The SF-OD/cc-pVQZ results for the first and second singlet states deviate from the experimental values by 0.061 and 0.022 eV, respectively. The SF-CIS(D)/cc-pVQZ numbers are off by 0.15 and 0.10 eV. However, since the experimentally measured value is the energy separation between the zero-point vibrational levels, it includes changes in ZPEs. These changes, estimated by using CISD frequencies [11], are about 0.017 eV and 0.005 eV for the $\tilde{X}^3B_1 - \tilde{a}^1A_1$ and the $\tilde{X}^3B_1 - \tilde{b}^1B_1$ transitions, respectively. Therefore, the ZPE-corrected SF-OD/cc-pVQZ values are within 0.044 and 0.017 eV of the experiment (i.e., 1.0 kcal/mol and 0.4 kcal/mol, respectively). The SF-OD values, obtained by using the most stable CBS-3pb extrapolation, deviate by
Table 2.3. Total energies (hartree) for the ground $\tilde{X}^3B_1$ state of CH$_2$, and adiabatic excitation energies (eV) for the three singlet states$^a$

<table>
<thead>
<tr>
<th></th>
<th>$\tilde{X}^3B_1$</th>
<th>$\tilde{a}^1A_1$</th>
<th>$\tilde{b}^1B_1$</th>
<th>$\tilde{c}^1A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF</td>
<td>-38.937956</td>
<td>1.236</td>
<td></td>
<td>2.772</td>
</tr>
<tr>
<td>CCSD</td>
<td>-39.080919</td>
<td>0.545</td>
<td></td>
<td>2.054</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>-39.083856</td>
<td>0.505</td>
<td></td>
<td>1.907</td>
</tr>
<tr>
<td>B-CCD</td>
<td>-39.080815</td>
<td>0.545</td>
<td>0.467</td>
<td>2.054</td>
</tr>
<tr>
<td>B-CCD(T)</td>
<td>-39.083859</td>
<td>0.505</td>
<td>0.315</td>
<td>1.907</td>
</tr>
<tr>
<td>CIS</td>
<td>-38.92886</td>
<td>0.989</td>
<td>1.748</td>
<td></td>
</tr>
<tr>
<td>CIS(D)</td>
<td>-39.05823</td>
<td>0.655</td>
<td>1.506</td>
<td></td>
</tr>
<tr>
<td>EOM-CCSD</td>
<td>-39.08066</td>
<td>0.538</td>
<td>1.566</td>
<td>3.843</td>
</tr>
<tr>
<td>EOM-OD</td>
<td>-39.08077</td>
<td>0.543</td>
<td>1.569</td>
<td>3.847</td>
</tr>
<tr>
<td>SF-CIS/TZ2P</td>
<td>-38.93254</td>
<td>0.883</td>
<td>1.875</td>
<td>3.599</td>
</tr>
<tr>
<td>SF-CIS(D)/TZ2P</td>
<td>-39.05586</td>
<td>0.613</td>
<td>1.646</td>
<td>2.953</td>
</tr>
<tr>
<td>SF-OD/TZ2P</td>
<td>-39.08045</td>
<td>0.514</td>
<td>1.564</td>
<td>2.715</td>
</tr>
<tr>
<td>FCI [38]</td>
<td>-39.066738</td>
<td>0.483</td>
<td>1.542</td>
<td>2.674</td>
</tr>
</tbody>
</table>

$^a$ FCI/TZ2P optimized geometries [38], see footnote 5.

0.040 and 0.005 eV from the experimental values, and when including ZPE-corrections, they are within 0.023 and 0.010 eV from the experiment.

Table 2.3 compares the SF results against traditional (non-SF) methods. The TZ2P basis is used to enable comparison against the FCI results [38]. While in the FCI calculations one core and one virtual orbitals have been frozen, all electrons/orbitals are active in present calculations.

The first three rows in the Table 2.3 present the ST gaps computed by the least balanced approach, e.g., by taking the difference between the total energies for the triplet and singlet states calculated by the ground state models. Here we consider the SCF, CCSD, and CCSD(T) methods. Note that such a
procedure is not capable of describing the open-shell $\tilde{b}^1B_1$ singlet. In general, it can be applied only to calculate energy gap between the lowest triplet and the lowest closed-shell-type singlet state. However, in this case it is also possible to evaluate the energy of the second $A_1$ singlet state (even though this state is of the same symmetry as the lowest singlet, the symmetries of orbitals in the reference determinant are different, e.g., $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$ is the Hartree-Fock determinant for the $\tilde{a}^1A_1$ state, whereas $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$ — for $\tilde{c}^1A_1$). Due to the inherently unbalanced treatment of the singlet and triplet states by single-reference wave functions, only the correlated CCSD and CCSD(T) methods yield accurate results for $\Delta E_{ST}$ for $\tilde{a}^1A_1$ (errors against FCI are 0.063 and 0.022 eV, respectively). However, both methods are about 0.7 eV off for the $\tilde{c}^1A_1$ state.

The next two rows in the Table 2.3 present results for the B-CCD and B-CCD(T) models [the computational cost of B-CCD/B-CCD(T) is similar to that of the CCSD/CCSD(T) models]. Following the approach of Schreiner and coworkers [30, 31], the triplet state energy is calculated by using the spin-unrestricted wave function, the closed-shell singlet’s energy — by using the spin-restricted wave function, and the energy of the open-shell singlet — by using the spin-unrestricted spin-contaminated wave function. As expected, the B-CCD/B-CCD(T) results are almost identical to those of CCSD/CCSD(T) — both in terms of total energies and energy differences. Thus, for the $\tilde{a}^1A_1$
state the B-CCD/B-CCD(T) errors against FCI are 0.063/0.022 eV, respectively. The excitation energy for the open-shell singlet state, however, is about 1 eV off! Moreover, by definition\(^6\) this approach will almost always place the open-shell singlet below the closed-shell one, thus reversing the states’ ordering in methylene.

The next four rows in Table 2.3 present a more balanced approach than the direct energy difference one, that is when the ST gaps are calculated by using single-reference excited state theories. Even though the closed-shell reference description of the lowest singlet state is not very accurate in methylene, the cancellation of errors results in improved values of the ST splittings. For example, the CIS value is closer to FCI by 0.25 eV than the value calculated by SCF energy differences. In the case of the correlated CCSD model, the improvement is less dramatic: 0.007 eV (thus, EOM-CCSD error equals 0.055 eV). More importantly, however, is that the excited state models can also describe the open-shell singlet state. Moreover, models which explicitly include double excitations (e.g., EOM-OD or EOM-CCSD) can even describe the second

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\(^6\)In variational methods, the energy of an approximate wave function can be lowered by breaking its spin or point group symmetry. Thus, for any variational model (e.g., Hartree-Fock or CI), energies of spin-contaminated solutions are always lower than those of the spin-pure ones. Rigorously, this may not be the case for non-variational methods such as CCSD or B-CCD. Practically, however, spin-contaminated energies are usually lower than spin-pure ones for non-variational methods as well. Spin-contamination of coupled-cluster wave functions has been recently discussed in Ref. [68].
closed-shell singlet, even though such description is not very accurate (e.g., the EOM-OD values are more than 1 eV off).

By using the SF approach, the accuracy of single-reference theories is considerably improved. Moreover, all three singlet states can now be described with a similar accuracy. For example, the SF-CIS error for the lowest singlet is 0.11 eV smaller than that of the CIS. Moreover, the second closed shell singlet, which is not accessible by the non-SF CIS, is now described with roughly the same accuracy as the other states. The SF-OD results are within 0.04 eV from the FCI ones for all three singlet states. As Fig. 2.4 demonstrates, this difference between the SF and non-SF models is systematic: regardless of the basis set used, all SF models are closer to the experimental value than the corresponding non-SF approaches.

\[ \text{NH}_2^+ \]

Table 2.4 presents the adiabatic energy separations between the ground triplet \( \tilde{X}^3B_1 \) state and the three low-lying singlet states of \( \text{NH}_2^+ \) calculated in the TZ2P(f,d) basis set at the CISD/TZ2P(f,d) optimized geometries [12] (see footnotes 4 and 5). The difference between SF-OD and CASSCF SOCI [12] does not exceed 0.04 eV. By including the ZPE corrections estimated by using CISD frequencies [12], the SF-OD value for the \( \tilde{X}^3B_1 - \tilde{a}^1A_1 \) transition is within 0.02
Table 2.4. Total energies (hartree) for the ground states of NH$_2^+$, SiH$_2$, and PH$_2^+$, and adiabatic excitation energies (eV) for the three low-lying states$^a$

<table>
<thead>
<tr>
<th></th>
<th>$X^3B_1$</th>
<th>$a^1A_1$</th>
<th>$b^1B_1$</th>
<th>$c^1A_1$ ($c^1\Sigma_g^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF-CIS</td>
<td>-55.22731</td>
<td>1.673</td>
<td>2.151</td>
<td>4.375</td>
</tr>
<tr>
<td>SF-CIS(D)</td>
<td>-55.37545</td>
<td>1.342</td>
<td>1.959</td>
<td>3.635</td>
</tr>
<tr>
<td>SF-OD</td>
<td>-55.40259</td>
<td>1.305</td>
<td>1.941</td>
<td>3.419</td>
</tr>
<tr>
<td>CASSCF SOCI$^b$</td>
<td>-55.388368</td>
<td>1.281</td>
<td>1.935</td>
<td>3.380</td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF-CIS</td>
<td>-290.03701</td>
<td>0.503</td>
<td>2.199</td>
<td>3.945</td>
</tr>
<tr>
<td>SF-CIS(D)</td>
<td>-290.27260</td>
<td>0.776</td>
<td>2.122</td>
<td>3.850</td>
</tr>
<tr>
<td>SF-OD</td>
<td>-290.29961</td>
<td>0.866</td>
<td>1.994</td>
<td>3.537</td>
</tr>
<tr>
<td>CASSCF SOCI$^b$</td>
<td>-290.166351</td>
<td>0.871</td>
<td>1.992</td>
<td>3.486</td>
</tr>
<tr>
<td>Expt.$^c$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF-CIS</td>
<td>-341.55130</td>
<td>0.388</td>
<td>2.166</td>
<td>4.541</td>
</tr>
<tr>
<td>SF-CIS(D)</td>
<td>-341.71948</td>
<td>0.682</td>
<td>2.134</td>
<td>4.015</td>
</tr>
<tr>
<td>SF-OD</td>
<td>-341.74916</td>
<td>0.761</td>
<td>2.015</td>
<td>3.728</td>
</tr>
<tr>
<td>CASSCF SOCI$^b$</td>
<td>-341.695054</td>
<td>0.760</td>
<td>2.009</td>
<td>3.686</td>
</tr>
<tr>
<td>Expt.$^f$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ CISD/TZ2P(f,d) optimized geometries [12–14], TZ2P(f,d) basis set (see footnotes 4 and 5).

$^b$ CASSCF SOCI values are from Refs. [12–14].

$^c$ [40]

$^d$ Ref. [41].

$^e$ Ref. [44].

$^f$ Ref. [42].

eV from the experimental result [40]. The SF-CIS(D) error is also small and equals 0.08 eV.

**SiH$_2$**

Table 2.4 shows the adiabatic energy separations between the ground and three excited states of SiH$_2$. The CISD/TZ2P(f,d) optimized geometries and the
TZ2P(f,d) basis, have been used [13] (see footnotes 4 and 5). As in the previous cases, SF-OD agrees very well with CASSCF SOCI [13]. The difference is less than 0.01 eV for the $\tilde{X}^1A_1 - \tilde{a}^3B_1$ and $\tilde{X}^1A_1 - \tilde{A}^1B_1$ transitions, and 0.05 eV — for the $\tilde{X}^1A_1 - \tilde{B}^1A_1$ one. The ZPE corrected [13] SF-OD value for the $\tilde{X}^1A_1 - \tilde{a}^3B_1$ transition is within the experimental error [41]. The corresponding value for the $\tilde{X}^1A_1 - \tilde{A}^1B_1$ transition is within 0.07 eV from the experiment [44].

$\text{PH}_2^+$

CISD/TZ2P(f,d) optimized geometries [14] and a TZ2P(f,d) basis have been used to calculate the adiabatic excitation energies in $\text{PH}_2^+$ (see footnotes 4 and 5). Table 2.4 compares the SF results against the CASSCF SOCI ones [14], and the experiment [42]. As in the case of $\text{SiH}_2$, there is excellent agreement between the SF-OD and CASSCF SOCI results, the largest difference being 0.04 eV for the $\tilde{X}^1A_1 - \tilde{A}^1B_1$ transition. The available experimental data are not very accurate [42]. However, they are in overall agreement with the theoretical values.
Table 2.5. Singlet-triplet ($^1\Delta - ^3\Sigma$) adiabatic energy separations (eV) in selected diatomic molecules$^a$

<table>
<thead>
<tr>
<th></th>
<th>Basis</th>
<th>SF-CIS</th>
<th>SF-CIS(D)</th>
<th>SF-OD</th>
<th>Expt. [45]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>cc-pVTZ</td>
<td>1.778</td>
<td>1.658</td>
<td>1.558</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cc-pVQZ</td>
<td>1.764</td>
<td>1.611</td>
<td>1.605</td>
<td></td>
</tr>
<tr>
<td>NF</td>
<td>cc-pVTZ</td>
<td>1.775</td>
<td>1.527</td>
<td>1.487</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cc-pVQZ</td>
<td>1.770</td>
<td>1.531</td>
<td>1.491</td>
<td></td>
</tr>
<tr>
<td>OH$^+$</td>
<td>cc-pVTZ</td>
<td>2.329</td>
<td>2.223</td>
<td>2.190</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cc-pVQZ</td>
<td>2.323</td>
<td>2.178</td>
<td>2.189</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>cc-pVTZ</td>
<td>1.445</td>
<td>1.076</td>
<td>0.980</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cc-pVQZ</td>
<td>1.447</td>
<td>1.061</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Experimental geometries used [45], see footnote 7.

2.3.3 Diatomic molecules with a diradical singlet state

The set of diatomic molecules with a diradical singlet state (NH, NF, OH$^+$, and O$_2$) have been studied using the cc-pVTZ and cc-pVQZ bases [58]. The adiabatic $^1\Delta - ^3\Sigma$ excitation energies are calculated by using experimental geometries$^7$ [45]. Table 2.5 compares the SF results with the experimental values. [45]

Overall, the agreement between the SF models and the experiment is very good: the SF-OD/cc-pVQZ results for NF and OH$^+$ are within 0.01 eV from the experiment, whereas for NH and O$_2$ the deviation is about 0.05 and 0.08 eV. The SF-CIS(D) numbers are within 0.04 eV from the SF-OD ones.

$^7$The following equilibrium bond lengths for the $^1\Delta$ and $^3\Sigma$ states are used [45]: 1.034 Å and 1.036 Å for NH; 1.308 Å and 1.317 Å for NF; 1.215 Å and 1.207 Å for O$_2$. For OH$^+$, the experimental geometry of the $^3\Sigma$ state ($r_e=1.029$ Å) is used for both states (theoretical calculations [34] predict that the difference in the $r_e$ of these states is very small, i.e. $\approx 0.001$ Å).
2.3.4 Benzynes

The ground state of the benzyne isomers is a closed-shell singlet state of $\Psi^s_1$ type [Eq. (1.1) from Sec. 2.1]: $^1A_1$ in $C_{2v}$ (o- and m-benzynes) and $^1A_g$ in $D_{2h}$ (p-benzyne) symmetries. The lowest excited state is a triplet state: $^3B_2$ in o- and m-benzynes, and $^3B_{1u}$ in p-benzyne (see Ref. [49] for analysis of the molecular orbitals in p-benzyne). The diradical character increases as the distance between the unpaired electrons increases in the ortho→meta→para- sequence. The increase in diradical character results in a singlet-triplet energy gap decrease in the same order. The strong diradical character of the singlet p-benzyne results in orbital instabilities for the singlet state [49].

![Equilibrium geometries for the singlet and triplet states of benzynes](image_url)

**Figure 2.5.** Equilibrium geometries for the singlet (upper values) and triplet (lower values) states of benzynes. Bond lengths are in angstroms, angles — in degrees, and nuclear repulsion energies — in hartrees. Structures are optimized at the SF-DFT/6-311G* level.
Fig. 2.5 summarizes the equilibrium structures of benzyne isomers in their singlet and triplet states calculated by the SF-DFT method\textsuperscript{8} [69] in the 6-311G* basis [70]. We have also employed SF-DFT to calculate ZPEs. Two pure angular momentum basis sets are used in this subsection: 6-31G* [71], and a basis composed of the cc-pVTZ basis on carbon and the cc-pVDZ basis on hydrogen.

Table 2.6 shows the adiabatic energy splittings between the ground singlet state and the first excited triplet state of the benzyne isomers. With ZPE corrections, the SF-OD/6-31G* results for o- and m-benzyne are within 0.17 eV (4 kcal/mol) of the experiment [50], and within 0.03 eV (0.7 kcal/mol) for p-benzyne. However, the corresponding cc-pVTZ values estimated by the energy separability formula [Eq. (8.1)] are within 0.03 eV (0.7 kcal/mol) of the experiment for all benzyne isomers. The SF-DFT results deviate from the experimental values by 0.22 eV (5 kcal/mol), 0.09 eV (2 kcal/mol), and 0.023 eV (0.5 kcal/mol) for o-, m-, and p-benzyne, respectively.

We have also calculated the vertical excitation energies for several low-lying states. Due to the extensive orbital degeneracy, the density of the excited states is rather high in benzenes. As a result, the open-shell singlet $^1B_2/ ^1B_{1u}$

\textsuperscript{8}We used the functional composed of the equal mixture of the following exchange and correlation parts: 50\% Hartree-Fock + 8 \% Slater + 42 \% Becke for exchange, and 19\% VWN + 81\% LYP for correlation.
Table 2.6. Ortho-, meta-, and para-benzenes. Total ground state energies (hartree) and adiabatic excitation energies (eV) to the lowest triplet state

<table>
<thead>
<tr>
<th></th>
<th>$^1A_1$</th>
<th>$^3B_2$</th>
<th>$^1A_1$</th>
<th>$^3B_2$</th>
<th>$^1A_g$</th>
<th>$^3B_{1u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF-DFT$^b$</td>
<td>-230.77510</td>
<td>1.872</td>
<td>-230.77510</td>
<td>1.872</td>
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<tr>
<td>SF-CIS/6-31G*</td>
<td>-229.42629</td>
<td>0.960</td>
<td>-229.42629</td>
<td>0.960</td>
<td>-229.42629</td>
<td>0.960</td>
</tr>
<tr>
<td>SF-OD/6-31G*</td>
<td>-230.19490</td>
<td>1.490</td>
<td>-230.19490</td>
<td>1.490</td>
<td>-230.19490</td>
<td>1.490</td>
</tr>
<tr>
<td>SF-CIS/cc-pVTZ$^c$</td>
<td>-229.49504</td>
<td>1.007</td>
<td>-229.49504</td>
<td>1.007</td>
<td>-229.49504</td>
<td>1.007</td>
</tr>
<tr>
<td>SF-OD/cc-pVTZ$^{c,d}$</td>
<td>-230.50269</td>
<td>1.632</td>
<td>-230.50269</td>
<td>1.632</td>
<td>-230.50269</td>
<td>1.632</td>
</tr>
<tr>
<td>Expt. [50]</td>
<td>1.628 ± 0.013</td>
<td>0.911 ± 0.014</td>
<td>0.165 ± 0.016</td>
<td>1.628 ± 0.013</td>
<td>0.911 ± 0.014</td>
<td>0.165 ± 0.016</td>
</tr>
<tr>
<td>$\Delta$ ZPE$^e$</td>
<td>-0.028</td>
<td>0.043</td>
<td>0.021</td>
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<td></td>
</tr>
<tr>
<td>Expt.-$\Delta$ ZPE</td>
<td>1.656</td>
<td>0.868</td>
<td>0.144</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ SF-DFT/6-311G* optimized geometries (see Fig. 2.5);
$^b$ 6-311G* basis;
$^c$ cc-pVTZ basis on carbon and cc-pVDZ basis on hydrogen;
$^d$ Estimated using Eq. (8.1);
$^e$ Calculated at the SF-DFT/6-311G* level.
[Eq. (1.4)] and the second closed shell singlet $^1A_1/^1A_g$ [Eq. (1.2)] strongly interact with other excited states derived by excitation of electrons from the $\pi$-system. In the energy interval from 4 to 7 eV, there are about seven states including two quintet states.

2.3.5 Trimethylenemethane (TMM)

Three basis sets have been used in this section: (i) the DZP basis set$^9$; (ii) a basis composed of the cc-pVTZ basis on the carbon and the cc-pVDZ on the hydrogen; and (iii) the full cc-pVTZ basis set. The SF-DFT/6-31G* method$^{10}$ has been used to calculate equilibrium geometries. We find that (i) the ground state SF-DFT geometry is very close to the CCSD(T) one; and (ii) the relative structural changes between states are very close to those predicted by MCSCF.

TMM is an example of a non-Kekulé system: even though it is fully conjugated, each of its Kekulé structures has at least two non $\pi$-bonded atoms. The $\pi$-system of TMM is shown in Fig. 2.6: four $\pi$-electrons are distributed over four molecular $\pi$-type orbitals. Due to the exact degeneracy between the two $\epsilon'$ orbitals at the $D_{3h}$ structure, Hund rule predicts the ground state of the

$^9$The DZP basis for carbon is the same as in Sec. 2.3.1. The DZP basis for hydrogen is a Huzinaga-Dunning [55, 56] basis augmented by a single set of polarization functions [$\alpha_p(H)=1.00$]. Pure angular momentum d-functions are used.

$^{10}$We used the functional composed of the equal mixture of the following exchange and correlation parts: 50% Hartree-Fock + 8 % Slater + 42 % Becke for exchange, and 19% VWN + 81% LYP for correlation.
Figure 2.6. The π-system of TMM and the electronic configurations of the three lowest states. $C_2v$ labels are used at the ground state equilibrium geometry ($D_{3h}$), where the $1a_2$ and $2b_1$ orbitals are two degenerate $e'$ components. Two different distortions can lift the degeneracy between these orbitals (and the two lowest excited states, i.e. $1A_1$ and $1B_2$): one is a $C_2v$ distortion, which leaves the molecule planar, whereas another involves a $90^\circ$ rotation of one of the CH$_2$ groups. The former distortion stabilizes the $1a_2$ orbital and the closed-shell $1A_1$ singlet state (shown on the left), whereas the latter favors the $2b_1$ orbital and the open-shell $1B_2$ singlet state (shown on the right). Note that at the twisted $C_2v$ geometry, the $b_1$ and $b_2$ labels interchange

molecule to be a triplet $3A'_2$ state. This is confirmed by both the experimental and theoretical findings [23–25, 48, 72, 73].

The vertical excited states are summarized in Table 2.7 ($C_2v$ symmetry labels are used). The three lowest states are the diradical singlet states of Eqns. (1.1)-(1.2). However, excited states that derive from excitation of other π electrons are also relatively low in energy. The first closed-shell singlet $1A_1$ [Eq. (1.1)] and open-shell singlet $1B_2$ [Eq. (1.4)] are degenerate at the $D_{3h}$
Table 2.7. TMM. Total energies (hartree) for the ground \( ^3A'_2 \) state and vertical excitation energies (eV) for the low-lying excited states

<table>
<thead>
<tr>
<th>Method</th>
<th>( ^3A'_2 )</th>
<th>( ^1A_1/{}^1B_2 )</th>
<th>( ^2{}^1A_1 )</th>
<th>( ^1A_1/{}^1B_2 )</th>
<th>( ^5B_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF-DFT(50/50)/6-31G*</td>
<td>-155.779717</td>
<td>1.049</td>
<td>3.404</td>
<td>6.103</td>
<td></td>
</tr>
<tr>
<td>SF-CIS/DZP</td>
<td>-154.90553</td>
<td>1.154</td>
<td>6.627</td>
<td>8.428</td>
<td>5.712</td>
</tr>
<tr>
<td>SF-CIS(D)/DZP</td>
<td>-155.43585</td>
<td>1.160</td>
<td>3.821</td>
<td>6.018</td>
<td>6.729</td>
</tr>
<tr>
<td>SF-OD/DZP</td>
<td>-155.51414</td>
<td>1.198</td>
<td>4.000</td>
<td>5.941</td>
<td>7.221</td>
</tr>
<tr>
<td>SF-CIS/cc-pVTZ(^b)</td>
<td>-154.91822</td>
<td>1.150</td>
<td>6.534</td>
<td>8.359</td>
<td>5.706</td>
</tr>
<tr>
<td>SF-CIS(D)/cc-pVTZ(^b)</td>
<td>-155.54809</td>
<td>1.144</td>
<td>3.585</td>
<td>5.819</td>
<td>6.755</td>
</tr>
<tr>
<td>SF-OD/cc-pVTZ(^b)</td>
<td>-155.62016</td>
<td>1.180</td>
<td>3.864</td>
<td>5.963</td>
<td>7.208</td>
</tr>
</tbody>
</table>

\(^a\) SF-DFT/6-31G* optimized geometries (see Fig. 2.7);
\(^b\) cc-pVTZ basis on carbon and cc-pVDZ basis on hydrogen.

geometry (because of the degeneracy of \( a_2 \) and \( 2b_1 \) orbitals)\(^{11}\). The second closed-shell singlet \( 2^1A_1 \) [Eq. (1.2)] is followed by a pair of degenerate triplets, \( ^3A_1 \) and \( ^3B_2 \), obtained by excitation of one electron from the doubly occupied \( 1b_1 \) orbital to the \( a_2 \) or \( 2b_1 \) degenerate orbitals. Finally, there is a quintet \( ^5B_2 \) state in which all \( \pi \)-orbitals are singly occupied.

The equilibrium structures for the four lowest states of TMM are summarized in Fig. 2.7\(^{12}\). In accordance with the Jahn-Teller theorem, the degeneracy between the closed-shell and open-shell singlets can be lifted in lower symmetry.

\(^{11}\)This is similar to the \( \text{NH}_2^+ \) diradical at linear geometry where the \( \tilde{a}^1A_1 \) and \( \tilde{b}^1B_1 \) states become degenerate as two components of the \( ^1\Delta_g \) state.

\(^{12}\)Note that the PES of the open-shell singlet has no minimum at the \( C_{2v} \) planar structure. Likewise, the PES of the triplet state has no minimum at the \( C_{2v} \) 90° twisted structure. This can be demonstrated by the vibrational analysis which yields one imaginary frequency corresponding to the rotation of methylene group for the structures obtained by the constrained optimization. We do not discuss these saddle points, even though these structures have been previously reported [23].
Figure 2.7. Equilibrium geometries for the four lowest electronic states of TMM. Bond lengths are in angstroms, angles — in degrees, and nuclear repulsion energies — in hartrees. Structures are optimized at the SF-DFT/6-31G* level.

The closed-shell singlet of Ψ₁⁺ type is stabilized at the planar C₂ᵥ geometry, with one short C-C bond. The open-shell singlet of Ψ₃⁻ type prefers an equilibrium structure with one long C-C bond and a 90° twisted methylene group. The real minimum of the open-shell singlet is a C₂ structure with a rotated methylene group (e.g., the dihedral angle equals 79.0°). However, the potential energy surface along the twisting coordinate is rather flat, i.e., the energy difference between the C₂ᵥ (90.0° twisted) and the equilibrium C₂ (79.0° twisted) structures is only 0.001 eV (0.03 kcal/mol). Thus, for the sake of simplicity, we have used a twisted C₂ᵥ structure as the equilibrium geometry for the open-shell singlet ¹B₂ (at this geometry, this state should be labelled as ¹B₁). As mentioned
in Ref. [23], this state has not been observed in the experimental photoelectron spectrum [48], because of unfavorable Franck-Condon factors, even though adiabatically this state is the lowest singlet state.

Table 2.8 summarizes the adiabatic excitation energies of the three low-lying singlet states calculated by the SF and MCSCF/MCQDPT2 methods (see Fig. 2.7 for equilibrium geometries). Two different active spaces and three basis sets (see above) have been used in the multi-configurational calculations. The small (4×4) active space includes four π-orbitals and four electrons. The larger (10×10) active space includes six additional carbon-carbon σ and σ* orbitals and six additional electrons participating in the C-C bonding.

As seen from Table 2.8, the MCSCF and MCQDPT2 results are very insensitive to the active space and the basis set. For the $^3A'_2 \rightarrow ^1B_1$ transition, increasing the active space changes the MCSCF excitation energy by 0.06 eV (1.4 kcal/mol), while the perturbative correction decreases the importance of the active space size and equalizes the excitation energies. For the $^3A'_2 \rightarrow ^1A_1$ transition, the situation is reverse: while the MCSCF excitation energy does not depend on active space size, the MCQDPT2 energy decreases by about 0.04 eV (0.9 kcal/mol) in a 10×10 active space. The basis set increase changes the MCQDPT2 $^3A'_2 \rightarrow ^1B_1$ excitation energy by only 0.035 eV (0.8 kcal/mol), while the $^3A'_2 \rightarrow ^1A_1$ energy is unchanged. Moreover, there is practically no difference between the mixed cc-pVTZ/cc-pVDZ and the full cc-pVTZ basis sets.
Table 2.8. TMM. Total energies (hartree) for the ground $^3A'_2$ state and adiabatic excitation energies (eV) for the low-lying excited states$^a$

<table>
<thead>
<tr>
<th>Method</th>
<th>$^3A'_2$</th>
<th>$^1B_1$</th>
<th>$^1A_1$</th>
<th>$^2^1A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF-DFT(50/50)/6-31G$^*$</td>
<td>-155.77972</td>
<td>0.745</td>
<td>0.866</td>
<td>3.397</td>
</tr>
<tr>
<td>SF-CIS/DZP</td>
<td>-154.90553</td>
<td>1.018</td>
<td>0.882</td>
<td>6.616</td>
</tr>
<tr>
<td>SF-CIS(D)/DZP</td>
<td>-155.43585</td>
<td>0.987</td>
<td>0.885</td>
<td>3.826</td>
</tr>
<tr>
<td>SF-OD/DZP</td>
<td>-155.51414</td>
<td>0.697</td>
<td>0.936</td>
<td>4.023</td>
</tr>
<tr>
<td>MCSCF(4,4)/DZP</td>
<td>-155.936880</td>
<td>0.643</td>
<td>0.843</td>
<td></td>
</tr>
<tr>
<td>MCQDPT2(4,4)/DZP</td>
<td>-155.423414</td>
<td>0.676</td>
<td>0.863</td>
<td></td>
</tr>
<tr>
<td>MCSCF(10,10)/DZP</td>
<td>-155.010122</td>
<td>0.704</td>
<td>0.834</td>
<td></td>
</tr>
<tr>
<td>MCQDPT2(10,10)/DZP</td>
<td>-155.422866</td>
<td>0.674</td>
<td>0.824</td>
<td></td>
</tr>
<tr>
<td>SF-CIS/cc-pVTZ$^c$</td>
<td>-154.91822</td>
<td>1.017</td>
<td>0.883</td>
<td>6.508</td>
</tr>
<tr>
<td>SF-CIS(D)/cc-pVTZ$^c$</td>
<td>-155.54809</td>
<td>1.025</td>
<td>0.893</td>
<td>3.570</td>
</tr>
<tr>
<td>SF-OD/cc-pVTZ$^c$</td>
<td>-155.62016</td>
<td>0.744</td>
<td>0.941</td>
<td>3.858</td>
</tr>
<tr>
<td>MCSCF(4,4)/cc-pVTZ$^c$</td>
<td>-154.949102</td>
<td>0.648</td>
<td>0.843</td>
<td></td>
</tr>
<tr>
<td>MCQDPT2(4,4)/cc-pVTZ$^c$</td>
<td>-155.541780</td>
<td>0.715</td>
<td>0.865</td>
<td></td>
</tr>
<tr>
<td>MCSCF(10,10)/cc-pVTZ$^c$</td>
<td>-155.023549</td>
<td>0.708</td>
<td>0.833</td>
<td></td>
</tr>
<tr>
<td>MCQDPT2(10,10)/cc-pVTZ$^c$</td>
<td>-155.538683</td>
<td>0.715</td>
<td>0.830</td>
<td></td>
</tr>
<tr>
<td>MCSCF(4,4)/cc-pVTZ</td>
<td>-154.959329</td>
<td>0.644</td>
<td>0.841</td>
<td></td>
</tr>
<tr>
<td>MCQDPT2(4,4)/cc-pVTZ</td>
<td>-155.571449</td>
<td>0.711</td>
<td>0.862</td>
<td></td>
</tr>
<tr>
<td>MCSCF(10,10)/cc-pVTZ</td>
<td>-155.033829</td>
<td>0.705</td>
<td>0.832</td>
<td></td>
</tr>
<tr>
<td>MCQDPT2(10,10)/cc-pVTZ</td>
<td>-155.568282</td>
<td>0.710</td>
<td>0.828</td>
<td></td>
</tr>
<tr>
<td>Expt. [48]</td>
<td></td>
<td></td>
<td>0.699±0.006</td>
<td></td>
</tr>
<tr>
<td>$\Delta$ ZPE$^b$</td>
<td>-0.042</td>
<td>-0.088</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>Expt.-$\Delta$ ZPE</td>
<td></td>
<td></td>
<td>0.787</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ SF-DFT optimized geometries (see Fig. 2.7);

$^b$ Calculated at the SF-DFT/6-31G$^*$ level;

$^c$ cc-pVTZ basis on carbon and cc-pVDZ basis on hydrogen.

The SF-OD results differ from MCQDPT2(10×10) by 0.02 eV (0.5 kcal/mol) for the $^3A'_2 \rightarrow ^1B_1$ transition, and by 0.11 eV (2.6 kcal/mol) for the $^3A'_2 \rightarrow ^1A_1$ transition. The ZPE-corrected SF-OD results for the $^3A'_2 \rightarrow ^1A_1$ splitting deviate from the experiment by 0.15 eV (3.4 kcal/mol).
Bonding and its spectroscopic signatures in the four lowest electronic states of TMM are discussed in details in Chapter 3, and more accurate values of adiabatic energy separations between the states are given in Chapter 1.7. Moreover, the photoelectron spectrum of TMM is modelled in Chapter 7.

2.4 Conclusions

The SF approach describes closed and open shell singlet and triplet states within a single reference formalism as spin-flipping, e.g., $\alpha \rightarrow \beta$, excitations from a high-spin triplet ($M_s=1$) reference state for which both dynamical and non-dynamical correlation effects are much smaller than for the corresponding singlet state [67, 74, 75]. In this work, several SF models of increased complexity have been applied to calculate vertical and adiabatic energy separations between low-lying states of diradicals. Due to the single-reference nature of the high-spin triplet diradicals’ states, the SF models yield systematically more accurate results than their traditional (non-SF) counterparts. Our results demonstrate that the SF approach extends the scope of applicability of single-reference methods from well-behaved systems (e.g., closed shell molecules around the equilibrium geometries) to situations plagued by electronic degeneracy, e.g., diradicals and bond-breaking.
For all the diradicals considered here, the SF variant of the EOM-OD model yields energy separations that are within less than 3 kcal/mol of the experimental or the highly accurate MR values. In most cases the errors are about 1 kcal/mol. Drawing from the performance of single-reference methods for well-behaved molecules, we expect that a perturbative account of triple excitations will bring the corresponding SF-CC model into the \textit{chemical accuracy}, i.e., \(< 1\) kcal/mol, range. As shown in Chapter 8, the performance of EOM-SF-CC(2,3), i.e., the EOM-CC model with inclusion of triple excitations in the EOM part, is superior to that of EOM-SF-CCSD and yields typical errors of less than 1 kcal/mol. The less computationally demanding SF-CIS(D) model consistently yields results that are within 0.1-0.25 eV of the SF-OD ones. Moreover, SF-CIS(D) can be used to extrapolate the large basis set results of the more computationally expensive SF-CC methods.

Regarding comparison with MR techniques, the following advantages of the SF approach are particularly attractive: (i) lower computational cost and scaling\textsuperscript{13}; (ii) the multi-state nature of the SF method, i.e., its ability to calculate

\textsuperscript{13}The scaling of the spin-orbital implementation of the SF-CIS model is \(N^5\) (due to integral transformation), however, it can easily be reduced to approximately \(N^2\) by implementing the direct algorithm for the CIS procedure [76]. The scaling of the SF-CIS(D) model is \(N^6\), and the \(N^6\) step is non-iterative. Similarly to their non SF counterparts, the SF-CISD, SF-CCSD, and SF-OD models scale as \(N^6\). The scaling of the MR models is factorial due to the MCSCF part.
several excited states at once, rather than in a state-by-state fashion; (iii) sim-
eral formalism, e.g., the analytic gradient theory is rather straightforward for
the SF models — in spin-orbital formulation, it is identical to the corresponding
non SF theories [77–80]; (iv) the “black-box” nature of the (single-reference)
SF methods which do not involve active space and/or configurations selection.
Reference List


[59] D. Woon and T.H. Dunning, to be published.


Chapter 3

Electronic structure of the
trimethylenemethane diradical in its ground
and electronically excited states: Bonding,
equilibrium geometries and vibrational
frequencies

3.1 Introduction

Trimethylenemethane (TMM) is an example of a non-Kekulé system (see Fig. 3.1). The π-system of TMM consists of four π-electrons which can be distributed over four molecular π-type orbitals in a number of different ways (Figs. 2.6). The unusual electronic structure of TMM was recognized by Moffit and Coulson more than 50 years ago [1]. Two years later, in 1950,
Longuet-Higgins analyzed the electronic structure of several non-Kekulé molecules, TMM included [2]. Since then, TMM has attracted avid attention of theoreticians [3–31] and experimentalists [32–39].

![TMM and Kekulé structures](image)

**Figure 3.1.** TMM (left) and its Kekulé structures (right): the π-system of the molecule is fully conjugated, but each of its Kekulé structures has at least two non-π-bonded atoms

In addition to its fascinating electronic structure, there are other reasons for such a persistent interest. For example, TMM is an intermediate in the formation and rearrangements of methylenecyclopropanes [40, 41]. Other practical applications of TMM derivatives include organic ferromagnets [42, 43], synthetic reagents [44], and DNA cleaving agents [45].

TMM was first isolated in a matrix in 1966 by Dowd [32], who recorded its ESR spectrum. In 1976, the triplet multiplicity of the ground state of TMM was confirmed by the EPR experiment [33]. Dowd had also attempted to determine the singlet-triplet splitting in TMM [34, 35], which was measured later by photoelectron spectroscopy [38]. Recently, the infrared spectrum of the triplet ground state was reported [36, 37]. Additional information about TMM's vibrational
frequencies was derived from the photoelectron spectrum of the corresponding anion [39].

Previous theoretical studies of TMM included investigation of the potential energy surfaces (PESs) of the two lowest singlet states by Borden and Davidson [11]. Energy profiles along the reaction coordinate of the methylenecyclopropane rearrangement which proceeds through the TMM intermediate, were also studied [12, 13]. Numerous attempts were made to accurately determine the singlet-triplet splittings in the molecule [14–30]. Theoretical predictions of the vibrational frequencies of the triplet TMM were reported in Refs. [31, 37].

In this Chapter, we quantitatively analyze the bonding in different electronic states of TMM, and determine spectroscopic signatures of changes in bonding upon electronic excitation. Qualitatively, the electronic structure of TMM can be described by using a simple molecular orbital picture as has been done in the earlier studies [1, 2]. Later, these qualitative conclusions have been confirmed by \textit{ab initio} calculations of optimized geometries of the triplet and the two lowest singlets [11]: the observed changes in bond lengths were consistent with earlier predictions. However, due to the methodological difficulties (see Sec. 1.3), it was not possible to calculate equilibrium geometries and harmonic frequencies with quantitative accuracy. Moreover, the cumbersome nature of the available methods discouraged researches from studying higher excited states. By using the SF method, we calculated accurate equilibrium structures and vibrational
frequencies of the ground and the three lowest excited states of TMM, and characterized higher excited states.

### 3.2 Computational details

TMM’s equilibrium geometries (see Fig. 2.7) and vibrational frequencies were obtained by using the SF-DFT [46] method with a 6-31G* basis set [47]. Additional calculations were performed by using the SF-CIS(D) and the SF-CCSD methods [48, 49]. For the ground triplet state, which can be accurately described by single-reference methods, we also present results calculated by the CCSD(T) method [50] in a cc-pVTZ basis set [51]. 6-31G* and cc-pVTZ bases were used with pure angular momentum polarization functions.

The SF optimized geometries, frequencies, and total energies for the triplet state have been calculated by using the $M_s = 0$ SF state rather than the $M_s = 1$ reference state. In all the SF calculations, spin-unrestricted triplet references were used. All electrons were active unless specified otherwise.

To streamline the discussion, $C_2v$ symmetry labels are used for all the states including those whose equilibrium structures are of different symmetries, e.g., $D_{3h}$ or $C_2$. The correct symmetry labels are given when needed.

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1 We used the functional composed of the equal mixture of the following exchange and correlation parts: 50% Hartree-Fock + 8 % Slater + 42 % Becke for exchange, and 19% VWN + 81% LYP for correlation.
3.3 Results and discussion

3.3.1 Low-lying excited states of TMM

The π-system of TMM is presented in Fig. 2.6. It consists of four π-electrons distributed over four molecular π-type orbitals, two of which are exactly degenerate at the $D_{3h}$ symmetry [these are $\phi_1$ and $\phi_2$ from Eqns. (1.1)-(1.6)]. Therefore, in accordance with Hund’s rule, the ground state of the molecule should be the $^3A_2^\prime$ ($^3B_2$) triplet state. By rearranging two unpaired electrons in two degenerate orbitals, three different singlet states can be generated: $\Psi_{1-3}^s$ from Eqns. (1.1)-(1.4), two of which (Ψ$^s_1$ and Ψ$^s_3$) being exactly degenerate at $D_{3h}$. These states are traditional diradical states derived from the two-electrons-in-two-orbitals model [52]. However, the electronic structure of TMM is more complicated because all four of its π-orbitals are close in energy. Thus, a more appropriate description should include four electrons and four orbitals. Indeed, as we will see later, states derived by excitations of other π-electrons within the four orbital subspace are relatively low in energy. To distinguish between different types of electronic states, we will refer to the states described by Eqns. (1.1)-(1.6) as the diradical states.

The electronic states of TMM derived from distributing four electrons on four π-orbitals are shown in Fig. 3.2. The vertical excitation energies used in Fig. 3.2 are calculated at the SF-CCSD method in a mixed basis (cc-pVTZ on carbons
Figure 3.2. Low-lying electronic states of TMM. The excitation energies are calculated at the $X^3A'_2$ ($^3B_2$) equilibrium geometry by the SF-CCSD method ($C_{2v}$ labels). The degeneracy between the $1^1B_2$ / $1^1A_1$ and the $2^3B_2$ / $1^3A_1$ states can be lifted by lower symmetry distortions. The high-spin component of the $X^3B_2$ state is used as the reference in the SF calculations. The vertical excitation energies for the $1^3A_1$ and $2^3B_2$ states are obtained using the $1^3B_2$ reference and $cc$-pVDZ on hydrogens. The first three singlet states are of a diradical type, i.e., $\Psi_{1-3}$ from Eqns. (1.1)-(1.4). The first closed-shell $1^1A_1$ and the open-shell $1^1B_2$ singlets are exactly degenerate in $D_{3h}$ symmetry. In accordance with the Jahn-Teller theorem [53], the degeneracy between these singlets can be lifted at lower symmetry. The closed-shell singlet is stabilized at the planar $C_{2v}$ geometry, with one short CC bond. The open-shell singlet prefers an equilibrium
structure with one long CC bond and a twisted methylene group (planar $C_{2v}$
structure with one long CC bond corresponds to a transition state between two
equivalent minima [11]). These two states have been characterized in several
previous studies [11, 24, 29, 30]. The second closed-shell singlet, $2^1A_1$ [14], is
composed of the same determinants as the $1^1A_1$ state [this is the $\Psi_2^s$ state from
Eq. (1.2)]. Since this state prefers structures at which the diradical orbitals are
exactly degenerate, its equilibrium geometry is of $D_{3h}$ symmetry. This is similar
to the $2^1A_1$ state of methylene and nitrenium: as explained in footnote 11 to
Chapter 2, this state favors a nearly linear (CH$_2$) or linear (NH$_2^+$) structures
when the $3a_1$ and $1b_1$ diradical orbitals become (nearly) degenerate. The next
two states, $1^3A_1$ and $2^3B_2$, are degenerate triplets derived from excitations
of one electron from the doubly occupied $1b_1$ orbital to either the $a_2$ or the
$2b_1$ degenerate orbitals. These states can also undergo different Jahn-Teller
distortions. The quintet $^5B_2$ state has all the $\pi$-orbitals singly occupied and
prefers $D_{3h}$ geometry.

Note that only the $X^3B_2$ and $1^5B_2$ states can be described by a single Slater
determinant. All other states from Fig. 3.2 are two-configurational. The tradi-
tional recipe for calculating these states would be to employ the MCSCF model
(two-configurational SCF being a minimal level of theory) with the subsequent
inclusion of dynamical correlation. Such calculations are usually performed in a
state-by-state fashion. Moreover, even large active space MCSCF calculations
would fail to reproduce the exact \(1^1A_1/1^1B_2\) and \(1^3A_1/2^3B_2\) degeneracies at \(D_{3h}\), unless state averaging is performed. The SF method employs the \(X^3B_2\) state (which also happens to be the true ground state of TMM) as the reference, and treats all other states as spin-flipping excitations. Note that the determinants employed in all the singlets and the quintet state (Fig. 3.2) are formally single electron excitations (with a spin-flip) from the reference high-spin triplet determinant. That is why the SF approach provides a balanced description of all the singlet states of Fig. 3.2. For example, the exact degeneracies mentioned above are correctly described by any SF model. Moreover, all the states of Fig. 3.2 are obtained in a single SF calculation.

\(^2\)Unlike the singlet states, the SF description of the \(1^3A_1\) and \(2^3B_2\) states is not perfectly balanced: while one of the configurations in both triplets is a single electron excitation from the \(X^3B_2\) reference, the second is formally a double excitation. Moreover, both states are strongly mixed with two higher triplet configurations: \(1b_2^22b_13b_1\) and \(1b_2^22a_13b_1\). This imbalance results in a considerable spin contamination of the \(1^3A_1\) and \(2^3B_2\) states. However, the exact degeneracy between the states is preserved. Much better description of these triplets can be achieved in the SF calculation by using the quintet reference, i.e., a high-spin \((M_s = 2)\) component of the \(5^3B_2\) state. Note that from this reference, the high-spin \((M_s = 1)\) components of all the triplets (i.e., the ground \(3^3A'_2\) state, the \(1^3A_1\), and \(2^3B_2\) triplets) are single spin-flipping excitations. At the SF-CCSD level in a mixed basis set (cc-pVTZ on carbon and cc-pVDZ on hydrogen), the vertical energy gaps between the \(X^3B_2\) and \(1^3A_1/2^3B_2\) states calculated from the triplet and quintet references are 6.005 eV and 4.610 eV, respectively. Alternatively, the description of these states can be improved by inclusion of triples excitations, as described in Section 1.7.
3.3.2 Equilibrium geometries of the $X^3A'_2$, $1^1B_1$, $1^1A_1$, and $2^1A_1$ states of TMM

Equilibrium geometries of the four lowest states of TMM are given in Section 2.3.5. The $X^3A'_2$ and $2^1A_1$ states have $D_{3h}$ equilibrium geometries. The $1^1A_1$ state has planar $C_{2v}$ structure with one short CC bond and two long CC bonds, whereas the $1^1B_1$ state has a non-planar structure with two short and one long CC bonds, and a twisted methylene group. At the SF-DFT/6-31G* level, the $C_{2v}$, $90^\circ$ twisted structure is a local minimum on the $1^1B_1$ surface, i.e., it does not have imaginary frequencies. However, the energy of the $C_2$ structure with the dihedral angle of $79.0^\circ$ is slightly lower in energy. We have not found any $C_s$ minima (corresponding to the $90^\circ$ twisted and pyramidized CH$_2$ group).

Overall, the potential surface along the twisting coordinate is rather flat, e.g., the energy difference between the $C_{2v}$ ($90^\circ$ twisted) and the $C_2$ ($79.0^\circ$ twisted) structures is only 0.001 eV (0.03 kcal/mol) at the SF-DFT/6-31G* level of theory. Both geometries are given in Fig. 3.3b. The vibrational analysis discussed in the next subsection confirms that the properties of both conformers are very similar.

Fig. 3.4 compares the equilibrium structures of the molecule calculated by the SF, MCSCF, and CCSD(T) (triplet only) methods. The most interesting structural parameters are the lengths of the CC bonds since they reflect changes
Figure 3.3. a) Geometries of the ground $^3A'_2$ state optimized at the CCSD(T) / cc-pVTZ (upper numbers) and SF-DFT/6-31G* (lower numbers) levels. b) Geometries of the open-shell singlet optimized by the SF-DFT/6-31G* method. Upper numbers: $C_{2v}$ twisted structure; lower numbers: $C_2$ twisted structure. Bond lengths are in angstroms, angles — in degrees, and nuclear repulsion energies — in hartrees.

In the $^1B_1$ state there are one long and two short bonds, whereas the $^1A_1$ state has one short and two long bonds.

As shown in Fig. 3.4, the SF-CIS(D) and SF-DFT triplet’s geometries are much closer to the (highly accurate) CCSD(T) values than the MCSCF structure with bonds that are 0.04 Å too long. The SF-DFT structures are very
Figure 3.4. The CC bond lengths in the ground triplet and the two lowest singlet states of TMM. The SF-CIS(D) and SF-DFT triplet bond lengths are very close to the CCSD(T) ones. MCSCF consistently overestimates bond lengths. State-to-state structural changes are similar in all methods close to the SF-CIS(D) ones. The relative structural changes between the states are well reproduced by all the methods.

In order to understand the bonding in different electronic states of TMM, we compare the corresponding bond lengths with the typical values for single
Figure 3.5. The CC bond lengths in the ground and the three lowest excited states of TMM. Solid horizontal lines correspond to the values of a single (twisted ethylene) and double (ethylene) bond lengths. Dashed horizontal lines show the $\pi$-bond orders (BO) of $\frac{1}{2}$, $\frac{2}{3}$, and $\frac{3}{4}$. Ethane (dash-dot-dot line), benzene (dotted line) and allyl (dash-dot line) bonds are also shown.

and double bonds, as in other studies establishing correlation between “bond order”-like quantities and bond lengths (see, for example, Refs. [54, 55] and references therein). This is presented in Fig. 3.5. We employ the Lewis definition
of bond order, i.e., a number of electron pairs shared between two atoms, rather than bond orders calculated from electron density (for a brief summary of different definitions, see Ref. [54]).

Our choice of reference systems has been guided by the following considerations: (i) the hybridization of the participating carbons should be the same as in TMM$^3$, and (ii) the valence angles should be not strained (i.e., should be close to an optimal value for a given hybridization). Moreover, we prefer to use geometries obtained by accurate electronic structure calculations, unless anharmonicity corrections are available for the experimentally determined structures. The $r_0$ vs $r_e$ difference can be much larger than the intrinsic errors of an electronic structure method. For example, in benzene, the anharmonicity corrections change the value of the CC bond from 1.391 to 1.399 Å [58], whereas the CCSD(T)/cc-pVQZ mean absolute errors of in bond lengths are about 0.002 Å [59].

In all four lowest states of TMM, the carbons are sp$^2$ hybridized and the CCC valence angles are close to 120$^o$. The choice of the reference double CC bond between the sp$^2$ hybridized carbons is straightforward: ethylene in its ground state has a full double bond and satisfies both of the above criteria. Thus, we

\footnote{The length of a carbon-carbon single bond depends strongly on the hybridization of participating atoms [57]: the increase in the s-character causes bond contraction. Thus, the single bond length between two sp$^2$-sp$^3$ hybridized centers increases in the following order: sp$^2$-sp$^2$, sp$^2$-sp$^3$, sp$^3$-sp$^3$. Of course, when p-electrons from sp$^2$-hybridized atoms are available for bonding, the bond order increases due to $\pi$-bonding, and the bond contracts further.}
accept 1.333 Å\(^4\) as the reference value for a full double bond (the \(\pi\)-bond order is 1). Choosing a typical single bond is more complicated. Ethane is not an appropriate candidate, because its carbons are sp\(^3\)-hybridized and, therefore, its CC bond is longer than the single bond between two sp\(^2\) hybridized carbons (see footnote 3). A more relevant example is twisted ethylene where both carbons are sp\(^2\) hybridized, while the \(\pi\)-bond is broken due to the zero overlap between the \(p\)-orbitals at the 90° twisted geometry. We accept the corresponding bond length of 1.470 Å \([48]\) as a typical single bond value (\(\pi\)-bond order is 0)\(^5\). Butadiene is another molecule with single and double bonds between sp\(^2\) hybridized carbons. However, due to conjugation, its single bond is slightly shorter whereas the double bond is longer than in ethylene (the corresponding values are 1.467 Å and 1.343 Å, respectively \([62]\)). Benzene and the allyl radical are examples of sp\(^2\) systems with \(\pi\)-bond orders of \(\frac{1}{2}\) and \(\frac{3}{4}\), respectively. The corresponding bond lengths are 1.391 Å \([58]\)\(^6\) and 1.387 Å \([63]\).

To analyze the bonding, we consider a simple model which assumes that the length of a bond with a partial \(\pi\)-character is inversely proportional to the

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\(^4\)The equilibrium structure of ethylene is calculated at the CCSD(T)/cc-pVTZ level. The experimental CC bond in ethylene equals 1.339 Å \([60]\). The discrepancy is much larger than the method’s intrinsic error of about 0.002 Å and is due to anharmonicity.

\(^5\)This value is surprisingly close to 1.479 Å suggested by Dewar and Schmeising in 1960 as a typical value of a single bond between sp\(^2\) hybridized carbons \([61]\).

\(^6\)Again, as in case of ethylene, the experimental (1.399 Å \([60]\)) and high level theoretical (1.391 Å \([58]\)) CC bondlengths are very different due to anharmonicities.
π-bond order. Once reference values for single and double CC bonds are agreed upon, the above assumption enables one to calculate a π-bond order for a given bond length, or, alternatively, to estimate an expected bond length for any intermediate bond order. As can be seen from Fig. 3.5, the bond lengths in benzene (π-bond order of \( \frac{1}{2} \)) are slightly shorter than predicted by the model. Conversely, the allyl radical bonds are longer than the value obtained by assuming that all three electrons participate in two π-bonds (i.e., a π-bond order of \( \frac{3}{4} \)). The latter discrepancy can be explained by the nearly non-bonding character of the \( a_2 \) singly occupied allyl orbital.

Assuming that the \( 1b_1, 2b_1, \) and \( 1a_2 \) orbitals of TMM are of a bonding character, the π-bond order in the \( 3A'_2 \) and \( 2^1A_1 \) states is \( \frac{2}{3} \) (four π-electrons equally distributed between three CC-bonds). Fig. 3.5 shows that the bond lengths in these states are slightly longer than estimated by the model. This is probably due to the nearly non-bonding character of the \( 2b_1 \) and \( 1a_2 \) orbitals at \( D_{3h} \) (see Fig. 2.6). Another interesting observation is that the bond lengths in the singlet are shorter than in the triplet. This is because electrons with parallel spins form weaker bonds due to the Pauli exclusion principle.

In the \( 1^1A_1 \) state, two π-electrons participate in the short (upper) bond (thus, the π-character of this bond equals 1). Two other π-electrons contribute to the two longer (lower) bonds, however, the resulting bonding is very weak,
because of the small overlap between the two $\pi$-centers. As Fig. 3.5 demonstrates, this picture agrees well with the actual structures: the length of the shorter bond is close to the bond in ethylene, while the longer bonds are only slightly shorter than the bond with the zero $\pi$-character (e.g., twisted ethylene).

The bonding in the $^1B_1$ state is more complicated. Assuming that three $\pi$-electrons participate in the two shorter (lower) bonds, and one $\pi$-electron contributes to the longer (upper) bond, the corresponding $\pi$-bond orders are $\frac{3}{4}$ and 0, respectively (the order of the longer bond is zero because the $p$-orbitals of the upper and central carbons do not overlap at the twisted structure). Thus, this state is similar to the allyl radical with a twisted methylene group attached to it. However, as Fig. 3.5 shows, the upper bond is longer than the bond length in twisted ethylene, and the lower bonds are shorter than those in the allyl radical. This can be explained by an electron transfer from the upper to the lower part of the molecule. Indeed, according to the Mulliken and Lowdin population analysis of the electron density in $^1B_1$, the upper and central carbons are positively charged, while the lower carbons host negative charges. The degree of the charge separation can be characterized by the permanent dipole moment which is equal 0.12 Debye (the dipole is directed from the upper to the lower part of the molecule). The driving force for the charge transfer is additional stabilization achieved by moving non-bonding electrons into the weakly bonding molecular orbitals of allyl. This charge transfer results in a
contraction of the shorter (lower) bonds and an elongation of the longer (upper)
bond.

We also performed a natural bond analysis (NBO 4.0. package [64]) to
determine the bond orders in different states of TMM. However, the strongly
delocalized structures with three- or four-center bonds are not well described
by the NBO procedure. In a future study, we will employ an extension of NBO,
natural resonance theory [65, 66], which has been developed to describe bonding
in molecules with several resonance structures.

3.3.3 Harmonic vibrational frequencies of the $X^3A_2^\prime$, $1^1B_1$, $1^1A_1$, and
$2^1A_1$ states of TMM

For species with an unusual electronic structure, vibrational analysis is of par-
ticular importance, because vibrational frequencies reflect bond strengths, e.g.,
higher stretching frequencies correspond to stronger bonds, an increase in out-
of-plane (OPLA) or torsional frequencies may be due to an increase in $\pi$-bonds’
orders, etc. Thus, by comparing frequencies in different electronic states of
TMM, we can learn more about bonding in these states.

Two independent experimental studies of the TMM vibrational spectrum
were reported [36, 37, 39]. Maier and coworkers recorded gas phase infrared
spectra (IR) of the ground state TMM and its deuterated isotopomers [36,
37]. From the vibrational structure of the photoelectron spectrum of the TMM
negative ion measured by Wenthold et al. [39], some vibrational frequencies for
the ground $X^3A'_2$ triplet and the excited $1^1A_1$ singlet states were determined.
Therefore, for the ground $X^3A'_2$ state of TMM, an almost complete set of the
experimental vibrational frequencies is available. For the $1^1A_1$ state, however,
only one vibrational frequency, 325 cm$^{-1}$, is known [39]. No frequencies for other
singlets have been reported so far. Although the $1^1B_1$ state is adiabatically the
lowest singlet state, it has not been observed in the Wenthold’s experiment
because of unfavorable Franck-Condon factors.

A comparison of the calculated and experimental frequencies is not straight-
forward due to anharmonicities. Fortunately, the harmonic frequencies of the
triplet state can be calculated by the highly reliable CCSD(T) method, which
allows us to calibrate the SF method against CCSD(T).

Table 3.1 compares the vibrational frequencies for the ground $^3A'_2$ state
calculated by the SF-DFT and CCSD(T) methods with the experimental val-
ues [36, 37, 39]. The SF-DFT frequencies are systematically higher than the

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7The experimentally measured frequencies are the fundamentals, i.e., the energy differences
between the zero and first vibrational levels. The calculated harmonic frequencies are equal
to the fundamentals only for pure harmonic potentials. For a real anharmonic potential, the
fundamentals can be lower (this is often a case for stretching vibrations) or higher (as can happen for OPLA modes) than the harmonic frequencies. Moreover, anharmonic terms can
couple harmonic vibrational modes, which can strongly affect the observed intensities, e.g.,
some frequencies may not be observed due to anharmonicities.
Table 3.1. Vibrational frequencies, cm$^{-1}$, of the ground $X^3A'_2$ state of TMM

<table>
<thead>
<tr>
<th>Symm. Type</th>
<th>Expt.$^a$</th>
<th>Expt.$^b$</th>
<th>CCSD(T)$^c$</th>
<th>SF-DFT$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_1/\omega_2$</td>
<td>$e'$</td>
<td>CC scissors/rock</td>
<td>425</td>
<td>427 (0.01)</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>$a''_1$</td>
<td>H wag (OPLA)</td>
<td>473</td>
<td>485</td>
</tr>
<tr>
<td>$\omega_4/\omega_5$</td>
<td>$e''_{1}$</td>
<td>H wag (OPLA)</td>
<td>485</td>
<td>503</td>
</tr>
<tr>
<td>$\omega_6$</td>
<td>$a''_2$</td>
<td>CC torsion (OPLA)</td>
<td>499.0 (0.36)</td>
<td>518 (0.34)</td>
</tr>
<tr>
<td>$\omega_7/\omega_8$</td>
<td>$e''_{2}$</td>
<td>H torsion (OPLA)</td>
<td>732</td>
<td>728</td>
</tr>
<tr>
<td>$\omega_9$</td>
<td>$a''_2$</td>
<td>H torsion (OPLA)</td>
<td>755.5 (1.00)</td>
<td>727.5</td>
</tr>
<tr>
<td>$\omega_{10}$</td>
<td>$a'_1$</td>
<td>CC s-stretch</td>
<td>915</td>
<td>950</td>
</tr>
<tr>
<td>$\omega_{11}$</td>
<td>$a'_2$</td>
<td>H rock</td>
<td>961</td>
<td>1002</td>
</tr>
<tr>
<td>$\omega_{12}/\omega_{13}$</td>
<td>$e'$</td>
<td>H-rock</td>
<td>1030 (&lt;0.01)</td>
<td>1064</td>
</tr>
<tr>
<td>$\omega_{14}/\omega_{15}$</td>
<td>$e'$</td>
<td>CC a-stretch</td>
<td>1310</td>
<td>1371 (&lt;0.01)</td>
</tr>
<tr>
<td>$\omega_{16}/\omega_{17}$</td>
<td>$e'$</td>
<td>H scissors</td>
<td>1418.4 (0.15)</td>
<td>1518 (0.06)</td>
</tr>
<tr>
<td>$\omega_{18}$</td>
<td>$a'_1$</td>
<td>H scissors</td>
<td>1533</td>
<td>1593</td>
</tr>
<tr>
<td>$\omega_{19}/\omega_{20}$</td>
<td>$e'$</td>
<td>H s-stretch</td>
<td>3019-3031 (0.05)</td>
<td>3178 (0.10)</td>
</tr>
<tr>
<td>$\omega_{21}$</td>
<td>$a'_1$</td>
<td>H s-stretch</td>
<td>3186</td>
<td>3293</td>
</tr>
<tr>
<td>$\omega_{22}$</td>
<td>$a'_2$</td>
<td>H a-stretch</td>
<td>3261</td>
<td>3384</td>
</tr>
<tr>
<td>$\omega_{23}/\omega_{24}$</td>
<td>$e'$</td>
<td>H a-stretch</td>
<td>3100-3115 (0.04)</td>
<td>3266 (0.09)</td>
</tr>
</tbody>
</table>

$^a$ Ref. [36, 37]. Intensities relative to the strongest band are given in parentheses. Additional band at 1455.6 cm$^{-1}$ (0.05) has not been assigned.

$^b$ Ref. [39].

$^c$ Frequencies and geometry calculated by CCSD(T)/cc-pVTZ (see Fig. 3.3a). IR intensities relative to the strongest band are given in parentheses.

$^d$ Frequencies and geometry calculated by SF-DFT/6-31G* (see Fig. 3.3a).

$^e$ The absolute intensity is 94.30 km/mol.

CCSD(T) ones, the average relative difference$^8$ being 3.1% with a standard deviation ± 1.1%, and a maximum difference of 4.3% for the $\omega_{11}$ mode.

At the $D_{3h}$ symmetry, TMM has eight IR active vibrations (six of $e'$ symmetry and two of $a''_2$ symmetry). The experimental and calculated values of the IR

$^8$The relative differences between the SF-DFT and CCSD(T) frequencies is calculated as $(\omega_{i,CCSD(T)} - \omega_{i,SF-DFT})/\omega_{i,CCSD(T)} \cdot 100\%$. 

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intensities of the active modes are also given in Table 3.1 (values in parentheses). The measured IR spectrum consists of six bands (four single lines and two doublets). In Ref. [37], five of these bands are assigned as the skeleton and the hydrogen groups OPLA motions ($\omega_6$, $\omega_9$), the CH$_2$ scissoring mode ($\omega_{16}/\omega_{17}$), and the symmetric and asymmetric stretches in the CH$_2$ groups ($\omega_{19}/\omega_{20}$ and $\omega_{23}/\omega_{24}$). This assignment is consistent both with the CCSD(T) and SF-DFT results. The 1455.6 cm$^{-1}$ band with a relative intensity of 0.05 is interpreted as a combination vibration [37]. The normal mode analysis reveals that the following vibrations are strongly mixed: (i) the CC scissors/rock ($\omega_1/\omega_2$) and the hydrogens’ rocking vibrations ($\omega_{12}/\omega_{13}$) (their sum is 1457 cm$^{-1}$ at the CCSD(T)/cc-pVTZ level); and (ii) the skeleton asymmetric stretches ($\omega_{14}/\omega_{15}$) and the CH$_2$ scissors ($\omega_{16}/\omega_{17}$). The calculated frequencies of the latter vibrations are 1371 cm$^{-1}$ and 1518 cm$^{-1}$, respectively. Both pairs of mixed modes are IR active and can yield a band at 1455.6 cm$^{-1}$. Moreover, the doubled frequency of the most intense line in the spectrum, the OPLA hydrogens’ deformation ($\omega_9$), equals 1511 cm$^{-1}$ (experimental), which is close to the frequency of the observed line. Thus, at this level of theory it is not possible to determine the nature of this band. 

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9 The SF-DFT IR intensities are not available because the analytic gradients for this method have not yet been implemented.
Four vibrational frequencies of the $X^3A'_2$ ground state were determined from the photoelectron experiment [39]. They were assigned as the skeleton scissoring/rocking mode ($\omega_1/\omega_2$), the hydrogens OPLA torsion motion ($\omega_9$), and the symmetric and asymmetric carbon skeleton stretches ($\omega_{10}$ and $\omega_{14}/\omega_{15}$). These vibrations are active in the photoelectron spectrum, because they correspond to coordinates that connect the $C_{2v}$ geometry of the anion with the $D_{3h}$ structure of the $X^3A'_2$ state of the neutral TMM.

Table 3.2 presents the frequencies of the four lowest states of TMM. The frequencies for the $1^1B_1$ state are calculated at the lowest minimum of this state ($C_2$ structure), therefore, the symmetry labels for the vibrational modes are only approximate. Significant changes in the skeleton frequencies and in the OPLA hydrogen group vibrations reflect structural differences between the ground state and the first two excited singlets, $1^1A_1$ and $1^1B_1$ (see previous subsection). The rest of this subsection explains the observed changes in the calculated frequencies in terms of structural changes.

The frequencies of the CC rock ($\omega_2$), the wag and OPLA torsional motions of the upper CH$_2$ group ($\omega_4$ and $\omega_7$) increase in the $1^1A_1$ state and decrease in the $1^1B_1$ state (as compared with the $X^3A'_2$ triplet state). This is because

\footnote{The vibrational analysis shows that the $C_2$ and $C_{2v}$ twisted structures are very similar. The largest change is in the frequency corresponding to the rotation of the upper CH$_2$ group (H-wag, $\omega_4$): in $C_{2v}$ twisted structures this frequency is 187 cm$^{-1}$ (vs. 330 cm$^{-1}$ in $C_2$). Changes in other frequencies do not exceed 15 cm$^{-1}$.}
Table 3.2. Vibrational frequencies, cm$^{-1}$, of the $X^3A'_2$, $1^1B_1$, $1^1A_1$, and $2^1A_1$ states of TMM$^a$

<table>
<thead>
<tr>
<th>Symm.</th>
<th>Type</th>
<th>$X^3A'_2$</th>
<th>$1^1B_1$</th>
<th>$1^1A_1$</th>
<th>$2^1A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_1$</td>
<td>$a_1(e')$</td>
<td>CC scissors</td>
<td>440</td>
<td>477</td>
<td>337</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>$b_2(e')$</td>
<td>CC rock</td>
<td>440</td>
<td>391</td>
<td>504</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>$a_2(a''_1)$</td>
<td>all-H wag (OPLA)</td>
<td>485</td>
<td>649</td>
<td>146</td>
</tr>
<tr>
<td>$\omega_4$</td>
<td>$a_2(e'')$</td>
<td>up-H wag (OPLA)</td>
<td>503</td>
<td>330</td>
<td>713</td>
</tr>
<tr>
<td>$\omega_5$</td>
<td>$b_1(e''_1)$</td>
<td>down-H wag (OPLA)</td>
<td>503</td>
<td>601</td>
<td>290</td>
</tr>
<tr>
<td>$\omega_6$</td>
<td>$b_1(a''_2)$</td>
<td>CC torsion (OPLA)</td>
<td>531</td>
<td>420</td>
<td>460</td>
</tr>
<tr>
<td>$\omega_7$</td>
<td>$b_1(e''_2)$</td>
<td>up-H torsion (OPLA)</td>
<td>728</td>
<td>490</td>
<td>951</td>
</tr>
<tr>
<td>$\omega_8$</td>
<td>$a_2(e''_2)$</td>
<td>down-H torsion (OPLA)</td>
<td>728</td>
<td>887</td>
<td>530</td>
</tr>
<tr>
<td>$\omega_9$</td>
<td>$b_1(a''_2)$</td>
<td>all-H torsion (OPLA)</td>
<td>794</td>
<td>871</td>
<td>628</td>
</tr>
<tr>
<td>$\omega_{10}$</td>
<td>$a_1(a'_1)$</td>
<td>CC s-stretch</td>
<td>989</td>
<td>945</td>
<td>921</td>
</tr>
<tr>
<td>$\omega_{11}$</td>
<td>$b_2(a''_2)$</td>
<td>all-H s-stretch</td>
<td>1002</td>
<td>1033</td>
<td>994</td>
</tr>
<tr>
<td>$\omega_{12}$</td>
<td>$a_1(e'_1)$</td>
<td>down-H-rock</td>
<td>1064</td>
<td>1128</td>
<td>1082</td>
</tr>
<tr>
<td>$\omega_{13}$</td>
<td>$b_2(e'_2)$</td>
<td>up-H-rock</td>
<td>1064</td>
<td>1079</td>
<td>1207</td>
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<tr>
<td>$\omega_{14}$</td>
<td>$a_1(e'_2)$</td>
<td>CC a/s-stretch</td>
<td>1416</td>
<td>1474</td>
<td>1717</td>
</tr>
<tr>
<td>$\omega_{15}$</td>
<td>$b_2(e'_2)$</td>
<td>CC a/a-stretch</td>
<td>1416</td>
<td>1236</td>
<td>346</td>
</tr>
<tr>
<td>$\omega_{16}$</td>
<td>$a_1(e'_2)$</td>
<td>up-H scissors</td>
<td>1569</td>
<td>1639</td>
<td>1496</td>
</tr>
<tr>
<td>$\omega_{17}$</td>
<td>$b_2(e'_2)$</td>
<td>down-H scissors</td>
<td>1569</td>
<td>1570</td>
<td>1521</td>
</tr>
<tr>
<td>$\omega_{18}$</td>
<td>$a_1(a'_1)$</td>
<td>all-H scissors</td>
<td>1593</td>
<td>1549</td>
<td>1571</td>
</tr>
<tr>
<td>$\omega_{19}$</td>
<td>$a_1(e'_2)$</td>
<td>up-H s-stretch</td>
<td>3283</td>
<td>3287</td>
<td>3275</td>
</tr>
<tr>
<td>$\omega_{20}$</td>
<td>$b_2(e'_2)$</td>
<td>down-H s-stretch</td>
<td>3283</td>
<td>3286</td>
<td>3288</td>
</tr>
<tr>
<td>$\omega_{21}$</td>
<td>$a_1(a'_1)$</td>
<td>all-H s-stretch</td>
<td>3293</td>
<td>3297</td>
<td>3299</td>
</tr>
<tr>
<td>$\omega_{22}$</td>
<td>$b_2(a''_2)$</td>
<td>all-H a-stretch</td>
<td>3384</td>
<td>3391</td>
<td>3361</td>
</tr>
<tr>
<td>$\omega_{23}$</td>
<td>$a_1(e'_2)$</td>
<td>H a-stretch</td>
<td>3387</td>
<td>3393</td>
<td>3404</td>
</tr>
<tr>
<td>$\omega_{24}$</td>
<td>$b_2(e'_2)$</td>
<td>H a-stretch</td>
<td>3387</td>
<td>3388</td>
<td>3402</td>
</tr>
</tbody>
</table>

$^a$ All frequencies are calculated at the SF-DFT/6-31G* level at the SF-DFT optimized geometries (see Fig. 3.3). Symmetry labels are not applicable for the $1^1B_1$ state which has twisted $C_2$ equilibrium structure.

these modes involve vibration of the upper CC bond, which becomes stronger and shorter in the closed-shell singlet, and is weaker in the open-shell singlet. Conversely, vibrations involving the lower carbons [i.e., the CC scissoring mode ($\omega_1$), the wagging and OPLA motions of the lower CH$_2$ groups ($\omega_3$, $\omega_5$, $\omega_9$, and
ω₈), have higher frequencies in the 1^1B₁ state and lower frequencies in the 1^1A₁ state.

Analysis of the vibrational modes that involve both the upper and the lower parts of the molecule is more complicated. The molecule becomes softer with respect to the OPLA distortions, because the π-system is disturbed at the C₂ᵥ structures (as compared with the D₃h structure of the ground state). This results in decrease of the OPLA carbon frequency (ω₆) in both the open- and closed-shell singlets. The decrease in ω₆ is larger for the open-shell C₂ structure with one p-orbital having zero overlap with the other p-orbitals. The frequency of the symmetric skeleton stretching mode (ω₁₀) is lower in both singlet states because the molecular skeleton is less rigid in these states with respect to the triplet state. This is consistent with the following structural changes (see also Sec. 3.3.2). The sum of the CC bond lengths increases in the following sequence: X³A′₂, 1^1B₁, and 1^1A₁ state (the values are 4.206, 4.231, and 4.244 Å, respectively). Degeneracy between two asymmetric skeleton stretches at the D₃h symmetry is lifted at equilibrium geometries of both lowest singlets. The frequency of the a₁ vibration (ω₁₄), which is dominated by the out-of-phase vibration of the upper and two lower CC bonds, increases. The b₂ vibration (ω₁₅) (the out-of-phase vibration of the lower CC bonds, with the upper CC bond being frozen) becomes softer. In both cases, the difference is larger for the 1^1A₁ state for which the b₂ asymmetric stretch frequency equals 346 cm⁻¹.
We find that these modes are strongly mixed with the carbon scissoring and rocking vibrations and with the rocking motions of the CH\textsubscript{2} groups.

The second closed-shell singlet, 2\textsuperscript{1}A\textsubscript{1}, has $D_{3h}$ equilibrium structure with the CC bond lengths slightly shorter than in the ground state (see previous subsection). Consequently, the frequencies of the skeleton and hydrogen in-plane modes are higher in the 2\textsuperscript{1}A\textsubscript{1} state. However, the carbon OPLA vibrations and the wagging motions of the hydrogens are lower in the singlet state. The frequencies of the latter modes are related to the stability of the molecule with respect to the rearrangement from a diradical to a methylenecyclopropane structure. Relative to the triplet state, all three singlets have lower frequencies of the hydrogens wagging modes, which suggests that these states have lower barriers for such rearrangements. Moreover, the skeleton asymmetric stretch ($\omega_{15}$), a mode that connects open- and closed-shell singlet structures, has lower frequencies in both the 1\textsuperscript{1}B\textsubscript{1} and 1\textsuperscript{1}A\textsubscript{1} states than in the triplet state.

From the vibrational structure of the photoelectron spectrum, Wenthold et al. [38, 39] have determined one frequency of 325 cm\textsuperscript{-1} for the 1\textsuperscript{1}A\textsubscript{1} state. Our calculated harmonic frequencies suggest that the observed 325 cm\textsuperscript{-1} mode can be assigned to either the CC scissoring ($\omega_{1}=337$ cm\textsuperscript{-1}) or the CC asymmetric stretching ($\omega_{15}=346$ cm\textsuperscript{-1}) mode. Both vibrations are active in the ground triplet state in the photoelectron spectrum.
3.4 Conclusions

The SF method accurately describes diradicals within a single-reference formalism. The SF-DFT method is applied to the low-lying excited states of TMM. In addition to the previous benchmarks [46, 48, 67], we show that the SF-DFT triplet equilibrium properties are very close to the CCSD(T)/cc-pVTZ results. For example, the difference in the CC bond lengths is about 0.005 Å, and the average relative differences in the harmonic frequencies are about 3 %. Since the SF model treats all diradical states in a uniform fashion, we expect that the SF-DFT equilibrium structures and vibrational frequencies of all four lowest states of TMM to be of the similar accuracy. Using these structures and frequencies, we also analyze the bonding in the TMM ground and the lowest excited states. We find that the $1^1A_1$ state has a full double bond between the central and one of the peripheral carbons, while there is only very little interaction between two other carbons that host unpaired electrons. Although the $1^1B_1$ state is similar to the allyl radical with a twisted methylene group, the corresponding CC bonds in TMM are shorter than those in allyl because of electron transfer from the twisted methylene to the allyl moiety. The excited $2^1A_1$ state has stronger bonds relative to the ground $X^3A'_2$ state. Otherwise, these two states are very similar, i.e., both have $D_{3h}$ equilibrium structures. Overall, our results demonstrate that the SF method is a useful tool for studying diradicals.
Reference List


Chapter 4

Electronic structure of the

1,3,5-tridehydrobenzene triradical in its ground

and excited states

4.1 Introduction

Triradicals are molecules with three unpaired electrons. From the electronic structure point of view, they are species where three electrons are distributed in three (near) degenerate orbitals, as discussed in Section 1.4. Because of the more extensive electronic degeneracy, the \textit{ab initio} modelling of triradicals is even more complicated than that of diradicals. Contrary to diradicals, which often appear as intermediates or transition states in chemical reactions, triradicals are less common and their studies are scarce [1–4]. The interest in triradicals and
other species with several unpaired electrons stems from their role as building units of organic magnets [5–10].

A number of radical and diradical benzene’s derivatives (i.e., phenyls and benzynes) have been extensively studied both experimentally and theoretically [11–18]. Our studies investigates the corresponding triradical analog, 1,3,5-tridehydrobenzene (C₆H₃). Previous studies of C₆H₃ involve that of Bettinger et al. [19] who have reported the equilibrium structure of the ²A₁ ground state of this molecule calculated by the CCSD method in a polarized double-ζ basis. Wenthold and coworkers determined the heat of formation and bond dissociation energies of 1,3,5-tridehydrobenzene [20]. Later on, bonding and thermochemical properties in all three C₆H₃ isomers were investigated by Cristian and co-workers [21]. Positive and negative ions of 1,3,5-tridehydrobenzene have also been studied [22–25]. The most interesting feature of the didehydrophenyl cation is the so called double aromaticity [22, 23]. In addition to an aromatic π-system, there is a bonding σ- system derived from the unpaired electrons. While the cation is a closed shell system, the corresponding anion is of a diradical type. It was concluded from its reactivity [25] that the ground state of the anion is a singlet (in violation of Hund’s rule).

The present study investigates the electronic structure of the ground and lowest electronically excited states of 1,3,5-tridehydrobenzene. We report accurate equilibrium structures and frequencies, vertical and adiabatic excitation
energies, and analyze the bonding. The energy separations between states and their vibrational frequencies can aid in the interpretation of the photoelectron spectra of the 3,5-dehydrophenyl anion that will provide the experimental evidence of the electronic structure of 1,3,5-tridehydrobenzene.

4.2 Computational details

Equilibrium geometries and vibrational frequencies of the lowest electronically excited states of 1,3,5-tridehydrobenzene have been obtained by the CCSD(T) method. Adiabatic energy separations have been calculated by the CCSD, CCSD(T), SF-CIS(D), and SF-CCSD approaches. The SF-CCSD method has been used to calculate vertical excitation energies. Additional calculations have been performed by using the MCSCF and MCQDPT2 methods. Three basis sets with pure angular momentum polarization functions have been used: the 6-311G** basis [26], the cc-pVTZ basis [27] and a mixed basis set (cc-pVTZ on carbon and cc-pVDZ [27] on hydrogen). To calculate the equilibrium geometries of the 1,3,5-tridehydrobenzene anion, the SF-DFT method [28] and the basis set with diffuse functions, 6-311++G** [26, 29], have been used.
To estimate basis set effects, we have also used an extrapolation technique based on an energy separability scheme:

\[
E_{SF-CCSD}^{\text{large}} = E_{SF-CCSD}^{\text{small}} + (E_{SF-CIS(D)}^{\text{large}}) - E_{SF-CIS(D)}^{\text{small}}, \quad (4.1)
\]

where \( E_{\text{large}} \) and \( E_{\text{small}} \) are the total energies calculated in relatively large (e.g., cc-pVTZ) and small (e.g., 6-311G**) basis sets. This procedure assumes that the changes in the total energy due to the basis set increase are similar for the less and more correlated models [e.g., MP2 and CCSD, or SF-CIS(D) and SF-CCSD].

### 4.3 Results and discussion

Molecular orbitals of 1,3,5-tridehydrobenzene at \( D_{3h} \) geometry are shown in Fig. 4.1 (\( C_{2v} \) labels are used). The \( \pi \)-system of the molecule is as in benzene: it consists of three doubly occupied bonding orbitals and three virtual antibonding orbitals. Three \( sp^2 \) hybridized orbitals from the carbons that lost their hydrogens form three molecular orbitals of a \( \sigma \)-type (these are the \( \phi_1, \phi_2, \) and \( \phi_3 \) triradical orbitals of Figs. 1.3 and 1.4). Two of them, \( 11a_1 \) and \( 7b_2 \) (\( \phi_2 \) and \( \phi_3 \)), are exactly degenerate at the \( D_{3h} \) geometry (these are the two \( e' \) orbitals). The \( 10a_1 \) orbital (\( \phi_1 \)) is slightly lower in energy. Energetically, three \( \sigma \)-orbitals are located between the bonding and anti-bonding \( \pi \)-orbitals. It is
not obvious how three electrons will be distributed in these three $\sigma$-orbitals. If all three orbitals were exactly degenerate, the ground state of the molecule would be a quartet $^4B_2$ state as dictated by Hund’s rule. If, however, the energy gap between the $10a_1$ and the degenerate $11a_1/7b_2$ pair were large enough, the ground state would be a doublet state with a doubly occupied $10a_1$ orbital and a singly occupied $11a_1$ or $7b_2$ orbital. In 1,3,5-tridehydrobenzene, one-electron considerations win, and the doublets are lower in energy than the quartet both vertically and adiabatically.

The $^4B_2$ quartet state prefers the $D_{3h}$ geometry (the appropriate symmetry label is $^4A_1'$), with the distances between the radical centers being equal. At its equilibrium geometry, the two doublet states, $^2B_2$ and $^2A_1$, are degenerate. By the Jahn-Teller theorem [30], this degeneracy can be lifted at lower symmetry. The shape of the $11a_1$ and $7b_2$ orbitals (see Fig. 4.1), immediately suggests that the $^2A_1$ doublet will favor a structure with a shorter distance between the two upper dehydro-carbons. This structure is similar to the structure of m-benzyne in its ground singlet $^1A_1$ state, in agreement with the recent study of Wenthold et al. [20]. The optimized structure (under $C_{2v}$ constraint) of the second doublet, $^2B_2$, is less tight and squeezed in a perpendicular direction. This is not a
Figure 4.1. Molecular orbitals of 1,3,5-tridehydrobenzene at the $D_{3h}$ symmetry. $C_{2v}$ labels are used. The $\pi$-system is as in benzene: orbitals $1a_2$ and $2b_1$, and $2a_2$ and $3b_1$ are degenerate. The $\sigma$-system consists of three molecular orbitals, two of them ($11a_1$ and $7b_2$) are exactly degenerate.
real minimum but a transition state which connects equivalent minima corresponding to the $^2A_1$ doublet state. The $\pi$-system holds the molecule planar and is responsible for the very small amplitudes of the Jahn-Teller distortions. The diagram explaining the energy changes along the two Jahn-Teller distortions is given in Fig. 4.2.

At $D_{3h}$ structures, the $10a_1$ orbital and the degenerate $11a_1/7b_2$ pair are very close in energy. Subsequently, the wave functions of the both doublets are heavily multiconfigurational. However, at both $C_{2v}$ equilibrium geometries ($^2A_1$ and $^2B_2$), the orbitals are relatively well separated in energy. Therefore, at their equilibrium geometries, all the three lowest states are well described by the single-reference CCSD(T) method. Optimized geometries of the $^2A_1$, $^2B_2$, and $^4B_2$ states are shown in Fig. 4.3.

The 3,5-dehydrophenyl (1,3,5-tridehydrobenzene) anion ($C_6H_3^-$) which was synthesized and studied [25] would be a precursor of $C_6H_3$ in a photoelectron experiment [32]. As it follows from the MO picture, the anion is a diradical. Indeed, in the lowest electronic states of $C_6H_3^-$, the $10a_1$ $\sigma$-orbital is doubly occupied, while two other electrons are distributed in the $11a_1$ and $7b_2$ $\sigma$-orbitals.

1. In a system with a three-fold axis the potential surface of the Jahn-Teller distortions consists of three equivalent minima and three transition states connecting them [31]. Pseudorotation between each pair of the equivalent minima proceeds through one of the equivalent transition states, and vice versa.

2. This is different from, for example, trimethylenemethane, where the open-shell singlet $^1B_2$ undergoes a second-order Jahn-Teller distortion by rotating one of the methylene groups and disrupting the conjugated $\pi$-system of the molecule.
Figure 4.2. Jahn-Teller distortions in 1,3,5-tridehydrobenzene (C₆H₃, upper panel) and in the 1,3,5-tridehydrobenzene anion (C₆H₃⁻, lower panel). The ⁴B₂ (⁴A′₂) quartet state of C₆H₃ has D₃h structure for which the ²A₁ and ²B₂ doublets are exactly degenerate. The degeneracy between the doublets can be lifted at lower symmetry. The ²A₁ state is a real minimum, while the ²B₂ doublet is a transition state. The triplet ³B₂ (³A′₂) state of the 1,3,5-tridehydrobenzene anion is of D₃h symmetry. At this geometry, the open- and closed shell singlets are exactly degenerate and can undergo in the Jahn-Teller distortions. The lowest singlet ¹A₁ state has C₂ᵥ structure.
Figure 4.3. Optimized geometries of the $^4B_2$, $^2A_1$, and $^2B_2$ states of $C_6H_3$ (at the CCSD(T)/cc-pVTZ and CCSD(T)/6-311G** levels) and of the $^3B_2$ and $^1A_1$ state of $C_6H^-$ (at the SF-DFT/6-311++G** level). Bond lengths are in angstroms, angles — in degrees, and nuclear repulsion energies — in hartrees.

Hund’s rule predicts the ground state of the anion to be a triplet. However, the reactivity of the anion gives indirect evidence that its ground state is a singlet state, although the triplet ground state could not be ruled out [25]. As in case of the quartet state in $C_6H_3$, the triplet $^3B_2$ ($^3A'_2$) state of $C_6H^-$ prefers $D_{3h}$ geometry. We found that, in accordance with Hund’s rule, at this geometry the singlet states are higher in energy (see Fig. 4.2) [33]. The degeneracy between the closed- and open-shell singlets result in the Jahn-Teller distortions that
lift the symmetry of both singlets. While the open-shell singlet \(^1B_2\) is, most likely, a transition state, the closed-shell \(^1A_1\) singlet is a real minimum. Its structure of \(C_{2v}\) symmetry is similar to the structure of the \(^1^2A_1\) doublet state of the neutral. The equilibrium geometries of the \(^3B_2\) and \(^1A_1\) anion’s states are shown in Fig. 4.3. Our preliminary calculations [33] show that adiabatically the \(^3B_2\) and \(^1A_1\) states are very close in energy\(^3\).

### 4.3.1 Vertical and adiabatic excitation energies

Since determining vertical energy separations from photoelectron spectra is straightforward, the availability of calculated vertical excitation energies at the anion geometry is useful in the experimental design and interpretation. We present the vertical excitation energies from both singlet \(^1A_1\) and triplet \(^3B_2\) anion’s equilibrium geometries (Table 4.1), because the adiabatic energy gap between the singlet and triplet states of the anion is very small. At the \(D_{3h}\) geometry of the \(^3B_2\) (\(^3A'_2\)) state of \(C_6H_3^-\), there are three pairs of degenerate orbitals: two pairs of \(\pi\)-orbitals (\(1a_2/2b_1\) and \(2a_2/3b_1\)), and the \(11a_1/7b_2\) orbitals. Therefore, the \(^1^2A_1\) and \(^1^2B_2\) doublets (\(^2E'\) at \(D_{3h}\)) are degenerate. These two doublets correspond to the configurations \((e)\) and \((g)\) in Fig. 1.4.

At the SF-CCSD level in a mixed cc-pVTZ/cc-pVDZ basis (see Sec. 4.2), the

\(^3\)The singlet-triplet adiabatic energy separation is less than 1 kcal/mol on the SF-DFT/6-311++G** level, the singlet state being lower in energy.
Table 4.1. Vertical excitation energies (eV) of 1,3,5-tridehydrobenzene calculated at the equilibrium geometries of the $^3B_2$ and $^1A_1$ states of the 3,5-dehydrophenyl anion$^a$

<table>
<thead>
<tr>
<th>State Type</th>
<th>From $^3B_2$ geom. $^c$</th>
<th>From $^1A_1$ geom. $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^2A_1$ $\sigma \rightarrow \sigma$ (allowed, allowed)</td>
<td>-229.77026</td>
<td>-229.76228$^d$</td>
</tr>
<tr>
<td>$1^2B_2$ $\sigma \rightarrow \sigma$ (allowed, forbidden)</td>
<td>0.000</td>
<td>1.987</td>
</tr>
<tr>
<td>$1^4B_2$ $\sigma \rightarrow \sigma$ (allowed, forbidden)</td>
<td>0.808</td>
<td>2.358</td>
</tr>
<tr>
<td>$1^4B_1$ $\pi \rightarrow \sigma$ (allowed, forbidden)</td>
<td>2.324</td>
<td>3.560</td>
</tr>
<tr>
<td>$1^4A_2$ $\pi \rightarrow \sigma$ (allowed, forbidden)</td>
<td>2.324</td>
<td>3.733</td>
</tr>
<tr>
<td>$2^4A_2$ $\pi \rightarrow \sigma$ (allowed, forbidden)</td>
<td>3.922</td>
<td>7.492</td>
</tr>
<tr>
<td>$2^2A_1$ $\sigma \rightarrow \sigma$ (forbidden, allowed)</td>
<td>4.267</td>
<td>3.098</td>
</tr>
<tr>
<td>$2^2B_2$ $\sigma \rightarrow \sigma$ (forbidden, forbidden)</td>
<td>4.267</td>
<td>5.983</td>
</tr>
<tr>
<td>$1^6B_2$ $\pi \rightarrow \pi$ (forbidden, forbidden)</td>
<td>4.386</td>
<td>5.853</td>
</tr>
<tr>
<td>$1^6A_1$ $\pi \rightarrow \pi$ (forbidden, forbidden)</td>
<td>5.313</td>
<td>6.311</td>
</tr>
<tr>
<td>$2^6B_2$ $\pi \rightarrow \pi$ (forbidden, forbidden)</td>
<td>5.313</td>
<td>6.989</td>
</tr>
<tr>
<td>$3^2A_1$ $\sigma \rightarrow \sigma$ (forbidden, forbidden)</td>
<td>5.291</td>
<td>8.066</td>
</tr>
<tr>
<td>$3^2B_2$ $\sigma \rightarrow \sigma$ (forbidden, allowed)</td>
<td>6.069</td>
<td>7.232</td>
</tr>
<tr>
<td>$2^6A_1$ $\pi \rightarrow \pi$ (forbidden, forbidden)</td>
<td>6.467</td>
<td>8.420</td>
</tr>
</tbody>
</table>

$^a$ Vertical excitation energies are calculated by the SF-CCSD method in the mixed (cc-pVTZ on carbon and cc-pVDZ on hydrogen) basis set.

$b$ In parenthesis, it is shown whether a state is accessible through a one-electron transition from the triplet and the singlet states of the anion, respectively.

$c$ The equilibrium geometries of the anion are used (see Fig. 4.3).

$d$ This energy is 0.217 eV higher than the $1^2A_1$ state energy at the triplet anion geometry.

quartet $1^4B_2$ state is 0.8 eV higher in energy than the doublets. We used a high-spin component of this quartet as the SF-reference.

The next two degenerate states, the $1^4A_2$ and $1^4B_1$ quartets, are derived from the excitation of an electron from the $2b_1$ or $1a_2$ $\pi$-orbital to the $10a_1$ orbital (see Fig. 4.1). These degenerate states can also undergo Jahn-Teller distortions. These quartets lie approximately 2.3 eV above the doublets. The relatively low excitation energies of these states indicate a strong interaction between the $\pi$-
and $\sigma$-systems in 1,3,5-tridehydrobenzene. These quartets, as well as other states that include electron excitations between the $\pi$- and $\sigma$-orbitals, do not belong to the triradical states, i.e., states derived by distributing three electrons between three energetically close orbitals ($10a_1$, $11a_1$, and $7b_2$). As explained in Sec. 1.4, triradical states are well described by the SF approach. However, states derived by excitations out of the subspace of the three triradical orbitals are treated by the SF methods in a less balanced way. For example, the wave function for the $1^4A_2$ quartet consists of three determinants [similar to state (b) from Fig. 1.4]:

$$\Psi_{1A_2} \sim 2b_111a_17b_2|\alpha\alpha\beta\rangle + 2b_111a_17b_2|\alpha\beta\alpha\rangle + 2b_111a_17b_2|\beta\alpha\alpha\rangle$$  \hspace{1cm} (4.2)

One of these determinants, $11a_12b_17b_2|\beta\alpha\alpha\rangle$, is a single spin-flip excitation from the $10a_111a_17b_2|\alpha\alpha\alpha\rangle$ reference. However, two other determinants are doubly excited configurations with respect to the reference. Therefore, the SF description of this state is not well balanced, which is reflected in the spin contamination of the wave function$^4$. To understand how accurately these states are described by SF, we performed additional calculations (at a slightly different $D_{3h}$ geometry). Table 4.2 compares the SF-CCSD vertical excitation energies against those

$^4$This is similar to some excited states in radicals [34]. Despite this, EOM-CCSD treats such states accurately.
Table 4.2. Vertical excitation energies (eV)

<table>
<thead>
<tr>
<th>Method/basis</th>
<th>$1^2A_1/1^2B_2$</th>
<th>$1^4B_2$</th>
<th>$1^4B_1/1^4A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF/6-311G**</td>
<td>-228.851857</td>
<td>0.726</td>
<td>2.281</td>
</tr>
<tr>
<td>MCQPPT2/6-311G**</td>
<td>-229.575314</td>
<td>0.719</td>
<td>2.055</td>
</tr>
<tr>
<td>SF-CCSD/6-311G**</td>
<td>-229.679943</td>
<td>0.726</td>
<td>2.155</td>
</tr>
</tbody>
</table>

$^a$ Calculated at the $D_{3h}$ geometry.

calculated by the MCSCF and MCQPPT2 methods. As seen from Table 4.2, the SF-CCSD results are in excellent agreement with the MCQPPT2 ones both for the $1^2A_1/1^2B_2 - 1^4B_2$ transition (all these are the triradical states which are well described by SF) and for the $1^2A_1/1^2B_2 - 1^4B_1/1^4A_2$ transition (the $1^4B_1/1^4A_2$ states are spin-contaminated at the SF-CCSD level).

The next state in Table 4.1, $2^4A_2$, also involves $\pi - \sigma$ excitations. In the dominant configuration of this state, the $1b_1$, $11a_1$, and $7b_2$ orbitals are singly occupied, while the $2b_1$, $1a_2$, and $10a_1$ orbitals are doubly occupied. However, two configurations with orbitals $2b_1$, $10a_1$, and $7b_2$ or $1a_2$, $10a_1$, and $11a_1$ being singly occupied, have large coefficients. The next two states are a degenerate pair of the $2^2A_1$ and $2^2B_2$ doublets [(i) and (d) states from Fig. 1.4]. These states are similar to the closed- and open-shell singlets in diradical systems. They are degenerate at $D_{3h}$ geometries because of the exact degeneracy between the $11a_1$ and $7b_2$ orbitals (similar to the $1^1A_1$ and $1^1B_2$ states of TMM [35]). Four sextet

$^5$The active space includes all orbitals and electrons shown in Fig. 3, i.e., six $\pi$-orbitals and three $\sigma$-orbitals, and nine electrons ($9\times9$). Root averaging was used to calculate the degenerate states.
states, $1^6A_1$, $2^6A_1$, $1^6B_2$, and $2^6B_2$, two of them exactly degenerate, are derived from excitations from the $2b_1$ or $1a_2$ to the $3b_1$ or $2a_2$ $\pi$-orbitals. In this energy region, there are several other states derived from excitations between $\sigma$ and $\pi$ systems (not shown in Table 4.1). The counterpart of the $2^2A_1$ state (i) is the closed-shell doublet $3^2A_1$ (j) at 5.3 eV. The open-shell doublet $3^2B_2$ of type (c) lies at approximately 6.1 eV.

At the equilibrium geometry of the $1A_1$ anion’s state the energy of the $1^2A_1$ state of C$_6$H$_3$ is approximately 0.2 eV higher than its energy at the triplet anion’s geometry. The strongly distorted geometry of the anion’s singlet state leads to large energy splittings between the states that are degenerate at $D_{3h}$ symmetry. Thus, the $1^2B_2$ doublet state (which is degenerate with the $1^2A_1$ doublet at $D_{3h}$ geometry) lies about 2 eV higher in energy. The $1^4B_2$ quartet state is 2.4 eV higher in energy. Relative to the $D_{3h}$ geometry, the excitation energy of the closed shell doublet of type (i) in Fig. 1.4, $2^2A_1$, becomes lower, while the energy of its counterpart, the $2^2B_2$ doublet of type (j), rises.

The adiabatic energy separations between the ground $^2A_1$ and the excited $^2B_2$ and $^4B_2$ states are presented in Table 4.3. All adiabatic energies are calculated at the CCSD(T)/cc-pVTZ equilibrium geometries, except for the CCSD/6-311G** and CCSD(T)/6-311G** values which are calculated at the CCSD(T)/6-311G** geometries. The zero point energies (ZPE) are calculated
Table 4.3. Total energies (hartree) for the ground \( ^2A_1 \) state and adiabatic excitation energies (eV) for the low-lying excited states\(^a\)

<table>
<thead>
<tr>
<th>Method/basis</th>
<th>( ^2A_1 )</th>
<th>( ^2B_2 )</th>
<th>( ^4B_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD/6-311G**(^b)</td>
<td>-229.691737</td>
<td>-0.039</td>
<td>0.757</td>
</tr>
<tr>
<td>CCSD(T)/6-311G**(^b)</td>
<td>-229.748061</td>
<td>0.203</td>
<td>1.256</td>
</tr>
<tr>
<td>SF-CIS(D)/6-311G**</td>
<td>-229.602587</td>
<td>0.104</td>
<td>1.010</td>
</tr>
<tr>
<td>SF-CCSD/6-311G**</td>
<td>-229.695974</td>
<td>0.065</td>
<td>1.086</td>
</tr>
<tr>
<td>SF-CIS(D)/mixed(^c)</td>
<td>-229.699820</td>
<td>0.122</td>
<td>1.124</td>
</tr>
<tr>
<td>SF-CCSD/mixed(^c)</td>
<td>-229.793207</td>
<td>0.082</td>
<td>1.200</td>
</tr>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>-229.798697</td>
<td>0.018</td>
<td>0.885</td>
</tr>
<tr>
<td>CCSD(T)/cc-pVTZ</td>
<td>-229.864320</td>
<td>0.223</td>
<td>1.375</td>
</tr>
<tr>
<td>SF-CIS(D)/cc-pVTZ</td>
<td>-229.718160</td>
<td>0.122</td>
<td>1.117</td>
</tr>
<tr>
<td>SF-CCSD/cc-pVTZ(^d)</td>
<td>-229.793207</td>
<td>0.082</td>
<td>1.193</td>
</tr>
<tr>
<td>SF-CCSD/cc-pVTZ(^e)</td>
<td>-229.811547</td>
<td>0.082</td>
<td>1.193</td>
</tr>
<tr>
<td>( \Delta ZPE )(^f)</td>
<td>-0.021</td>
<td>0.010</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) All values are calculated at the CCSD(T)/cc-pVTZ optimized geometries (see Fig. 4.3), except when specified otherwise.

\(^b\) Calculated at the CCSD(T)/6-311G** optimized geometries.

\(^c\) Mixed basis set: cc-pVTZ on carbon and cc-pVDZ on hydrogen.

\(^d\) Determined by using Eq. (4.1) from the 6-311G** and cc-pVTZ bases.

\(^e\) Determined by using Eq. (4.1) from the mixed (cc-pVTZ on carbon and cc-pVDZ on hydrogen) and cc-pVTZ bases.

\(^f\) Calculated at the CCSD(T)/6-311G** level.

At the CCSD(T)/6-311G** level. At the highest level of theory, CCSD(T)/cc-pVTZ, the energy gap between the \( ^2A_1 \) and \( ^2B_2 \) doublets is 0.223 eV (5.14 kcal/mol) and the splitting between the \( ^2A_1 \) doublet and the \( ^4B_2 \) quartet is 1.375 eV (31.71 kcal/mol). The SF-CCSD energy separations in the mixed basis set are 0.082 eV (1.89 kcal/mol) and 1.200 eV (27.67 kcal/mol) for the \( ^2A_1 \) – \( ^2B_2 \) and \( ^2A_1 \) – \( ^4B_2 \) transitions, respectively. Applying Eq. (4.1), we have obtained similar results for the SF-CCSD/cc-pVTZ splittings: 0.082 eV and
1.193 eV. The SF-CIS(D) results are very close to the SF-CCSD ones: the discrepancy is less than 2 kcal/mol. The SF-CCSD values differ from the CCSD(T) ones by no more than 4 kcal/mol. The SF-CCSD energy separations between states are much closer to the CCSD(T) ones than the CCSD results are. We have observed the similar behavior of the SF methods in the methylene example (see Section 2.3.2).

4.3.2 Structures and vibrational frequencies of the $1^2A_1$, $1^2B_2$, and $1^4B_2$ states of $C_6H_3$

In the context of photoelectron spectroscopy, analyses of equilibrium properties of anion and neutral states are extremely important. This section discusses the structures and vibrational frequencies of the lowest electronic states of $C_6H_3$, while a detailed analysis of anion’s properties will be reported elsewhere.

Fig. 4.4 compares the structures of the lowest 1,3,5-tridehydrobenzene states with the structures of two m-benzyne’s states [35] and the benzene ground state [36]. As structural characteristics, we choose the C$_1$-C$_3$ and C$_1$-C$_5$ diagonal lengths (carbons 1, 3, and 5 are radical centers in 1,3,5-tridehydrobenzene, carbons 1 and 3 are radical centers in m-benzene), as well as the C$_2$-C$_4$ and C$_2$-C$_6$ diagonal lengths (these carbons are connected to hydrogens in all the molecules). These distances are shown in Fig. 4.4. In benzene, all the C-C diagonals are equal. In both the quartet state of 1,3,5-tridehydrobenzene and the triplet state
Figure 4.4. Diagonal distances in the $^4B_2$, $^2A_1$, and $^2B_2$ states of 1,3,5-tridehydrobenzene and in the $^3B_2$ and $^1A_1$ states of m-benzyne as compared with the corresponding distances in benzene. Upper panel (a) shows distances between the radical centers. Lower panel (b) presents distances between non-radical carbons (i.e., those which are connected to hydrogens in all molecules) of m-benzyne the diagonal lengths are contracted relative to benzene. This indicates that there is some bonding between the same-spin radical centers. This is because removing a hydrogen results in an increase in electronic density in the central part of the molecule. This additional electronic density bonds
the radical centers even in the high-spin states. Overall, the structures of the high-spin states of m-C₆H₄ and C₆H₃ are very similar. Likewise, there is also a similarity between the ¹A₁ state of m-benzene and the ¹²A₁ state of C₆H₃. However, the C₁-C₃ diagonal in 1,3,5-tridehydrobenzene is slightly shorter than the corresponding length in m-benzyne, due to the interaction of the unpaired electron on the C₃ carbon of 1,3,5-tridehydrobenzene with the electron density on the C₁ and C₅ carbons⁶. As expected, the structure of the ¹²B₂ transition state has a long C₁-C₅ diagonal and two short C₁-C₃ and C₃-C₅ diagonals. The structure is less tight than the structure of the ground ¹²A₁ state. Most of the diagonal lengths between the non-radical carbons in 1,3,5-tridehydrobenzene and m-benzyne are longer than the ones in benzene. However, this increase is smaller than the contraction of the distances between the dehydro-carbons, i.e., the overall rigidity of the molecular structures increases relative to benzene.

Table 4.4 presents the vibrational frequencies of the three lowest electronic states of C₆H₃. The frequencies of the skeleton modes are compared with the corresponding benzene’s vibrations. As mentioned above, the ¹²B₂ state is a transition state with one imaginary frequency, ω₅. This mode connects the structure with one of the real minima. The real minimum on the potential surface, the ¹²A₁ state, is also less stable to ring deformations, which correspond

⁶This interaction is stronger than, for example, the interaction of a radical center with non-radical carbons in phenyl: the corresponding length in phenyl is 2.370 Å [18] which is about 0.09 Å longer than the length in the ²A₁ state of 1,3,5-tridehydrobenzene.
Table 4.4. Vibrational frequencies (cm\(^{-1}\)) of the 1\(^2\)A\(_1\), 1\(^2\)B\(_2\), and 1\(^4\)B\(_2\) states of 1,3,5-tridehydrobenzene\(^a\)

<table>
<thead>
<tr>
<th>Symm.(^b)</th>
<th>Type of mode</th>
<th>benzene(^c)</th>
<th>1(^4)B(_2)</th>
<th>1(^2)A(_1)</th>
<th>1(^2)B(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_1)</td>
<td>(a_2 (e''_1))</td>
<td>Ring deform (OPLA)</td>
<td>410 ((\omega_20))</td>
<td>322</td>
<td>506</td>
</tr>
<tr>
<td>(\omega_2)</td>
<td>(b_1 (e''_1))</td>
<td>Ring deform (OPLA)</td>
<td>410 ((\omega_20))</td>
<td>322</td>
<td>415</td>
</tr>
<tr>
<td>(\omega_3)</td>
<td>(a_1 (a''_2))</td>
<td>Ring deform (OPLA)</td>
<td>703 ((\omega_8))</td>
<td>576</td>
<td>482</td>
</tr>
<tr>
<td>(\omega_4)</td>
<td>(a_1 (e'))</td>
<td>Ring deform</td>
<td>606 ((\omega_{18}))</td>
<td>607</td>
<td>382</td>
</tr>
<tr>
<td>(\omega_5)</td>
<td>(b_2 (e'))</td>
<td>Ring deform</td>
<td>606 ((\omega_{18}))</td>
<td>607</td>
<td>444</td>
</tr>
<tr>
<td>(\omega_6)</td>
<td>(b_1 (a''_2))</td>
<td>CH bend (OPLA)</td>
<td>749</td>
<td>742</td>
<td>739</td>
</tr>
<tr>
<td>(\omega_7)</td>
<td>(a_2 (e'_1))</td>
<td>CH bend (OPLA)</td>
<td>791</td>
<td>801</td>
<td>778</td>
</tr>
<tr>
<td>(\omega_8)</td>
<td>(b_1 (e''_1))</td>
<td>CH bend (OPLA)</td>
<td>791</td>
<td>803</td>
<td>827</td>
</tr>
<tr>
<td>(\omega_9)</td>
<td>(a_1 (a'_1))</td>
<td>Ring deform</td>
<td>1010 ((\omega_6))</td>
<td>965</td>
<td>798</td>
</tr>
<tr>
<td>(\omega_{10})</td>
<td>(a_1 (a'_1))</td>
<td>Ring str</td>
<td>992 ((\omega_2))</td>
<td>1028</td>
<td>1085</td>
</tr>
<tr>
<td>(\omega_{11})</td>
<td>(a_1 (e'))</td>
<td>Ring str+deform</td>
<td>1486 ((\omega_{13}))</td>
<td>1054</td>
<td>1068</td>
</tr>
<tr>
<td>(\omega_{12})</td>
<td>(b_2 (e'))</td>
<td>Ring str+deform</td>
<td>1486 ((\omega_{13}))</td>
<td>1054</td>
<td>991</td>
</tr>
<tr>
<td>(\omega_{13})</td>
<td>(b_2 (a'_2))</td>
<td>Ring str</td>
<td>1310 ((\omega_9))</td>
<td>1195</td>
<td>1225</td>
</tr>
<tr>
<td>(\omega_{14})</td>
<td>(b_2 (a'_2))</td>
<td>CH bend</td>
<td>1230</td>
<td>1208</td>
<td>1232</td>
</tr>
<tr>
<td>(\omega_{15})</td>
<td>(a_1 (e'))</td>
<td>CH bend</td>
<td>1361</td>
<td>1350</td>
<td>1281</td>
</tr>
<tr>
<td>(\omega_{16})</td>
<td>(b_2 (e'))</td>
<td>CH bend</td>
<td>1361</td>
<td>1323</td>
<td>1379</td>
</tr>
<tr>
<td>(\omega_{17})</td>
<td>(a_1 (e'))</td>
<td>Ring str</td>
<td>1596 ((\omega_{16}))</td>
<td>1569</td>
<td>1710</td>
</tr>
<tr>
<td>(\omega_{18})</td>
<td>(b_2 (e'))</td>
<td>Ring str</td>
<td>1596 ((\omega_{16}))</td>
<td>1569</td>
<td>1516</td>
</tr>
<tr>
<td>(\omega_{19})</td>
<td>(a_1 (e'))</td>
<td>CH str</td>
<td>3199</td>
<td>3231</td>
<td>3253</td>
</tr>
<tr>
<td>(\omega_{20})</td>
<td>(b_2 (e'))</td>
<td>CH str</td>
<td>3189</td>
<td>3230</td>
<td>3252</td>
</tr>
<tr>
<td>(\omega_{21})</td>
<td>(a_1 (a'_1))</td>
<td>CH str</td>
<td>3191</td>
<td>3248</td>
<td>3216</td>
</tr>
</tbody>
</table>

\(^a\) All \(C_6H_3\) frequencies are calculated at the CCSD(T)/6-311++G** level at the CCSD(T)/6-311++G** optimized geometries (see Fig. 4.3).

\(^b\) Symmetry labels are given in \(C_2\) and \(D_{3h}\) (in parentheses) symmetry groups.

\(^c\) Ref. [37], description of the benzene’s modes is given in Ref. [38].

to the pseudorotations (modes \(\omega_4 - \omega_5\)) relative to the undistorted quartet 1\(^4\)B\(_2\) state of \(C_6H_3\) and benzene. Due to \(\pi\)-system destabilization, lowering of the high-order symmetry of benzene makes the \(C_6H_3\) structures less stable with respect to other ring deformations (e.g., modes \(\omega_9\) and \(\omega_{11} - \omega_{12}\)). Moreover, the out-of-plane (OPLA) ring deformation frequencies (\(\omega_1 - \omega_3\)) of all the three
states of C₆H₃ are lower than in benzene. The decrease is due to the weaker conjugation of the π-system in the distorted (relative to benzene) structures of C₆H₃. Some ring stretching frequencies, however, do not significantly change or even become higher in C₆H₃ (e.g., the symmetric breathing mode ω₁₀ and ω₁₇−ω₁₈ modes). The behavior of these modes is consistent with the structural changes in the different C₆H₃ states discussed above.

4.4 Conclusions

The electronic structure of the 1,3,5-tridehydrobenzene triradical has been characterized by the SF and CCSD(T) methods. We find that the ground state of the molecule is the Jahn-Teller distorted doublet ²A₁ that has a C₂ᵥ structure similar to the geometry of m-benzyne. The second doublet state, ²B₂, which lies only 0.1-0.2 eV higher in energy is a transition state with one imaginary frequency. The 4A′₂ quartet state has D₃h symmetry and is 1.2-1.4 eV higher in energy. The analysis of the equilibrium properties of these states should be useful in planning and interpreting photoelectron experiments.
Reference List


[38] G. Herzberg, Molecular spectra and molecular structure; Infrared and Raman spectra of polyatomic molecules, volume III. van Nostrand Reinhold: New York, 1945.
Chapter 5

Electronic structure of the
dehydro-meta-xylylene (DMX) triradical

5.1 Introduction

5-dehydro-1,3-quinodimethane (5-dehydro-m-xylylene, DMX, Fig. 5.1), is a hydrocarbon with an unprecedented electronic ground state of three low-spin coupled unpaired electrons, i.e. an "open-shell doublet." Although low-spin open-shell states occur in molecules containing transition metals, the ground states of organic molecules are rarely of this type. Open-shell singlet ground state organic diradicals have been reported [1], however, DMX is the first example of an organic triradical with an open-shell doublet ground state.

Qualitatively, the preference for the open-shell doublet ground state in DMX can be understood by considering the electronic structure of m-xylylene (MX)
Figure 5.1. Molecular orbitals of the MX and DHT diradicals and of the DMX triradical and α,3-dehydrotoluene (DHT). The MX diradical has a triplet ground state \[5, 1\].

To determine the ground electronic state of a polyradical molecule with noninteracting radical centers, one can employ several qualitative models of a common origin. From the molecular orbital point of view, the most important consideration is whether the electronic densities of the orbitals that host unpaired electrons overlap. If the densities overlap, Hund’s rule would favor the high-spin coupling. Consequently, non-overlapping orbitals strongly suggest the low-spin ground state \[2\], because the opposite-spin coupling can be stabilized by interactions with low-lying molecular orbitals. The classic example is the cyclobutadiene diradical, which has the singlet ground state \[3\]. Although such cases are often referred to as violations of Hund’s rule, rigorously speaking, this is misleading because Hund’s rule (which is based on the Pauli exclusion principle) applies only to overlapping electronic density.

Another approach, known as the local Hund’s rule or the spin-polarization method, is often used to predict the ground state multiplicity. It does not require a priori knowledge of the shapes of the molecular orbitals. This model consists of two postulates: (i) each bond is formed by an \(\alpha - \beta\) electron pair; (ii) all electrons localized on one atom have the same spin orientation (due to local Hund’s rule). One can apply these two simple rules to predict (with an impressive success!) the multiplicity of any polyradical molecule with noninteracting radical centers. Note, however, that spin-polarization fails to predict ground state of \(\text{C}_6\text{H}_3\) isomers. For \(\pi\)-type polyradical hydrocarbons, spin-polarization approach is equivalent to the \((n^* - n)/2\) rule \[4\], where \(n^*\) stays for alternant (starred) and \(n\) — for nonalternant (nonstarred) carbons. In most situations, both molecular orbital and spin-polarization considerations yield identical results.
with two ferromagnetically coupled electrons in two $\pi$ molecular orbitals (Fig. 5.1). DHT, which is also shown in Fig. 5.1, is a $\sigma - \pi$ diradical with singlet-coupled unpaired electrons, as predicted by spin polarization. [7, 8] The features responsible for the MX and DHT ground state multiplicities are also present in DMX. The $\pi$-system is similar to that of MX, such that it should contain two ferromagnetically coupled electrons. Likewise, the interaction between the $\sigma$ and $\pi$ systems resembles that in DHT, and should therefore have a preference for anti-ferromagnetic coupling. The net result is a hydrocarbon with a $\sigma^1\pi^1\pi^1$ open-shell doublet ground state configuration.

More rigorously, the electronic structure of triradicals is described by 3-electrons-in-3-orbitals model (see Fig. 1.3). Different occupations of three nearly-degenerate triradical orbitals result in one quartet and eight doublet low-lying states shown in Fig. 1.4. The 8 lowest energy electronic states of DMX are shown in Fig. 5.2. Orbital near-degeneracies in the triradical result in multi-configurational wave functions for most of the low-lying electronic states, which greatly complicates electronic structure calculations. Fortunately, the recently introduced spin-flip (SF) approach, [9, 10], which describes the target electronic states as spin-flipping excitations from a high-spin reference state, is well-suited for these calculations. Unlike low-spin states, the high-spin states are not affected by orbital degeneracies and can be accurately described by a single-reference method. In the case of triradicals we employ the high-spin
Figure 5.2. Vertical excitation energies of DMX triradical calculated at the ROHF-SF-CCSD/6-311G** level at the SF-DFT/6-311G** optimized geometry of the ground $X^2B_2$ state

component of the quartet state as a reference and describe the doublets and the low-spin component of the quartet as "excited" states in the space of the single spin-flipping excitations [11]. The multi-state nature of the SF approach allows us to calculate an entire manifold of low-lying electronic states of DMX.
5.2 Computational details

Most of the results presented in this Chapter are obtained by the EOM-SF-CCSD model. Additional data were obtained by SF-CIS(D) and by SF-OD. Equilibrium geometries of the lowest states of DMX were optimized by the SF-DFT method in the 6-31G* [12] and 6-311G** [13] bases. In order to calculate thermochemical data, the CCSD(T) method in a mixed cc-pVTZ/cc-pVDZ [14] basis was used. In addition, we employed MCSCF and MRQDPT2.

5.3 Results and discussion

In agreement with the qualitative spin-polarization-based predictions, the ground state of DMX is the open-shell doublet $1^2B_2$ state (Fig. 5.2). The counterpart of the $1^2B_2$ state, the $1^4B_2$ quartet, is 0.16 eV higher in energy. Equilibrium geometries of these two states are similar (see Fig. 5.3). Interestingly, the $1^2B_1$ state that results from sequential electron addition (the aufbau principle) is more than 2 eV higher in energy than the open-shell $1^2B_2$, because it leads to the electron transfer between spatially separated $\pi$ and $\sigma$ systems.

Similar considerations explain the high excitation energy of the $2^2A_1$ state. The

---

2 The optimized SF-DFT geometries are not minima on the SF-CCSD and SF-OD potential surfaces. However, the equilibrium geometries of the doublet and quartet states are very close and the differences between the adiabatic and vertical energy gaps are very small, e.g., at the SF-DFT level, they are 0.004-0.005 eV.
lowest energy closed-shell type doublet (i.e., doublet with one of the triradical orbitals being occupied by a pair of electrons) is the 1^2A_1 state, which resembles the lowest energy singlet in MX.

Figure 5.3. Equilibrium geometries of the three lowest electronic states of DMX. The optimized geometries are not very sensitive to the basis set size. The changes in the bondlengths do not exceed the thousandths of angstrom. As expected, the structures of the covalent 1^2B_2 and 1^4B_2 states are very similar, whereas the equilibrium geometry of the ionic 1^2A_1 state is different.
Table 5.1. The total energies (hartrees) of the ground $1^2B_2$ state and the vertical excitation energies (eV) of the $1^4B_2$ state

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref. orbitals</th>
<th>$1^2B_2$</th>
<th>$1^4B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF-DFT</td>
<td>UDFT</td>
<td>-308.720103</td>
<td>0.159</td>
</tr>
<tr>
<td>SF-CIS(D)</td>
<td>ROHF</td>
<td>-307.835213</td>
<td>-0.258</td>
</tr>
<tr>
<td></td>
<td>UHF</td>
<td>-308.121012</td>
<td>1.189</td>
</tr>
<tr>
<td>SF-CCSD</td>
<td>UHF</td>
<td>-308.213445</td>
<td>0.503</td>
</tr>
<tr>
<td></td>
<td>B3LYP</td>
<td>-308.207660</td>
<td>0.244</td>
</tr>
<tr>
<td></td>
<td>ROHF</td>
<td>-308.209668</td>
<td>0.164</td>
</tr>
<tr>
<td>SF-OD</td>
<td></td>
<td>-308.209981</td>
<td>0.315</td>
</tr>
<tr>
<td>MCSCF(3×3)</td>
<td></td>
<td>-306.934693</td>
<td>-0.034</td>
</tr>
<tr>
<td>MRPT(3×3)</td>
<td>MCSCF(3×3)</td>
<td>-308.010216</td>
<td>0.012</td>
</tr>
<tr>
<td>MCSCF(9×9)</td>
<td></td>
<td>-307.035684</td>
<td>0.154</td>
</tr>
<tr>
<td>MRPT(9×9)</td>
<td>MCSCF(9×9)</td>
<td>-308.031112</td>
<td>0.099</td>
</tr>
</tbody>
</table>

* Calculated at the SF-DFT/6-311G* equilibrium geometry, see Fig. 5.3, in 6-311G** basis.

5.3.1 Accurate evaluation of the doublet-quartet energy gap

The doublet-quartet energy gap determines the reactivity of the molecule and reflects the strength of $\sigma - \pi$ interaction. The accurate description of $\sigma - \pi$ interaction is challenging because the stabilization of the low-spin state occurs primarily due to electron correlation effects, which should be treated at a high level of *ab initio* theory. Table 5.1 presents the vertical energy differences between the two lowest electronic states of DMX, the $1^2B_2$ doublet and the $1^4B_2$ quartet, calculated by different methods.
As expected, the low-level treatment, e.g., MCSCF with the minimal $3 \times 3$ active space, yields incorrect state ordering since it fails to describe the stabilization of the doublet state due to interaction between the triradical orbitals with benzene $\pi$-system. Increasing the active space and including the correlation effects by perturbation theory improve the results, placing the doublet below the quartet by 0.10-0.15 eV (2.3-3.4 kcal/mol). However, due to the limitations of PT, these results are not fully converged. More accurate description of this molecule would involve MR-CI with a reasonably large active space that includes at least some $\sigma$-orbitals, which are important for the doublet state stabilization. We were not able to perform such calculations with the available software.

For this system, EOM-SF-CCSD is very sensitive to the choice of reference orbitals. For example, the vertical doublet-quartet energy gap varies from 0.50 eV for the EOM-SF-CCSD that employs the UHF reference up to 0.16 eV for its ROHF based counterpart. The corresponding EOM-SF-OD value is 0.31 eV, which is in between the UHF and ROHF based EOM-SF-CCSD results. We also employed the B3LYP [15] reference orbitals, which were shown to be useful in describing symmetry breaking in radicals [16]. The B3LYP based SF-CCSD doublet-quartet gap is 0.24 eV, which is close to the ROHF-SF-CCSD value. Usually, the discrepancy between the SF-CCSD and SF-OD methods does not exceed thousandths of eV, whereas in case of DMX it is about hundred times
larger! The origin of this phenomenon is in spin-contamination of the reference and the EOM target states. For example, in the series ROHF-SF-CCSD → B3LYP-SF-CCSD → SF-OD → UHF-SF-CCSD, the spin contamination of both doublet and quartet spin-flip states increases dramatically. Similar behavior was observed in other $\sigma$-$\pi$ diradical systems [8] and in the EOM-EE-CCSD calculations of radicals [17]. To summarize, we believe that the most reliable value of the doublet-quartet gap is given by the ROHF SF-CCSD method (0.164 eV in 6-311G* basis). This is consistent with the SF-DFT value of 0.16 eV (3.6 kcal/mol). More accurate value of the doublet-quartet energy gap was obtained by using the active space EOM-SF-CC(2,3) method (see Chapter 8), which rectifies spin-contamination problem.

Interestingly, the SF-CIS(D) method, which often performs very well, fails to describe excited states of DMX. The UHF based SF-CIS(D) puts the doublet state 1 eV lower in energy, whereas ROHF-SF-CIS(D) overstabilizes the quartet by about 0.4 eV. This dramatic failure of SF-CIS(D) is due to an insufficient electron correlation treatment and the spin-contamination of excited states.

5.3.2 Thermochemistry

Triradical stabilization energy (TSE) is the energy required to separate a triradical into radical and diradical components. This value, which can be determined from heats of formation, provides a quantitative measure of interaction between
radical centers. The TSE for DMX corresponds to the energy change for the reaction $TSE_{LS}$ (low-spin TSE) shown in Fig. 5.4, where DMX and MX are in their ground doublet and triplet states, respectively. From the experimental results, the TSE of DMX is estimated to be $1 \pm 4$ kcal/mol, indicating very little interaction between the $\sigma$ and $\pi$ electrons in this open-shell doublet triradical [18].

**Triradical separation reaction:**

\[
\begin{align*}
\text{quartet} & \quad \text{+} \quad \text{circles} & \quad \rightarrow \quad \text{triplet} & \quad \text{+} \quad \text{circles} & \quad - TSE_{HS} \\
\downarrow \Delta E_{DQ} & \quad \text{doublet} & \quad \text{+} \quad \text{circles} & \quad \rightarrow \quad \text{triplet} & \quad \text{+} \quad \text{circles} & \quad - TSE_{LS}
\end{align*}
\]

\[TSE_{LS} = TSE_{HS} + \Delta E_{DQ}\]

**Figure 5.4.** Triradical separation reaction

The experimentally determined TSE can be compared to that obtained from *ab initio* calculations. In order to achieve a balanced description of all species involved in the reaction $TSE_{LS}$, we first calculate the high-spin TSE ($TSE_{HS}$), in which all diradicals and triradicals species are in their high-spin state. Since
Table 5.2. Calculation of high-spin TSE\(^a\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>geom.(^b)</th>
<th>UHF-CCSD(T)</th>
<th>ROHF-CCSD(T)</th>
<th>ZPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>(^1)A(_g)</td>
<td>CCSD(T)/cc-pVQZ(^c)</td>
<td>-231.8672976</td>
<td>-231.8672976</td>
<td>63.03(^d)</td>
</tr>
<tr>
<td>phenyl radical</td>
<td>(^2)A(_1)</td>
<td>B3LYP/6-311+G*</td>
<td>-231.1791191</td>
<td>-231.182727</td>
<td>54.60</td>
</tr>
<tr>
<td>benzyl radical</td>
<td>(^2)B(_2)</td>
<td>B3LYP/6-311+G*</td>
<td>-270.4648541</td>
<td>-270.467761</td>
<td>71.59</td>
</tr>
<tr>
<td>DHT</td>
<td>(^3)A(_\Pi)</td>
<td>B3LYP/6-311G**</td>
<td>-269.7807835</td>
<td>-269.782843</td>
<td>63.85</td>
</tr>
<tr>
<td>MX</td>
<td>(^3)B(_2)</td>
<td>SF-DFT/6-31G*</td>
<td>-309.0691055</td>
<td>-309.071534</td>
<td>80.91</td>
</tr>
<tr>
<td>DMX</td>
<td>(^4)B(_2)</td>
<td>SF-DFT/6-31G*</td>
<td>-308.3844084</td>
<td>-308.3864027</td>
<td>72.72(^e)</td>
</tr>
</tbody>
</table>

\(^a\) CCSD(T) energies are in hartree, ZPEs — in kcal/mol. CCSD(T) results are calculated in the cc-pVTZ/cc-pVDZ basis set, with all electrons active. If not mentioned otherwise, ZPEs are calculated at the same level as the equilibrium geometry.

\(^b\) Method for the geometry optimization.

\(^c\) From Ref. [19].

\(^d\) Calculated at the B3LYP/6-311G** level.

\(^e\) From Ref. [6].

All the species involved in the high-spin reaction are well described by single-reference methods, the CCSD(T) TSE\(_{HS}\) is very accurate (\(\pm 1\) kcal/mol). The low-spin TSE\(_{LS}\) is obtained by adding the DMX quartet-doublet energy difference \(\Delta E_{QD}\) , which is calculated at the SF-CCSD level (see Sec. 5.3.1), to TSE\(_{HS}\).

To calculate the high-spin TSE\(_{HS}\), we employed the CCSD(T) method with the ROHF reference as we found that the spin-contamination of the high-spin states affects the accuracy of CCSD and CCSD(T) results (see Table 5.2).

Our best estimate for TSE\(_{HS}\) is -0.35 kcal/mol, which, when combined with \(\Delta E_{QD} = 3.78\) kcal/mol for DMX, gives TSE = 3.43 kcal/mol for the ground state triradical. Thus, the calculated TSE indicates a weak but stabilizing...
interaction between $\sigma$ and $\pi$ radical centers in DMX, in agreement with the experimental result.

5.4 Conclusions

Accurate *ab initio* calculations allowed us to characterize electronic structure of DMX and to make a definite conclusion regarding its unique ground state, in which 3 unpaired electrons are coupled antiferromagnetically.
Reference List

Chapter 6

Efficient strategies for accurate calculations of electronic excitation and ionization energies:

Theory and application to dehydro-meta-xyylene anion (DMX$^-$)

6.1 Electronic structure of DMX$^-$

6.1.1 What DMX$^-$ is similar to?

The molecular orbitals of DMX$^-$, which are similar to those of DMX, were discussed in previous Chapter and are shown in Fig. 5.1. The lowest in energy is a $\sigma$-type $a_1$ (in-plane) orbital formed by the $sp^2$ hybridized carbon orbital. Two $\pi$-orbitals are formed by atomic p-orbitals on the methylene carbons and include contributions from the benzene $\pi$-system.
Two non-disjoint $\pi$-orbitals of DMX give rise to the triplet coupling of the two $\pi$-electrons, as in the ground state of the $\pi - \pi$ diradical analogue of DMX, meta-xylelene (MX). The $\sigma$-type $a_1$ orbital, however, does not overlap with any of $\pi$ orbitals, which leads to the antiferromagnetic coupling between the $\sigma$- and $\pi$-electrons. The corresponding $\sigma - \pi$ diradical, meta-didehydrotoluene (DHT), has a singlet ground state. The molecular orbitals of MX and DHT are also shown in Fig. 5.1. Thus, both triplet coupling between $\pi$-electrons and singlet coupling between $\pi$- and $\sigma$-centers are in favor of the open-shell doublet ground state for DMX, in which each of the triradical orbitals is singly occupied and the unpaired electrons are coupled antiferromagnetically.

Qualitatively, DMX can be described as consisting of either (i) phenyl and MX; or (ii) benzyl and DHT moieties. This suggests that, depending on which orbital an extra electron is placed to, the electronic states of the DMX$^-$ will belong to one of the following types, that is, (i) states originating from the phenyl anion and the MX diradical moieties (structure a); and (ii) states derived from the benzyl anion and the DHT diradical (structures b and b'), see Fig. 6.1. In the latter case, we can distinguish two different structures, b and b', depending on which of the two $\pi$ orbitals is doubly occupied. One may expect that the properties and energy separations between states of type (i), or manifold a, would be similar to those of the MX diradical, whereas the states of type (ii),
or manifolds $b$ and $b'$, would be similar to the electronic states of the DHT diradical.

Figure 6.1. The low-lying electronic states of MX (left panel), DHT (right panel), and DMX$^-$ (middle) at $C_{2v}$ geometries. The energy separation in the DMX$^-$ states originating from the phenyl anion and the MX diradical moieties (structure $a$) are similar to that of MX’s states, and the states correlating with a combination of the benzyl anion and the m-DHT diradical (manifolds $b$ and $b'$) resemble the electronic states of the DHT diradical.
Fig. 6.1 shows the electronic states of MX, DHT, and DMX\(^{-}\) (the left, right, and center parts, respectively\(^1\)). The ground electronic state of MX is triplet, which is confirmed by both the experimental and theoretical studies [1, 2]. The lowest singlet is of a closed-shell type, the adiabatic singlet-triplet gap being about 10 kcal/mol at the SF-DFT level of theory [2]. The open-shell singlet is considerably higher in energy. Such state ordering — triplet, closed-shell singlet, open-shell singlet — is typical for diradicals with overlapping electronic density of the diradical orbitals (e.g., see methylene example in Sec. 2.3.2).

The state ordering in DHT, a \(\sigma - \pi\) diradical, is different, because of the different nodal structure of \(\sigma\) and \(\pi\) orbitals. This results in an open-shell singlet ground state. The triplet state is about 1-3 kcal/mol higher in energy [3, 4]. The closed-shell singlet state is much higher in energy (about 62 kcal/mol vertically) [4] due to its ionic character that results from the electron transfer between the spatially separated \(\sigma\) and \(\pi\) orbitals.

The electronic states of DMX\(^{-}\) at planar \(C_{2v}\) geometries are shown in the middle of Fig. 6.1. States corresponding to the \(a\) and \(b/b'\) manifolds, i.e., MX and DHT like states, are shown to the left and to the right from the energy axis, respectively. As expected, the electronic states from manifold \(a\) are similar to

\(^1\)One can also compare the states of DMX\(^{-}\) with those of neutral DMX. For example, the vertical energy gap between the quartet and the closed-shell doublet in DMX is 13.6 kcal/mol which is comparable with 10 kcal/mol singlet-triplet energy separation in MX. Likewise, the energy separation between the open-shell doublet and the quartet is 3.8 kcal/mol, similarly to 3 kcal/mol singlet-triplet separation in DHT.
those of MX. Indeed, the lowest electronic state of \( \text{a} \) is triplet, while the closed-shell singlet lies 10.1 kcal/mol higher in energy. This energy difference is very similar to the singlet-triplet gap in MX. As mentioned above, \( \text{b} \) and \( \text{b}' \) manifolds are derived by placing an extra electron either on \( \pi_1 (\text{b}_1) \) or \( \pi_2 (\text{a}_2) \) molecular orbitals, respectively. Though the aufbau principle would favor placing an extra electron on the slightly lower \( \pi_1 \) orbital, a more diffuse character of \( \pi_2 \) favors a negative charge residing on \( \pi_2 \). In \( \text{b} \) and \( \text{b}' \), singlets are 0.2-0.8 kcal/mol and 1.2 kcal/mol lower than triplets, which is close to singlet-triplet energy separation in DHT. To summarize, there is a remarkable similarity between the electronic states of \( \text{DMX}^- \) and those of MX and DHT.

6.1.2 Equilibrium geometries of the lowest electronic states of \( \text{DMX}^- \)

Contrarily to DMX and MX, several low-lying electronic states of \( \text{DMX}^- \) do not preserve the \( C_{2v} \) symmetry. The driving force for the symmetry lowering in \( \text{DMX}^- \) is more efficient charge delocalization at twisted geometries due to the lifting of symmetry imposed constraints. In \( \text{DMX}^- \), the energy gain due to the more extensive delocalization appears to be more significant than energy penalty for breaking the conjugation in the \( \pi \)-system at non-planar geometries.

When the symmetry lowers from \( C_{2v} \) to \( C_2 \), the \( a_1 \) and \( a_2 \) irreducible representations (irreps) become the \( a \) irrep, while the \( b_1 \) and \( b_2 \) irreps become the \( b \)
Figure 6.2. Effects of symmetry reduction on the non-bonding molecular orbitals of DMX$^-$

irrep. Lowering the symmetry from $C_{2v}$ to planar $C_s$ allows mixing of $a_1$ and $b_2$, and of $a_2$ and $b_1$, which correlate with the $a'$ and $a''$ irreps, respectively$^2$. Figure 6.2 shows the corresponding changes in the DMX$^-$ molecular orbitals when the anion distorts from $C_{2v}$ to the $C_2$ and the planar $C_s$ symmetries. As one can

$^2$Lowering symmetry to the out-of-plane ("butterfly") $C_s$ mixes $a_1$ and $b_1$, and $a_2$ and $b_2$ irreps, i.e., at this distortion, $^3B_2$ and $^2A_2$ states would interact. Though none of low-lying states of DMX$^-$ belongs to the out-of-plane $C_s$ symmetry, there is an evidence that the out-of-plane $C_s$ states exist, for example, in the CN substituted DMX anion [5].
see, in $C_2$, two $a$ orbitals are obtained by a superposition of the distorted $a_1$ and $a_2$ orbitals, while $a_2$ and $b_1$ orbitals mix in $C_s$.

Figure 6.3 shows the natural charge distribution in different states of $\text{DMX}^-$. In the $C_{2v}$ triplet states (and there is a similar tendency in the corresponding open-shell singlets), the extra charge is mostly localized on the doubly occupied orbital, e.g., on the $\sigma$-type phenyl orbital in the $^3B_2$ state or on the $\pi_1$ ($b_1$) orbital in the $^3A_2$ state. At $C_{2v}$ geometry, in the closed-shell $a$ manifold singlet state more than a half of the charge is also localized on the $\sigma$ orbital. Some hints how the $C_{2v}$ structures of different electronic states of $\text{DMX}^-$ will relax by lowering the symmetry of the molecule can be obtained by analyzing potential surfaces of the $C_{2v}$ structures. As shown in Fig. 6.3, some of the electronic states of $\text{DMX}^-$ do not have a minimum in $C_{2v}$ as indicated by imaginary vibrational frequencies.

In the $^3B_2$ and $^3B_1$ triplet states, charge delocalization can be enhanced by lowering the symmetry from $C_{2v}$ to $C_2$, where these triplets exhibit resonance-type mixing since in lower $C_2$ symmetry group they both become $^3B$. At the DFT level, both $^3B_1$ and $^3B_2$ lower the symmetry to $C_2$ whereas at the higher [CCSD and CCSD(T)] levels, $^3B_1$ distorts to $C_2$ but $^3B_2$ remains planar. This is confirmed by vibrational analysis at the corresponding (B3LYP and CCSD) levels of theory. We believe that lowering the symmetry of $^3B_2$ at the DFT level is artificial and is due to a tendency of the DFT schemes to delocalize
Figure 6.3. Natural charge distribution (given in numbers and visualized by black and white circles on the carbon atoms) in the lowest electronic states of DMX$^-$. In each state, negative charge distribution follows the shape of a doubly occupied non-bonding orbital. For the states that exhibit symmetry breaking values of the imaginary frequencies are also given. The DFT artificial symmetry breaking in $^3B_2$ and $^3A_2$ is discussed in some details in text.
the electronic density in a molecule. As follows from equilibrium geometries of the low-lying electronic states of DMX$^-$ (see Fig. 6.4), the overall (artificial) geometry distortion of $^3B_2$ at the B3LYP level is very small, e.g., the out-of-plane angles do not exceed 12°.

\[ \text{E}_{\text{ref}}^\text{B3LYP/6-311+G*} = 309.0125 \]

\[ \text{E}_{\text{ref}}^\text{B3LYP/6-31G*} = 309.3370 \]

Figure 6.4. The equilibrium geometries of the lowest electronic states of DMX$^-$. B3LYP/6-311+G* and CCSD/6-31G* (italic) were used to calculate the geometries of all the triplets and the $^1A^1/^1A_1$ singlet, EOM-CCSD/6-31+G* (bold) was used for the $^1A_2$ and $^1B_1$ open-shell singlets. Both the $C_{2v}$ constrained (at the B3LYP/6-311+G* level, underlined) and $C_2$ equilibrium geometries of $^1A$ are shown. A structure corresponding to the artificial symmetry breaking in $^3B_2$ (observed at the B3LYP/6-311+G* level, underlined) is also given. Only the $C_{2v}$ constrained structures of $^3A_2$ and $^1A_2$ are reported (see footnote 3).
At the B3LYP level, the $^3A_2$ triplet lowers the symmetry to planar $C_s$ (where it can mix with $^3B_1$), whereas at the CCSD and CCSD(T) levels it preserves the $C_{2v}$ geometry. Again, as in the case of $^3B_2$, breaking the symmetry of the state by B3LYP appears to be artificial.

The closed-shell singlet state with the doubly occupied $\sigma$ and $\pi_1$ orbitals (the closed-shell singlet from the manifold $a$, see Fig. 6.1) has the $C_2$ equilibrium geometry, at which C5 no longer hosts the phenyl-type $sp^2$ hybridized orbital, but rather two $sp$-hybridized and two $\pi$ orbitals making double bonds with C4 and C6 carbons. Thus, the lower part of the molecule (C4-C5-C6) resembles the 1-2-propadiene and is only marginally charged. The majority of the charge is localized on the upper part of the molecule, which resembles the pentadienyl anion. Both moieties are connected by the two single carbon-carbon bonds between C3-C4 and C6-C1 (see Fig. 6.5). Similar structure appears, for example, in deprotonated cyclooctatetraene, which also forms an allene and a delocalized anion [6]. The equilibrium bond lengths and NBO analysis of $^1A$ are consistent with this bonding scheme.

---

$^3$Additional difficulties in finding potential surface minima of some states appear because of strong interaction between the states in the same symmetry irrep. For instance, the $^1B_1$ and $^1A_2$ open-shell singlets (interacting at planar $C_s$ symmetry) were found to exhibit conical intersection, with the minimum of potential surface of one of these states ($^1B_1$) likely to lie in immediate proximity to the region of intersection. Probably, similar behavior inheres in $^3A_2$ state.
It is commonly assumed that structures and properties of the states with same spatial occupancies are similar, as in the case of the triplet and open-shell singlet states of DHT [4], the quartet and the open-shell doublet of DMX [7], and the $A_2$ states of DMX$^-$ (the latter two states do not exhibit any distortion from $C_{2v}$). Moreover, the $C_{2v}$ restricted structures of the $B_1$ singlet-triplet pair of DMX$^-$’s states obey the same rule. However, charge delocalization in the $^1B_1$ open-shell is different from that in the $^3B_1$ triplet. While the $^3B_1$ triplet experiences the $C_2$ distortion, the $^1B_1$ open-shell distorts to planar $C_2$. This can be rationalized as follows: since in both $C_{2v}$ restricted $B_1$ states the charge

\textbf{Figure 6.5.} $C_{2v}$ constrained and equilibrium $C_2$ twisted structures of the $^1A_1$ ($^1A$) closed-shell singlet state and their bonding patterns
is mainly delocalized according to the shape of the $A_2$ orbital, either $C_2$ or $C_s$ distortion can lead to the charge delocalization (between $a_1$ and $a_2$ orbitals in $C_2$, and between $b_1$ and $a_2$ orbitals in $C_s$, see Fig. 6.2). The triplet distorts to $C_2$ to mix there with the lower $^3B_2$ state, while the $C_2$ distortion in singlet would lead to the interaction with the higher $^1B_2$. Instead, $^1B_1$ prefers to distort to $C_s$ where it interacts with the closely-lying $^1A_2$ (both $^1B_1$ and $^1A_2$ become the $A''$ states at the planar $C_s$ symmetry). Alternatively, this can be explained by the orbital mixing in $C_2$ that leads to overlapping the electronic densities of $a_1$ and $b_1$ orbitals (see Fig. 6.2), which increases the exchange integral and raises the energy of the singlet compared to the triplet, as follows from Hund’s rule. However, there is no such effect in the planar structure because the electronic density of the singly occupied $a_1$ and $b_1$ orbitals remains non-overlapping and the energy of the $^1B_1$ open-shell lowers due to the charge delocalization in the $\pi$-system.

### 6.2 Accurate electronic excitation and ionization energies of the electronic states

Adding an extra electron into the 3-electrons-on-3-orbitals system of the DMX triradical leads to the 4-electrons-on-3-orbitals pattern in DMX$^-$. This results in the extreme electronic degeneracies and heavily multi-configurational wave
functions. However, if the interaction between a doubly occupied orbital and two others is weak due to symmetry/nodal considerations or a spatial separation, the complexity of the DMX\(^-\) electronic structure reduces to the familiar 2-electrons-in-2-orbitals diradical case. For example, all three non-bonding orbitals are of different symmetry at C\(_{2v}\) geometries which, along with a weak overlap between the \(\sigma\)- and \(\pi\)-systems, strongly impede the electron transfer between the \(\sigma\)- and \(\pi\)-orbitals.

Extensive electronic near-degeneracies make the choice of an electronic structure method extremely important: an approximate model should provide a qualitatively correct description of an electronic wave function (non-dynamical correlation), and also include dynamical correlation, which is crucial for quantitative accuracy, especially in anions. Moreover, a balanced description of several states of interest is required – therefore, our preference is to use multi-state rather than state-to-state methods.

For a molecule such as DMX or DMX\(^-\), traditional strategy is to employ MR techniques. Indeed, with a reasonably chosen active-space, MCSCF would provide an appropriate zero-order wave function for both DMX and DMX\(^-\). In order to achieve quantitative accuracy, such zero-order wave function should be augmented by dynamical correlation, e.g., as in MRCI or MRPT. With such
an approach, all the electronic states are described with a presumably equal quality. Both one-state-at-a-time and state-averaging procedures can be used. In this work, we investigate the performance of ”brute force” approaches and that of schemes based on a combination of ground state single-reference and EOM methods on the example of the electronic excitation and ionization energies of the dehydro-meta-xylylene (DMX) anion.

6.2.1 Adiabatic excitation energies of DMX$^-$

Accurate calculation of the adiabatic excitation energies in DMX$^-$ is nontrivial due to significantly different equilibrium geometries and characters of its electronic states. Indeed, whereas the wave functions of the three triplets and the $^1A$ singlet are are dominated by a single electronic configuration, the open-shell singlets are two-configurational. Therefore, it is impossible to describe all six lowest electronic states of DMX$^-$ with an equal quality by using a single-reference technique. To solve this problem, we employ two different approaches. In the ”brute force” approach, the total energies of all the states are calculated by MCSCF and MRPT, and excitations energies are calculated as differences between the

$^4$Contrarily to the EOM approach, in which the total number of simultaneously calculated states does not affect the resulting excitation energies, in a state-averaged calculation by MCSCF, the energies of states will depend on the number of the states included. Whereas this uncertainty in excitation energies may not be important when vertical excitation energies are calculated, it can become an issue when the adiabatic excitation energies are of interest. For example, at some points of PES, it may be possible to calculate one root in a time, whereas at other points, degeneracy between the states may require root-averaging.
total energies of states. In the second approach, we combine the high-level single-reference method, e.g., CCSD(T), and the single-reference excited-states method, EOM-EE-CCSD, to accurately describe energy differences between different states.

We use CCSD(T) to calculate the total energies of all the triplets, \( ^3B_2 \), \( ^3B_1 \), and \( ^3A_2 \), and the closed-shell singlets, \( ^1A \) and \( ^2^1A_1 \). The latter singlet, \( ^2^1A_1 \), with electronic configuration \( a_1^0b_1^2a_2^2 \) (see Fig. 5.1 for orbital notations), can be used as a reference in the EOM-EE-CCSD calculations of the open-shell states. Indeed, both open-shell singles, \( ^1B_1 \) and \( ^1A_2 \), along with the corresponding triplets, \( ^3B_1 \) and \( ^3A_2 \), are singly excited states with respect to this state. Note that in the CCSD(T) calculations, the high-spin \( M_s = 1 \) components of the \( ^3B_1 \) and \( ^3A_2 \) triplets are used, and the triplets are single-configurational. In the EOM calculations, the low-spin \( M_s = 0 \) components of these triplets are found.

Thus, in order to calculate the adiabatic excitation energies of DMX\(^-\), we suggest two schemes depicted in Fig. 6.6. In these schemes, the energy differences between the states are calculated in two steps. In scheme a, we calculate the adiabatic energy difference between the triplet states and the \( ^1A - ^3B_2 \) energy difference by CCSD(T). The excitation energies of \( ^1A_2 \) and \( ^1B_1 \) are calculated by subtracting the energy separations \( \Delta E_{^1A_2 - ^3A_2} \) and \( \Delta E_{^1B_1 - ^3B_1} \) from the CCSD(T) energies of the corresponding triples. The latter singlet-triplet gaps are calculated at the geometries of the corresponding triplets, by using
Figure 6.6. Calculation of the adiabatic excitation energies in lowest states of DMX$^-$
EOM-EE-CCSD with the $2^1A_1$ reference state. Since the singlet-triplet pairs of the $B_1$ and $A_2$ states have the same spatial configurations, we expect each pair to be described by EOM-EE-CCSD with an equal quality. The main source of uncertainty and of possible error in scheme $a$ is accuracy of CCSD(T) for treatment of different triplet states. All triplets are moderately spin-contaminated, which can result in a loss of accuracy by CCSD(T). However, we believe scheme $a$ gives an accurate estimate of the excitation energies of DMX$^-$.  

In scheme $b$, we use CCSD(T) to calculate the energy difference between the lowest triplet $^3B_2$ and the two closed-shell singlets, $^1A$ and $2^1A_1$. Then we employ the latter state as the reference in EOM-EE-CCSD calculations and obtain the excitation energies of the $B_1$ and $A_2$ triplets and singlets relative to the $2^1A_1$ state. Thus, scheme $b$ eliminates the main drawback of scheme $a$ — using CCSD(T) for different spin-contaminated triplets. However, in scheme $b$, there is another source of an error. Whereas the energy separation between each pair of the $B_1$ and $A_2$ states is accurately described by EOM-EE-CCSD, it may not be so for the energy separation between different pairs of these states. For example, if one pair of states has slightly larger doubly excited character than the other, it will appear higher in energy relative to the other pair.

Numerical results obtained by using schemes $a$ and $b$ along with MR data are presented and discussed in Section 6.4.
6.2.2 Ionization potential of DMX$^-$

Accurate evaluation of the ionization energy can be a very challenging task for electronic structure calculations since it requires a balanced description of two different species, a molecule of interest and its negative ion. Using a single-reference method such as DFT or CCSD(T) is possible only if both anion and neutral are well behaved systems, e.g., when the neutral is a closed shell species, and the anion doesn’t exhibit symmetry breaking. And this is certainly not the case for DMX and DMX anion!

In order to calculate the adiabatic ionization energy of DMX$^-$, we employed several different schemes shown in Fig. 6.7. In the simplest and the most straightforward scheme $a$, the energy difference between the $2B_2$ state of DMX and the $3B_2$ state of DMX$^-$ is calculated by MCSCF or MRPT, i.e., methods which can treat the electronic structure of both neutral and anion molecules. Scheme $b$ is a two-step scheme. First, we calculate the energy difference between the high-spin states, $3B_2$ state of anion and the $4B_2$ state of neutral, by CCSD(T). And second, the energy difference between the $4B_2$ and $2B_2$ states of DMX is calculated by EOM-SF-CCSD. In schemes $c$ and $d$, first, we use EOM-IP-CCSD for accurate evaluation of the vertical ionization energy between the
Figure 6.7. Evaluation of the adiabatic ionization energy of the DMX$^-$
$^3B_2$ state of anion and $^4B_2$ state of neutral. Second, in order to make a transition from the vertical to adiabatic energy differences, the CCSD(T) energies of anion (scheme c) or neutral (scheme d) are calculated at the equilibrium geometries of $^3B_2$ and $^2B_2$. Finally, the vertical energy difference between the $^2B_2$ and $^4B_2$ states of neutral DMX are in a balanced way calculated by the EOM-SF-CCSD method. Schemes c and d are of equal quality, they differ by the geometry ($^3B_2$ or $^2B_2$) at which the EOM-IP-CCSD energy is calculated and by the potential surface ($^3B_2$ or $^4B_2$) at which the adiabatic shift is calculated.

### 6.3 Computational details

Equilibrium geometries of the triplet and closed-shell singlet states of DMX$^-$ were optimized at the CCSD/6-31G* [8, 9] and B3LYP/6-311+G* [10–12] levels, geometries of the open-shell singlets were obtained by EOM-EE-CCSD/6-31+G* [9, 12]. Geometries of lowest electronic states of DMX$^-$ calculated by appropriate methods are shown in Fig. 6.4. It is interesting that C$_2v$ constrained B3LYP geometries of the triplets are very similar to the geometries obtained by using CCSD. Also, there is no large difference between the B3LYP and CCSD C$_2$ geometries of the $^1A$ state. Moreover, the C$_{2v}$ geometries of both open-shell states of DMX$^-$ cannot be accurately calculated by using EOM-IP-CCSD because not all the configurations of the $^2B_2$ doublet can be obtained as singly excited (i.e., with detachment of one electron) from the $^3B_2$ reference state.
singlets, $^1A_2$ and $^1B_1$, are similar to those of the corresponding triplets, $^3A_2$ and $^3B_1$. Therefore, in order to calculate adiabatic excitation energies, we use the B3LYP/6-311+G* $C_2$ geometry for the $^1A$ state and the B3LYP/6-311+G* $C_{2v}$ constrained geometries for all the other states, that is, we calculate the energies of the $^1A_2$ and $^1B_1$ singlets at the geometries of the corresponding triplets. 

Adiabatic excitation energies and ionization potential of DMX$^-$ were calculated by the CCSD(T), EOM-EE-CCSD, EOM-SF-CCSD, and EOM-IP-CCSD in 6-311+G* basis set and by MCSCF and MRPT in 6-311G** basis (see Sections 6.2.1 and 6.2.2 for details). The active space for MR calculations consisted from 9 orbitals, i.e., 3 triradical orbitals shown in Fig. 5.1, and 3 doubly-occupied and 3 virtual benzene $\pi$ orbitals, and 10 or 9 electrons for DMX$^-$ and DMX, respectively. No root averaging was used, i.e., only one solution was sought in each calculation.

Additionally, we performed calculations by the active-space EOM-EE-CC(2,3) method (see Section 1.7), i.e., the EOM-CC model where the cluster amplitudes $T$ are truncated at the second order and the excitation amplitudes $R$ consist of zero, single, double, and triple excitations. In the active space variant of this method, EOM-EE-CC(2,3), only a small subset of triple excitations, determined by the choice of the active space, is included. As an active space for

---

6 We also performed test calculations at the EOM-CCSD optimized geometries of the $^1A_2$ and $^1B_1$ singlets. Calculated at these geometries, changes in the excitation energies of these states are less than 0.1 kcal/mol.
the EOM-EE-CC(2,3) calculations on DMX⁻, we chose three triradical orbitals shown in Fig. 5.1. This small active space includes the leading excitations of the $B_1$ and $A_2$ states. Moreover, it takes care of the instability of the reference, the $2^1A_1$ state, which is not the lowest closed-shell singlet. Benchmarks for the EOM-EE-CC(2,3) method, which can be found in Chapter 8, show that in the case of strong non-dynamical correlation, the accuracy of EOM-EE-CC(2,3) significantly exceeds that of EOM-EE-CCSD.

6.4 Results and discussion

Scheme $a$ was applied to calculate the excitation energies shown in Fig. 6.1. To compare the DMX⁻ states of manifold $a$ with the MX ones, we calculated the vertical rather than adiabatic energy separation between the $3B_2$ and $1A$ ($1A_1$ in $C_{2v}$) states of DMX⁻. Since at $C_{2v}$, the $1A$ singlet is less single-reference than at $C_2$, the EOM-SF-CCSD method, employing $3B_2$ state as the reference, was used for calculating the $3B_2 - 1A_1$ energy separation.

The adiabatic excitation energies of DMX⁻ calculated by different schemes are given in Table 6.1. MCSCF and MRPT results are shown in the last two column of the table. For all excited states, the difference between the MCSCF and MRPT values is 7-8 kcal/mol (0.30-0.35 eV), MCSCF data being closer to CCSD(T) values for the single-reference states. The only one from applied
Table 6.1. Total (hartree) and adiabatic excitation energies (kcal/mol) of the lowest electronic states of DMX$^{-a}$

<table>
<thead>
<tr>
<th>State</th>
<th>CCSD(T)</th>
<th>EOM (a)</th>
<th>EOM (b)</th>
<th>EOM-CC(2,3) (b)</th>
<th>MCSCF</th>
<th>MRQDPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3B_2$</td>
<td>-308.250087</td>
<td></td>
<td></td>
<td>-307.011161</td>
<td>-308.046218</td>
<td></td>
</tr>
<tr>
<td>$^1A_1^b$</td>
<td>11.90</td>
<td></td>
<td></td>
<td>14.44</td>
<td>6.14</td>
<td></td>
</tr>
<tr>
<td>$^1A^c$</td>
<td>1.48</td>
<td></td>
<td></td>
<td>3.19</td>
<td>-4.04</td>
<td></td>
</tr>
<tr>
<td>$^1B_1^e$</td>
<td></td>
<td>8.53</td>
<td>15.45</td>
<td>7.16</td>
<td>8.93</td>
<td>1.15</td>
</tr>
<tr>
<td>$^3B_1$</td>
<td>8.71</td>
<td>8.71</td>
<td>15.63</td>
<td>7.61</td>
<td>9.63</td>
<td>1.62</td>
</tr>
<tr>
<td>$^1A_2^d$</td>
<td></td>
<td>11.18</td>
<td>11.39</td>
<td>7.37</td>
<td>10.81</td>
<td>3.93</td>
</tr>
<tr>
<td>$^3A_2$</td>
<td>12.15</td>
<td>12.15</td>
<td>12.36</td>
<td>9.17</td>
<td>16.15</td>
<td>5.34</td>
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<tr>
<td>$^2^1A_1@^3B_1$ geom.$^c$</td>
<td>77.53</td>
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<td>308.061178</td>
<td>308.064657</td>
<td></td>
<td></td>
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<tr>
<td>$^2^1A_1@^3A_2$ geom.$^c$</td>
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<td>308.062815</td>
<td>308.062815</td>
<td>308.066671</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 6-311+G* basis set was employed for all calculations except of MCSCF and MRPT, where 6-311G** was used.
$^b$ B3LYP/6-311+G* geometries used (see Fig. 6.4); see text for details.
$^c$ Calculated at the geometry of $^3B_1$.
$^d$ Calculated at the geometry of $^3A_2$.
$^e$ This state has the electronic configuration $a_1^0b_1^2a_2^2$ and used as a reference for EOM-EE-CC calculations of $B_1$ and $A_2$ states.
methods, MRPT places the $^1A$ state as the ground state. This contradicts both to other calculated data and to experiment [13]. Thus, the applied multi-reference methodology fails to give an unambiguous answer about the order of electronic states of DMX$^-$. 

It appears that in schemes $a$ and $b$ (see Fig. 6.6), the order of $B_1$ and $A_2$ states is different: whereas scheme $a$ places the $B_1$ states lower than the $A_2$ ones, scheme $b$ gives the reverse order. In order to clarify the situation, we improved the quality of scheme $b$ by replacing the EOM-EE-CCSD method by EOM-EE-CC(2,3). With this improvement, the state order in scheme $b$ coincides with that in scheme $a$, i.e., the $B_1$ states lie lower in energy than the $A_2$ states. The differences in excitation energies from these two schemes is now less than 3 kcal/mol.

Therefore, the state ordering in DMX$^-$ is as follows: $^3B_2$, $^1A$, $^1B_1$, $^3B_1$, $^1A_2$, $^3A_2$.

Tables 6.2 and 6.3 summarize the results of calculations of adiabatic ionization potential of DMX$^ -$. The MCSCF and MRPT values (scheme $a$) are erroneous. The results of two-step scheme $b$ are slightly lower than the experimental value. As expected, the ionization energies calculated by schemes $c$ and $d$ are very similar, 24.6 kcal/mol and 24.2 kcal/mol, respectively. These results are in excellent agreement with the experimental value of 24.9 ± 2.0
Table 6.2. Calculating adiabatic ionization energy of DMX\(^-\), kcal/mol\(^a\)

<table>
<thead>
<tr>
<th>Method</th>
<th>State</th>
<th>Geometry</th>
<th>(\Delta E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)</td>
<td>(^3B_2)</td>
<td>(^3B_2)(^-)(^2B_2)</td>
<td>14.13</td>
</tr>
<tr>
<td></td>
<td>(^4B_2)</td>
<td>(^3B_2)(^-)(^2B_2)</td>
<td>6.70</td>
</tr>
<tr>
<td></td>
<td>(^3B_2)(^-)(^4B_2)</td>
<td>(^3B_2)(^-)(^2B_2)</td>
<td>24.29</td>
</tr>
<tr>
<td>IP</td>
<td>(^3B_2)(^-)(^4B_2)</td>
<td>(^3B_2)</td>
<td>35.07</td>
</tr>
<tr>
<td></td>
<td>(^3B_2)(^-)(^4B_2)</td>
<td>(^2B_2)</td>
<td>13.83</td>
</tr>
<tr>
<td>SF</td>
<td>(^4B_2)(^-)(^2B_2)</td>
<td>(^2B_2)</td>
<td>3.78</td>
</tr>
<tr>
<td>MCSCF</td>
<td>(^3B_2)(^-)(^2B_2)</td>
<td>(^3B_2)(^-)(^2B_2)</td>
<td>-15.39</td>
</tr>
<tr>
<td>MRPT</td>
<td>(^3B_2)(^-)(^2B_2)</td>
<td>(^3B_2)(^-)(^2B_2)</td>
<td>9.48</td>
</tr>
</tbody>
</table>

\(^a\) See Fig. 6.7 for details.

Table 6.3. Adiabatic ionization energy (kcal/mol) of DMX\(^-\) calculated by different schemes

<table>
<thead>
<tr>
<th>Scheme</th>
<th>method</th>
<th>IP(_{\text{adiab}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>scheme (a)</td>
<td>MCSCF</td>
<td>-15.39</td>
</tr>
<tr>
<td></td>
<td>MRPT</td>
<td>9.48</td>
</tr>
<tr>
<td>scheme (b)</td>
<td>CCSD(T), EOM-SF-CCSD</td>
<td>20.51</td>
</tr>
<tr>
<td>scheme (c)</td>
<td>CCSD(T), EOM-SF-CCSD, EOM-IP-CCSD</td>
<td>24.58</td>
</tr>
<tr>
<td>scheme (d)</td>
<td>CCSD(T), EOM-SF-CCSD, EOM-IP-CCSD</td>
<td>24.18</td>
</tr>
<tr>
<td>Experiment(^a)</td>
<td></td>
<td>24.9 ± 2.0</td>
</tr>
</tbody>
</table>

\(^a\) Experiment from Ref. [13].

kcal/mol [13]. Thus, the three-step procedure for calculating the adiabatic ionization potential of DMX\(^-\) produces the accurate result.

### 6.5 Conclusions

Accurate description of electronic states of DMX\(^-\), 4-electrons-in-3-orbital system, is a challenging task for any ab initio method. This is even more so for
calculating of the DMX⁻’s ionization potential, when, additionally, the ground state of neutral DMX, a 3-configurational open-shell doublet wave function, should be described accurately. We show that the ”brute force” approach, i.e., calculation of the total energies of the excited states by multi-reference MCSCF and MRPT, fails to give the correct order of the electronic states and reasonable IP. Contrarily, the EOM based two-step schemes yield the correct state ordering and accurate excitation energies. The results of the three-step schemes for calculation of adiabatic IP, which include EOM-IP-CCSD, EOM-SF-CCSD, and CCSD(T), are in excellent agreement with experiment.
Reference List


Chapter 7

Photoelectron spectroscopy

Ab initio calculations are in particular important for the design and interpretation of experiments. Photoelectron spectroscopy is an excellent example of an experiment where accurate analysis and assignment of the results is virtually impossible without supplementary ab initio calculations. This Chapter discusses practical aspects of such modelling and presents calculations of the photoelectron spectrum (PES) of the TMM anion, including assignment and comparison with the experimental spectrum [1, 2].

7.1 Introduction to photoelectron spectroscopy

Consider the photodetachment of a stable negative ion $X^{-}$ with a photon of energy $\hbar \nu$ producing a neutral molecule $X$ and an electron:

$$X^{-} \rightarrow^{\hbar \nu} X + e^{-}$$ (7.1)
The energy of the photon is distributed between the kinetic energy of the detached electron (eKE) and internal energy of the molecule:

\[ eKE = h\nu - EA - E_{\text{neutral}}^{\text{int}} + E_{\text{anion}}^{\text{int}}, \]  

(7.2)

where EA is the adiabatic electron affinity of X (which is equal to IP, the adiabatic ionization potential of X\(^-\)), and \( E_{\text{neutral}}^{\text{int}} \) and \( E_{\text{anion}}^{\text{int}} \) represent the internal energy, i.e., electronic, vibrational, rotational, etc., of the neutral and the anion, respectively. In most of experimental setups, the internal state of the anion is reasonably well controlled. Therefore, the measurement of eKE determines the internal energies of the states of the neutral in a straightforward way. Figure 7.1 illustrates the energy distribution in a photodetachment experiment.

In addition to the energy differences, eKE measurements can provide information about the relative geometries of the anion and the neutral. Consider the photodetachment from a diatomic anion. In the Franck-Condon approximation, i.e., when the nuclear and electron motions are separated, the relative yield of electrons, i.e., the intensity of the signal I, is proportional to the spatial overlap of the vibrational wave functions of the anion, \( \Psi''_\nu \), and the neutral, \( \Psi'_\nu \):

\[ I \propto v_e \cdot |\tau_e|^2 \cdot |\langle \Psi''_\nu(Q)|\Psi'_\nu(Q)\rangle|^2, \]  

(7.3)
where $Q$ is the normal coordinate, i.e., the bond length in the case of diatomic molecule. Eq. 7.3 assumes that the asymptotic velocity $v_e$ and the electron transition dipole moment $\tau_e = \langle \Psi''_e(Q) | H | \Psi'_{el}(Q) \rangle$ are approximately constant over the energy range of one vibrational transition. However, both $v_e$ and $\tau_e$ can be very different for transitions to different electronic states of neutral.

Figure 7.2 demonstrates the photodetachment process involving three different electronic states of neutral, 0, 1, and 2. The change in bond lengths...
Figure 7.2. One-dimensional Franck-Condon factors and the shape of photoelectron spectrum

between the anion and the neutral states, \( \Delta Q \), is different for these states. For state 0, \( \Delta Q \simeq 0 \), which results in no or very short vibrational progression. Larger displacements result in longer vibrational band (state 1). Finally, at very large \( \Delta Q \), the vibrational band becomes so broad that the relative intensity of each peak is too small to resolve, and the state becomes invisible due the small spatial overlap of the anion and neutral vibrational wave functions, i.e., the
Franck-Condon factors. Thus, the shape of the vibrational band provides the information about relative geometries of the anion and neutral. The modelled spectra calculated with $\Delta Q$ in range from 0 to 1.6 Å/$\sqrt{amu}$ are shown in Appendix B. The spacing between the peaks in the vibrational progression reflects the spacing between the vibrational levels of the neutral state, see Fig. 7.1.

For polyatomic molecules with $N$ normal modes, similar considerations result in the separable normal mode approximation:

$$FC = \prod_{i=1}^{N} |\langle \Psi''_{\nu_i}(Q_i) | \Psi'_{\nu_i}(Q_i) \rangle|^2,$$

(7.4)

where Franck-Condon factor $FC$ is the spatial overlap of the vibrational wave functions for the $i$th vibrational mode of the anion, $\Psi''_{\nu_i}$, and the neutral, $\Psi'_{\nu_i}$. That is, the overall spectrum consists of several vibrational progressions along different normal modes (see Fig. 7.3). As shown in Fig. 7.2, only the vibrational progressions of the "active" normal modes, i.e., modes with $\Delta Q \neq 0$, will appear in spectrum. If the anion and the neutral belong to the same spatial symmetry group, only normal modes of the fully symmetric irreducible representation can be active.

The photoelectron spectrum can also include hot bands, i.e., transitions from the vibrationally excited levels of the anion. These hot bands, which are
Figure 7.3. PES with two active vibrational modes. Stars (*), pluses (+), and circles (o) correspond to the “long” progression of the vibrational mode $\nu = 850 \text{ cm}^{-1}$ combined with 0, 1, or 2 quanta of the $\nu = 600 \text{ cm}^{-1}$ mode, respectively.

temperature dependant, can provide some information about the vibrational levels of the anion.

Eqns. (7.3) and (7.4) assume that: (i) the vibrational modes of anion and neutral are harmonic, (ii) the vibrational and electronic degrees of freedom are separable (the Franck-Condon approximation) [3], (iii) the normal modes of anion and neutral are noninteracting (no anharmonic couplings), and (iv) the
normal modes are "parallel", i.e., the normal coordinates in the anion and neutral are the same. These approximations can be relaxed in more sophisticated schemes of PES modelling. For example, one can include electronic degrees of freedom, or account for the normal mode changes between the anion and the neutral (Duschinsky rotations) [4, 5], which requires calculation of multidimensional Franck-Condon factors. In the following, we limit our discussion by modelling the photoelectron spectra based on approximations (i)-(iv).

7.2 Modelling PES of diradical’s and triradical’s precursors

In this section, we discuss the challenges of modelling PES of diradical and triradical precursors. Figure 7.4 shows transitions from the anion to the diradical and the triradical neutral states visible in PES (i.e., one-electron transitions). The precursor of a neutral diradical is a doublet radical anion, and three diradical states, triplet, open-shell, and closed-shell singlets [these are states of Eqns. (1.5), (1.4), and (1.1), respectively], can be visible in PES. In the case of neutral triradical, the anion has 4-electrons-in-3-orbitals pattern, which can result in either singlet or triplet ground state. Starting from the singlet anion, two closed-shell doublets of the neutral [states (g) and (i) from Fig. 1.4] will be visible, whereas starting from the triplet anion, the quartet, two closed-shell
and two open-shell doublets of the neutral triradical [states (a), (e), (g), (c), and (d), respectively] can be obtained.

**Figure 7.4.** Allowed transitions in PES targeting diradicals and triradicals

Modelling PES targeting diradicals and triradicals is challenging with respect to the choice of an *ab initio* technique, since the potential surfaces of the species with very different electronic character should be accurately described. The appropriate techniques for describing diradicals and triradicals were discussed in details in the previous Chapters. The accurate description of the radical anion with 3-electrons-in-2-orbitals pattern can also be rather tricky due to extensive degeneracies and possible symmetry breaking. In some circumstances, the anion can be described by a single-reference method, such as CCSD(T), or by SF from the high spin quartet reference, provided that such a stable state exists. Treating the anion precursor of the triradical with 4-electrons-in-3-orbitals pattern can
be even more challenging. Anions of these types are discussed in Chapters 4 and 6.

Any PES modelling requires accurate energy separations between the states. Strategies for calculating accurate energy splittings in diradicals and triradicals are given in the previous Chapters. An example of accurate calculation of the adiabatic electron affinity in a triradical is given in Chapter 6.

Moreover, modelling PES requires the information about potential energy surfaces, i.e., the equilibrium geometries and vibrational frequencies of all the electronic states involved. Ideally, potential energy surfaces of all the states should be described at the same level of theory. However, it is almost impossible to find a single \textit{ab initio} method that will accurately describe the electronic states of both the anion and the neutral due to the non-trivial electronic structure of these species. Therefore, we describe each state separately, by the most appropriate method.

\textit{Ab initio} calculations yield the equilibrium geometry of the electronic state. Comparing geometries of two electronic states gives the geometry displacements in Cartesian coordinates \((dx, dy, dz)\). The required set of distortions along the normal modes, \(\Delta Q_i\), can be calculated by the program NMODES developed in our group and described in Appendix A.
To model PES, I employed the FORTRAN program PES4 from Berkeley [6]. Comments on its usage based on the \textit{ab initio} calculations are given in Appendix B.

### 7.3 Modelling PES of the TMM anion

The electronic structure of the TMM diradical is discussed in details in Section 2.3.5 and Chapter 3. The equilibrium geometries and vibrational frequencies of the low-lying electronic states of TMM are given in Fig. 2.7 and 3.3 and in Tables 3.1 and 3.2. Here we focus on the electronic structure of the TMM anion.

Similarly to neutral TMM, the TMM anion is also a Jahn-Teller (JT) system. At $D_{3h}$ geometries, two doublet states are degenerate. Each of them can be stabilized by different $C_{2v}$ distortions. As in other JT systems, one of the doublets, $^2B_1$, is not a minimum but a transition state at its $C_{2v}$ optimized geometry. In TMM, the corresponding JT state, $^1B_1$, finds its minimum due to the secondary out-of-plane distortion. Overall, equilibrium geometries of the JT doublets are similar to the $C_{2v}$ geometries of the JT singlets of neutral TMM. At the $D_{3h}$, doublets are degenerate and would not be correctly described by a single-reference method due to symmetry breaking. However, at $C_{2v}$ the degeneracy is lifted and the doublets become accessible by a single-reference
method. Geometries and vibrational frequencies of the $^{2}A_{2}$ and $^{2}B_{1}$ doublet states were calculated at the B3LYP/aug-cc-pVTZ level [7–9].

According to Fig. 7.4, the three lowest electronic states of TMM, $X^{3}A'_{2}$, $1^{1}B_{1}$, and $1^{1}A_{1}$, can be visible in PES. However, additional constraint arises due to the twisted equilibrium geometry of the open-shell $1^{1}B_{1}$ singlet which results in an unfavorable Franck-Condon factor (see Fig. 7.2, state 2) that makes this state invisible in PES.

Table 7.1 summarizes the geometry distortions $\Delta Q$ along the normal modes between the anion and the neutral states. In both the $X^{3}A'_{2}$ and $1^{1}A_{1}$ states of TMM, the largest geometry distortion occurs along the CC scissoring mode. The next important are the symmetric and anti-symmetric skeleton stretches in $X^{3}A'_{2}$ and the anti-symmetric skeleton stretch and a couple of hydrogen modes in $1^{1}A_{1}$.

Distortions to both the planar $^{1}B_{2}$ and twisted $^{1}B_{1}$ states are presented in Table 7.1. Since the $^{1}B_{2}$ state is not a minimum on the potential energy surface but has two imaginary frequencies (mode 9 — JT imaginary mode, and mode 0 — rotation of methylene group), the transition to this state will be very broad. On the other hand, the $^{1}B_{1}$ state has huge geometry distortions along the coordinates corresponding to the rotation of methylene group, which renders this states inactive in PES.
Table 7.1. Geometry distortions along the normal modes in the \( X^3A'_2 \), \( 1^1B_1 \), and \( 1^1A_1 \) states of TMM\(^a\)

<table>
<thead>
<tr>
<th>Symm. Type</th>
<th>( ^2A_2 ) anion freq</th>
<th>( X^3A'_2 ) freq</th>
<th>( 1^1B_1 ) freq</th>
<th>( 1^1B_2 ) freq</th>
<th>( 1^1A_1 ) freq</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>freq</td>
<td>( \Delta Q )</td>
<td>freq</td>
<td>( \Delta Q )</td>
<td>freq</td>
</tr>
<tr>
<td>( a_2(a''_1) )</td>
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</tr>
<tr>
<td>all-H wag (OPLA)</td>
<td>253</td>
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<td>649</td>
<td>0.611</td>
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<tr>
<td>( b_1(e'') )</td>
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<tr>
<td>down-H wag (OPLA)</td>
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<td>584</td>
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<td></td>
</tr>
<tr>
<td>up-H torsion (OPLA)</td>
<td>327</td>
<td>728</td>
<td>490</td>
<td>329</td>
<td>951</td>
</tr>
<tr>
<td>( b_1(a''_2) )</td>
<td></td>
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</tr>
<tr>
<td>all-H torsion (OPLA)</td>
<td>454</td>
<td>794</td>
<td>871</td>
<td>852</td>
<td>628</td>
</tr>
<tr>
<td>( a_1(e') )</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CC scissors</td>
<td>486</td>
<td>440</td>
<td>0.366</td>
<td>477</td>
<td>0.297</td>
</tr>
<tr>
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<td></td>
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</tr>
<tr>
<td>down-H torsion (OPLA)</td>
<td>512</td>
<td>728</td>
<td>887</td>
<td>621</td>
<td>811</td>
</tr>
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<tr>
<td>up-H wag (OPLA)</td>
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<td>503</td>
<td>330</td>
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<td>713</td>
</tr>
<tr>
<td>( b_1(a''_2) )</td>
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<tr>
<td>CC torsion (OPLA)</td>
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<td>531</td>
<td>420</td>
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</tr>
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<tr>
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<td>989</td>
<td>0.112</td>
<td>945</td>
<td>-0.61</td>
</tr>
<tr>
<td>( b_2(a''_2) )</td>
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<td></td>
</tr>
<tr>
<td>all-H rock</td>
<td>955</td>
<td>1002</td>
<td>1033</td>
<td>993</td>
<td>994</td>
</tr>
<tr>
<td>( b_2(e') )</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>up-H-rock</td>
<td>1010</td>
<td>1064</td>
<td>1079</td>
<td>1130</td>
<td>1207</td>
</tr>
<tr>
<td>( a_1(e') )</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>down-H-rock</td>
<td>1032</td>
<td>1064</td>
<td>0.014</td>
<td>1128</td>
<td>0.127</td>
</tr>
<tr>
<td>( b_2(e') )</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CC a/a-stretch</td>
<td>1223</td>
<td>1416</td>
<td>1236</td>
<td>457i</td>
<td>346</td>
</tr>
<tr>
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<td></td>
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<tr>
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</tr>
<tr>
<td>( b_2(e') )</td>
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<tr>
<td>down-H scissors</td>
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<td>1569</td>
<td>1570</td>
<td>1539</td>
<td>1521</td>
</tr>
<tr>
<td>( a_1(e') )</td>
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<tr>
<td>up-H scissors</td>
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<td>1569</td>
<td>0.035</td>
<td>1639</td>
<td>-0.310</td>
</tr>
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<td>all-H scissors</td>
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<tr>
<td>up-H s-stretch</td>
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<td>3283</td>
<td>0.004</td>
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<td>0.851</td>
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<td>3286</td>
<td>3269</td>
<td>3288</td>
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<td>all-H s-stretch</td>
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<td>-0.298</td>
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<td>( b_2(a''_2) )</td>
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<td>all-H a-stretch</td>
<td>3183</td>
<td>3384</td>
<td>3391</td>
<td>3375</td>
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<tr>
<td>( b_2(e') )</td>
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<tr>
<td>H a-stretch</td>
<td>3208</td>
<td>3387</td>
<td>3388</td>
<td>3415</td>
<td>3402</td>
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<tr>
<td>( a_1(e') )</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H a-stretch</td>
<td>3208</td>
<td>3387</td>
<td>0.004</td>
<td>3393</td>
<td>0.027</td>
</tr>
</tbody>
</table>

\( ^a \) Vibrational frequencies in cm\(^{-1} \), geometry distortions in A/\(\sqrt{a.m.u.}\). Equilibrium geometries and vibrational frequencies of anion and neutral are calculated by B3LYP/aug-cc-pVTZ and SF-DFT/6-31G*, respectively.

\( ^b \) Symmetry labels are not applicable for the \( 1^1B_1 \) state that has twisted \( C_2 \) equilibrium structure.
The modelled spectrum of TMM$^-$ is shown in Figure 7.5. 10 normal modes were used in modelling of the triplet state. These are the active modes 5, 9, 14, 16, 17, as well as modes without displacement but with large differences in frequencies between the anion and neutral (modes 0, 1, 2, 3, and 4), see Table 7.1. The latter modes can appear in PES as hot bands. Modelling of the singlet $^1A_1$ state included 9 modes, i.e., modes with $\Delta Q \neq 0$ (5, 12, 14, and 16)
and modes contributing to hot bands (0, 1, 2, 3, and 13). More information on modelling procedure can be found in Appendix B.

Figure 7.6. PES of TMM$^-$ in the triplet region. The empty circles show the intensities of the transitions, i.e, the stick-spectrum. The bold black line (the modelled spectrum) is obtained by convolution of the stick spectrum by Gaussians.

Figures 7.6 and 7.7 compare the triplet and singlet regions, respectively, of the calculated and the experimental spectra [1, 2]. The triplet region of PES is better resolved. In modelled spectrum, peaks A, B, C, and D are due to the progression of the CC-scissoring mode 5. Peaks K, L, and M correspond
Figure 7.7. PES of TMM\(^{-}\) in the singlet region

to one quantum of skeleton symmetric stretch (9) and 0-2 quanta of mode 5. Peak x is a hot band, i.e., it is a transition from the excited vibrational level of anion (with one quantum of mode 5) to the ground vibrational level of neutral. Peaks a,b, and c are also hot bands. Three transitions contribute to each of these peaks: these are excitations from the first vibrational level of anion to the first vibrational level of neutral along the modes 0, 1, and 2, i.e., \(0^{1-1}\), \(1^{1-1}\), \(2^{1-1}\). Moreover, the peaks b and c have one and two quanta of the skeleton
scissoring mode, respectively. Therefore, as follows from Fig. 7.6, the triplet spectrum is dominated by the mode with the largest $\Delta Q$, i.e., the skeleton scissors. Overall, modelled and experimental spectra of the triplet state are in a very good agreement.

The singlet region of the PES shown in Fig. 7.7 is less structured. The calculated spectrum is dominated by the skeleton scissoring mode. The shoulders on the main peaks are due to the hot bands, similarly to a, b, c peaks in the triplet region. The small peak at about 1.07 eV is a hot band transition from the excited by one quantum of mode 5 vibrational state of anion. Unlike the triplet spectrum, the calculated and experimental spectra of the singlet state do not agree well with each other. First of all, the character of the progression along mode 5 is different in the modelled and the experimental PES, i.e., in the calculated spectrum, this mode has longer progression. This suggests that the relative geometries of the $^1A_1$ singlet and the anion are not accurate enough. Since in the triplet modelled spectrum, the overall shape of this progression was in a good agreement with the experiment, we conclude that the problem is in the geometry of the $^1A_1$ singlet rather than in that of the anion. Another problematic feature is the peaks of experimental spectra shown in Fig. 7.7 by asterisks. They are thought to be not the hot bands but the transitions along the mode with a very low frequency, about 90 cm$^{-1}$. No such frequency was found in the calculated vibrational spectrum of the $^1A_1$ singlet. Another issue is
that the experimental PES in the singlet region has overall more condensed signal than the calculated spectrum. This can be due to a variety of reasons, e.g., the hot band activity in the experimental PES may be underestimated in calculated spectrum, or, there are indeed other active vibrational transitions, which are not reproduced by the calculations, or, that the signal from the open-shell singlet, though unresolved, contributes to this region. To conclude, additional calculations at a higher level of theory are required to understand the spectrum of the singlet state.
Reference List


Chapter 8

Benchmark results for EOM-CC(2,3) for open-shell species

Hirata, Nooijen, and Bartlett [1] benchmarked EOM-EE-CC(2,3), as well as other EOM-EE-CC models, on the excited states of CH\(^+\) using the closed-shell reference. Our study extends the benchmark set by including the following open-shell systems: (i) two problematic radicals, CH and CO\(^+\); (ii) the CH\(_2\) diradical; (iii) the trimethylenemethane (TMM) diradical; and (iv) the dehydro-meta-xylylene (DMX) triradical. To obtain EOM-CC(2,3) results apt for comparison with experiment for the two latter systems, we employed an extrapolation technique based on an energy separability scheme [2]:

\[
E_{EOM-CC(2,3)}^{large} = E_{EOM-CC(2,3)}^{small} + (E_{EOM-CCSD}^{large} - E_{EOM-CCSD}^{small}), \quad (8.1)
\]
where $E^{\text{large}}$ and $E^{\text{small}}$ refer to the total energies calculated in large (e.g., cc-pVTZ) and small (e.g., 6-31G*) basis sets. This procedure assumes that changes in the total energy due to the basis set increase are similar for the less and more correlated models [e.g., MP2 and CCSD, or EOM-CCSD and EOM-CCSD(2,3)].

Our benchmark study addresses the following questions: (i) the extent of the effect of spin-contamination on the accuracy of EOM-CC(2,3); (ii) the sensitivity of EOM-CC(2,3) to a choice of the reference (UHF vs. ROHF); (iii) the choice of active space and accuracy of EOM-CC(2,3).

### 8.1 CO$^+$ and CH radicals

Due to their challenging electronic structure, the CH and CO$^+$ radicals have been extensively studied [3–5]. To compare the EOM-CC(2,3) data against the MRCI results from Ref. [4] and against spin-restricted LRT-CCSD [4] and CC3 [5], we performed our calculations in the Sadlej-pVTZ (PBS) basis set [6] with frozen core orbitals. To investigate the performance of EOM-CC(2,3), we performed additional set of calculations in non-diffuse 6-311G$^*$ [7] (CO$^+$) and cc-pVTZ [8] (CH) basis sets$^1$.

$^1$Diffuse orbitals are problematic for an active space method. Different approaches exist to alleviate this problem, e.g., using natural orbitals instead of molecular ones. However, this issue is out of scope of this work.
Table 8.1. Total energies of the ground state (hartree) and vertical excitation energies (eV) of the two low-lying excited states of CO\(^+\) calculated using different EOM-CC methods with ROHF and UHF references\(^a\)

<table>
<thead>
<tr>
<th>Method</th>
<th>(X^2\Sigma^+)</th>
<th>(A^2\Pi)</th>
<th>(B^2\Sigma^+)</th>
</tr>
</thead>
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<tr>
<td>PBS basis</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>UHF-EOM-EE-CCSD</td>
<td>-112.566265</td>
<td>3.533</td>
<td>6.199</td>
</tr>
<tr>
<td>ROHF-EOM-EE-CCSD</td>
<td>-112.566036</td>
<td>3.230</td>
<td>6.011</td>
</tr>
<tr>
<td>UHF-EOM-EE-CC(2,3)</td>
<td>-112.579033</td>
<td>3.369</td>
<td>5.890</td>
</tr>
<tr>
<td>ROHF-EOM-EE-CC(2,3)</td>
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<td>3.353</td>
<td>5.866</td>
</tr>
<tr>
<td>SR-CCSD(^b)</td>
<td></td>
<td>3.22</td>
<td>6.07</td>
</tr>
<tr>
<td>UHF-CC3(^c)</td>
<td></td>
<td>3.330</td>
<td>5.811</td>
</tr>
<tr>
<td>ROHF-CC3(^c)</td>
<td></td>
<td>3.290</td>
<td>5.725</td>
</tr>
<tr>
<td>MRCI</td>
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<td>3.30</td>
<td>5.88</td>
</tr>
<tr>
<td>6-311G* basis</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>UHF-EOM-EE-CCSD</td>
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<td>3.577</td>
<td>6.189</td>
</tr>
<tr>
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<td>5.851</td>
</tr>
<tr>
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<td>5.871</td>
</tr>
<tr>
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<td>5.992</td>
</tr>
<tr>
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<td>5.846</td>
</tr>
<tr>
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<td>5.808</td>
</tr>
<tr>
<td>Experiment(^e)</td>
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<td>3.26</td>
<td>5.82</td>
</tr>
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</table>

\(^a\) Calculations performed at the experimental ground state geometry [9] \([r(CO)=1.115\,\AA]\) using the PBS and 6-311G* basis sets with frozen core orbitals.

\(^b\) Results from Ref. [4].

\(^c\) Results from Ref. [5].

\(^d\) EOM-CC(2,3) with six-orbital active space; see text for details.

\(^e\) Experimental results from Ref. [9].

CO\(^+\) is an example of a radical with the considerably spin-contaminated reference, and, consequently, spin-contaminated excited states. As shown in Table 8.1, the spin-contamination manifests itself in large differences between the UHF-EOM-CCSD and ROHF-EOM-CCSD excitation energies (0.2–0.3 eV). However, for EOM-CC(2,3), there is only a minimal difference (\(\sim\) 0.02 eV).
between the ROHF and UHF values. Similar behavior, i.e., significant reduction of spin-contamination with inclusion of triple excitations, was previously reported for other models with triple excitations, e.g., CC3 [5]. For CO\(^+\), the accuracy of EOM-CC(2,3) exceeds that of SR-CCSD-LRT, and is similar to the accuracy of CC3; the differences between EOM-CC(2,3) and MRCI results do not exceed 0.07 eV.

![Diagram](image)

**Figure 8.1.** Electronic structure of CO\(^+\) radical. Orbital labels are given in \(C_2\)\(_v\) symmetry group. The two lowest excited states of CO\(^+\) are dominated by excitations from the \(4a_1^2\) and \(1b_1^2/1b_2^2\) to \(5a_1^1\) orbital. Thus, these orbitals form the minimal active space for the active-space EOM-CC(2,3) calculations. Inclusion of the anti-bonding \(\pi\)-orbitals in the active space is also important.

As an active space for the \(^2\Pi\) and \(^2\Sigma^+\) valence states of CO\(^+\), we chose the following set of orbitals: \(4a_1^2, 1b_1^3, 1b_2^3, 5a_1^1, 2b_1^0, 2b_2^0\), i.e., in addition to singly-occupied \(5a_1^1\), we augmented the active space by three highest doubly-occupied
and two lowest virtual orbitals. These orbitals are shown in Figure 8.1. The $4a_2^1, 1b_1^1, 1b_2^1, 5a_1^1$ orbitals form the minimal active space for the $^2\Pi$ and $^2\Sigma^+$ states (see Sec. 1.7.4), whereas $2b_0^0$ and $2b_2^0$ were added as orbitals being next important for description of these states. The importance of these orbitals was derived from the analysis of the EOM-CCSD amplitudes, which revealed large excitation amplitudes involving these two virtual orbitals.

As follows from Table 8.1, EOM-CC(2,3) is a definite improvement over EOM-CCSD and the differences between active-space and full EOM-CC(2,3) values do not exceed 0.05 eV.

![Figure 8.2](image)

**Figure 8.2.** Electronic structure of the CH (tri)radical. Orbital labels are given in the $C_{2v}$ symmetry group. Distribution of three electrons in $2a_1, 1b_1$ and $1b_2$ triradical orbitals results in a number of low-lying electronic states shown on the right. Active-space EOM-CC(2,3) with these three orbitals as the active space yields accurate results.
The electronic structure of the CH radical is described in Fig. 8.2. From methodological point of view, CH is a triradical because it has three electrons distributed over three nearly degenerate orbitals \((2a_1, 1b_1, 1b_2)\) in \(C_{2v}\) symmetry group notations). The lowest electronic states of CH are given in the right panel of Fig. 8.2. The ground state of CH, a doubly degenerate \(2\Pi\) state, is closely followed by the \(4\Sigma^-\) quartet state. About 3 eV higher lies the \(2\Delta\) state (one of its components is of a "closed-shell" type, and another is of an "open-shell" type). Slightly higher is the "open-shell" \(2\Sigma^-\) doublet, and, finally, there is the \(2\Sigma^+\) state.

Table 8.2 summarizes vertical excitation energies of CH calculated by different CC methods. Clearly, using the ground state wave function as a reference for EOM-CC will lead to intrinsic problems in description of many if not all excited states, since only one component of the \(2\Pi\) state (\(3a_1^2, 1b_1^1\) or \(3a_1^2, 1b_2^1\)) is used as a reference determinant. As a result, the second component of this state appears as an EOM state [column \(2\Pi(EOM)\) in Table 8.2], i.e., the degeneracy between the two components of \(2\Pi\) is not reproduced. Another problem arises with the description of electronic states which include configurations that are formally doubly excited with respect to the reference, e.g., configurations (3) and (10) from Fig. 1.3. Configuration (3) is a so-called "pseudo-double" excitation with respect to the reference determinant [configuration (5)], it
Table 8.2. Total energies of the ground state (hartree) and vertical excitation energies (eV) of several low-lying excited states of CH radical calculated using various CC methods with ROHF and UHF references

<table>
<thead>
<tr>
<th>Method</th>
<th>( X^2\Pi )</th>
<th>( X^2\Pi ) (EOM)</th>
<th>( a^1\Sigma^- )</th>
<th>( A^2\Delta^c )</th>
<th>( A^2\Delta^d )</th>
<th>( B^2\Sigma^- )</th>
<th>( C^2\Sigma^+ )</th>
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</thead>
<tbody>
<tr>
<td>UHF-EOM-EE-CCSD</td>
<td>-38.385379</td>
<td>0.011</td>
<td>0.944</td>
<td>3.221</td>
<td>3.331</td>
<td>4.404</td>
<td>5.312</td>
</tr>
<tr>
<td>ROHF-EOM-EE-CCSD</td>
<td>-38.385681</td>
<td>0.005</td>
<td>0.908</td>
<td>3.215</td>
<td>3.304</td>
<td>4.230</td>
<td>5.199</td>
</tr>
<tr>
<td>UHF-EOM-EE-CC(2,3)</td>
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<td>0.011</td>
<td>0.659</td>
<td>3.030</td>
<td>3.026</td>
<td>3.328</td>
<td>4.107</td>
</tr>
<tr>
<td>ROHF-EOM-EE-CC(2,3)</td>
<td>-38.38582</td>
<td>0.010</td>
<td>0.654</td>
<td>3.023</td>
<td>3.022</td>
<td>3.325</td>
<td>4.102</td>
</tr>
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<td>0.624</td>
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<td>3.030</td>
<td>3.341</td>
<td>4.114</td>
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<td>3.025</td>
<td>3.347</td>
<td>4.108</td>
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<td>UHF-EOM-SF-CC(2,3)</td>
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<td>0.636</td>
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<td>3.000</td>
<td>3.316</td>
<td>4.056</td>
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<td>2.999</td>
<td>3.318</td>
<td>4.055</td>
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<tr>
<td>CCSD-psT-LRT</td>
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<td>3.14</td>
<td>3.48</td>
<td>5.16</td>
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<tr>
<td>UHF-CC3 (^f)</td>
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<td></td>
<td></td>
<td>3.173</td>
<td>3.643</td>
<td>4.517</td>
<td></td>
</tr>
<tr>
<td>ROHF-CC3 (^f)</td>
<td></td>
<td></td>
<td></td>
<td>3.160</td>
<td>3.576</td>
<td>4.472</td>
<td></td>
</tr>
<tr>
<td>MRCI</td>
<td></td>
<td></td>
<td></td>
<td>2.96</td>
<td>3.31</td>
<td>4.03</td>
<td></td>
</tr>
<tr>
<td>Exp. (adiabatic) (^g)</td>
<td></td>
<td>0.725</td>
<td></td>
<td>2.875</td>
<td>3.229</td>
<td>3.943</td>
<td></td>
</tr>
<tr>
<td>Exp. (vert) (^h)</td>
<td></td>
<td>0.745</td>
<td></td>
<td>2.880</td>
<td>3.263</td>
<td>3.943</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Calculations performed at the experimental ground state geometry [9] \([r(CH)=1.1198\,\text{Å}]\) using the PBS basis set with one frozen core orbital.

\(^b\) The energy of the \( X^2\Pi \) state found in the EOM procedure (see text).

\(^c\) The open-shell component of the \( A^2\Delta \) state.

\(^d\) The closed-shell component of the \( A^2\Delta \) state.

\(^e\) Results from Ref. [4].

\(^f\) Results from Ref. [5].

\(^g\) Experimental results from Ref. [9].

\(^h\) Values are estimated based on the adiabatic energy differences and harmonic vibrational frequencies [9] of the potential surfaces of the excited states.
appears in the quartet $^4\Sigma^-$, in the "open-shell" component of the $^2\Delta$ state, and in the $^2\Sigma^-$ doublet. Configuration (10) contributes to the "closed-shell" component of the $^2\Delta$ state, in which the weight of this configuration is not very large, and to the $^2\Sigma^+$ state, where configuration (10) is dominant. Thus, all these states (excluding, perhaps, the closed-shell component of $^2\Delta$) are expected to suffer from unbalanced description by any EOM-CC model, which employs the ground state as a reference. Inclusion of triples (or quadruples) will reduce this intrinsic imbalance, but will not fully eliminate it.

As follows from Table 8.2, both UHF and ROHF based EOM-CCSD fail to describe $^2\Sigma^-$ and $^2\Sigma^+$ states. Two components of $^2\Delta$ state, which lost their degeneracy due to different excitation levels of leading configurations, and the $^4\Sigma^-$ quartet are about 0.2-0.3 eV off relative to the MRCI results. EOM-CC(2,3) dramatically improves description of the excited states of CH. For all the states considered, the largest deviation from the MRCI results is 0.08 eV. Differences between the UHF and ROHF data are less than 0.01 eV. For CH, EOM-CC(2,3) performs much better than the CCSD-pst-LRT or CC3 methods.

As expected, EOM-CC(2,3) does not fully restore the degeneracy between different components of the multi-component states ($^2\Pi$ and $^2\Delta$). An alternative (and methodologically correct) way to treat this problem is by using the SF rather than EE variant of EOM-CC. As demonstrated in Refs. [10] and [11],
EOM-SF-CCSD accurately describes all triradical states by taking the high-spin component of the quartet state as a reference. As a result, even EOM-SF-CCSD results are in excellent agreement with MRCI ones (discrepancies are less than 0.1 eV), the EOM-SF-CC(2,3) data further improving. As an important consequence of using the method that provides the balanced description of the excited states, the multi-component states appear as exactly degenerate both in EOM-SF-CCSD and EOM-SF-CC(2,3). Moreover, the spin-contamination of SF states is very small even at the EOM-SF-CCSD level: the UHF and ROHF data differ by less than 0.01 eV.

The EOM-CC(2,3) results are shown in Table 8.3. As an active space for both the EE and SF variants of EOM-CC(2,3), we choose three triradical orbitals \((3a_1, 1b_1, 1b_2)\). This is a minimal active space since all considered excitations occur within these orbitals. For both UHF and ROHF based EOM-EE-CC(2,3), this active space yields excellent results: the differences between the active-space and full EOM-EE-CC(2,3) are less than 0.05 eV and 0.03 eV, for UHF and ROHF, respectively. For the SF variant, the active-space EOM-SF-CC(2,3) also improves the performance of EOM-SF-CCSD and approaches the accuracy of full EOM-SF-CC(2,3): active-space and full EOM-SF-CC(2,3) results differ by less than 0.02 eV. However, the relative improvement of active-space EOM-CC(2,3) over EOM-CCSD is much more modest for the SF than EE variant. For example, for the \(^2\Sigma^+\) state, active-space EOM-EE-CC(2,3) recovers
Table 8.3. Total energies of the ground state (hartree) and vertical excitation energies (eV) of several low-lying excited states of CH radical calculated using the active-space EOM-EE-CC(2,3) and EOM-SF-CC(2,3) methods with ROHF and UHF references.

<table>
<thead>
<tr>
<th>Method</th>
<th>(X^2\Pi)</th>
<th>(X^2\Pi) (EOM)</th>
<th>(a^1\Sigma^-)</th>
<th>(A^2\Delta) (^{c})</th>
<th>(A^2\Delta) (^{d})</th>
<th>(B^2\Sigma^-)</th>
<th>(C^2\Sigma^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF-EOM-EE-CCSD</td>
<td>-38.407096</td>
<td>0.015</td>
<td>1.024</td>
<td>3.210</td>
<td>3.223</td>
<td>4.590</td>
<td>5.521</td>
</tr>
<tr>
<td>UHF-EOM-EE-CC(2,3)</td>
<td>-38.408764</td>
<td>0.009</td>
<td>0.751</td>
<td>3.031</td>
<td>3.021</td>
<td>3.356</td>
<td>4.156</td>
</tr>
<tr>
<td>UHF-EOM-EE-CC(2,3)</td>
<td>-38.411018</td>
<td>0.017</td>
<td>0.743</td>
<td>3.009</td>
<td>3.004</td>
<td>3.343</td>
<td>4.113</td>
</tr>
<tr>
<td>ROHF-EOM-EE-CCSD</td>
<td>-38.406975</td>
<td>0.007</td>
<td>0.991</td>
<td>3.205</td>
<td>3.295</td>
<td>4.402</td>
<td>5.402</td>
</tr>
<tr>
<td>ROHF-EOM-EE-CC(2,3)</td>
<td>-38.408772</td>
<td>0.001</td>
<td>0.723</td>
<td>3.000</td>
<td>3.010</td>
<td>3.342</td>
<td>4.141</td>
</tr>
<tr>
<td>ROHF-EOM-EE-CC(2,3)</td>
<td>-38.410986</td>
<td>0.016</td>
<td>0.738</td>
<td>3.000</td>
<td>2.998</td>
<td>3.340</td>
<td>4.117</td>
</tr>
<tr>
<td>UHF-EOM-SF-CCSD</td>
<td>-38.407473</td>
<td>0.000</td>
<td>0.687</td>
<td>2.991</td>
<td>2.991</td>
<td>3.343</td>
<td>4.118</td>
</tr>
<tr>
<td>UHF-EOM-SF-CC(2,3)</td>
<td>-38.408372</td>
<td>0.000</td>
<td>0.697</td>
<td>2.964</td>
<td>2.964</td>
<td>3.325</td>
<td>4.070</td>
</tr>
<tr>
<td>UHF-EOM-SF-CC(2,3)</td>
<td>-38.410184</td>
<td>0.000</td>
<td>0.709</td>
<td>2.965</td>
<td>2.965</td>
<td>3.332</td>
<td>4.056</td>
</tr>
<tr>
<td>Exp. (adiabatic)</td>
<td></td>
<td>0.725</td>
<td>2.875</td>
<td>3.229</td>
<td>3.943</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp. (vert)</td>
<td></td>
<td>0.745</td>
<td>2.880</td>
<td>3.263</td>
<td>3.943</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Calculations performed at the experimental ground state geometry \([9]\) \(r(\text{CH})=1.1198\text{Å}\) using the cc-pVTZ basis set with one frozen core orbital.

\(^b\) The energy of the \(X^2\Pi\) state found in the EOM procedure.

\(^c\) The open-shell component of the \(A^2\Delta\) state.

\(^d\) The closed-shell component of the \(A^2\Delta\) state.

\(^e\) EOM-CC(2,3) with three-orbital active space; see text for detail.

\(^f\) Experimental results from Ref. \([9]\).

\(^g\) Values are estimated based on the adiabatic energy differences and harmonic vibrational frequencies \([9]\) of the potential surfaces of the excited states.
about 1.3 eV of discrepancy between the CCSD and CC(2,3) energies, whereas
the corresponding gain of EOM-EE-CC(2,3) is only 0.05 eV. This observation
does not suggest that the chosen active space is more appropriate for EOM-EE-
CC(2,3) than for EOM-SF-CC(2,3). Rather: (i) the inclusion of semi-internal
triples efficiently solved the problem caused by non-dynamical correlation, i.e.,
the active space improved the EOM-EE-CCSD results corrupted by orbital
degeneracies; and (ii) a small subset of triples was not sufficient to recover
the dynamical correlation correction available through using full triples.

8.2 CH₂ diradical

The CH₂ diradical is a popular benchmark system [12–15]. Following our bench-
mark study presented in Chapter 2, we now investigate how EOM-CC(2,3)
improves the performance of the SF and EE variants of EOM-CCSD. We also
consider the active-space EOM-CC(2,3) and analyze the performance of EOM-
CC(2,3), which employs a deliberately poor reference, the excited 2¹A₁ deter-
minant.

Adiabatic excitation energies of CH₂ calculated by EOM-CCSD and EOM-
CC(2,3) as well as the FCI results from Ref. [15] are summarized in Table 8.4.
Using the 1¹A₁ state as a reference (EE approach), the triplet 3B₁ and the open-
shell 1B₁ singlet appear as the EOM states with dominant single-excitation
Table 8.4. Total energies of the ground state (hartree) and adiabatic excitation energies (eV) of the CH$_2$ diradical calculated by different EOM-EE-CC and EOM-SF-CC methods in comparison to the FCI energies$^a$

<table>
<thead>
<tr>
<th>Method</th>
<th>$^3B_1$</th>
<th>$^1A_1$</th>
<th>$^1B_1$</th>
<th>$^2A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOM-EE-CCSD</td>
<td>-39.063114</td>
<td>0.526</td>
<td>1.565</td>
<td>3.799</td>
</tr>
<tr>
<td>EOM-EE-CC(2,3)$^b$</td>
<td>-39.063163</td>
<td>0.488</td>
<td>1.545</td>
<td>2.757</td>
</tr>
<tr>
<td>EOM-EE-CC(2,3)</td>
<td>-39.065456</td>
<td>0.454</td>
<td>1.539</td>
<td>2.689</td>
</tr>
<tr>
<td>EOM-EE-CCSD ($^2A_1$ ref)</td>
<td>-39.057717</td>
<td>1.921</td>
<td>1.439</td>
<td>1.894</td>
</tr>
<tr>
<td>EOM-EE-CC(2,3)$^b$ ($^2A_1$ ref)</td>
<td>-39.062944</td>
<td>0.692</td>
<td>1.541</td>
<td>2.734</td>
</tr>
<tr>
<td>EOM-EE-CC(2,3) ($^2A_1$ ref)</td>
<td>-39.065375</td>
<td>0.657</td>
<td>1.541</td>
<td>2.676</td>
</tr>
<tr>
<td>EOM-SF-CCSD $^c$</td>
<td>-39.062846</td>
<td>0.510</td>
<td>1.564</td>
<td>2.715</td>
</tr>
<tr>
<td>EOM-SF-CC(2,3)$^{b,c}$</td>
<td>-39.063078</td>
<td>0.497</td>
<td>1.554</td>
<td>2.705</td>
</tr>
<tr>
<td>EOM-SF-CC(2,3) $^c$</td>
<td>-39.065208</td>
<td>0.477</td>
<td>1.542</td>
<td>2.664</td>
</tr>
<tr>
<td>FCI$^d$</td>
<td>39.066738</td>
<td>0.483</td>
<td>1.542</td>
<td>2.674</td>
</tr>
</tbody>
</table>

$^a$TZ2P basis set from Ref. [12], one frozen core and one frozen virtual orbital; FCI/TZ2P optimized geometries [15].
$^b$ EOM-CC(2,3) with two-orbital active space; see text for details.
$^c$ UHF reference used for SF calculations.
$^d$ FCI results from Ref. [15].

character. The discrepancy between EOM-EE-CCSD and FCI for these two states is less than 0.05 eV. However, the second closed-shell $^2A_1$ singlet is dominated by the double excitation from this reference. As a result, EOM-EE-CCSD description is very poor: the error is more than 1 eV. The SF model treats all four diradical states as the excited spin-flipped states from the high-spin triplet reference determinant. Consequently, all the above states have dominant single-excitation character and are described by EOM-SF-CCSD in a balanced way: errors against FCI are less than 0.04 eV.
EOM-CC(2,3) represent an improvement over both EE-EOM and SF-EOM: the errors against FCI are 0.03 eV and 0.01 eV, respectively.

As the minimal active space for the EOM-CC(2,3), we choose two diradical orbitals, $3a_1$ and $1b_1$. As follows from Table 8.4, the accuracy of active-space EOM-CC(2,3) closely follows that of full EOM-CC(2,3); errors against FCI are less than 0.1 eV and 0.03 eV for EE and SF variants, respectively.

To test how robust EOM-EE-CC(2,3) with respect to the reference choice, we calculated the electronic states of CH$_2$ starting from the excited $2^1A_1$ reference determinant. As shown in Table 8.4, EOM-CCSD fails to describe both the $1^1A_1$ and $2^1A_1$ closed-shell singlets. The results of EOM-CC(2,3) are much better: the $1^1B_1$ and $2^1A_1$ states are in excellent agreement with FCI, the $1^1A_1$ state is only 0.18 eV off. The active-space variant also performs well, e.g., the active-space energies are within 0.06 eV from the full EOM-CC(2,3) values. To conclude, the inclusion of triples in EOM-CC(2,3) dramatically improves the EOM-CCSD energies even when a poorly described state is used as a reference; small but correctly selected active space gives accurate results as well.
8.3 TMM

Electronic structure of TMM, the fascinating non-Kekulé molecule, was discussed in details in Section 2.3.5 and Chapter 3. The π-system of TMM consists of four π-electrons which can be distributed over four molecular π-type orbitals (Fig. 2.6). As demonstrated in previous Chapters, the TMM diradical can be described in a balanced way by the SF methods, however, the discrepancy between available experimental and theoretical multi-reference results was perceptible. In this section, we investigate the effect of triples on adiabatic excitation energies of four low-lying electronic states of TMM.

Two bases were used: a small 6-31G* [16] and a larger cc-pVTZ basis sets. To compare EOM-SF-CC(2,3) results with experiment, we applied the energy separability scheme (8.1), where large and small correspond to cc-pVTZ and 6-31G* bases, respectively. Equilibrium geometries and zero-point energies (ZPE) of TMM’s states are from Ref. [17].

Distribution of two electrons in two diradical orbitals ($2b_1$ and $1a_2$) determines the electronic state of TMM. Thus, this is the minimal active space for EOM-SF-CC(2,3). However, inclusion of two other π orbitals in active space is also important. Therefore, we employed two different active spaces: the minimal diradical active space ($2b_1$ and $1a_2$ orbitals), and a larger 4-π-orbital active space ($1b_1, 2b_1, 1a_2, 3b_1$), see Fig. 2.6 for orbital notations.
Table 8.5. Total energies of the ground state (hartree) and adiabatic excitation energies (eV) of the TMM diradical calculated by different EOM-SF-CC methods in comparison to the multi-reference and experimental values$^a$

<table>
<thead>
<tr>
<th>Method</th>
<th>$^3A_2$</th>
<th>$^1B_1$</th>
<th>$^1A_1$</th>
<th>$^2A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G* basis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EOM-SF-CCSD</td>
<td>-155.365751</td>
<td>0.510</td>
<td>0.919</td>
<td>4.337</td>
</tr>
<tr>
<td>EOM-SF-CC(2,3)$^b$</td>
<td>-155.368385</td>
<td>0.555</td>
<td>0.830</td>
<td>4.356</td>
</tr>
<tr>
<td>EOM-SF-CC(2,3)$^c$</td>
<td>-155.370897</td>
<td>0.657</td>
<td>0.784</td>
<td>4.171</td>
</tr>
<tr>
<td>EOM-SF-CC(2,3)</td>
<td>-155.373271</td>
<td>0.653</td>
<td>0.774</td>
<td>4.028</td>
</tr>
<tr>
<td>cc-pVTZ basis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EOM-SF-CCSD</td>
<td>-155.589945</td>
<td>0.554</td>
<td>0.933</td>
<td>3.860</td>
</tr>
<tr>
<td>EOM-SF-CC(2,3)$_{extrap,d}$</td>
<td>-155.597465</td>
<td>0.697</td>
<td>0.788</td>
<td>3.551</td>
</tr>
<tr>
<td>MCSCF(10/10)$^a$</td>
<td>-155.033829</td>
<td>0.705</td>
<td>0.832</td>
<td></td>
</tr>
<tr>
<td>MCQDPT2(10/10)$^a$</td>
<td>-155.568282</td>
<td>0.710</td>
<td>0.828</td>
<td></td>
</tr>
<tr>
<td>Experiment$^e$ - $\Delta ZPE$</td>
<td></td>
<td></td>
<td></td>
<td>0.787</td>
</tr>
</tbody>
</table>

$^a$ Equilibrium geometries and ZPEs of TMM’s states as long as multi-reference data are from Ref. [18]; four frozen core and four frozen virtual orbitals.

$^b$ EOM-SF-CC(2,3) with two-orbital active space; see text for detail.

$^c$ EOM-SF-CC(2,3) with four-orbital active space; see text for detail.

$^d$ Extrapolated results by using Eq. (8.1).

$^e$ Experimental data are from Ref. [19].

The results for full and active-space EOM-SF-CC(2,3), which are summarized in Table 8.5, reveal that triple excitations are very important for this molecule. Indeed, inclusion of triples changes the energies of all three excited states by 0.15 - 0.3 eV. Note that on the EOM-SF-CCSD level, two closed-shell singlets are too high in energy whereas the open-shell (and highly spin-contaminated) $^1B_1$ is over-stabilized. This suggests that correlation of the excited states of TMM occurs by different mechanisms. Consequently, the selection of a common to all states and yet compact active-space is not trivial. As follows from
Table 8.5, the minimal two-orbital active space (similar to that employed for the CH$_2$ diradical) only slightly improves the EOM-SF-CCSD results. A larger 4-orbital active space brings the energies of $1^1A_1$ and $1^1B_1$ to within 0.01 eV from full EOM-SF-CC(2,3) ones, however, the energy of $2^1A_1$ is still 0.15 eV off. We noticed that in the latter state, higher in energy virtual $\pi$ orbitals contribute significantly to the excitation amplitudes, therefore, a larger or different active space is required to achieve the accuracy of full EOM-CC(2,3).

The basis set effects in TMM are also state dependent. In the two lowest states, $1^1B_1$ and $1^1A_1$, increase in basis set from 6-31G* to cc-pVTZ slightly raises the excitation energies (by 0.02 - 0.03 eV). However, in the $2^1A_1$ state, there is a tremendous 0.5 eV drop in the excitation energy. Using the energy separability scheme extrapolations brings the EOM-SF-CC(2,3) results for $1^1A_1$ to the excellent agreement with the experiment. The excitation energy for open-shell $1^1B_1$ agrees well with the MCQDPT2 data.

We conclude that for the molecule with such a non-trivial electronic structure as TMM, both dynamical and non-dynamical correlation are important. Our extrapolated EOM-CC(2,3) values give accurate estimate of the excitation energies of the considered electronic states of TMM.
8.4 DMX

The electronic structure of the DMX triradical was discussed in detail in Chapter 5. Molecular orbitals of DMX are given in Fig. 8.3. The three lowest in energy orbitals shown in this figure are doubly occupied in the lowest electronic states of DMX, the three highest in energy orbitals are unoccupied. Distribution of three electrons in three middle triradical orbitals determines the electronic state of DMX. Of these three, the lowest in energy is the $a_1$ orbital. This $\sigma$-type orbital is formed by the $sp^2$ hybridized atomic orbital on carbon and lies in the molecular plane. Two $\pi$-orbitals are dominated by atomic p-orbitals on the methylene carbons. According to the spin-polarization principle (and confirmed by the SF calculations), the ground state of DMX is the doublet of the open-shell type, with 3 genuinely unpaired anti-ferromagnetically coupled electrons. In this state, each electron occupies its own orbital. DMX is the first example of the hydrocarbon molecule with the open-shell doublet ground state, contrarily to the Hund’s rule and aufbau principle.

The SF approach yields accurate energy separations between the lowest electronic states of DMX. However, the electronic states in this molecule suffer from strong spin-contamination. The spin-contamination in DMX originates from the instabilities in the $\sigma - \pi$ type high-spin state used as the SF reference. Other examples of spin-contamination of this type were observed in didehydrotoluens.
Figure 8.3. Molecular orbitals of DMX. The $\pi$-system and the $\sigma$-type phenyl like orbital are presented. Whereas the electronic state is determined by electron distribution over three triradical orbitals (minimal active space), the inclusion in active space of benzene $\pi$-orbitals is crucial for eliminating spin-contamination and producing accurate excitation energies.
Table 8.6. Total energies of the ground state (hartree) and vertical excitation energies (eV) of the DMX triradical calculated by different EOM-SF-CC methods

<table>
<thead>
<tr>
<th>Method</th>
<th>$^2B_2$</th>
<th>$^4B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>6-31G basis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UHF-EOM-SF-CCSD</td>
<td>-307.498124</td>
<td>0.546</td>
</tr>
<tr>
<td>UHF-EOM-SF-CC(2,3)$^b$</td>
<td>-307.494383</td>
<td>0.318</td>
</tr>
<tr>
<td>UHF-EOM-SF-CC(2,3)$^c$</td>
<td>-307.495853</td>
<td>0.198</td>
</tr>
<tr>
<td>ROHF-EOM-SF-CCSD</td>
<td>-307.495757</td>
<td>0.272</td>
</tr>
<tr>
<td>ROHF-EOM-SF-CC(2,3)$^b$</td>
<td>-307.493400</td>
<td>0.179</td>
</tr>
<tr>
<td>ROHF-EOM-SF-CC(2,3)$^c$</td>
<td>-307.495619</td>
<td>0.158</td>
</tr>
<tr>
<td><strong>6-311G</strong> basis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UHF-EOM-SF-CCSD</td>
<td>-308.213445</td>
<td>0.503</td>
</tr>
<tr>
<td>ROHF-EOM-SF-CCSD</td>
<td>-308.209668</td>
<td>0.164</td>
</tr>
<tr>
<td>UHF-EOM-SF-CC(2,3)$^{c,d,extrap}$</td>
<td>0.155</td>
<td></td>
</tr>
<tr>
<td>ROHF-EOM-SF-CC(2,3)$^{c,d,extrap}$</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>Experiment$^a$</td>
<td>0.04 ± 0.17</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Equilibrium geometry of the ground state of DMX and experimental data are from Ref. [21]; frozen core orbitals.

$^b$ EOM-SF-CC(2,3) with three active orbitals; see text for detail.

$^c$ EOM-SF-CC(2,3) with nine active orbitals; see text for detail.

$^d$ Extrapolated results by using Eq. (8.1).

and in the $^1B_1$ (twisted) state of TMM. Here we investigate the effect of the triple excitations on this type of spin-contamination by EOM-CC(2,3). Two active spaces were considered, the minimal triradical active space (i.e., orbitals $1a_1, 3b_1, 2a_2$ from Fig. 8.3), and the larger 9-orbital active space which includes all orbitals from Fig. 8.3.

Two basis sets, 6-31G [20] and 6-311G** [7], were used in this section. To compare our results with experiment, we used the energy separability scheme of Eq. (8.1). The equilibrium geometry of the $^2B_2$ state is taken from Ref. [21].
The vertical energy separations between the lowest doublet and quartet states calculated at different levels of theory are given in Table 8.6. The spin-contamination of the reference and the excited states at the EOM-SF-CCSD level leads to the large (more than 0.3 eV!) difference between the UHF and ROHF values. Using the 3-orbital active space reduces but not completely eliminates this difference. This is expected, because the minimal active space does not target the origin of the spin-contamination — mixing in to the excited state character excitations from other orbitals. Results are much more promising in the 9-orbital active space: the difference between UHF and ROHF based data and spin-contamination are very small (0.04 eV). We expect that the doublet-quartet separation obtained with this 9-orbital active space is very close to the full EOM-SF-CC(2,3) one.

Extrapolating the active-space EOM-CC(2,3) values to the larger basis set give the results very close to ones obtained from the thermochemical experiment [21].

**8.5 Conclusions**

We benchmarked the EE and SF variants of EOM-CC(2,3) on the CO\(^+\) and CH radicals, and on the CH\(_2\) diradical. In all cases, we observed an excellent agreement between EOM-CC(2,3) and MRCI or FCI results: the errors are
hundredths of eV for well described states and up to 0.1-0.2 eV for states with significant double excitations. The accuracy of the active-space models closely follows that of full EOM-CC(2,3). In two larger systems, the TMM diradical and the DMX triradical, we employed the energy separability scheme to compare EOM-CC(2,3) results with experiment. In both cases, calculated results are in an excellent agreement with experimental values.
Reference List


Chapter 9

Conclusions and future work

This work discusses many aspects of the electronic structure of open-shell species, e.g., structural characteristics and bonding patterns in the different electronic states and their spectroscopic signatures, the strength of interaction between radical centers and accurate thermochemistry, as well as Jahn-Teller distortions and evaluation of ionization potentials. All these fascinating facets of electronic structure of open-shell species are worth speculation only if the energy differences between the valence electronic states and their structural characteristics are accurate. Therefore, the largest part of my work was devoted to the implementation and benchmarking of the excited state method that provides higher accuracy in the evaluation of excitation energies, EOM-CC(2,3). This method, which in our implementation can be applied both to closed- and open-shell molecules, opens new horizons in studying intriguing properties of radicals, diradicals, and triradicals.
Several directions may be pursued in the future research to explore the ideas described in this thesis.

For example, for almost any system discussed here there remain unanswered questions, e.g., source of discrepancy between the experimental and calculated PES of the singlet state of TMM, the ground state multiplicity of the 1,3,5-tridehydrobenzene anion and its PES, the origin of spin-contamination in $\sigma - \pi$ diradicals and triradicals, and so on. Many of these questions can be addressed by applying more accurate ab initio techniques, e.g., a method including higher excitations and/or larger basis set.

The second set of interesting problems concerns generalization of certain phenomena inherent to a given molecule to other more or less similar molecular systems. For example, thinking of low-lying electronic states of DMX$^-$, one can ask a question how different substitutions, e.g., N, OH, or NH$_2$, would affect the relative order of these states. One can also explore the accuracy and applicability of our schemes for calculating thermochemistry and ionization potentials on other molecular systems. Many questions of this type can be studied by means of ab initio tools, which have been used and developed in this work.
Yet another interesting and very important direction is development of computer codes. For example, it would be useful to extend the implemented EOM-CC(2,3) method to full EOM-CCSDT, and to implement calculations of transition and excited state properties, as well as analytic energy gradients for EOM-CC(2,3). Furthermore, one can implement the quadruple excitations. Though quadruples are very computationally demanding, their effect could be evaluated through the energy additivity schemes, or by using the active space techniques.

Certainly, the topic briefly discussed in Chapter 7 — modelling of photoelectron spectra — deserves further investigation and development. Both applicational and methodological projects are available in this direction, e.g., one can implement and test the Duschinski rotations of normal modes, go beyond the Franck-Condon approximation, and include anharmonic corrections. In general, modelling of PES is a very important and exciting field of study that interfaces theory and experiment.

To summarize, the research described in this thesis generated many fascinating questions ranging from applications to methodology. As any scientific project, this work answered a couple of questions and opened a myriad of unanswered ones.
Bibliography

[1] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1 , as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.


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[236] D. Woon and T.H. Dunning. to be published.


Appendix A

Transformation of the Cartesian displacements into the displacements along the normal modes

A.1 Theory

For an $M$-atomic system, it is customary to use normal coordinates $\{Q_i\}_{i=1}^N$ (where $N = 3M - 6$ for a non-linear molecule and $N = 3M - 5$ for a linear one). The non-unitary transformations between Cartesian ($\{X_i\}_{i=1}^{3M}$) and normal ($\{Q_i\}_{i=1}^N$) coordinates are defined as follows:

\[
Q_i = \sum_{j=1}^{3M} R_{ij} X_j \tag{A.1}
\]

\[
X_i = \sum_{j=1}^N L_{ij} Q_j \tag{A.2}
\]

\[
RL = I, \tag{A.3}
\]
where $I$ is an $N \times N$ unit matrix, $I_{ij} = \delta_{ij}$. The transformation matrices $R$ ($N \times 3M$) and $L$ ($3M \times N$) are found by solving the normal mode problem:

\begin{align}
UL &= TL\Lambda, \quad \Lambda_{ij} = \delta_{ij}\omega_i^2 \\
L^TTL &= I \\
R &= L^T,
\end{align}

where $T$ is a diagonal matrix composed of atomic masses, $\omega_i$ is the vibrational frequency of mode $i$, and $U$ is the Hessian matrix evaluated at the equilibrium geometry $\{X_{eq}\}$:

\begin{equation}
U_{ij} = \frac{\partial^2 V(X_{eq}, \ldots, X_{3M})}{\partial X_i \partial X_j}.
\end{equation}

The transformations between Cartesian to normal coordinates can be written in a matrix form are:

\begin{equation}
Q = RX \quad \text{and} \quad X = LQ,
\end{equation}

where $X$ and $Q$ are column vectors composed of Cartesian or normal coordinates, respectively.

Some electronic structure programs (e.g., Q-CHEM) solve eigenproblem (A.4) and print the matrix $L$ in the output. Alternatively, eigenproblem (A.4) can be modified as follows:

\begin{equation}
\tilde{U}\tilde{L} = \tilde{L}\Lambda,
\end{equation}
where $\tilde{U} \equiv T^{-0.5}UT^{-0.5}$ and $\tilde{L} \equiv T^{0.5}L$. Some packages, e.g. ACES II, solve (A.9) and print $\tilde{L}$. Note that $\tilde{L}$ is normalized and dimensionless: $\tilde{L}^+\tilde{L} = 1$.

Transformation $R$ is related to $\tilde{L}$ as follows: $R = \tilde{L}^+T^{0.5}$.

Due to the fact that transformation matrices are rectangular (because the translational and rotational motions are projected out), be aware of singularities, which result the following features:

\[
\tilde{L}\tilde{L}^+ \neq 1 \quad (A.10)
\]
\[
LR \neq 1 \quad (A.11)
\]

Nevertheless, when performing double transformation (from Cartesian to normal and then back from normal to Cartesian), the resulting Cartesian coordinates are the same as the original set, the small numeric differences are due to the admixture of rotations and translations — this can be verified by calculating nuclear repulsion energies. Small residual differences are due to the lost of precision in the normal modes printed from ab initio programs.

Sometimes it is convenient to calculate changes in normal modes relative to their equilibrium values:

\[
\Delta Q = Q - Q^{eq} = RX - RX^{eq} = R\Delta X \quad (A.12)
\]
A.2 NMODES program

The program NMODES calculates the displacements along the normal modes from the Cartesian displacements and visa versa. The program is written in C++ by A.I. Krylov and S.V. Levchenko.

A.2.1 Input

The following input files are required:

- **molecule** — file containing equilibrium coordinates, for which the normal modes are printed in the output of an *ab initio* package (QChem or ACES II);

  format:
  
  first string: 0(1) Angstroms(a.u.)
  second string: Atom name X Y Z
  third string: Atom name X Y Z
  ...

  example:
  
  CF\textsubscript{2} molecule, geometry in angstroms

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>C</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-1.096929</td>
<td>0.000000</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>1.096929</td>
<td>0.000000</td>
</tr>
</tbody>
</table>

- **normmods.in** — file containing normal modes from an *ab initio* package

  format:
Note that only atom names and elements of transformation matrix should be left in the output from the package, i.e., all symmetry labels, IR intensities, frequencies, etc. have to be deleted. Normal modes should be given in blocks of three modes per string (this is how they are printed in output).

**example:**
CF$_2$, Q-CHEM output, non-linear geometry:

<table>
<thead>
<tr>
<th>1</th>
<th>3</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.000 0.000 -0.328</td>
<td>0.864 0.000 0.000 0.000 0.000 0.882</td>
</tr>
<tr>
<td>F</td>
<td>-0.660 0.000 0.104</td>
<td>-0.273 0.000 -0.228 -0.182 0.000 -0.279</td>
</tr>
<tr>
<td>F</td>
<td>0.660 0.000 0.104</td>
<td>-0.273 0.000 0.228 0.182 0.000 -0.279</td>
</tr>
</tbody>
</table>

**example:**
CH$_2$F, Q-CHEM output, non-linear geometry:

<table>
<thead>
<tr>
<th>1</th>
<th>4</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>.000 .698 .000</td>
<td>-.168 .000 -.583 .072 .000 .737</td>
</tr>
<tr>
<td>C</td>
<td>.000 -.159 .000</td>
<td>.125 .000 .026 -.043 .000 .481</td>
</tr>
<tr>
<td>F</td>
<td>.000 .026 .000</td>
<td>-.058 .000 -.025 .020 .000 -.358</td>
</tr>
<tr>
<td>H</td>
<td>.000 .698 .000</td>
<td>-.219 .000 .750 .066 .000 .292</td>
</tr>
<tr>
<td>H</td>
<td>.358 .000 .656</td>
<td>-.458 .000 .223 .783 .000 -.373</td>
</tr>
<tr>
<td>C</td>
<td>-.008 .000 -.109</td>
<td>-.027 .000 -.052 -.103 .000 .013</td>
</tr>
<tr>
<td>F</td>
<td>.004 .000 .004</td>
<td>.000 .000 .001 .000 .000 .000</td>
</tr>
<tr>
<td>H</td>
<td>-.338 .000 .562</td>
<td>.774 .000 .372 .437 .000 .213</td>
</tr>
</tbody>
</table>
• **coordlist.in** — file containing values of Cartesian/normal coordinates to be transformed into normal/Cartesian coordinates

**format:**

From Cartesian to normal:

<table>
<thead>
<tr>
<th>From Cartesian to normal:</th>
<th>1</th>
<th>number of entries</th>
<th>0(1) Angstroms(a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom name</td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>Atom name</td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
</tr>
</tbody>
</table>

From normal to Cartesian:

<table>
<thead>
<tr>
<th>From normal to Cartesian:</th>
<th>0</th>
<th># of entries</th>
<th>0(1) Angstroms(a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMode #</td>
<td></td>
<td>value of displacement along norm. coord.</td>
<td></td>
</tr>
<tr>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
</tr>
</tbody>
</table>

**example:**

*CF$_2$, three different Cartesian geometries given in angstroms:*

<table>
<thead>
<tr>
<th>From Cartesian to normal:</th>
<th>1</th>
<th>3</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.688451</td>
</tr>
<tr>
<td>F</td>
<td>-1.096929</td>
<td>0.000000</td>
<td>-0.228885</td>
</tr>
<tr>
<td>F</td>
<td>1.096929</td>
<td>0.000000</td>
<td>-0.228885</td>
</tr>
<tr>
<td>C</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.592683</td>
</tr>
<tr>
<td>F</td>
<td>-1.027251</td>
<td>0.000000</td>
<td>-0.197317</td>
</tr>
<tr>
<td>F</td>
<td>1.027251</td>
<td>0.000000</td>
<td>-0.197317</td>
</tr>
<tr>
<td>C</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.499135</td>
</tr>
<tr>
<td>F</td>
<td>-1.129819</td>
<td>0.000000</td>
<td>-0.166022</td>
</tr>
<tr>
<td>F</td>
<td>1.129819</td>
<td>0.000000</td>
<td>-0.166022</td>
</tr>
</tbody>
</table>
example:

CF₂, 3 normal displacements given in atomic units, bohr-amu

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.550978</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-0.939817</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.804281</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-1.253423</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Compile command is: `make` (it will create executable file called `nmodes`).

To run, link or copy the `nmodes` file to the directory with inputs, and type 'nmodes'. Output is sent to stdout. To redirect into the file `outfile`, use 'nmodes > outfile'.

We use atomic mass units throughout. If atomic units are desired, uncomment the following line in the file main.C:

```c
//SqrtT.Scale(sqrt(amu2aum))
```

**A.2.2 Output**

Output of the program is long and messy. To validate the results, check the matrix called `RL` in the output: it should be unitary. Basically, one needs the last section of the output. For each geometry given in `coordlist.in` ("Displacement #i"), the following information will be printed (the output is for the transformation from Cartesian to normal coordinates):
Displacement #i
Cartesian displacements DX, bohr:

0 0.000000
1 0.000000
2 0.338430
3 -0.275365
4 0.000000
5 -0.169215
6 0.275365
7 0.000000
8 -0.169215

NModes displacements DQ, au-sqrt(amu):

0 -0.000000
1 0.501437
2 -0.273029

NModes displacements DQ, angstrom-sqrt(amu):

0 -0.000000
1 0.265350
2 -0.144481

It is recommended to always start your coordlist.in file from the geometry at which the normal modes are calculated. Than the entry for the "Displacement #0" should consist of zeros.

When using the PES4 program for modelling photoelectron spectra, (this program is discussed in Appendix B, the displacements along the normal modes should be in Å√amu, i.e., the "NModes displacements DQ, angstrom-sqrt(amu):" entry gives the right values of ΔQ.
Appendix B

Modelling of PES

Here we describe the procedure of modelling photoelectron spectra using PES4 program [D.W. Arnold, PhD thesis, US Berkeley, 1994]. Detailed description of PES4 is given in the program manual. Here I summarize the most important steps of using PES4.

PES4 requires the following input files:

- **sample.ene** — file for the experimental data. In our case, it should be empty

- **plot.par** — file with a general setup:

  ********************************************
sample.ene — name of the experimental (empty) file
1000000 — number of counts in main peak (leave it as it is!)
0.0000 — time width of experimental apparatus, ns
12.0000 — energy width, meV
4.0000 — maximum energy to display in spectrum
1.000 — simulating scaling factor
φ — this is small ”φ”, it should be on the second place. Keep it there!
*********************************************************

Time and energy widths in the **plot.par** determine the width of the Gaussians in the modelled spectrum. Time or energy widths of experimental machines are usually 10-15 meV.

- **input.par** — file with *ab initio* data.

Here is the example from the modelling of the triplet region of TMM (see Sec. 7.3):

```plaintext
P (P)olyatomic/(D)iatomic molecule
1 number of electronic states - the program doesn’t calculate the interaction between the electronic states but only prints several (scaled) spectra together
0.431 origin of electronic state #1 (IP or IP+δEexited)
10 number of vibrational modes
N different temperature for each mode (Y/N)
200 temperature: higher temperature results in larger number of hot bands.
N degenerate vibrational mode (Y/N)
253 485 harmonic frequencies for anion and neutral from *ab initio* (mode 1)
0.0 0.0 anharmonicities for anion and neutral — no need in them for short progressions
0.0 anion bond length (Qanion)
0.0 neutral bond length (Qneutral): the program uses ΔQ = Qanion - Qneutral
2 4 number of vibrational levels in anion and neutral (should be larger for long progressions)
N degenerate vibrational mode (Y/N), etc.
267 503
0.0 0.0
```

258
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 0.0</td>
<td>2 4</td>
<td>N</td>
</tr>
<tr>
<td>296 440</td>
<td>0.0 0.0</td>
<td>0.0 0.0</td>
</tr>
<tr>
<td>327 728</td>
<td>0.0 0.0</td>
<td>0.0 0.0</td>
</tr>
<tr>
<td>454 794</td>
<td>0.0 0.0</td>
<td>0.0 0.0</td>
</tr>
<tr>
<td>486 440</td>
<td>0.0 0.0</td>
<td>0.0 0.366</td>
</tr>
<tr>
<td>920 989</td>
<td>0.0 0.0</td>
<td>0.0 0.112</td>
</tr>
<tr>
<td>1392 1416</td>
<td>0.0 0.0</td>
<td>0.0 0.050</td>
</tr>
<tr>
<td>1493 1569</td>
<td>0.0 0.0</td>
<td>0.0 0.035</td>
</tr>
<tr>
<td>1507 1593</td>
<td>0.0 0.0</td>
<td>0.0 0.030</td>
</tr>
</tbody>
</table>

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Temperature and hot bands: as a starting point, take experimental temperature (150-200K). In principle, different modes can have different temperatures, but we do not have sufficient information about this. To make the modelled spectrum look "fuller" and appear more similar to the experimental one, one needs to include modes that yield hot bands. These are the non-active low-frequency modes (<500 cm\(^{-1}\)) with some change of frequency between the anion and the neutral. Then the modelled PES will have hot band transitions like \(\nu^{1-1}\) and overtones \(\nu^{0-2}\).

PES4 prints the following output files:

- **fort.7** — stick spectrum in one-coulomb format (I never used this file)

- **fort.11** — spectrum convoluted by Gaussians in two coulomb format (intensity vs energy). Just plot it!

- **fort.12** — summary of the input parameters and the calculated one-dimensional Franck-Condon factors. Take a look at it!

- **input.ass** — summary of all transitions ordered by energy with assignments. Very useful file! Plot it together with fort.11 and analyze (see spectra 7.6 and 7.7).
I commented the part of PES4 program that generated long prompts (they were really annoying). Now it asks only the name of the .par file (should be entered without suffix .par) and makes the job.

Often, the spectrum is dominated by one or several modes with large $\Delta Q$. The spectra from Figures B.1-B.4 illustrate this point. Indeed, for modelling PES, the most important thing is the accurate determination of relative geometries. Vibrational frequencies can be scaled, energy differences between states can be shifted, but without accurate geometries, the modelled PES never will look like the experimental one!
Figure B.1. PES with one active mode, $\Delta Q = 0.05 - 0.20$
Figure B.2. PES with one active mode, $\Delta Q = 0.25 - 0.50$
Figure B.3. PES with one active mode, $\Delta Q = 0.60 - 0.90$
Figure B.4. PES with one active mode, $\Delta Q = 1.00 - 1.60$
Appendix C

Choosing correct Hartree-Fock reference in Q-CHEM

Axiom 1: Any quantum chemist runs ab initio calculations.

Axiom 2: Any ab initio calculation starts from Hartree-Fock.

Theorem: Any quantum chemist who is worth his/her computers knows how to converge Hartree-Fock.

This Appendix is supposed to shed light on how to become a successful quantum chemist using Q-CHEM.
C.1 Q-CHEM keywords controlling HF convergence

Q-CHEM has several options that control the Hartree-Fock (HF) procedure. All of them are described in details in the Q-CHEM manual. Here I summarize the options that I found the most useful.

- **BASIS2** — this option uses the smaller basis (BASIS2) to project the guess to the larger basis. It is useful when dealing with very large or diffuse basis sets.

- **MOM\_START=1** — this option preserves the orbital occupations given by initial guess during the HF iterations. Works well!

- **$\text{occupied}$** keyword — a separate section of input that changes the order of HF orbitals in the guess. Should always be used together with MOM\_START option. This keyword works for RHF and UHF only.

- **GUESS=READ** — this means that the guess will be taken from the previous job. May be used together with MOM\_START and/or $\text{occupied}$ options. The GUESS=READ option can be used in many different ways, e.g., one can read from the job having different geometry, which presumably stabilizes the state of interest, from the state of different multiplicity, e.g., to obtain the tricky triplet, one can read from the singlet, and so on.
The only requirement is that the basis set is the same. This is universal option but requires some imagination and experience. Try it!

- **SCF_ALGORITHM:**
  
  - **DIIS** is usually most robust in keeping the original guess. However, tight convergence may be very slow.
  
  - **GDM** has better convergence on the last iterations, but is unstable with respect to the reference and can easily loose it.
  
  - **DIIS_GDM** does DIIS on the first iterations and switches to GDM later on. Has advantages of both DIIS and GDM.

### C.2 ROHF convergence of high-spin states

The ROHF convergence of high-spin states is generally less stable than the UHF one. Additional problem arises because the \texttt{occupied} keyword does not work with ROHF.

*Example:* the DMX anion. Suppose one needs a triplet with the \(b_2\) orbital being doubly occupied and the \(a_1\) and \(a_2\) orbitals being singly occupied (\(b_2^2a_1a_2\)). Default ROHF calculation gives \(a_1^2a_2a_2\) reference.

I suggest the following scheme for dealing with this situation (see also the corresponding input file below):
1. Run the HF calculation for the *closed-shell singlet* by detaching two electrons (in the case of DMX\(^-\), this is a cation). We want to obtain the singlet with the same doubly-occupied orbital as one in the desired triplet, i.e., \( a_1^2 b_0^0 a_2^0 \).

2. If the obtained occupancies of the cation are different from those we need, run the second HF job that will read the orbitals from the first calculation (\texttt{GUESS=READ}) and reorder them in the necessary way (use \texttt{MOM\_START} and \texttt{\$occupied} keywords, see Sec. C.1).

3. Read these orbitals (\texttt{GUESS=READ}) as a guess for the triplet state. You may need to stabilize this solution by using \texttt{MOM\_START} keyword, but often using \texttt{DIIS} (but not \texttt{DIIS\_GDM}) would be enough. Here is the triplet!

\begin{verbatim}
Input:

***********************************************
$comment
job 1: closed-shell singlet cation
$end

$molecule
+1 1
C 0.000000 0.000000 0.990770
H 0.000000 0.000000 2.081970
C -1.233954 0.000000 0.290926
C -2.444677 0.000000 1.001437
H -2.464545 0.000000 2.089088
269

***********************************************
\end{verbatim}
H -3.400657 0.000000 0.486785
C -1.175344 0.000000 -1.151599
H -2.151707 0.000000 -1.649364
C 0.000000 0.000000 -1.928130
C 1.175344 0.000000 -1.151599
H 2.151707 0.000000 -1.649364
C 1.233954 0.000000 0.290926
C 2.444677 0.000000 1.001437
H 2.464545 0.000000 2.089088
H 3.400657 0.000000 0.486785
$end

$rem
jobtype SP
unrestricted FALSE
LEVCOR NONE
EXCHANGE HF
BASIS 6-31+G*
PURCAR 1
SCF_GUESS CORE
SCF_CONVERGENCE 7
SCF_ALGORITHM DIIS
$end

@@@
$comment
job 2: closed-shell singlet cation, orbital reorder
$end

$molecule
+1 1
C 0.000000 0.000000 0.990770
H 0.000000 0.000000 2.081970
C -1.233954 0.000000 0.290926
C -2.444677 0.000000 1.001437
H -2.464545 0.000000 2.089088
H -3.400657 0.000000 0.486785
C -1.175344 0.000000 -1.151599
H -2.151707 0.000000 -1.649364
C 0.000000 0.000000 -1.928130
C 1.175344 0.000000 -1.151599
H 2.151707 0.000000 -1.649364
C 1.233954 0.000000 0.290926
C 2.444677 0.000000 1.001437
H 2.464545 0.000000 2.089088
H 3.400657 0.000000 0.486785
$end

$rem
jobtype SP
unrestricted FALSE
LEVCOR NONE
EXCHANGE HF
BASIS 6-31+G*
PURCAR 1
SCF_GUESS READ
SCF_CONVERGENCE 7
SCF_ALGORITHM DIIS
MOM_START = 1
$end

$occupied
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 28 1 2 3 4 5 6 7 8 9 10 11
12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 28
$end

@@@
acomment
job 3: triplet anion
$end

$molecule
-1 3
C 0.000000 0.000000 0.990770
H 0.000000 0.000000 2.081970
C -1.233954 0.000000 0.290926
C -2.444677 0.000000 1.001437
H -2.464545 0.000000 2.089088
H -3.400657 0.000000 0.486785

271
C -1.175344 0.000000 -1.151599
H -2.151707 0.000000 -1.649364
C 0.000000 0.000000 -1.928130
C 1.175344 0.000000 -1.151599
H 2.151707 0.000000 -1.649364
C 1.233954 0.000000 0.290926
C 2.444677 0.000000 1.001437
H 2.464545 0.000000 2.089088
H 3.400657 0.000000 0.486785
$end

$rem
jobtype SP
unrestricted FALSE
LEVCOR NONE
EXCHANGE HF
BASIS 6-31+G*
PURCAR 1
SCF_GUESS READ
SCF_CONVERGENCE 7
SCF_ALGORITHM DIIS
$end

*******************************************************************************
Appendix D

Comments on practical calculations by the

EOM-CC(2,3) method

Any *ab initio* calculation that involves triple excitations is a computationally demanding task. The EOM-CC(2,3) method, discussed in details in Chapter 1.7, is not an exception. In this Appendix, practical aspects of performing the EOM-CC(2,3) calculations are described.

D.1 Input parameters

**CC_DO_TRIPLES = 1** this keyword initializes EOM-CC(2,3) calculations

(default is 0)

Next two options are for preconverging EOM-CCSD block of the Hamiltonian:
CC\_DO\_SMALL\_TRIPLES = \textit{n} does \textit{n} EOM-CCSD iterations, then switches to EOM(3)-CCSD using the EOM-CCSD vectors as a guess for EOM-CC(2,3) (default is 0);

\textbf{CC\_PRECONV\_SD} = \textit{1} solves the EOM-CCSD equations, prints energies, then uses EOM-CCSD vectors as initial vectors in EOM-CC(2,3) (default is 0)

The following options are for the active space EOM-CC(2,3) calculations:

\textbf{CC\_RESTR\_AMPL} = \textit{0} forces the integrals, \(T\), and \(R\) amplitudes to be determined in the full space even though the \textbf{CC\_REST\_OCC} and \textbf{CC\_REST\_VIR} keywords are used (default is 1);

\textbf{CC\_RESTR\_TRIPLES} = \textit{1} restricts \(R_3\) amplitudes to the active space, i.e., one electron should be removed from the active occupied orbital and one electron should be added to the active virtual orbital

The keywords controlling the active space:

\textbf{CC\_REST\_OCC} = \textit{n} gives the number of the restricted occupied orbitals including frozen occupied orbitals;

\textbf{CC\_REST\_VIR} = \textit{n} gives the number of restricted virtual orbitals including frozen virtual orbitals
To select the active space, orbitals can be reordered by supplementing an additional file, `moorder.dat`, in the working directory. It consists of two rows of numbers (α and β sets), starting from 0, and ending with (n-1), where n is the total number of orbitals, i.e., including frozen orbitals. In the following example, orbitals 16 and 17 are swapped:

```
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 17 16
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54
55 56 57 58 59 60 61 62 63 64 65 66 67
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 17 16
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54
55 56 57 58 59 60 61 62 63 64 65 66 67
```

Note that the `CC_DOEXDIAG` option, which controls whether the full (exact) or the reduced diagonal of the Hamiltonian is used as a preconditioner in Davidson’s procedure, should be turned off (=0), as EOM-CC(2,3) converges poorly with the full diagonal.

Inclusion of triple excitations in the EOM part allows double spin-flip calculations, i.e., \(\alpha \alpha \rightarrow \beta \beta\). The corresponding keyword is `CC_SPIN_FLIP_MS = 2`, which should be used together with `CC_SPIN_FLIP = 1`. Default for the `CC_SPIN_FLIP_MS` keyword is 0 for \(\alpha \rightarrow \alpha\) and 1 for \(\alpha \rightarrow \beta\) excitations.
Along with EON-CC(2,3), the CISDT method has been also implemented. It can be invoked by specifying \texttt{CC\_MAXITER = 0} and \texttt{CC\_DO\_CISDT = 1}. EE, SF, and double SF variants of CISDT are available. Note that double SF CISDT is a size-extensive model. The active space CISDT calculations can be performed similarly to the active space EOM-CC(2,3) ones.

\section*{D.2 Full EOM-CC(2,3)}

Running the full EOM-CC(2,3) calculations is straightforward. The main bottlenecks are the storage of the data on a hard drive and the CPU time. I could run calculations with about 80 basis functions for a molecule consisting of 4 first row atoms (NO dimer). The number of basis functions can be larger for smaller systems.

It is recommended to preconverge the EOM-CCSD block of Hamiltonian (see the previous Section for the corresponding keywords). \textit{In EE calculations, one needs to always solve for at least one low-spin root in the first symmetry irrep in order to obtain the correlated EOM energy of the reference.}

\section*{D.3 Active space EOM-CC(2,3)}

Active space calculations are less demanding with respect to the size of a hard drive. The main bottlenecks here are the memory usage and the CPU time.
Both arise due to the increased number of orbital blocks in the active space calculations. In the current implementation, each block can contain from 0 up to 16 orbitals of the same symmetry irrep, occupancy, and spin-symmetry. For example, for a typical molecule of $C_{2v}$ symmetry, in a small/moderate basis set (e.g., TMM in 6-31G*), the number of blocks for each index is:

occupied: $(\alpha + \beta) \cdot (a_1 + a_2 + b_1 + b_2) = 2 \cdot 4 = 8$;

virtuals: $(\alpha + \beta) \cdot (2 \cdot a_1 + a_2 + b_1 + 2 \cdot b_2) = 2 \cdot 6 = 12$ (usually there are more than 16 $a_1$ and $b_2$ virtual orbitals).

In EOM-CCSD, the total number of blocks is $O^2V^2 = 8^2 \cdot 12^2 = 9216$. In EOM-CC(2,3) the number of blocks in the EOM part is $O^3V^3 = 8^3 \cdot 12^3 = 884736$. In active space EOM-CC(2,3), additional fragmentation of blocks occurs to distinguish between the restricted and active orbitals. For example, if the active space includes occupied and virtual orbitals of all symmetry irreps (this will be a very large active space), the number of occupied and virtual blocks for each index is 16 and 20, respectively, and the total number of blocks increases to $3.3 \cdot 10^7$. Not all of the blocks contain real information, some blocks are zeros because of the spatial or spin-symmetry requirements. For the $C_{2v}$ symmetry group, the number of non-zero blocks is about 10-12 times less than the total number of blocks, i.e., $3 \cdot 10^6$. This is the number of non-zero blocks in one vector. Davidson diagonalization procedure requires $(2 \cdot \text{MAX\_VECTORS} + 2 \cdot \text{NROOTS})$ vectors, where MAX\_VECTORS is the maximum number of...
vectors in the subspace, and NROOTS is the number of the roots to solve for. Taking NROOTS=2 and MAX VECTORS=20, we obtain 44 vectors with the total number of non-zero blocks being $1.3 \times 10^8$.

In our implementation, each block is a logical unit of information. Along with real data, which are kept on a hard drive at all the times except of their direct usage, each non-zero block contains an auxiliary information about its size, structure, relative position with respect to other blocks, location on a hard drive, and so on. The auxiliary information about blocks is *always* kept in memory. Currently, the approximate size of this auxiliary information is about 400 bytes per block. It means, that in order to keep information about one vector ($3 \times 10^6$ blocks), 1.2 GB of memory is required! The information about 44 vectors amounts 53 GB. Moreover, the huge number of blocks significantly slows down the code.

To make the calculations of active space EOM-CC(2,3) feasible, we need to reduce the total number of blocks. One way to do this is to reduce the symmetry of the molecule to lower or $C_1$ symmetry group (of course, this will result in more expensive calculation). For example, lowering the symmetry group from $C_{2v}$ to $C_s$ would results in reducing the total number of blocks in active space EOM-CC(2,3) calculations in about $2^6 = 64$ times, and the number of non-zero blocks in about 30 times (the relative portion of non-zero blocks in $C_s$ symmetry group is smaller compared to that in $C_{2v}$). There is only one known
to me way of reducing the symmetry group in Q-CHEM — by slightly distorting the molecular geometry.

Alternatively, one may keep the MAX_VECTORS and NROOTS parameters of Davidson’s diagonalization procedure as small as possible (this mainly concerns the MAX_VECTORS parameter). For example, specifying MAX_VECTORS = 12 instead of 20 would require 30% less memory.

One more trick concerns specifying the active space. In a desperate situation of a severe lack of memory, should the two previous options fail, one can try to modify (increase) the active space in such a way that the fragmentation of active and restricted orbitals would be less. For example, if there is one restricted occupied $b_1$ orbital and one active occupied $B_1$ orbital, adding the restricted $b_1$ to the active space will reduce the number of blocks, by the price of increasing the number of FLOPS. In principle, adding extra orbital to the active space should increase the accuracy of calculations, however, a special care should be taken about the (near) degenerate pairs of orbitals, which should be handled in the same way, i.e., both active or both restricted.