

Chapter 1

Brief Review of the Background

1.1 Introduction

In last few decades, electronic-structure theory has been developed to the extent, so as to provide extremely helpful data in the interpretation of experimental measurements of a broad range of molecular structure and properties of importance in rotational and vibrational spectroscopies [1], UV spectroscopies [2, 3], magnetic-resonance spectroscopies [4, 5], linear and nonlinear optics [5-7], and so on. Quantum chemical computations allow us to accurately predict the spectroscopic constants. These constant can be calculated at various levels of electronic-structure theory, capable of approaching the exact value in a controlled, systematic manner, using established hierarchical levels of theory. In present time, methodological developments toward larger systems are being made in different laboratories, promising to make calculations of molecular properties of systems containing hundreds and thousands of atoms routine in the near future. Advances in the wavefunction based correlation methods, computational algorithms as well as computer hardware, have made it plausible not only to reach the accuracy and precision in the results, comparable with those obtained in experiments, but also in extending it to molecules of bigger size which were untractable even till, just about a decade ago.



This document was created with the Win2PDF “print to PDF” printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

Apart from the MRCC formalisms, parallel developments such as equation-of-motion (EOM) CC [33–39] and related methods are also noteworthy. These methods, due to single-reference (SR) framework and relatively simpler formalism, have been very popular for about a couple of decades and provide a handy tool for computing excitation energies (EE), ionization energies (or ionization potentials) (IP) and electron-attachment energies (or electron affinities) (EA). For one valence problems, such that singly ionized or single-electron-attached states of closed-shell system, the energies and derivatives obtained from EOM-CC and FS-MRCC methods are formally equivalent [40] as long as the methods use the same truncation scheme for the vectors. However, this equivalence is lost at higher valence problems. Moreover, whereas FSMRCC is rigorously size-extensive, the EOM-CC is not. However, if same truncation scheme is employed for EOM eigen-vectors as well as the CC vectors, the corresponding EOM-CC variant happens to be core-extensive, though not valence-extensive. This property is also referred to as size-intensivity. Other approaches such as symmetry adapted cluster (SAC) CI [41], MRCI [42], CC linear response (LR) [43], Green’s function method [44], MRPT [45], quasi-degenerate (QD) PT [46], etc. are also known for handling certain kinds of static correlation.

While MRCC and EOM-CC approaches have been well established for computation of energies, gradients and properties of molecules, their applicability is hindered due to the computational cost. For example, for single and double substitution (SD) these methods scale roughly, with sixth power of the computational size of the system. Inclusion of triples would increase the scaling to the eighth power. Therefore, the development of cost effective approximations to these methods becomes necessary. One way to do this is by approximating the CC, MRCC/EOM-CC vectors as done by several researchers [47–52]. However, these approaches can achieve only limited saving in terms of computational cost. The major source of the high computational cost of these methods are the electron repulsion integrals (ERI’s), which are four index quantities and have high storage requirements. Developments in this line of cost-saving resulted in the approaches such as the resolution of identity (RI) [53–59] and the cholesky decomposition (CD) schemes [60–67]. In RI, an auxiliary basis is used to approximate products of Gaussian functions. The four index ERI’s are thus approximated as sum over the products of one-electron densities obtained



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

corrections, which resulted in the many body perturbation theory (MBPT). MBPT is fully size-extensive. The MBPT (or MPPT) give systematic and step-wise improvement to the wavefunction characterised by order of perturbation. The method in which the energy is correct up to n -th order is commonly denoted by MP_n . MP_n theories were rapidly developed and programmed in the mid-70ies[89–94] started working with MP perturbation theory. The computational developments of MP_2 [89, 95], MP_3 [90, 91], MP_4 [91, 92, 96, 97], MP_5 [94, 98, 99] and MP_6 [100–103] were reported and MPPT (or MBPT) became more popular.

According to this theory, the zeroth order wavefunction is HF wavefunction, whereas the zeroth order Hamiltonian is the electronic Hamiltonian with actual inter-electronic repulsion potential replaced by the effective potential obtained in HF.

Now, Hamiltonian term is summation of unperturbed and perturbed term in equation 1.1,

$$\hat{H} = \lambda^0 \hat{H}^0 + \lambda^1 \hat{V} \quad (1.38)$$

where, the $\lambda = 0$ corresponds to the unperturbed Hamiltonian \hat{H}_0 . Wavefunction Ψ and energy E also have unperturbed and perturbed term,

$$\begin{aligned} \Psi_i &= \lambda^0 \Psi_i^0 + \lambda^1 \Psi_i^{(1)} + \frac{\lambda^2}{2!} \Psi_i^{(2)} + \frac{\lambda^3}{3!} \Psi_i^{(3)} + \dots + \frac{\lambda^K}{K!} \Psi_i^{(K)} + \dots \\ E_i &= \lambda^0 E_i^0 + \lambda^1 E_i^{(1)} + \frac{\lambda^2}{2!} E_i^{(2)} + \frac{\lambda^3}{3!} E_i^{(3)} + \dots + \frac{\lambda^K}{K!} E_i^{(K)} + \dots \end{aligned}$$

We obtain SWE in the given form,

$$\begin{aligned} \hat{H} \Psi_i &= E_i \Psi_i \quad (1.39) \\ (\lambda^0 \hat{H}^0 + \lambda^1 \hat{V})(\lambda^0 \Psi_i^0 + \lambda^1 \Psi_i^{(1)} + \dots) &= (\lambda^0 E_i^0 + \lambda^1 E_i^{(1)} + \dots)(\lambda^0 \Psi_i^0 + \lambda^1 \Psi_i^{(1)} + \dots) \end{aligned}$$

Associating the factors of λ^K in this equation gives a k^{th} -order perturbation equation, where $K = 0, 1, 2, \dots, N$.

$$\hat{H}^0 \Psi_i^0 - E_i^0 \Psi_i^0 \quad \leftarrow \text{Corresponding to } \lambda^0 \text{ terms} \quad (1.40)$$

$$\hat{H}^0 \Psi_i^1 + \hat{V} \Psi_i^0 = E_i^0 \Psi_i^1 + E_i^1 \Psi_i^0 \quad \leftarrow \text{Corresponding to } \lambda^1 \text{ terms} \quad (1.41)$$

$$\hat{H}^0 \Psi_i^2 + \hat{V} \Psi_i^1 = E_i^0 \Psi_i^2 + E_i^1 \Psi_i^2 + E_i^2 \Psi_i^0 \quad \leftarrow \text{Corresponding to } \lambda^2 \text{ terms} \quad (1.42)$$

\vdots and so on.

λ^0 associated terms in equation 1.40 provide first order correlation energy correction which is given by,

$$E_{MP1} = \sum i^{\text{occ}} \epsilon_i - \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle = \sum i^{\text{occ}} \epsilon_i + V_{00} E_{HF} \quad (1.43)$$

This equation 1.43 is known as MP theorem which holds for electron density, dipole moments and other one-electron properties [13]. The MP2 correlation energy correction is given by equation,

$$E_{MP2} = \sum_{1>0} \frac{V_{01} V_{10}}{E_0 - E_1} \quad (1.44)$$

where, $1 = \Psi_i^a$ Single excitation term do not contribute because $\langle \phi_0 | \hat{V} | \phi_i \rangle = 0$ as a outcome of the Brillouin theorem. Finite matrix elements V_{01} are only obtained for double excitations (ϕ_{ij}^{ab}). Higher excitations are excluded because of the Slater-Condon rules. The second order correction takes the following form after applying the Slater-conden rules,

$$E_{MP2} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{\langle ij || ab \rangle \langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (1.45)$$

Similary, one can obtain the higher order perturbation energy correction term (e.g. MP3).

$$E_{MP3} = \sum_{1>0} \sum_{3>0} \frac{V_{01} V_{13} V_{30}}{(E_0 - E_1)(E_0 - E_3)} \quad (1.46)$$

and so on.

1.5.1 The RI-MP2 and CD-MP2 methods

An extra alternative path to diminish the scaling and storage requirements is by approximating the four-index electron repulsion integrals(ERI) $(\mu\nu|\lambda\sigma)$ by resolution of identity(RI) [53–59]. The ERIs are the major source for computational cost and hence, computational time in conventional MP2 calculations. The computational cost can be significantly reduced using RI as discussed in a number of articles and reviews [55, 56, 104]. For closed-shell MP2, RI was first implemented by Feyereisen and co-workers [55].

RI is mathematically defined by $I = \sum_{\mu} |\mu\rangle\langle\mu|$ and is introduced in the MP_2 expression to give

$$E_{MP_2} = \sum_{ij}^{occ} \sum_{ab}^{vir} \sum_{\mu,\nu}^M \frac{\langle ia\mu | \langle \mu | jb \rangle [2 \langle ia\mu | \langle \mu | jb \rangle - \langle ib\mu | \langle \mu | ja \rangle]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (1.47)$$

In the limit of complete auxiliary basis μ , RI is exact, (that is, RI-MP2 would be equivalent to MP2). However, for incomplete auxiliary basis, RI gives approximate results. The finite auxiliary basis is usually preoptimized for given basis so as to get most accurate results with low computational cost. Typically, the auxiliary basis optimized for RI-MP2 is about 3–4 times larger than that of the normal basis set. $\langle ia\mu |$ represents the three index overlap integrals and, $\langle \mu | jb \rangle$ represent the 3-index ERIs.

The computational cost of Coulomb term of MP2 energy correction (the first term in the square bracket in Eq. 1.47) is reduced from $O(N^4)$ to $O(MN^2)$ as explained by Almlöf and co-workers [56]. This cost reduction is not possible for exchange term (the second term in the square bracket in Eq. 1.47). RI has been extended to various other methods including DFT, CC, EOM-CCSD, etc [68].

Another alternative approach to reduce the scaling and storage requirements is by approximating the four-index ERIs by Cholesky decomposition approach [60–67]. Cholesky decomposition (CD) and RI are closely related [60, 65, 105–107]. In 1977, Beebe and Linderberg [60] suggested to reduce the rank of the ERI supermatrix $V_{(\mu\nu|\lambda\sigma)}$ with the

help of a Cholesky decomposition,

$$V_{(\mu\nu|\lambda\sigma)} = (\mu\nu|\lambda\sigma) = \sum_{P=1}^M B_{\mu\nu}^P B_{\lambda\sigma}^P \quad (1.48)$$

The supermatrix $V_{(\mu\nu|\lambda\sigma)}$ is decomposed in terms of Cholesky densities $B_{\mu\nu}^P$ as given in equation 1.48. The computational details of Cholesky algorithm is discussed later in the thesis (see Chapter 4).

1.6 Coupled Cluster (CC) theory

Coupled cluster is a well-established method. Unlike CI it is nonlinear in structure. Use of exponential excitation operator instead of the linear operator is the genesis of the coupled-cluster method. The non-variational coupled cluster theory [15, 16] consider that the exact wavefunction can be developed by the action of an exponential operator on a single Slater determinant.

$$|\Psi_0\rangle = e^{\hat{T}} |\Phi_0\rangle \quad (1.49)$$

where, \hat{T} is hole-particle excitations on Φ_0 or Φ_{HF} , it can be decomposed as,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_n \quad (1.50)$$

with

$$\begin{aligned} \hat{T}_1 &= \sum_{i \in occ} \sum_{a \in virt} t_i^a \{a_a^\dagger a_i\} \\ \hat{T}_2 &= \sum_{i,j \in occ} \sum_{a,b \in virt} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\} \end{aligned}$$

and, an n -orbital cluster operator may be explained as,

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{i,j,\dots \in occ} \sum_{a,b,\dots \in virt} t_{ij,\dots}^{ab,\dots} \{a_a^\dagger a_b^\dagger \dots a_j a_i\} \quad (1.51)$$

Where, i, j, k , etc are occupied spin orbitals and a, b, c , are the virtual orbitals. With Φ_0 as hole-particle vacuum, a^\dagger, b^\dagger are the particle creation operators and i, j are the hole creation operators.

Standard Coupled-cluster equations are obtained by method of projecting the Schrödinger's equation to the Hartree-Fock and excited determinants,

$$\hat{H}e^{\hat{T}}|\Phi_0\rangle = Ee^{\hat{T}}|\Phi_0\rangle \quad (1.52)$$

Pre-multiplying by $e^{-\hat{T}}$ left projecting with $\langle \Phi_0|$, it follows,

$$\langle \Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E \quad (1.53)$$

where, we recognize in Eq. 1.53 that $\Phi_0\rangle$ is normalized. Using the Campbell-Baker-Hausdorff formula [81] for the similarity transformation, it can be easily shown that the ‘unlinked’ terms in the CC expansion vanish and one obtains

$$E - \langle \Phi_0|(\hat{H}e^{\hat{T}})_C|\Phi_0\rangle \quad (1.54)$$

where, the subscript C in the above equation indicates that only connected terms (all \hat{T} 's must be contracted with \hat{H}) should be used. Left projections of $(\hat{H}e^{\hat{T}})_C|\Phi_0\rangle$ with excited determinants result in the equations for CC vectors or CC amplitudes.

$$\langle \Phi_{ij,\dots}^{ab,\dots}|(\hat{H}e^{\hat{T}})_C|\Phi_0\rangle = 0 \quad (1.55)$$

The *connectedness* of \hat{T} with \hat{H} results in natural termination of the CC vector equations after the quartic terms. Moreover, irrespective of truncation scheme in the CC vectors, the energy expression uses only one-body and two-body terms. The *connectedness* of the

terms also ensures size-extensivity of the method. Moreover, due to exponential nature, the truncated CC also ensures excitations upto all ranks, thereby ensuring retention of the size-consistency (as long as the reference wavefunction is size-consistent). If not truncated, the method is called Full CC and is equivalent to Full CI, but much more expensive due to non-linearity of the equations and hence, unattractive. The beauty of CC is that it remains size-extensive (and size-consistent, for size-consistent references), even if \hat{T} are truncated. Truncating \hat{T} as $\hat{T} = \hat{T}_1 + \hat{T}_2$ results in the CCSD method.

Coupled-cluster singles doubles Method (CCSD)

Hamiltonian consists of one and two body particles which is represented by,

$$\hat{H}_N - \hat{F}_N + \hat{V}_N \quad (1.56)$$

and, according to equations 1.50 and 1.51,

$$e^{\hat{T}} = 1 + (\hat{T}_1 + \hat{T}_2) + (\hat{T}_1 + \hat{T}_2)^2 + (\hat{T}_1 + \hat{T}_2)^3 + (\hat{T}_1 + \hat{T}_2)^4 + \dots \quad (1.57)$$

or,

$$\begin{aligned} e^{\hat{T}} = & 1 \\ & + \hat{T}_1 + \hat{T}_2 \\ & + \frac{1}{2!} \hat{T}_1^2 + \frac{1}{2!} \hat{T}_2^2 + \hat{T}_1 \hat{T}_2 \\ & + \frac{1}{3!} \hat{T}_1^3 + \frac{1}{3!} \hat{T}_2^3 + \frac{1}{3!} \hat{T}_1^2 \hat{T}_2 + \frac{1}{3!} \hat{T}_1 \hat{T}_2^2 \\ & + \frac{1}{4!} \hat{T}_1^4 + \frac{1}{4!} \hat{T}_2^4 \end{aligned} \quad (1.58)$$

After multiplication of equation 1.58 and equation 1.56, we obtain following equation,

$$\begin{aligned}
 \hat{T}_1 &= \sum_{ia} t_i^a \{a_a^\dagger a_i\} = \begin{array}{c} \diagup \\ \diagdown \\ \text{---} \\ \diagup \\ \diagdown \end{array} + 1 \\
 \hat{T}_2 &= \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\} = \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \text{---} \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} + 2 \\
 \hat{T}_3 &= \frac{1}{36} \sum_{ijkabc} t_{ijk}^{abc} \{a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i\} = \begin{array}{c} \diagup \quad \diagdown \quad \diagup \\ \diagdown \quad \diagup \quad \diagdown \\ \text{---} \\ \diagup \quad \diagdown \quad \diagup \\ \diagdown \quad \diagup \quad \diagdown \end{array} + 3
 \end{aligned}$$

 FIGURE 1.5: Diagrammatic representation^[a] of the \hat{T}_1 , \hat{T}_2 and \hat{T}_3 excitation operators

 [a] \rightarrow [108]

$$\begin{aligned}
 \hat{F}_N &= \sum_{ab} f_{ab} \{a_a^\dagger a_b\} + \sum_{ij} f_{ij} \{a_i^\dagger a_j\} + \sum_{ia} f_{ia} \{a_i^\dagger a_a\} + \sum_{ia} f_{ai} \{a_a^\dagger a_i\} \\
 &= \begin{array}{c} \diagdown \quad \text{---} \quad \diagup \\ \diagup \quad \diagdown \end{array} + \begin{array}{c} \diagdown \quad \text{---} \quad \diagup \\ \diagup \quad \diagdown \end{array} + \begin{array}{c} \text{---} \quad \diagup \\ \diagdown \end{array} + \begin{array}{c} \diagup \\ \text{---} \quad \diagdown \end{array} \\
 &\quad \quad \quad 0 \quad \quad \quad 0 \quad \quad \quad -1 \quad \quad \quad +1
 \end{aligned}$$

 FIGURE 1.6: Diagrammatic representation^[a] of each fragment if the one-particle component of the Hamiltonian operator, \hat{F}_N .

 [a] \rightarrow [108]

$$\begin{aligned}
 \hat{H}_N e^{\hat{T}} &= \underbrace{\hat{F}_N}_{\text{disconnected diagram}} + \hat{V}_N \\
 &+ \hat{F}_N \hat{T}_1 + \hat{F}_N \hat{T}_2 + \hat{V}_N \hat{T}_1 + \hat{V}_N \hat{T}_2 \\
 &+ \frac{1}{2!} \hat{V}_N \hat{T}_1^2 + \underbrace{\frac{1}{2!} \hat{V}_N \hat{T}_2^2}_{\text{disconnected diagram}} + \hat{V}_N \hat{T}_1 \hat{T}_2 \\
 &+ \frac{1}{3!} \hat{V}_N \hat{T}_1^3 + \underbrace{\frac{1}{3!} \hat{V}_N \hat{T}_2^3}_{\text{disconnected diagram}} + \frac{1}{3!} \hat{V}_N \hat{T}_1^2 \hat{T}_2 + \underbrace{\frac{1}{3!} \hat{V}_N \hat{T}_1 \hat{T}_2^2}_{\text{disconnected diagram}} \\
 &+ \frac{1}{4!} \hat{V}_N \hat{T}_1^4 + \underbrace{\frac{1}{4!} \hat{V}_N \hat{T}_2^4}_{\text{disconnected diagram}} \tag{1.59}
 \end{aligned}$$

$$\begin{aligned}
 \hat{V}_N &= \frac{1}{4} \sum_{abcd} \langle ab || cd \rangle \{ a_i^\dagger a_b^\dagger a_c a_d \} + \frac{1}{4} \sum_{ijkl} \langle ij || kl \rangle \{ a_i^\dagger a_j^\dagger a_k a_l \} + \sum_{iabc} \langle ia || bj \rangle \{ a_i^\dagger a_c^\dagger a_b a_c \} \\
 &+ \frac{1}{2} \sum_{abcd} \langle ai || bc \rangle \{ a_i^\dagger a_c^\dagger a_b a_d \} + \frac{1}{2} \sum_{ijkl} \langle ij || ka \rangle \{ a_i^\dagger a_j^\dagger a_k a_l \} + \frac{1}{2} \sum_{abci} \langle ab || ca \rangle \{ a_i^\dagger a_b^\dagger a_c a_c \} \\
 &+ \frac{1}{2} \sum_{iabc} \langle ia || bk \rangle \{ a_i^\dagger a_c^\dagger a_k a_b \} + \frac{1}{4} \sum_{abcd} \langle ab || kj \rangle \{ a_i^\dagger a_b^\dagger a_j a_c \} + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle \{ a_i^\dagger a_j^\dagger a_b a_a \} \\
 &= \begin{array}{ccc}
 \begin{array}{c} \text{Diagram 1} \\ \text{0} \end{array} & + & \begin{array}{c} \text{Diagram 2} \\ \text{0} \end{array} & + & \begin{array}{c} \text{Diagram 3} \\ \text{0} \end{array} \\
 \begin{array}{c} \text{Diagram 4} \\ \text{-1} \end{array} & + & \begin{array}{c} \text{Diagram 5} \\ \text{-1} \end{array} & + & \begin{array}{c} \text{Diagram 6} \\ \text{+1} \end{array} \\
 \begin{array}{c} \text{Diagram 7} \\ \text{+1} \end{array} & + & \begin{array}{c} \text{Diagram 8} \\ \text{+2} \end{array} & + & \begin{array}{c} \text{Diagram 9} \\ \text{-2} \end{array}
 \end{array}
 \end{aligned}$$

FIGURE 1.7: Diagrammatic representation^[a] of each fragment if the two-particle component of the Hamiltonian operator, \hat{V}_N .

[a] → [108]

Here, the rightmost diagram in this matrix element is \hat{T} , thus its interaction line must lie at the bottom of the final diagram and \hat{H}_N must lie above the \hat{T} interaction lines. \hat{T}_1 and \hat{T}_2 diagrams produces an excitation levels of +1 and +2, respectively.

To obtain the desired amplitudes (t_i^a and t_{ij}^{ab}) and the energy (E_0^{corr}), amplitudes and energy equations have to be solved.

$$\langle \Phi_0 | (\hat{H}_N e^{(\hat{T}_1 + \hat{T}_2)}) | \Phi_0 \rangle = E_0^{corr} \quad (1.60)$$

$$\langle \Phi_i^a | (\hat{H}_N e^{(\hat{T}_1 + \hat{T}_2)})_c | \Phi_0 \rangle = 0 \quad (1.61)$$

$$\langle \Phi_{ij}^{ab} | (\hat{H}_N e^{(\hat{T}_1 + \hat{T}_2)})_c | \Phi_0 \rangle = 0 \quad (1.62)$$

For the desired solution, we have to take the only connected term from the equation 1.59.

$$\begin{aligned}
(\hat{H}_N e^{\hat{T}})_c &= (\hat{V}_N \\
&+ \hat{F}_N \hat{T}_1 + \hat{F}_N \hat{T}_2 + \hat{V}_N \hat{T}_1 + \hat{V}_N \hat{T}_2 \\
&+ \frac{1}{2!} \hat{V}_N \hat{T}_1^2 + \hat{V}_N \hat{T}_1 \hat{T}_2 \\
&+ \frac{1}{3!} \hat{V}_N \hat{T}_1^3 + \frac{1}{3!} \hat{V}_N \hat{T}_1^2 \hat{T}_2 \\
&+ \frac{1}{4!} \hat{V}_N \hat{T}_1^4)_c
\end{aligned} \tag{1.63}$$

The CC amplitudes are obtained by solving the simultaneous equations arising from left projecting the similarity-transformed Hamiltonian operator with One-body CCSD equation provides the desired amplitude which has only two open skyward lines and we obtain the below equation.

$$\underbrace{\hat{F}_N \hat{T}_1 + \hat{V}_N \hat{T}_1 + \hat{V}_N \hat{T}_2}_{\text{Linear CC}} + \underbrace{\hat{V}_N \hat{T}_1 \hat{T}_2 + \hat{V}_N \hat{T}_1^3}_{\text{High order CC}} = 0 \tag{1.64}$$

Two-body CCSD equation provides the desired amplitude which has four open skyward lines and we obtain the below equation.

$$\underbrace{\hat{F}_N \hat{T}_2 + \hat{V}_N \hat{T}_1 + \hat{V}_N \hat{T}_2}_{\text{Linear CC}} + \underbrace{\hat{V}_N \hat{T}_1^2 + \hat{V}_N \hat{T}_1 \hat{T}_2 + \hat{V}_N \hat{T}_2^2 + \hat{V}_N \hat{T}_1^2 \hat{T}_2 + \hat{V}_N \hat{T}_1^3 + \hat{V}_N \hat{T}_1^4}_{\text{High order CC}} = 0 \tag{1.65}$$

These simultaneous non-linear equations are solved iteratively. The CCSD correlation energy can be computed after solving for the CC amplitudes.

$$E_{CCSD} - E_0 = \hat{V}_N \hat{T}_2 + \hat{V}_N \hat{T}_1^2 \tag{1.66}$$

Higher order approximate coupled-cluster methods

The CCSD method scales with sixth power of the computational size and can now be used for small to moderate size molecules. For small molecules, if computational facility permits, one can go for more accurate approximations such as CCSD(T) which is a perturbative triples correction to CCSD and has one non-iterative step of $O(N^7)$ after the CCSD equations are converged. It is considered as gold-standard in computational electronic structure methods. More accuracy is obtained by including full triples, which is straightforward extension of CCSD. The utilisation of CC approximations including higher excitations is limited due to their complexity and computational cost [109].

1.7 Equation of motion method (EOM)

Among the various available theoretical methods, the EOM-CC [33–39] has been one of the most attractive options for direct computation of excited state energy calculations (e.g. EE, IP and EA) due to accuracy and scope for systematic improvements in the description of total and difference energies.

The EOM-CC is generally employed with singles and double substitution (EOM-CCSD) which provides an accuracy of 0.1-0.01 eV for low-lying excited states and about 0.5 eV for principle ionized/electron-attached states. Inclusion of triples enables one to go for enhanced accuracy, particularly for studying strong near-degeneracies and high-lying excitations, obviously at the expense of added computational cost. The inclusion of partial, as well as, full triples has been tried within the framework of EOM-CC method [38, 43, 47, 48, 74, 110–114].

The equation-of-motion coupled cluster method approximates the excited state wavefunction by application of a linear excitation operator to the general coupled cluster ground state. In case of RHF and UHF reference, T_1 is zero. Using these T' amplitudes one can define a modified effective \bar{H}' , which can be used as the reference for subsequent

EOM calculation. Since \hat{H} is not Hermitian. Therefore, wavefunction exists in different left and right eigen vectors.

Firstly, we understand the left eigen vector.

$$\langle \tilde{\Psi} | = \langle \phi_0 | \hat{L} e^{-\hat{T}} \quad (1.67)$$

The operator \hat{L} may be explained in analogy to the cluster operator; \hat{T} as a sum of cluster operators;

$$\hat{L} = \hat{L}_0 + \hat{L}_1 + \hat{L}_2 + \dots + \hat{L}_n \quad (1.68)$$

Where;

$$\hat{L}_n = \left(\frac{1}{n!} \right)^2 \sum_{ij..ab..}^n L_{ab..}^{ij..} i^\dagger j^\dagger \dots ba \quad (1.69)$$

For m^{th} deexcitation -

$$\hat{L}_n(m) = \left(\frac{1}{n!} \right)^2 \sum_{ij..ab..}^n L_{ab..}^{ij..}(m) i^\dagger j^\dagger \dots ba \quad (1.70)$$

Therefore, the ground state coupled cluster energy may be written as -

$$E = \langle \tilde{\Psi} | \hat{H} | \Psi \rangle = \langle \tilde{\Psi} | \hat{H} e^{-\hat{T}} | \phi_0 \rangle \quad (1.71)$$

and,

$$E = \langle \phi_0 | \hat{L} e^{-\hat{T}} \hat{H} e^{-\hat{T}} | \phi_0 \rangle = \langle \phi_0 | \hat{L} \bar{H} | \phi_0 \rangle \quad (1.72)$$

Here, right and left eigen wavefunctions are assumed to be normalized -

$$\langle \phi_0 | \hat{L} | \phi_0 \rangle = 1 \quad (1.73)$$

Similarly, excitation operator \hat{R} (right eigen vector).

$$|\tilde{\Psi}\rangle = e^{-\hat{T}} \hat{R} | \phi_0 \rangle \quad (1.74)$$

The operator \hat{R} also explained \hat{L} operator;

$$\hat{R} = \hat{R}_0 + \hat{R}_1 + \hat{R}_2 + \dots + \hat{R}_n \quad (1.75)$$

Where;

$$\hat{R}_n = \left(\frac{1}{n!} \right)^2 \sum_{ij..ab..}^n R_{ij..}^{ab..} a^\dagger b^\dagger \dots ij \quad (1.76)$$

For k^{th} de-excitation:

$$\hat{R}_n(k) = \left(\frac{1}{n!} \right)^2 \sum_{ij..ab..}^n R_{ij..}^{ab..} (k) a^\dagger b^\dagger \dots ij \quad (1.77)$$

Therefore, the ground state coupled cluster energy would be MP2 written as -

$$\begin{aligned}
E &= \langle \tilde{\Psi} | \hat{H} | \Psi \rangle \\
E &= \langle \phi_0 | \hat{L} e^{-\hat{T}} \hat{H} | \Psi \rangle \\
E &= \langle \phi_0 | \hat{L} e^{-\hat{T}} \hat{H} e^{-\hat{T}} \hat{R} | \phi_0 \rangle \\
E &= \langle \phi_0 | \hat{L} \bar{H} \hat{R} | \phi_0 \rangle
\end{aligned} \tag{1.78}$$

For m^{th} de-excitation and K^{th} excitation -

$$E = \langle \phi_0 | \hat{L}(m) \bar{H} \hat{R}(k) | \phi_0 \rangle \tag{1.79}$$

Since,

$$\bar{H} \hat{R}(k) | \phi_0 \rangle = E_k \hat{R}(k) | \phi_0 \rangle \tag{1.80}$$

Therefore,

$$\begin{aligned}
E &= \langle \phi_0 | \hat{L}(m) E_k \hat{R}(k) | \phi_0 \rangle \\
E &= E_k \langle \phi_0 | \hat{L}(m) \hat{R}(k) | \phi_0 \rangle \\
E &= E_k \delta_{mk}
\end{aligned} \tag{1.81}$$

Therefore, \hat{L} and \hat{R} biorthogonal to each other and can be normalized -

$$\langle \phi_0 | \hat{L}(m) \hat{R}(k) | \phi_0 \rangle = \delta_{mk} \tag{1.82}$$

Now,

$$\bar{H}|\phi_0\rangle = E|\phi_0\rangle \quad (1.83)$$

This equation shows an eigen value problem [36] in which similarity transformed Hamiltonian is used. \bar{H} is non-symmetric since \hat{T} is not Hermitian. Now, the energy equation is given by,

$$E_{cc} = \langle\phi_0|\bar{H}|\phi_0\rangle \quad (1.84)$$

and, amplitude equations are given by,

$$\begin{aligned} 0 &= \langle\phi_i^a|(H - E_{cc})|\phi_0\rangle \\ 0 &= \langle\phi_{ij}^{ab}|(\bar{H} - E_{cc})|\phi_0\rangle \end{aligned} \quad (1.85)$$

Matrix form of H_{CCSD} is shown by -

$$\bar{H}_{CC} = \begin{bmatrix} \langle\phi_0|\bar{H}|\phi_0\rangle & \langle\phi_0|\bar{H}|\phi_i^a\rangle & \langle\phi_0|\bar{H}|\phi_{ij}^{ab}\rangle \\ \langle\phi_i^a|\bar{H}|\phi_0\rangle & \langle\phi_i^a|\bar{H}|\phi_i^a\rangle & \langle\phi_i^a|\bar{H}|\phi_{ij}^{ab}\rangle \\ \langle\phi_{ij}^{ab}|\bar{H}|\phi_0\rangle & \langle\phi_{ij}^{ab}|\bar{H}|\phi_i^a\rangle & \langle\phi_{ij}^{ab}|\bar{H}|\phi_{ij}^{ab}\rangle \end{bmatrix}$$

Using equation 1.84 and 1.85, we obtain,

$$\bar{H}_{CCSD} = \begin{bmatrix} E_{cc} & \langle\phi_0|\bar{H}|\phi_i^a\rangle & \langle\phi_0|\bar{H}|\phi_{ij}^{ab}\rangle \\ 0 & \langle\phi_i^a|\bar{H}|\phi_i^a\rangle & \langle\phi_i^a|\bar{H}|\phi_{ij}^{ab}\rangle \\ 0 & \langle\phi_{ij}^{ab}|\bar{H}|\phi_i^a\rangle & \langle\phi_{ij}^{ab}|\bar{H}|\phi_{ij}^{ab}\rangle \end{bmatrix}$$

Let us consider, ground state, single and double excitation represented by O, S and D. Thus,

$$\langle \phi_0 | \bar{H} | \phi_i^a \rangle = \bar{H}_{OS} \quad (1.86)$$

$$\langle \phi_0 | \bar{H} | \phi_{ij}^{ab} \rangle = \bar{H}_{OD} \quad (1.87)$$

$$\langle \phi_i^a | \bar{H} | \phi_i^a \rangle = \bar{H}_{SS} \quad (1.88)$$

$$\langle \phi_i^a | \bar{H} | \phi_{ij}^{ab} \rangle = \bar{H}_{SD} \quad (1.89)$$

$$\langle \phi_{ij}^{ab} | \bar{H} | \phi_i^a \rangle = \bar{H}_{DS} \quad (1.90)$$

$$\langle \phi_{ij}^{ab} | \bar{H} | \phi_{ij}^{ab} \rangle = \bar{H}_{DD} \quad (1.91)$$

Now, matrix equation becomes -

$$\bar{H}_{CCSD} = \begin{bmatrix} E_{cc} & \bar{H}_{OS} & \bar{H}_{OD} \\ 0 & \bar{H}_{SS} & \bar{H}_{SD} \\ 0 & \bar{H}_{DS} & \bar{H}_{DD} \end{bmatrix}$$

We get k^{th} excitation energy by subtracting E_{cc} from equation 1.80,

$$(\bar{H} - E_{cc})\hat{R}_k|\phi_0\rangle = (E_k - E_{cc})|\phi_0\rangle \quad (1.92)$$

Since \hat{T} and \hat{R} are truncated at same level. Therefore, EOM-CCSD equation becomes,

$$\begin{pmatrix} 0 & \bar{H}_{OS} & \bar{H}_{OD} \\ 0 & \bar{H}_{SS} - E_{cc} & \bar{H}_{SD} \\ 0 & \bar{H}_{DS} & \bar{H}_{DD} - E_{cc} \end{pmatrix} \begin{pmatrix} R_0 \\ R_1 \\ R_2 \end{pmatrix} = \omega_k \begin{pmatrix} R_0 \\ R_1 \\ R_2 \end{pmatrix} \quad (1.93)$$

Where, $\omega_k = E_k - E_{cc} = k^{th}$ excitation energy. Here, E_{cc} appears only in the diagonal parts of the matrix. Equation 1.93 is solved by the generalized Davidson diagonalization iterative procedure [115] which involves the calculations of r_0 , r_i^a and r_{ij}^{ab} .

1.8 Fock-space multi-reference coupled cluster method (FS-MRCC)

The spectacular success of SRCC in predicting energies and energy derivatives [28, 116, 117] of non-degenerate ground states of molecules fueled the research in extending the ideas to understand the near-degeneracies in the electronic states. The prominence of static correlation over the dynamical one in the near degenerate states demanded for multiconfigurational description of the reference wavefunction. This resulted in the spectrum of what are knowns multi-reference (MR) CC methods [17–27]. In these methods, the dynamical correlation effects are brought in via action of a wave-operator on the multi-determinantal reference. While these methods have many similarities, they differ in the way the static correlation is treated and consequently in the types of degeneracies they can handle.

The MRCC methods based on effective-Hamiltonian framework can be broadly classified into two types, namely, SUMRCC or VSMRCC or HSMRCC [19, 27] and VUMRCC or FSMRCC [17, 18, 21–26].

The former method is convenient for studying near-degeneracies arising during bond dissociation and similar phenomena, while the latter is more suited for studying near-degeneracies arising from ionization, electron-attachments, electronic excitations, etc in the system. Both these methods often suffer from the intruder states problem. The intermediate Hamiltonian approach [21, 24, 26] is found to be very robust in eliminating the problem of intruder states by introduction of intermediate subspace for better separation of active and inactive subspaces.

The intruder states can also be avoided in state-specific manner as shown by Mahapatra et al [118] and Meller et al [119]. A suitable choice of active subspace can often avoid intruder states problem within the conventional FSMRCC framework for most of the

one-valence cases, particularly, when one is interested in computing only a few low-lying states.

FSMRCC uses a valence universal wave-operator acting on the model space configurations that can be viewed to be formed by creation of hole(s) and/or particle(s) with respect to a common hole-particle vacuum. A suitable RHF configuration is usually chosen as the vacuum. For example, a mono-radical state may be obtained by ionization of a closed-shell anion or electron-attachment of a cation resulting in respectively, the IP and EA variants of FSMRCC. To illustrate the formalism, we start with an N -electron RHF configuration as a vacuum. Removal of an electron from an occupied orbital of RHF is termed as creation of hole, whereas addition of electron to a virtual orbital is termed as creation of particle. The model space determinants include h -holes and p -particles categorised within the sets of what we call active holes and active particles.

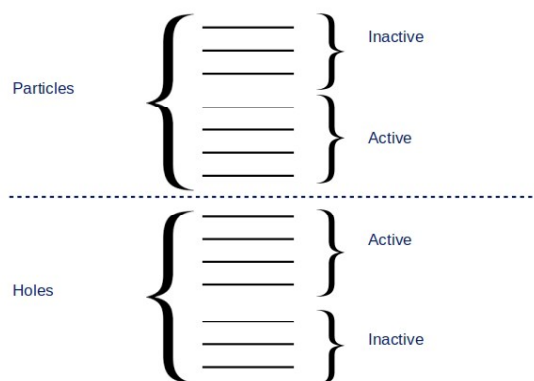


FIGURE 1.8: Schematic depiction of the classification of the hole and particle orbitals into active and inactive orbitals.

In brief, we can explain by graphical representation 1.9 -

“Single arrow lines show the inactive hole and particle; double arrows lines show active hole and particle and arrow with circle represent to both active and inactive.”

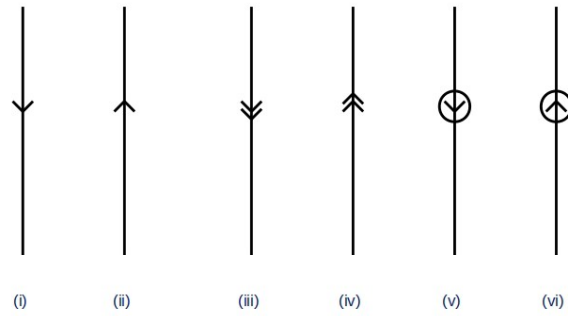


FIGURE 1.9: Hole and particle representation

The model space consists of the configurations $\{\Phi_i^{(p,h)}\}$ each of which has p -active particles and h -active holes. Thus, the MR wavefunction is thus, a linear combination of the model space configurations.

$$|\Psi_\mu^{(p,h)}\rangle = \sum_i C_{i\mu}^{(p,h)} |\Phi_i^{(p,h)}\rangle \quad (1.94)$$

The projection operator for model space is explained by given equation,

$$P^{(p,h)} = \sum_i |\Phi_i^{(p,h)}\rangle \langle \Phi_i^{(p,h)}| \quad (1.95)$$

The virtual space is the orthogonal component of the model space and its projection is given by

$$Q^{(p,h)} = 1 - P^{(p,h)} \quad (1.96)$$

The MR description of the starting wavefunction (Eq. 1.94) takes care of the static electron correlation. The relatively weaker component – the dynamical electron correlation is effected through a valence universal wave operator Ω which is parameterized so that its action would take one from model space to the virtual space. To generate exact

states for the (p, h) valence system, the wave operator must be capable of creating all valid excitations from the model space. Subsequently, Ω should include cluster operators $\{\tilde{T}^{(p,h)}\}$ which are defined as follows,

$$\tilde{T}^{(p,h)} = \sum_{k=0}^p \sum_{l=0}^h T^{(k,l)} \quad (1.97)$$

The superscripted bracket in the right-hand side of the above expression 1.97 shows that the cluster operator T can destroy exactly k active particles and l active holes, in enhancement to the creation of holes and particles. The $\tilde{T}^{(p,h)}$ operator subsumes all such lower cluster $T^{(k,l)}$ operators. Using these operators, the Ω is defined as follows,

$$\Omega = \{e^{\tilde{T}^{(p,h)}}\} \quad (1.98)$$

The brace-bracket in equation 1.98 shows normal ordering of the cluster-operators. The SWE for the manifold of quasi-degenerate states can be written as,

$$\begin{aligned} H|\Psi_i^{(p,h)}\rangle &= E_i|\Psi_i^{(p,h)}\rangle \\ &\text{which leads to} \\ H\Omega\left(\sum_i C_{i\mu}^{(p,h)}\Phi_i^{(p,h)}\right) &= E_\mu\Omega\left(\sum_i C_{i\mu}^{(p,h)}\Phi_i^{(p,h)}\right) \end{aligned} \quad (1.99)$$

The effective Hamiltonian for (p, h) valence system can be described such that,

$$\sum_j (H_{\text{eff}}^{(p,h)})_{ij} C_{j\mu} = E_\mu C_{i\mu} \quad (1.100)$$

$$(H_{\text{eff}}^{(p,h)})_{ij} = \langle \Phi_i^{(k,l)} | \Omega^{-1} H \Omega | \Phi_j^{(k,l)} \rangle$$

which can be described as-

$$H_{\text{eff}}^{(p,h)} = P^{(p,h)}\Omega^{-1}H\Omega P^{(p,h)} \quad (1.101)$$

The form of the inverse of Ω , in usual may not be well defined. Hence, the above explanation is rarely used to obtain effective Hamiltonian.

Alternatively, the Bloch-Lindgren approach is generally used to define the effective Hamiltonian. The Bloch equation is just a modified form of SWE.

$$H\Omega P = \Omega H_{\text{eff}} P \quad (1.102)$$

This approach not only eliminates the requirement of Ω^{-1} , but also provides an essential criterion that must be fulfilled by the effective Hamiltonian. The effective Hamiltonian is, in general, non-hermitian. The Bloch projection approach, involves left projection of above equation by P and Q .

$$\begin{aligned} P^{(k,l)}[H\Omega - \Omega H_{\text{eff}}^{(k,l)}]P^{(k,l)} &= 0 \\ Q^{(k,l)}[H\Omega - \Omega H_{\text{eff}}^{(k,l)}]P^{(k,l)} &= 0 \\ & ; \forall k = 0, \dots, p; l = 0, \dots, h \end{aligned} \quad (1.103)$$

The normalization condition is indirectly specified through parameterization of Ω . In the case of complete model spaces (CMS), the intermediate normalization is commonly employed.

The diagonalization of the effective Hamiltonian within the P space provides the energies of the corresponding states and the left and the right eigenvectors.

$$H_{\text{eff}}^{(p,h)}C^{(p,h)} = C^{(p,h)}E$$

$$\tilde{C}^{(p,h)} H_{eff}^{(p,h)} = E \tilde{C}^{(p,h)} \quad (1.104)$$

$$\tilde{C}^{(p,h)} C^{(p,h)} = C^{(p,h)} \tilde{C}^{(p,h)} = 1 \quad (1.105)$$

The normal ordering, avoids the contractions amongst various cluster operators resulting in the sub-system embedding condition (SEC) which is nothing but the partial hierarchical decoupling of cluster equations. As a result, the lower valence cluster equations are completely decoupled from the respective higher valence cluster equations. Hence, the Bloch equations need to be progressively solved, starting from the lowest valence $(0,0)$ sector, step by step up to (p,h) valence sector.

Pal and co-workers [120–124] formulated and implemented LR in FSMRCCSD framework and computed dipole moments of moments of doublet radicals and of closed-shell molecules in excited electronic states. The method may be viewed as extension of Monkhorst’s approach in SRCC [116] to MRCC and being non-variational, requires explicit differentiation of Bloch equation concerning the uniform external field. In presence of time-independent uniform external field, the parameters $\Upsilon = \{H_{eff}^{(p,h)}, C^{(p,h)}, \tilde{C}^{(p,h)}, E, \Omega\}$ become perturbation dependent and can be expanded in Taylor series of g .

$$\Upsilon(g) = \Upsilon^{(0)} + g\Upsilon^{(1)} + \frac{1}{2!}g^2\Upsilon^{(2)} + \frac{1}{3!}g^3\Upsilon^{(3)} + \dots \quad (1.106)$$

The first order differentiation of the Bloch equations results in the the equations for the MRCC derivative amplitudes and the derivative effective Hamiltonian. The dipole moments corresponding to the near-degenerate states appearing as roots of the effective Hamiltonian are obtained up on solving the following equations.

$$\sum_i \{(H_{eff}^{(1)})_{ji} C_{i\mu}^{(0)} + (H_{eff}^{(0)})_{ji} C_{i\mu}^{(1)}\} = E_{\mu}^{(1)} C_{j\mu}^{(0)} + E_{\mu}^{(0)} C_{j\mu}^{(1)} \quad (1.107)$$

Due to non-variational nature of the method, the generalized Hellman-Feynman theorem does not hold and for higher order energy derivatives, the method becomes unattractive.

Constrained variation approach (CVA) FSMRCCSD

Following the LR developments in SRCC, such as Z-vector technique [117] and the equivalent constrained variation approach (CVA) [28], their extensions to FSMRCC were attempted, which includes Z-vector formulation by Pal and co-workers [125], CVA linear response formulation by Szalay [126] and independently by Pal and co-workers [29–32, 127]. The computational implementation of CVA-FSMRCCSD was done by Manohar et al [29, 30] for analytical dipole moments and analytical dipole polarizability of doublet radicals. The CVA-FSMRCC method of Pal and co-workers gives response of a specific root of the multiple roots of FSMRCC. One has to project a single desired state (root of effective Hamiltonian) for doing constrained variation.

$$E_\mu = \sum_{ij} \tilde{C}_{\mu i}^{(p,h)} (H_{\text{eff}})_{ij}^{(p,h)} C_{j\mu}^{(p,h)} \quad (1.108)$$

We formulate the Lagrangian to minimize the energy expression 1.108, with the constraint that the MRCC equations 1.103 are satisfied for the state μ .

$$\begin{aligned} \mathfrak{S} = & \sum_{ij} \tilde{C}_{\mu i}^{(p,h)} (H_{\text{eff}})_{ij}^{(p,h)} C_{j\mu}^{(p,h)} \\ & + \sum_{k=0}^p \sum_{l=0}^h \{ P^{(k,l)} \Lambda^{(k,l)} P^{(k,l)} P^{(k,l)} [H\Omega - \Omega H_{\text{eff}}^{(k,l)}] P^{(k,l)} \\ & + P^{(k,l)} \Lambda^{(k,l)} Q^{(k,l)} Q^{(k,l)} [H\Omega - \Omega H_{\text{eff}}^{(k,l)}] P^{(k,l)} \} \\ & + E_\mu \left[\sum_{ij} \tilde{C}_{\mu i}^{(p,h)} C_{j\mu}^{(p,h)} - 1 \right] \end{aligned} \quad (1.109)$$

As in SRCC, the energy derivatives obey the $2n + 1$ rule with respect to MRCC cluster amplitude derivatives and $2n + 2$ rule with respect to the Lagrange multiplier derivatives.

Other Developments

Apart from the methods discussed above, the methods such as SAC-CI [41], MRCI [42], MRPT [45], QDPT [46], ST-EOM-CC [128], Green function approach, CC-LRT, etc are also well-known for their capability in treating static and dynamic correlation. An entirely alternative approach to the wavefunction based method is the popular density functional theory (DFT) [129]. The problem with DFT is that exact form of exchange-correlation (XC) functional is not known. The plethora of XC functionals have been developed for handling a variety of electronic structure problems. Though these functionals can provide high accuracy within their domain of applicability, they fail very badly if not properly chosen. However, due to simplicity and compactness, DFT is being widely used. The TD-DFT [130] has extended its applicability further the developments to near-degenerate electronic states, as well.

With this, we conclude our review of various theoretical & computational methods that provide the background to our PhD research work that is presented in the next few chapters.



This document was created with the Win2PDF “print to PDF” printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

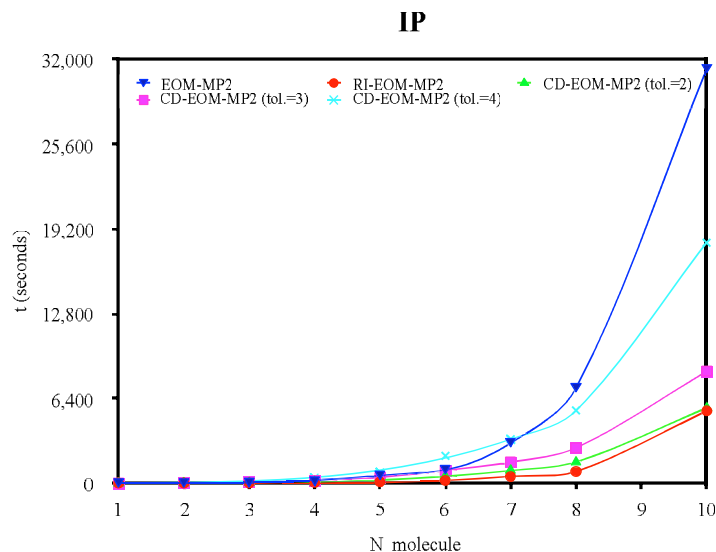


FIGURE 3.3: Plot of Total time vs no water clusters for IP variant of EOM-MP2

Fig 3.3 and 3.4 provide a plot of time required for the computation of a single root (for IP and EA variants of EOM-MP2 and RI and CD approximations) versus the no of water molecules. The data used for plotting can be found in Table 3.1 and 3.2. It can be seen that use of RI/CD approximation leads to significant speed-up for IP and EA. Total computational timing depends mainly upon two factors. One of them is formal scaling and other is the I/O.

In the case of IP and EA the formal scaling of EOM part of the computation is $O(N^5)$, while the CCSD part of computation, which is $O(N^6)$, is eliminated and replaced by the MP2 approximation in EOM-MP2, which scales as $O(N^4)$. Thus, for IP and EA variants, there is reduction in scaling as one goes from EOM-CCSD to EOM-MP2. The RI or CD implementation would further reduce the computational cost resulting in further speed up. Following Eq. 2.22 and the related discussion, we present the plots of $\ln t$ versus $\ln n_{molecule}$ for IP and EA variants of all the methods in Figures 3.5 and 3.6, respectively. The graphs clearly show reduction in the computational timings for IP and EA variants. The EOM parts of these variants employ less number of intermediates as compared to those required in EE and SF. Thus, significant speed-up is already gained at EOM-MP2 level. Thus

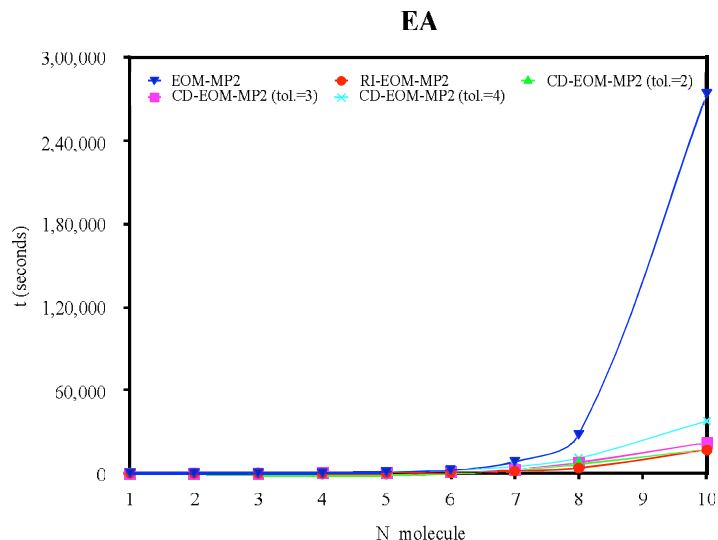


FIGURE 3.4: Plot of Total time vs no water clusters for EA variant of EOM-MP2

the advantage of RI/CD would be seen only wherever I/O bottlenecks are reduced. The reduction in computational timing is much more prominent in EA, where the four-particle integrals leads to significant I/O bottleneck. The absence of four four-particle integrals makes RI/CD based methods less advantageous in IP than that in EA. As in case of EE and SF, among all the methods, the CD-EOM-MP2 with $\delta = 10^{-2}$ is the fastest, followed by the one with $\delta = 10^{-3}$ and then the CD-EOM-MP2 with $\delta = 10^{-4}$. The computational timings of RI are a little more than those of CD with $\delta = 10^{-2}$ but quite lesser than those of CD($\delta = 10^{-3}$), a trend very similar to the one observed in case of EE and SF variants.

TABLE 3.1: Computational timings for EOM-CCSD, EOM-MP2, RI-EOM-MP2 and CD-EOM-MP2 (in seconds) for IP energy calculations of water clusters using cc-pVDZ basis

Cluster	EOM-CCSD	EOM-MP2	RI-MP2	CD-MP2		
				$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	13.98	11.95	11.84	13.08	14.10	16.94
Dimer	30.69	17.99	14.39	23.94	35.49	57.79
Trimer	115.43	47.26	23.80	48.80	78.23	164.65
Tetramer	533.32	141.15	51.80	119.98	197.40	416.00
Pentamer	1641.56	580.77	108.59	215.65	415.43	831.27
Hexamer	4402.71	1016.19	219.60	539.77	956.55	2071.59
Heptamer	12169.52	3046.57	517.67	967.92	1597.25	3318.21

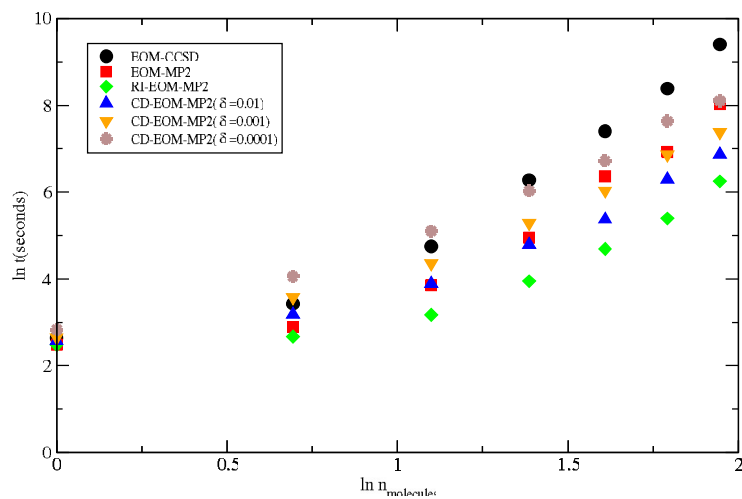


FIGURE 3.5: Plot of $\ln(\text{time})$ vs $\ln(\text{no water clusters})$ for IP variant of EOM-MP2

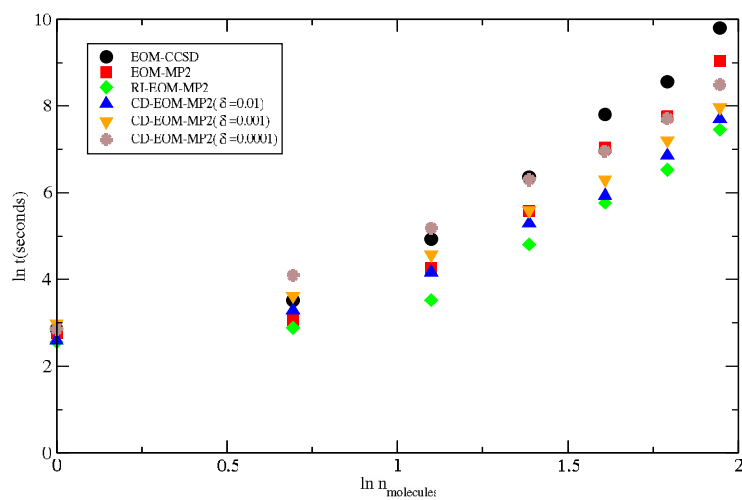


FIGURE 3.6: Plot of $\ln(\text{time})$ vs $\ln(\text{no water clusters})$ for EA variant of EOM-MP2

TABLE 3.2: Computational timings for EOM-CCSD, EOM-MP2, RI-EOM-MP2 and CD-EOM-MP2 (in seconds) for EA energy calculations of water clusters using cc-pVDZ basis

Cluster	EOM-CCSD	EOM-MP2	RI-MP2	CD-MP2		
				$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	17.35	15.89	12.92	13.51	19.67	17.32
Dimer	33.75	21.72	17.88	26.70	37.26	59.94
Trimer	138.22	70.68	33.90	64.59	97.02	178.36
Tetramer	533.97	141.15	51.80	119.06	266.45	545.87
Pentamer	2443.44	1141.59	319.34	375.64	544.33	1052.83
Hexamer	5214.61	2347.02	683.92	949.09	1344.40	2424.51
Heptamer	18053.36	8404.21	1725.44	2202.48	2887.38	4877.56

3.3.2 Energies of water clusters

The energy-gap between two target states 3.3 and 3.4 gives the canonical EOM-MP2 total energies for IP, and EA target states and the relative energies of RI-EOM-MP2 and CD-EOM-MP2 methods for these variants. The corresponding excitation energies are summarized in 3.5 and 3.6.

TABLE 3.3: EOM-CCSD total target state energies (hartrees) of water clusters and errors (eV) of RI-EOM-MP2 and CD-EOM-MP2 relative to EOM-MP2 for IP

Cluster	EOM-MP2	RI-MP2	CD-MP2		
			$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	-75.81264	0.000	0.003	0.002	0.000
Dimer	-152.11678	0.000	0.015	0.005	0.000
Trimer	-228.38223	0.000	0.008	0.039	0.001
Tetramer	-304.66502	0.001	0.022	0.012	0.001
Pentamer	-380.86701	0.000	0.045	0.017	0.001
Hexamer	-457.24425	0.001	0.078	0.021	0.001
Heptamer	-533.52662	0.001	0.052	0.025	0.002

The standard deviations of TEs in canonical EOM-MP2 method relative to EOM-CCSD for IP and EA variants are 0.404 and 0.431 eV, respectively. This gives an idea about the error bar of EOM-MP2 methods. However, in this study, we present our RI/CD-EOM-MP2 results relative to canonical EOM-MP2 results, because that is the maximum accuracy possible to achieve in our RI/CD EOM-MP2 method. The TE values in RI-EOM-MP2 method are generally higher than the canonical EOM-MP2 values for all the variants.

TABLE 3.4: EOM-CCSD total target state energies (hartrees) of water clusters and errors (eV) of RI-EOM-MP2 and CD-EOM-MP2 relative to EOM-MP2 for EA

Cluster	EOM-MP2	RI-MP2	CD-MP2		
			$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	-76.23479	0.000	0.004	0.002	0.000
Dimer	-152.51585	0.000	0.006	0.005	0.000
Trimer	-228.79288	0.000	0.033	0.009	0.001
Tetramer	-305.07643	0.000	0.031	0.012	0.001
Pentamer	-381.28175	0.001	0.016	0.038	0.001
Hexamer	-457.64114	0.000	0.066	0.021	0.001
Heptamer	-533.92405	0.001	0.041	0.025	0.002

TABLE 3.5: First ionization energies ($E_{target} - E_{reference}$)(eV) of water clusters computed using EOM-MP2, RI-EOM-MP2 and CD-EOM-MP2 methods and cc-pVDZ basis

Cluster	MP2	RI-MP2	CD-MP2		
			$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	0.775	0.775	0.769	0.774	0.775
Dimer	0.527	0.527	0.519	0.527	0.527
Trimer	0.644	0.644	0.638	0.643	0.644
Tetramer	0.638	0.638	0.633	0.636	0.638
Pentamer	0.426	0.426	0.418	0.424	0.425
Hexamer	0.432	0.432	0.424	0.430	0.431
Heptamer	0.491	0.491	0.482	0.490	0.491

The maximum deviations of TEs in RI-EOM-MP2 relative to EOM-MP2 for all the EOM methods are 0.001 eV, only. However, the errors in CD variants depends strongly on the tolerance used. The standard deviation in CD-EOM-MP2 ($\delta = 10^{-2}$) TEs relative to EOM-MP2 for IP and EA variants are 0.028 and 0.021 eV, respectively. They are an order of magnitude less than the typical error bar of 0.2 eV -0.3 eV reported for EOM methods [139].

TABLE 3.6: First electron affinities energies ($E_{target} - E_{reference}$)(eV) of water clusters computed using EOM-MP2, RI-EOM-MP2 and CD-EOM-MP2 methods and cc-pVDZ basis

Cluster	MP2	RI-MP2	CD-MP2		
			$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	0.775	0.775	0.769	0.774	0.775
Dimer	0.527	0.527	0.519	0.527	0.527
Trimer	0.644	0.644	0.638	0.643	0.644
Tetramer	0.638	0.638	0.633	0.636	0.638
Pentamer	0.426	0.426	0.418	0.424	0.425
Hexamer	0.432	0.432	0.424	0.430	0.431
Heptamer	0.491	0.491	0.482	0.490	0.491

The error decreases on tightening the tolerance criteria. The standard deviation in errors with $\delta = 10^{-3}$ for IP and EA variants are 0.013 and 0.13 eV, respectively. The maximum deviations come down to 0.002 eV with $\delta = 10^{-4}$. It should be noted that the TE in CD-EOM-MP2 is always higher than their canonical version for all the flavors of EOM.

The DEs are much well reproduced in both RI and CD EOM-MP2 than that observed for TE. Table 3.5 and 3.6 presents the DE values for all flavors of EOM-MP2. The maximum deviations of DE in RI-EOM-MP2 is 0.001 eV for all flavors of EOM. The accuracy of CD-EOM-MP2 is strongly dependent on the decomposition threshold. The maximum deviation of DE with $\delta = 10^{-2}$ for IP and EA variants are 0.005 and 0.009 eV, respectively. The maximum error gets reduced to 0.002 and 0.002 eV, for IP and EA variants, respectively with Cholesky decomposition threshold $\delta = 10^{-3}$. The maximum errors come down within 0.001 eV with $\delta = 10^{-4}$.

Table 3.7 and 3.8 summarises DTEs (ΔE_{12}) of water clusters computed for IP and EA variants of RI-EOM-MP2 and CD-EOM-MP2. Both RI-EOM-MP2 and CD-EOM-MP2 predict the DTEs with good accuracy.

TABLE 3.7: Energy difference (eV) between lowest two IP target energy levels for water clusters computed using EOM-MP2, EOM-MP2, RI-EOM-MP2 and CD-EOM-MP2 methods and cc-pVDZ basis

Cluster	MP2	RI-MP2	CD-MP2		
			$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	2.259	2.259	2.261	2.259	2.259
Dimer	1.355	1.355	1.357	1.354	1.355
Trimer	0.140	0.140	0.134	0.140	0.140
Tetramer	1.322	1.322	1.324	1.322	1.322

For IP, the CD-EOM-MP2 with $\delta = 10^{-4}$ and RI-EOM-MP2 gives identical value as that of canonical EOM-MP2, whereas for CD-EOM-MP2 with $\delta = 10^{-2}, 10^{-3}$, the maximum deviation increases to 0.006 eV and 0.001 eV, respectively. For EA, the maximum deviation for CD-EOM-MP2 with $\delta = 10^{-2}$ is 0.003 eV, whereas, CD-EOM-MP2 with $\delta = 10^{-4}$ gives identical value as that of canonical one. The maximum deviation for EA in the CD-EOM-MP2 with $\delta = 10^{-3}$ and RI-EOM-MP2 is 0.001 eV.

TABLE 3.8: Energy difference (eV) between lowest two EA target energy levels for water clusters computed using EOM-MP2, EOM-MP2, RI-EOM-MP2 and CD-EOM-MP2 methods and cc-pVDZ basis

Cluster	MP2	RI-MP2	CD-MP2		
			$\delta = 10^{-2}$	$\delta = 10^{-3}$	$\delta = 10^{-4}$
Monomer	0.728	0.729	0.730	0.729	0.728
Dimer	0.847	0.847	0.850	0.847	0.847
Trimer	0.575	0.575	0.575	0.575	0.575
Tetramer	0.563	0.563	0.564	0.563	0.563

3.3.3 Electron Affinity of DNA bases

The weakly bound electrons in DNA nucleic acid bases (NAB) lead to a diverse range of interesting properties [141–144], which has fascinated generations of theoreticians and experimentalists. A wide range of theories, starting from DFT [145–148] with different functionals and basis set, to state of the art coupled cluster methods [149, 150] were used in the simulation of electron attachment to NAB.

However, the addition of an extra electron to NAB leads to multiple quasi-degenerate configurations, the simulation of which calls for a method which can go beyond the single determinant picture. The EOM-CC method is quite capable of treating such quasi-degenerate situations and can calculate electron attachment corresponding to multiple states in a single run [37]. The EOM-IP-CC has been extensively used by Krylov and co-workers [151–154] to study the ionization-induced changes in NAB.

However, the EOM-CC studies on the electron affinities of NAB are rather limited. To the best of our knowledge, the one available comes from the work of Pal and co-workers [155] and that also restricts its attention to isolated bases only. The large basis set required to model the NAB bound anions often makes conventional EOM-CC calculations difficult to perform beyond isolated DNA bases. However, our RI/CD based EOM-MP2 method because of its lower storage and memory requirements can be an efficient alternative. The electron affinity values of NAB in different theoretical methods are presented in 3.9.

TABLE 3.9: Vertical electron affinities (eV) of DNA and RNA nucleobases obtained by different theoretical methods

Method ^a	uracil	thymine	cytosine	adenine	guanine
experimental range ^b	-0.30~0.22	-0.53~0.29	-0.55~0.32	-0.56~0.45	-2.07~0.08
DFT range ^c	-1.09~0.11	-1.05~0.28	-1.42~0.31	-1.57~0.34	-1.30
PMP2//MP2/aug-cc-pVDZ ^d	-0.56	-0.58	-0.73	-0.99	
CCSD//CCSD/aug-cc-pVDZ ^d	-0.63	-0.65	-0.77		
CCSD(T)//CCSD/aug-cc-pVDZ ^d	-0.64	-0.65	-0.79		
CASPT2/ANO-L 4321/321//CASSCF/ANO-L 431/21 ^d	-0.49	-0.45	-0.59	-0.74	-0.94
EOM-EA-CCSD/aug-cc-pVDZ/B3LYP/6-311++G** ^e	-0.23	-0.28	-0.27	-0.44	-0.23
EOM-EA-CCSD/aug-cc-pVTZ(-1f)/B3LYP/6-311++G** ^e	-0.20	-0.24	-0.24	-0.40	-0.19
RI-EOM-EA-MP2/aug-cc-pVDZ ^f	-0.20	-0.26	-0.27	-0.46	-0.28
RI-EOM-EA-MP2/aug-cc-pVTZ ^f	-0.12	-0.17	-0.17	-0.35	-0.19

^a W/X/Y/Z denotes the single point calculations are done using W method using X basis set.

The geometry was optimized using Y method and Z basis set.

^b Values taken from ref[156-158].

^c Values taken from ref[159].

^d Values taken from ref[149].

^e Values taken from ref[155].

^f present work.

It can be seen that the electron affinities in all the theoretical methods are negative, which is consistent with the experimental results. It indicates the electron attached states of NAB are not bound states, rather quasi-bound or resonance states. It can be seen that the DFT method gives most scattered results ranging from highly negative values to values close to zero. The MP2 method leads to negative values. The CCSD and CCSD(T) method also leads to highly negative values and the values are almost identical to each other. However, the used basis set is too small to perform any meaningful comparison with experiments.

The CASPT2 method, on the other hand, gives much less negative values. It can be seen that EOM based methods give the best agreement with experiments. The RI-EOM-MP2/aug-cc-pVDZ computed EA values are in good agreement with the EOM-CCSD/aug-cc-pVDZ results of Pal and co-workers [155]. On using the aug-cc-pVTZ basis, the absolute values of RI-EOM-MP2 computed EAs decrease by 0.04-0.08 eV from the corresponding EOM-CCSD results. However, it is justifiable, as Pal and co-workers [155] removed one of the f functions from their basis set and used aug-cc-pVDZ basis set for hydrogen. Whereas, in the present study the standard aug-cc-pVTZ basis set is used for all elements and it is well known that EA of NAB increases(i.e becomes less negative) with increase in basis set.

The deviation is within the accuracy range of EOM-CCSD method. Among all the nucleobases, the uracil shows highest EA values of -0.12 eV in RI-EOM-MP2/aug-cc-pVTZ level of theory, which is in excellent agreement with the optimized virtual orbital space (OVOS) based CCSD(T)/aug-cc-pVTZ value of -0.15 eV reported by Urban and co-workers [150]. The lowest electron affinity of -0.35 eV is displayed by adenine, which is much lower than the other theoretical methods, though it agrees well with the experimental value. The small storage requirements and favorable computational scaling of RI/CD of EOM-MP2 allows to calculate EA values beyond single DNA bases, but that is outside the scope of the present study and will be followed in some future work.

3.4 Conclusion

We have presented the formulation of cost-effective RI and CD based EOM-MP2 approximations to EOM-CCSD [70]. The MP2 approximation reduces the timing and cost by eliminating iterative CCSD procedure. Moreover, use of RI (or CD) reduces the cost further with respect to the computational size of the system, thereby widening the applicability of EOM-MP2 to molecules of larger size such as DNA nucleobases. Although the RI/CD approximating doesn't change overall scaling of the methods, it greatly reduces the storage requirements and I/O bottlenecks and thereby resulting in a major speed-up.

The iterative decomposition procedure in CD-EOM-MP2 is the rate-determining step and can alter the overall timing of the job depending on the CD threshold chosen. In terms of accuracy, RI-EOM-MP2 and CD-EOM-MP2 with $\delta = 10^{-3}$ are comparable and provide fairly good results for DEs with maximum absolute error (MAE) with respect to the conventional EOM-MP2 to be of 0.002 eV for IPs and EAs. For DTEs, these methods perform even better with the MAE of 0.001 eV with respect to the EOM-MP2 values for IP and EA.

In case of availability of pre-optimized auxiliary basis, RI-EOM-MP2 is a preferred method over CD-EOM-MP2 as it saves the time required for iterative CD procedure. However, CD-EOM-MP2 can be used for a more general choice of basis and suitable threshold can be chosen to tune the desired accuracy. The small storage requirements and favorable computational scaling of RI/CD-EOM-MP2 allows one to use these methods for computing IPs and EAs of large molecules and clusters, which is beyond the reach of both the canonical EOM-MP2 as well as RI/CD-EOM-CCSD.

Chapter 4

Cholesky Representation of CVA-FSMRCCSD : Analytical dipole moment of doublet radicals

4.1 Introduction

In previous chapters, we have discussed the cost-effective computation of energies and energy differences of molecules in excited, ionized and electron-attached states. Optical properties such as dipole moments, polarizabilities play important role in electronic structure of molecules. Therefore, it is important to test the accuracy of a cost-effective technique in computing these properties.

In this chapter, we present the Cholesky representation of CVA-FSMRCCSD for computing analytical dipole moments of some doublet radicals. The lowest electron-attached state of some doublet radicals is a non-degenerate closed shell state. Such radicals can be viewed as ionized states of corresponding closed shell anions, for example, the OH, CN and SiN radicals. One can use the IP variant of CVA-FSMRCCSD to compute the dipole

moments of these radicals. On the other hand, some radicals have their first ionized state of closed shell character. These radicals can, therefore, be viewed as electron-attached states of the corresponding non-degenerate closed shell cations, for example, the CH, CCH, SiH and BO radicals. The EA variant of CVA-FSMRCCSD can be conveniently employed for computing dipole moments of these radicals.

4.2 Theory

CVA-FSMRCC method for the first order properties

The FSMRCC and CVA-FSMRCC theory has already been described in Chapter 1 for a general (p, h) -valence sector. Here, we write the algebra specifically for one valence sector of FS to discuss the formulation of CVA in FSMRCC context. We fix our notations for the quantities as follows. The $[m]$ in the superscript indicates the m -valence sector, so that, $m = 0$ would correspond to the vacuum, $m = 1$ would correspond to either IP or EA, that is, the $(0, 1)$ or $(1, 0)$ sector, respectively, as applicable, and so on. The (n) in the superscript indicates the n^{th} order derivatives of the quantity with respect to the external field. The configurations of this CMS are given by,

$$|\Psi_{\mu}^{[1]}\rangle = \sum_i C_{i\mu} |\Phi_i^{[1]}\rangle \quad (4.1)$$

The dynamical electron correlation effects are brought in through a universal wave operator Ω .

$$\Omega = \{e^{\hat{T}^{[1]}}\} \quad (4.2)$$

$$\hat{T}^{[1]} = T^{[1]} + T^{[0]} \quad (4.3)$$

The wave operator Ω is parameterized such that the states generated by its action on the reference function satisfy Bloch-Lindgren equation for effective Hamiltonian given by equation 1.102. The lower valence cluster operator equations are decoupled from the higher valence ones which is known as subsystem embedding condition (SEC).

The diagonalization of the effective Hamiltonian within the P space gives the energies of the corresponding states and the left and the right eigen vectors.

$$\begin{aligned} H_{\text{eff}}^{[1]}C^{[1]} &= C^{[1]}E \\ \tilde{C}^{[1]}H_{\text{eff}}^{[1]} &= E\tilde{C}^{[1]} \end{aligned} \quad (4.4)$$

Explicit differentiation of the above equations leads to the non-variational LR of FSMRCC and involves solution of derivatives of Ω and $H_{\text{eff}}^{[1]}$ for every mode of perturbation separately.

We now briefly discuss the CVA-FSMRCC method for [1] Fock space. The energy of a specific state of the ionized system is given by,

$$E_{\mu} = \sum_{ij} \tilde{C}_{\mu i}^{[1]} (H_{\text{eff}}^{[1]})_{ij} C_{j\mu}^{[1]} \quad (4.5)$$

We construct the Lagrangian to minimize the energy expression given above, with the constraint that the MRCC equations are satisfied for the state μ .

$$\begin{aligned}
\mathfrak{S} = & \sum_{ij} \tilde{C}_{\mu i}^{[1]} (H_{eff})_{ij}^{[1]} C_{j\mu}^{[1]} \\
& + P^{[1]} \Lambda^{[1]} P^{[1]} P^{[1]} [H\Omega - \Omega H_{eff}^{[1]}] P^{[1]} \\
& + P^{[1]} \Lambda^{[1]} Q^{[1]} Q^{[1]} [H\Omega - \Omega H_{eff}^{[1]}] P^{[1]} \\
& + P^{[0]} \Lambda^{[0]} P^{[0]} P^{[0]} H\Omega P^{[0]} \\
& + P^{[0]} \Lambda^{[0]} Q^{[0]} Q^{[0]} H\Omega P^{[0]} \\
& - E_{\mu} \left(\sum_{ij} \tilde{C}_{\mu i}^{[1]} C_{j\mu}^{[1]} - 1 \right) \tag{4.6}
\end{aligned}$$

The Λ in equation 4.6 are the Lagrange multipliers. However, in case of CMS, the effective Hamiltonian has an explicit expression in terms of cluster operators, as a consequence of which, the closed part in the Lagrange multipliers vanishes. The equation 4.6 thus reduces to,

$$\begin{aligned}
\mathfrak{S} = & \sum_{ij} \tilde{C}_{\mu i}^{[1]} (H_{eff})_{ij}^{[1]} C_{j\mu}^{[1]} \\
& + P^{[1]} \Lambda^{[1]} Q^{[1]} Q^{[1]} [H\Omega - \Omega H_{eff}^{[1]}] P^{[1]} \\
& + P^{[0]} \Lambda^{[0]} Q^{[0]} Q^{[0]} H\Omega P^{[0]} \\
& - E_{\mu} \left(\sum_{ij} \tilde{C}_{\mu i}^{[1]} C_{j\mu}^{[1]} - 1 \right) \tag{4.7}
\end{aligned}$$

Differentiation of equation 4.7 with respect to Λ results in expression for cluster amplitudes (i.e., the Bloch equation). It is obviously seen that the equations for Ω amplitudes are decoupled from the Λ amplitudes. The Λ equations are, however, coupled with the Ω amplitudes. These are obtained by making equation 4.7 stationary with respect to the cluster amplitudes. In presence of external field, the Lagrangian and the parameters $\Upsilon = \{H_{eff}, C, \tilde{C}, E, \Omega, \Lambda\}$ become perturbation dependent. These can be expanded in Taylor series.

$$\Upsilon(g) = \Upsilon^{(0)} + g\Upsilon^{(1)} + \frac{1}{2!}g^2\Upsilon^{(2)} + \frac{1}{3!}g^3\Upsilon^{(3)} + \dots \tag{4.8}$$

The Lagrangian defined in equation 4.7 can be differentiated with respect to the field g to obtain the Lagrangians at every order. The zeroth order and the first order Lagrangians can therefore, be written as

$$\begin{aligned}
\mathfrak{S}^{(0)} = & \left(\tilde{C}^{[1](0)} H_{eff}^{[1](0)} C^{[1](0)} \right)_{\mu\mu} \\
& + P^{[1]} \Lambda^{[1](0)} [H^{(0)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{[1](0)}] P^{[1]} \\
& + P^{[0]} \Lambda^{0} [H^{(0)} \Omega^{(0)}] P^{[0]} \\
& - E_{\mu} \left(\sum_{ij} \tilde{C}_{\mu i}^{[1](0)} C_{j\mu}^{[1](0)} - 1 \right)
\end{aligned} \tag{4.9}$$

$$\begin{aligned}
\mathfrak{S}^{(1)} = & \left(\tilde{C}^{1} H_{eff}^{[1](0)} C^{[1](0)} \right)_{\mu\mu} + \left(\tilde{C}^{[1](0)} H_{eff}^{1} C^{[1](0)} \right)_{\mu\mu} \\
& + \left(\tilde{C}^{[1](0)} H_{eff}^{[1](0)} C^{1} \right)_{\mu\mu} \\
& + P^{[1]} \Lambda^{1} [H^{(0)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{[1](0)}] P^{[1]} \\
& + P^{[1]} \Lambda^{[1](0)} [H^{(1)} \Omega^{(0)} + H^{(0)} \Omega^{(1)} - \Omega^{(1)} H_{eff}^{[1](0)} - \Omega^{(0)} H_{eff}^{1}] P^{[1]} \\
& + P^{[0]} \Lambda^{[0](1)} H^{(0)} \Omega^{(0)} P^{[0]} + P^{[0]} \Lambda^{0} H^{(1)} \Omega^{(0)} + H^{(0)} \Omega^{(1)} P^{[0]} \\
& - E_{\mu}^{(0)} \sum_{ij} \left(\tilde{C}_{\mu i}^{[1](0)} C_{j\mu}^{1} + \tilde{C}_{\mu i}^{1} C_{j\mu}^{[1](0)} \right) \\
& - E_{\mu}^{(1)} \left(\sum_{ij} \tilde{C}_{\mu i}^{[1](0)} C_{j\mu}^{[1](0)} - 1 \right)
\end{aligned} \tag{4.10}$$

The equations 4.9 and 4.10 give the energy and the first order energy derivative for the state μ . Because of stationarity of Lagrangian with respect to Λ and Ω , the above expressions are further simplified. The energy derivatives follow $(2n+1)$ rule with respect to the Ω amplitudes and $(2n+2)$ rule with respect to Λ amplitudes. There is a $(2n+1)$ rule for the eigen-vectors $\tilde{C}^{[1]}$ and $C^{[1]}$ for evaluation of energy derivatives. With these, the expressions for Lagrangians given in equation 4.9 and 4.10 simplify. We denote this simplified Lagrangian as

\mathfrak{S}_{opt} .

$$\mathfrak{S}_{opt}^{(0)} = \left(\tilde{C}^{[1](0)} H_{eff}^{[1](0)} C^{[1](0)} \right)_{\mu\mu} \quad (4.11)$$

$$\begin{aligned} \mathfrak{S}_{opt}^{(1)} = & \left(\tilde{C}^{[1](0)} H_{eff\Omega^{(0)}}^{1} C^{[1](0)} \right)_{\mu\mu} \\ & + P^{[1]} \Lambda^{[1](0)} [H^{(1)} \Omega^{(0)} - \Omega^{(0)} H_{eff\Omega^{(0)}}^{1}] P^{[1]} \\ & + P^{[0]} \Lambda^{0} H^{(1)} \Omega^{(0)} P^{[0]} \end{aligned} \quad (4.12)$$

The subscript $\Omega^{(0)}$ indicates that the derivative effective Hamiltonian does not contain any term formed from derivatives of the cluster amplitudes. The first order properties can thus be obtained simply with the knowledge of Ω and Λ amplitudes only. Differentiation of equation 4.9 with respect to Λ amplitudes leads the equations for Ω amplitudes – the Bloch equations.

The Λ are obtained by differentiating equation 4.9 with respect to Ω amplitudes. It may be noticed that the coupling within the Λ amplitudes in various valence sectors is exactly opposite of SEC. Thus, one has to solve for the Λ amplitudes successively from the highest valence sector to the lowest valence sector.

The CVA method is a single-root method. The Λ amplitudes depend on the desired state of the molecule. Therefore, for every state one has to calculate the Λ amplitudes separately. In contrast, the non-variational response of FSMRCC [120, 121] has a multiple-root structure. However, the expensive evaluation of wavefunction derivatives for each mode of perturbation is avoided in CVA-FSMRCC. Also, the single-root feature makes CVA more attractive for the cases like curve-crossing studies of excited states, etc. than the non-variational response method. It can be seen that the Λ equations for one-valence problem are same as the “zeta equations” in the EOMCC method [37, 160, 161].

4.3 CD Approach for CVA-FSMRCCSD

We briefly present the iterative procedure of CD. Following are the steps involved in computing Cholesky vectors:

1. From the ERI matrix, fetch the diagonal elements, $\langle pp|qq \rangle$ (Dirac notation used: $\langle p(1)p(2)|q(1)q(2) \rangle$) and store them in a separate array. Identify the largest element of the array and label it as $\langle p'p'|q'q' \rangle$.
2. Define $D_{p'q',rs}^{(0)} = \langle p'r|q's \rangle$.
3. Compute the first Cholesky vectors: $B_{rs}^{(1)} = D_{p'q',rs}^{(0)} / \text{sqrt} D_{p'q',p'q'}^{(0)}$ for all r, s .
4. Update the residual of the diagonal by subtracting the Cholesky vector obtained in previous iterations: $D_{pq|rs}^{(k)} = D_{pq|rs}^{(k-1)} - B_{pq}^{(k)} B_{rs}^{(k)}$. (The diagonal element is obtained when $rs = pq$). Compute the diagonal elements of next iteration, identify the largest element in the updated diagonal and repeat the Step 3 with $B^{(k)}$ and $D^{(k-1)}$, if the largest element of the diagonal is still larger than the chosen tolerance. If the largest element in the diagonal becomes smaller than the chosen tolerance, the Cholesky decomposition procedure is said to have converged.

While the above CD procedure can in principle be done on ERI's in either AO or MO basis, in the present work, we have implemented the same in MO basis. The required intermediates for CC, FSMRCC and CVA were programmed from the CD vectors. The number of Cholesky vectors equals to the number of CD iterations, which in turn depends on the Cholesky tolerance ($\delta = 10^{-tol}$). If N_{CD} is the number of Cholesky vectors and N_{basis} is the number of basis functions, then in general, N_{CD}/N_{basis} ranges roughly around $0.1 \sim 0.5$ for $\delta = 10^{-1}$; around $2 \sim 2.5$ for $\delta = 10^{-2}$; and around $4 \sim 4.5$ for $\delta = 10^{-3}$. Cholesky vectors, thus have a size $O(N^3)$ as compared to $O(N^4)$ of the ERI's.

Further sorting of the Cholesky vectors into occupied-occupied, occupied-virtual and virtual-virtual may be beneficial in using them in CC/FSMRCC equation. Use of Cholesky vectors instead of ERI's would reduce the scaling of the terms in which the running

indices in the summation belong to single electron. For example, scaling of terms like $\sum_{k,c} \langle ac|ik \rangle t_{kj}^{cb}$ can be reduced by about one order if $\langle ac|ik \rangle$ is expressed as $\sum_{\mu} B_{ia}^{(\mu)} B_{kc}^{(\mu)}$ (We use the orbital notations as $i, j, k \in occ$, $a, b, c \in virt$ and the index μ is the order of the Cholesky vector $\mu = 1, \dots, N_{CD}$). However, in case of the terms such as $\sum_{c,d} \langle ab|cd \rangle t_{ij}^{cd}$, where, the summation is over the indices of two different electrons, expressing the ERI's, $\langle ab|cd \rangle$ as $\sum_{\mu} B_{ac}^{(\mu)} B_{bd}^{(\mu)}$ would not gain in terms of scaling, though there would be reduction in a pre-factor.

Thus, though scaling of many individual terms in the CC/MRCC/CVA equations can be reduced by an order, the overall scaling does not reduce. However, one does not require to write to the disk, the large size ERI's like, for example, $\langle ab|cd \rangle$, as the Cholesky vectors $B_{ac}^{(N_{CD})}$, which build them are smaller in size and can be stored in RAM.

4.4 Results and Discussion

4.4.1 Computational details

The ground state geometries of *OH* and *CH* radicals were optimized at RI-MP2/cc-pVDZ level of theory using Q-CHEM 4.4 [135]. The equilibrium geometries of *BO*, *CCH*, *CN*, *SiN* radicals were obtained from various sources [162, 163].

The single point computations of dipole moment was done using cc-pVTZ basis [164–166]. Locally modified version of Gamess [167] was used for running RHF and fetching the ERI's, dipole integrals, AO-MO coefficients, etc for post-HF computations. The dipole moments are all reported in debyes.

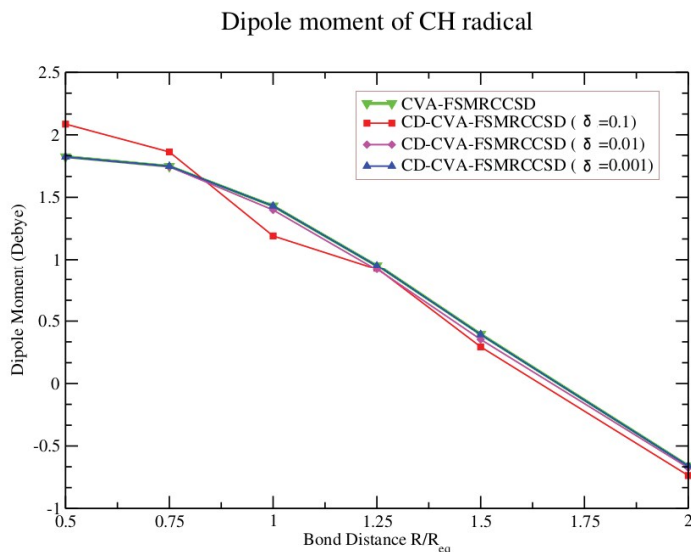


FIGURE 4.1: Plot of Bond distance vs Dipole moment for CH radical

4.4.2 CH radical

The dipole moments of CH radical (for $^2\Pi$ state) at various internuclear distances are presented in Table 4.1 and plotted in Figures 4.1. In this system, we start with RHF of CH^+ cation as vacuum and compute the properties for EA states.

TABLE 4.1: Dipole moment (D) of CH radical

$\mu_{e,z}/D$	Bond Length	CVA-FSMRCCSD	CD-CVA-FSMRCCSD		
			$\delta = 10^{-1}$	$\delta = 10^{-2}$	$\delta = 10^{-3}$
	0.50 R_{eq}	1.82479	2.08577	1.82308	1.82473
	0.75 R_{eq}	1.74824	1.86315	1.74484	1.74839
	R_{eq}	1.43056	1.19074	1.39851	1.43002
	1.25 R_{eq}	0.95107	0.92361	0.91792	0.94948
	1.50 R_{eq}	0.39427	0.29326	0.35273	0.39204
	2.00 R_{eq}	-0.65861	-0.73668	-0.67450	-0.65932

The qualitative trends in dipole moments computed with CD-CVA-FSMRCCSD with $\delta = 10^{-1}, 10^{-2}, 10^{-3}$ are very similar to that of the conventional CVA-FSMRCCSD. The $\delta = 10^{-1}$ gives rather very poor results for dipole moments. For dipole moment, the maximum absolute errors are 0.24 D for $\delta = 10^{-1}$; 0.042 D for $\delta = 10^{-2}$ and 0.017 D for $\delta = 10^{-3}$.



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

One more measure of accuracy is the non-parallelity error (NPE). It is usually used to compare the trends in the potential energy surfaces obtained by an approximate method versus the exact results or those obtained by most accurate method like FCI. However, the definition can be extended to check the trends in any property upon bond stretching. The NPE is defined as the difference between maximum and minimum relative errors in property, relative to the reference value. In this context, the CVA-FSMRCCSD dipole moments of the radical computed at different bond-distances are the reference values. The deviations of CD-CVA-FSMRCCSD relative to these can be calculated and NPE is just the difference between the largest positive error and the largest negative error. (In case if all the errors are positive, smallest positive error is considered in stead of the largest negative one, while if all the errors are negative, the smallest negative error is taken instead of largest positive one). Using this definition, we find that the NPE of CD-CVA-FSMRCCSD relative to CVA-FSMRCCSD in computing the dipole moments of CH radical is 0.36 D for $\delta = 10^{-1}$, 0.04 D for $\delta = 10^{-2}$ and as small as 0.00086 D for $\delta = 10^{-3}$.

4.4.3 OH radical

Table 4.2 presents the dipole moments of OH radical (for $^2\Pi$ state) at various internuclear distances. The results are also plotted in Figures 4.2. For OH radical, we start with RHF of OH^- anion as vacuum and compute the properties for the desired IP states.

TABLE 4.2: Dipole moment (D) of OH radical

	Bond Length	CVA-FSMRCCSD	CD-CVA-FSMRCCSD		
			$\delta = 10^{-1}$	$\delta = 10^{-2}$	$\delta = 10^{-3}$
$\mu_{e,z}/D$	0.50 R_{eq}	1.31120	1.28834	1.31168	1.31103
	0.75 R_{eq}	1.46000	1.46732	1.46254	1.46000
	R_{eq}	1.57438	1.64292	1.57870	1.57392
	1.25 R_{eq}	1.64261	1.78289	1.64866	1.64227
	1.50 R_{eq}	1.71707	2.05485	1.73320	1.71677
	2.00 R_{eq}	2.38482	2.61631	2.39166	2.38496

Like in CH radical, here also we get the qualitative trends of CD-CVA-FSMRCCSD very similar to those of CVA-FSMRCCSD for dipole moments. For dipole moment, the maximum absolute errors are 0.338 D for $\delta = 10^{-1}$; 0.016 D for $\delta = 10^{-2}$ and 0.0005 D

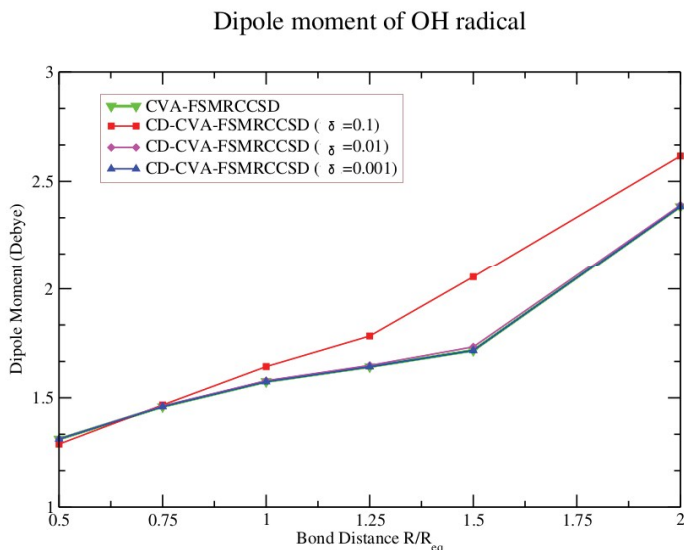


FIGURE 4.2: Plot of Bond distance vs Dipole moment for OH radical

for $\delta = 10^{-3}$. The $\delta = 10^{-1}$ results are very poor as in case of *CH* radical. The NPE of CD-CVA-FSMRCCSD relative to CVA-FSMRCCSD for dipole moments of OH radical also reduces with tighter convergence criterion, as in case of *CH* radical. The NPE is 0.36 D for $\delta = 10^{-1}$, 0.0156 D for $\delta = 10^{-2}$ and as small as 0.00031 D for $\delta = 10^{-3}$.

4.4.4 *BO*, *CCH*, *SiH*, *CN* and *SiN* radicals

Geometry of *BO*, *CCH*, *SiH*, *CN* and *SiN* radicals are shown in Appendix B. The dipole moments of radicals in ground (X^{2+}) state is summarised in the table 4.3.

For *BO*, *CCH* and *SiH*, we start with RHF of the corresponding cations and compute the properties for respective EA states, whereas for *CN* and *SiN*, we start with the RHF of the corresponding anions followed by computation of properties for the respective IP states. The absolute errors in dipole moment of *BO*, *CCH*, *SiH*, *CN* and *SiN* radicals are 0.0013 D, 0.00002 D, 0.0002 D, 0.0001 D and 0.0004 D for $\delta = 10^{-3}$, respectively.

TABLE 4.3: Dipole moment (D) of *BO*, *CCH*, *SiH*, *CN* and *SiN* radicals in ground (X^{2+}) state

Methods	<i>BO</i>	<i>CCH</i>	<i>SiH</i>	<i>CN</i>	<i>SiN</i>
CVA-FSMRCCSD	2.60296	0.94756	0.13593	0.18002	2.67202
CD-CVA-FSMRCCSD					
$\delta = 10^{-1}$	1.99189	-1.34360	0.67423	-0.01023	2.67423
$\delta = 10^{-2}$	2.68707	0.93381	0.10436	0.16708	2.63112
$\delta = 10^{-3}$	2.60430	0.94758	0.13576	0.17995	2.67237

For $\delta = 10^{-2}$, absolute errors in dipole moment are respectively, 0.0841, 0.0137, 0.0316, 0.0129 and 0.0409 D, whereas, for $\delta = 10^{-1}$, they are quite large. The values are 0.6111, 2.2912, 0.5367, 0.1903 and 0.0022 D, respectively. For CD-CVA-FSMRCCSD with $\delta = 10^{-2}$ and 10^{-3} , we see that the percentage absolute errors for these radicals is less than the maximum absolute errors in case of CH and OH radicals.

4.5 Conclusion

In this chapter, we have presented dipole moments of various radicals computed analytically using CD-CVA-FSMRCCSD for IP and EA cases. CD with $\delta = 10^{-3}$ yields very accurate values of dipole moments at equilibrium as well as stretched geometries as illustrated for *CH* and *OH* radicals. The maximum absolute error for dipole moment are 0.03 % and 0.57 % and for polarizability 0.07 % and 0.06 % of *OH* and *CH*, respectively for this tolerance and the number of Cholesky vectors is about 4-4.5 times that of the number of basis functions.

Increasing the tolerance of $\delta = 10^{-2}$ reduces the number of Cholesky vectors to 2-2.5 times that of the number of basis functions with reduction in the accuracy of the computed properties. The resulting maximum absolute errors for dipole moment are 0.94 % and 10.54 % of *OH* and *CH*, respectively. Further increase in the tolerance is strongly discouraged as with $\delta = 10^{-1}$, the dipole moment, no longer remain reliable because of the high maximum absolute errors of 19.67 %, 25.62 % in dipole moment, which is obvious as the number of Cholesky vectors is smaller than even the number of basis functions.

Chapter 5

Cholesky Representation of CVA-FSMRCCSD : Analytical polarizability of doublet radicals

5.1 Introduction

In previous Chapter, we discussed the CD-CVA-FSMRCCSD formulation for computing dipole moments of doublet radicals. In continuation, we present in this chapter, extension of the one-valence CD-CVA-FSMRCC ansatz for computing the second-order analytical properties. Specifically, we test the method for static dipole polarizabilities of doublet radicals. There also have been developments in other CC based formulations [168, 169] for obtaining higher order properties, although not rigorously analytical. Thus, till date, the CVA-FSMRCC is the only known method to have reported analytically computed dipole polarizabilities of doublet radicals, which signifies the relevance of presenting the Cholesky representation of the method.

5.2 Theory

5.3 CVA-FSMRCC method for the second order properties

In continuation with the theory discussed in Chapter 4, we now proceed with the second order of Lagrangian and it resembles with second order energy derivatives. This is obtained by differentiating equation 4.7 twice with respect to g for specific root of the effective Hamiltonian.

$$\begin{aligned}
\mathfrak{S}^{(2)} = & \left(\tilde{C}^{[1](2)} H_{eff}^{[1](0)} C^{[1](0)} \right)_{\mu\mu} + \left(\tilde{C}^{1} H_{eff}^{1} C^{[1](0)} \right)_{\mu\mu} \\
& + 2 \left(\tilde{C}^{1} H_{eff}^{[1](0)} C^{1} \right)_{\mu\mu} + \left(\tilde{C}^{[1](0)} H_{eff}^{[1](2)} C^{[1](0)} \right)_{\mu\mu} \\
& + \left(\tilde{C}^{[1](0)} H_{eff}^{1} C^{1} \right)_{\mu\mu} + \left(\tilde{C}^{[1](0)} H_{eff}^{[1](0)} C^{[1](2)} \right)_{\mu\mu} \\
& + P^{[1]} \Lambda^{[1](2)} [H^{(0)} \Omega^{(0)} - \Omega^{(0)} H_{eff}^{[1](0)}] P^{[1]} \\
& + P^{[1]} \Lambda^{1} [H^{(1)} \Omega^{(0)} + H^{(0)} \Omega^{(1)} - \Omega^{(0)} H_{eff}^{1} - \Omega^{(1)} H_{eff}^{[1](0)}] P^{[1]} \\
& + P^{[1]} \Lambda^{[1](0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} + H^{(0)} \Omega^{(2)}] P^{[1]} \\
& - P^{[1]} \Lambda^{[1](0)} [\Omega^{(0)} H_{eff}^{[1](2)} + \Omega^{(1)} H_{eff}^{1} + \Omega^{(2)} H_{eff}^{[1](0)}] P^{[1]} \\
& + P^{[0]} \Lambda^{[0](2)} [H^{(0)} \Omega^{(0)}] P^{[0]} + P^{[0]} \Lambda^{[0](1)} [H^{(1)} \Omega^{(0)} + H^{(0)} \Omega^{(1)}] P^{[0]} \\
& + P^{[0]} \Lambda^{0} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} + H^{(0)} \Omega^{(2)}] P^{[0]} \\
& - E_{\mu}^{(0)} \sum_{ij} \left(\tilde{C}_{\mu i}^{[1](2)} C_{j\mu}^{[1](0)} + 2 \tilde{C}_{\mu i}^{1} C_{j\mu}^{1} + \tilde{C}_{\mu i}^{[1](0)} C_{j\mu}^{[1](2)} \right) \\
& - E_{\mu}^{(1)} \sum_{ij} \left(\tilde{C}_{\mu i}^{1} C_{j\mu}^{[1](0)} + \tilde{C}_{\mu i}^{[1](0)} C_{j\mu}^{1} \right) \\
& - E_{\mu}^{(2)} \sum_{ij} \left(\tilde{C}_{\mu i}^{[1](0)} C_{j\mu}^{[1](0)} - 1 \right)
\end{aligned} \tag{5.1}$$

Following Shamasundar *et. al.* [127], some terms in Eq. (5.1) mutually cancel whereas several others vanish because of $(2n+1)$ and $(2n+2)$ rules [170]. If there is no operator

form for H^2 , then equation 5.1 reduces after eliminating the vanishing terms to the following.

$$\begin{aligned}
\mathfrak{S}_{opt}^{(2)} = & \left(\tilde{C}^{[1](0)} H_{eff}^{[1](2)} \Omega^{(1)} C^{[1](0)} \right)_{\mu\mu} \\
& + P^{[1]} \Lambda^{[1](0)} [H^{(2)} \Omega^{(0)} + H^{(1)} \Omega^{(1)} - (\Omega^{(0)} H_{eff}^{[1](2)})_{\Omega^{(1)}}] P^{[1]} \\
& + P^{[0]} \Lambda^{0} [H^{(1)} \Omega^{(1)} + H^{(0)} \Omega_{\Omega^{(1)}}^{(2)}] P^{[0]} \\
& + 2 \left(\sum_{ij} \tilde{C}_{\mu i}^{1} H_{eff}^{[1](0)} C_{j\mu}^{1} - E_{\mu}^{(0)} \sum_i \tilde{C}_{\mu i}^{1} C_{i\mu}^{1} \right) \quad (5.2)
\end{aligned}$$

The subscripts $\Omega^{(0)}$ and $\Omega^{(1)}$ indicate that the corresponding terms are formed using up to zeroth and first derivatives of the cluster amplitudes respectively. The second-order properties can thus be obtained only with the knowledge of cluster amplitudes, eigenvectors and their first derivatives with respect to the field and an additional set of perturbation independent vectors, i.e. the Λ -vectors.

Due to the single-root nature of the CVA method, one has to obtain the Λ amplitudes separately for every state unlike the non-variational response of FSMRCC [120, 121], which has a multiple-root structure. However, the expensive evaluation of wavefunction derivatives for each mode of perturbation is avoided in CVA-FSMRCC. This feature becomes more prominent while obtaining higher-order properties like polarizability. Also, the single-root feature makes CVA more attractive for cases like curve-crossing studies of excited states, etc. than the non-variational response method. maybe noted that for a one-valence problem, FSMRCC method is equivalent to EOM-CC [37, 161]. However, developments in the higher-order linear response of EOM-CC have yet not been reported.

The computational approaches used for obtaining first-order energy derivatives are transparently extended in case of second-order derivatives. An additional step of evaluation of $T^{[0]}$ derivative amplitudes and storage of the resulting intermediates with Hamiltonian gets introduced this case.

5.4 Results and Discussion

5.4.1 Computational details

Computational details have already discussed in chapter 4. The single point computations of polarizabilities was done using cc-pVTZ basis set [164, 165]. Locally modified version of Gamess [167] was used for running RHF and fetching the ERI's, dipole integrals, AO-MO coefficients, etc for post-HF computations. The polarizabilities are all reported in atomic units.

5.4.2 CH radical

The polarizabilities of CH radical (for $^2\Pi$ state) at various internuclear distances are presented in Table 5.1 and plotted in Figures 5.1. In this system, we start with RHF of CH^+ cation as vacuum and compute the properties for EA states.

TABLE 5.1: Polarizability (a.u.) of CH radical

	Bond Length	CVA-FSMRCCSD			CD-CVA-FSMRCCSD		
			$\delta = 10^{-1}$	$\delta = 10^{-2}$	$\delta = 10^{-3}$		
$\alpha_{zz}/a.u.$	0.50 R_{eq}	8.1947	9.8857	8.2504	8.1965		
	0.75 R_{eq}	10.8539	13.6062	10.8949	10.8569		
	R_{eq}	15.2544	19.2323	15.4352	15.2577		
	1.25 R_{eq}	21.0149	24.8827	21.0539	21.0242		
	1.50 R_{eq}	26.5392	29.1065	26.6478	26.5430		
	2.00 R_{eq}	28.2290	25.3607	27.8555	28.2121		

The NPE of CD-CVA-FSMRCCSD for polarizabilities of CH radicals, with CVA-FSMRCCSD results as reference for $\delta = 10^{-1}$, 10^{-2} and 10^{-3} , are, respectively, 6.84, 0.55 and 0.026 a.u.

The qualitative trends in polarizabilities computed with CD-CVA-FSMRCCSD with $\delta = 10^{-1}, 10^{-2}, 10^{-3}$ are very similar to that of the conventional CVA-FSMRCCSD. The $\delta = 10^{-1}$ gives rather very poor results for polarizabilities. For polarizability, the maximum absolute errors are 3.978 a.u. for $\delta = 10^{-1}$; 0.374 a.u. for $\delta = 10^{-2}$ and 0.017 a.u. for $\delta = 10^{-3}$.

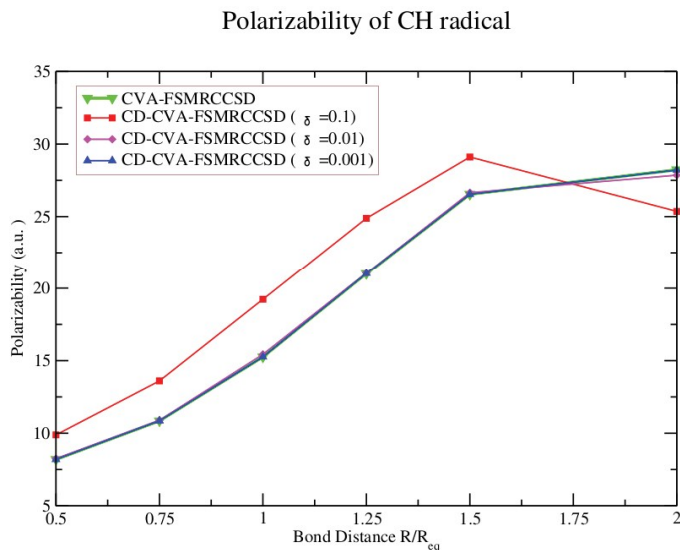


FIGURE 5.1: Plot of Bond distance vs Polarizability for CH radical

5.4.3 OH radical

Table 5.2 presents the polarizabilities of OH radical (for ${}^2\Pi$ state) at various internuclear distances. The results are also plotted in Figure 5.2. For OH radical, we start with RHF of OH^- anion as vacuum and compute the properties for the desired IP states.

TABLE 5.2: Polarizability (a.u.) of OH radical

	Bond Length	CVA-FSMRCCSD	CD-CVA-FSMRCCSD		
			$\delta = 10^{-1}$	$\delta = 10^{-2}$	$\delta = 10^{-3}$
$\alpha_{zz}/ a.u.$	$0.50 R_{eq}$	4.9504	5.0296	4.9645	4.9505
	$0.75 R_{eq}$	7.1111	7.0986	7.1138	7.1109
	R_{eq}	10.5565	10.8232	10.5866	10.5583
	$1.25 R_{eq}$	15.0253	15.4825	15.0400	15.0276
	$1.50 R_{eq}$	18.9673	20.1744	18.9557	18.9687
	$2.00 R_{eq}$	20.6540	18.9675	20.2901	20.6393

Like in CH radical, here also we get the qualitative trends of CD-CVA-FSMRCCSD very similar to those of CVA-FSMRCCSD for polarizabilities. For polarizability, the maximum absolute errors are 1.687 a.u. for $\delta = 10^{-1}$; 0.364 a.u. for $\delta = 10^{-2}$ and 0.015 a.u. for $\delta = 10^{-3}$. The NPE of CD-CVA-FSMRCCSD for OH radical polarizabilities relative to the CVA-FSMRCCSD method as reference are, respectively, 2.89, 0.39 and 0.017 a.u., for $\delta = 10^{-1}$, 10^{-2} and 10^{-3} .

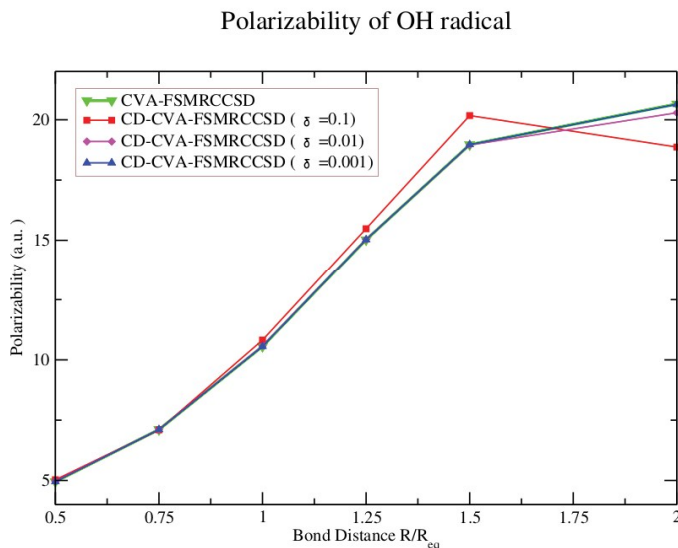


FIGURE 5.2: Plot of Bond distance vs Polarizability for OH radical

5.4.4 BO, CCH, SiH, CN and SiN radicals

Geometry of *BO*, *CCH*, *SiH*, *CN* and *SiN* radicals are shown in Appendix. The polarizabilities of radicals in ground (X^{2+}) state is summarised in the table 5.3. For *BO*, *CCH* and *SiH*, we start with RHF of the corresponding cations and compute the properties for respective EA states, whereas for *CN* and *SiN*, we start with the RHF of the corresponding anions followed by computation of properties for the respective IP states. The maximum absolute errors for $\delta = 10^3$ for these radicals are respectively, 0.003, 0.008, 0.0237, 0.010 and 0.050 a.u., respectively.

TABLE 5.3: Polarizability (a.u.) ($\alpha_{zz}/a.u.$) of *BO*, *CCH*, *SiH*, *CN* and *SiN* radicals in ground (X^{2+}) state

Methods	<i>BO</i>	<i>CCH</i>	<i>SiH</i>	<i>CN</i>	<i>SiN</i>
CVA-FSMRCCSD	19.1957	23.5350	37.9561	20.3795	49.4426
CD-CVA-FSMRCCSD					
$\delta = 10^{-1}$	20.8522	-44.1379	49.0389	22.6224	62.8690
$\delta = 10^{-2}$	19.2311	23.6568	38.0453	20.5629	50.4191
$\delta = 10^{-3}$	19.1931	23.5425	37.9798	20.3893	49.4929

For $\delta = 10^{-2}$, the errors increase to 0.0355, 0.1218, 0.0892, 0.1834 and 0.9765 a.u. respectively, whereas for $\delta = 10^{-1}$, some jobs failed to converge in CCH, SiH and SiN radicals. The error for BO and CN are 1.6566 and 2.2429 a.u., respectively for CD $\delta = 10^{-1}$. For CD-CVA-FSMRCCSD with $\delta = 10^{-2}$ and 10^{-3} , we see that the percentage absolute errors for these radicals is less than the maximum absolute errors in case of CH and OH radicals.

5.5 Conclusion

In this chapter, we have presented dipole polarizabilities [71] of various radicals computed analytically using CD-CVA-FSMRCCSD for IP and EA cases. CD with $\delta = 10^{-3}$ yields very accurate values of polarizabilities at equilibrium as well as stretched geometries as illustrated for *CH* and *OH* radicals. The maximum absolute error for polarizability 0.07 % and 0.06 % of *OH* and *CH*, respectively for this tolerance and the number of Cholesky vectors is about 4-4.5 times that of the number of basis functions.

Increasing the tolerance of $\delta = 10^{-2}$ reduces the number of Cholesky vectors to 2-2.5 times that of the number of basis functions with reduction in the accuracy of the computed properties. The resulting maximum absolute errors for polarizability 1.76 % and 1.32 % of *OH* and *CH*, respectively. Further increase in the tolerance is strongly discouraged as with $\delta = 10^{-1}$, the polarizability no longer remain reliable because of the high maximum absolute errors of 8.17 %, 26.08 % in polarizability of *OH* and *CH*, which is obvious as the number of Cholesky vectors is smaller than even the number of basis functions.

Chapter 6

Conclusion

6.1 General Conclusions

In the present thesis, we studied the effect of employing density fitting techniques such as RI and CD on accuracy and computational cost in computing energies and properties of molecules in near-degenerate electronic states.

For energies, we started with the EOM-MP2 method and incorporated the RI and CD representations of the method in a locally modified developmental version of Q-Chem. Speaking qualitatively, we find that both RI and CD implementations give good speed up without much compromise on accuracy. However, quantitative analysis of the results give better insight. The since, EOM-MP2 eliminates the iterative CC procedure and approximates the CC vectors by their MP2 guess values, the speed-ups in RI and CD would arise majorly due to reduction in the prefactor in computation of EOM equations and in the I/O requirements. This in turn, depends the number and types of intermediates required in the original EOM-MP2 method. EOM-IP-MP2 does not have costly intermediates in its expressions and thereby, has less scope for speed-up upon RI/CD implementation as expected. In case of EA, the speed-up gained relative to EOM-MP2 is significant

because the RI/CD reduce the cost of computing four-particle and three-particle-one-hole intermediates by density fitting. The speed-up gained in EE and SF is also due to reduction in computation of such terms. However, in these, all kinds of intermediates are used and effect of RI/CD will be less significant on the computational cheaper terms such as two-particle-two-hole, one-particle-three-hole and four-hole intermediates. If we compare the timings with that of EOM-CCSD, then all the methods will show tremendous speed up. But, the credit goes to EOM-MP2 level.

As far as accuracy is concerned, CD with $\delta = 10^{-4}$ gives the results almost as accurate as the conventional variant. However, this requires the rank of the CD vectors to be about about 6 \sim 7 times larger than the number of basis functions and is thus, highly discouraged as would hardly save any computational cost. The accuracy of CD with $\delta = 10^{-3}$ results in accuracy comparable with that of RI and the rank of the Cholesky tensors is about 4 \sim 4.5 times the number of basis functions. The standard deviation and maximum of this method are also comparable with those of RI. The $\delta = 10^{-2}$ gives only semiquantitative accuracy in the results, with the rank of the tensors only about 2 \sim 2.5 times the number of basis functions. In general, the errors introduced due to RI and CD of given rank are most prominent in computation of the total energies. The errors are much less significant in case of gaps between reference-target states and target-target states. Thus, the least accurate approximation like CD-EOM-MP2 with $\delta = 10^{-2}$ may perform well in case of weakly near-degenerate systems of relatively larger computational size and will definitely give qualitatively more correct description than the less accurate alternatives like TD-DFT and popular methods. Thus, for given set of atoms, basis functions and method, if a preoptimized auxiliary basis is already available, it is beneficial to go for RI for better accuracy with less cost. However, this may not be the situation for many cases and CD turns out to be a convenient tool. Moreover, with advances in parallel computing facilities, CD can be better explored for more speed-ups up on parallelization. While the EE, SF, IP and EA variants of EOM-MP2 differ quantitatively for RI and CD timings and accuracy, the qualitative trends are very similar for all the variants, as discussed in detail in Chapters 2 and 3. In general, from the accuracy point of view, the RI/CD-EOM-MP2 are most suited for target-target and reference-target energy gaps rather than total energies.

Motivated with the accuracy of CD in computing difference energies in EE, SF, IP and EA variants of EOM-MP2, we studied the applicability of CD for computing response properties of molecules. We, therefore, implemented CD on CVA-FSMRCCSD codes for computing analytical first and second order energy derivatives. Specifically, we have done the CD implementation on IP and EA variants of CVA-FSMRCCSD. In the FSMRCC context, these correspond to the model spaces of $(0, 1)$ and $(1, 0)$ FS sectors. The required ERI's and MO coefficients were fetched from a locally modified version of Gamess. We computed analytical dipole moments and analytical static dipole polarizabilities of doublet radicals using CD-CVA-FSMRCCSD and compared its accuracy relative to the conventional CVA-FSMRCCSD method. We studied the accuracy of the method for CD tolerance set as 10^{-1} , 10^{-2} and 10^{-3} , respectively. The comparative study of CD-CVA-FSMRCCSD timings versus the conventional CVA-FSMRCCSD ones could not be done because our stand alone codes yet need to be cleaned up further and optimized more for a rigorous study of computational time, although we do agree that the research in that direction could be equally interesting. As per the discussions in the Chapters 4 and 5, as far as accuracy is concerned, CD is found to perform much better for properties than for energies. As seen for bond-stretching of OH and CH radicals, tightening of CD threshold not only reduces the maximum absolute error in dipole moments, but also reduces the NPE. The trend is also observed in computation of polarizabilities of the radicals, though the percentage absolute errors are slightly more for polarizabilities than for the dipole moments.

6.2 Future Scope of the Research Work

The outcomes in the thesis presented here open up interesting avenues for further work. As discussed in the thesis, the RI/CD approximations scale down only the 'coulomb'-type terms. There have been attempts of approximations that scale down the 'exchange' type terms. While these approaches have been studied for EOM-CCSD, extension of the methods to EOM-MP2 and also for FSMRCCSD, CVA-FSMRCCSD, etc might be interesting as that may actually result in reduction of overall scaling of the methods. Since RI/CD reduces cost of a few terms, it would be interesting to extend this technique for three-body and

higher-body approximations of EOM-CC and MRCC for which conventional ansatz may be computationally challenging. As discussed above, the percentage errors in computing polarizability are in general, greater than those in computing dipole moments. One of the important factors for this is probably the neglect of the orbital relaxation due to external field. The orbital relaxation may be less prominent for first order properties like dipole moment, but may be very crucial for higher order properties. Inclusion of orbital relaxation will also enable for computational extensions of CVA-FSMRCCSD as well as its CD representation to computing higher order properties like hyperpolarizabilities of doublet radicals. The extension of the method to computing magnetic properties would also be challenging and interesting.

Appendix A

The Geometries

All the geometries and their energies reported here are in atomic units.

Water Cluster Geometries

EOM calculations done using cc-pVDZ basis

TABLE A.1: Water Monomer

I	Atom	X	Y	Z
1	O	0.0000000000	0.0000000000	0.1173000000
2	H	-0.7572000000	-0.0000000000	-0.4692000000
3	H	0.7572000000	0.0000000000	-0.4692000000

Standard Nuclear Orientation (Angstroms)

Nuclear Repulsion Energy = 9.1895337609 hartrees

SCF energy = -76.04139352 hartrees

MP2 energy = -76.26327320 hartrees

CCSD total energy = -76.27078698 hartrees

TABLE A.2: Water Dimer

I	Atom	X	Y	Z
1	O	-1.5127378002	-0.0030990744	0.1219878960
2	H	-1.9127237990	0.0190629754	-0.7508981287
3	H	-0.5593548001	0.0021948755	-0.0491951049
4	O	1.3851232002	0.0024320693	-0.1105280959
5	H	1.7458122999	-0.7687614223	0.3376216986
6	H	1.7471830988	0.7528396120	0.3707931343

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 9.1895337609 \text{ hartrees}$$

$$\text{SCF energy} = -152.08814379 \text{ hartrees}$$

$$\text{MP2 energy} = -152.53522842 \text{ hartrees}$$

$$\text{CCSD total energy} = -152.54978468 \text{ hartrees}$$

TABLE A.3: Water Trimer

I	Atom	X	Y	Z
1	O	1.5064100480	0.5852050713	-0.0835157175
2	H	0.6557334483	1.0629780145	-0.0182207968
3	H	2.0826464679	1.0015697829	0.5687483407
4	O	-0.2398302617	-1.5962040985	0.1105871003
5	H	-0.1819953913	-2.2414240223	-0.6049168981
6	H	0.5877771003	-1.0778180704	0.0511711834
7	O	-1.2655614706	1.0035656289	-0.0939039827
8	H	-1.9269358822	1.2849068035	0.5497759551
9	H	-1.2253722685	0.0292546783	-0.0118969848

Standard Nuclear Orientation (Angstroms)

$$\begin{aligned}\text{Nuclear Repulsion Energy} &= 84.1987027522 \text{ hartrees} \\ \text{SCF energy} &= -228.13936341 \text{ hartrees} \\ \text{MP2 energy} &= -228.81654929 \text{ hartrees} \\ \text{CCSD total energy} &= -228.83726058 \text{ hartrees}\end{aligned}$$



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

TABLE A.4: Water Tetramer

I	Atom	X	Y	Z
1	O	-1.3157308351	-1.4161516574	0.0050817484
2	O	-1.4161515285	1.3157314018	-0.0050816943
3	O	1.4161518610	-1.3157210413	-0.0050812342
4	O	1.3157318975	1.4161421722	0.0050811801
5	H	-1.8140914037	-1.7648730409	-0.7424384043
6	H	-1.4886721748	-0.4444937900	0.0141405947
7	H	-0.4444919534	1.4886632856	-0.0141378834
8	H	-1.7648795068	1.8140924682	0.7424350500
9	H	1.7648749236	-1.8140801924	0.7424390803
10	H	0.4444946235	-1.4886659128	-0.0141402165
11	H	1.4886602532	0.4444819705	0.0141375052
12	H	1.8140940802	1.7648682086	-0.7424357259

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 141.5569434397 \text{ hartrees}$$

$$\text{SCF energy} = -304.19258133 \text{ hartrees}$$

$$\text{MP2 energy} = -305.09986783 \text{ hartrees}$$

$$\text{CCSD total energy} = -305.12641164 \text{ hartrees}$$

TABLE A.5: Water Pentamer

I	Atom	X	Y	Z
1	O	0.9198030436	-2.1016120414	0.2720645367
2	O	-1.7101331834	-1.5570647807	-0.0999184599
3	O	-2.0111428154	1.1377564846	-0.0135995403
4	O	2.2990037191	0.2146836655	-0.0433103755
5	O	0.4733580845	2.2302535239	0.1000913760
6	H	1.4548979752	-1.2779399127	0.1575594961
7	H	1.5419560055	-1.9083078184	-0.4379025714
8	H	2.8138905148	0.3100125742	-0.8520245979
9	H	1.6860633288	0.9890293134	-0.0204469389
10	H	0.4716895440	3.0143825901	-0.4592529672
11	H	-0.4465492958	1.8694519145	0.0625017844
12	H	-2.5995857781	1.3072951261	0.7305816145
13	H	-1.9410936194	0.1531262940	-0.0732756847
14	H	-1.9856247318	-2.0510381155	-0.8798085361
15	H	-0.7627547315	-1.7981467811	0.0494481059

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 204.5036659804 \text{ hartrees}$$

$$\text{SCF energy} = -380.15731741 \text{ hartrees}$$

$$\text{MP2 energy} = -381.29743420 \text{ hartrees}$$

$$\text{CCSD total energy} = -381.32894483 \text{ hartrees}$$

TABLE A.6: Water Hexamer

I	Atom	X	Y	Z
1	H	0.2445335213	-1.4295970476	-1.1756170484
2	O	-0.7244706404	-1.5915708055	-1.1667922867
3	H	-1.0962631451	-0.8247509940	-1.6285654237
4	H	2.7170423023	-1.3903700358	-0.9102880647
5	O	1.9240597518	-0.8483503324	-0.8184536722
6	H	1.8372931849	-0.6542682504	0.1500529144
7	H	-2.0429791666	-1.3859967435	1.7885503298
8	O	-1.4610774414	-0.7958022540	1.2939457841
9	H	-1.2324148726	-1.2751909326	0.4556290991
10	H	0.3953517498	-0.2619634294	1.7975030275
11	O	1.3069562228	0.0514146460	1.6572831047
12	H	1.1780670170	0.9168273933	1.2165049752
13	H	1.3803183959	1.4242669011	-0.9331902743
14	O	0.9185523519	2.0277668819	-0.3309642172
15	H	-0.0256575214	1.8719966869	-0.5245400461
16	H	-2.5511601752	1.8509670613	-0.5960671088
17	O	-1.8239780232	1.2163476193	-0.6147015289
18	H	-1.9244690619	0.6796333490	0.1974901499

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 301.9290937526 \text{ hartrees}$$

$$\text{SCF energy} = -456.29069694 \text{ hartrees}$$

$$\text{MP2 energy} = -457.65699383 \text{ hartrees}$$

$$\text{CCSD total energy} = -457.69664868 \text{ hartrees}$$

TABLE A.7: Water Heptamer

I	Atom	X	Y	Y
1	O	2.8265799600	-0.5859861722	0.2569373345
2	H	3.7388439505	-0.3889787926	0.0130555959
3	H	2.3087349612	-0.5205051813	-0.5817225861
4	O	-0.2241412570	2.0746308304	-0.7590273778
5	H	-0.3787543260	2.9621232407	-1.1046672674
6	H	-1.1196812274	1.6683906108	-0.6501768892
7	O	-1.0864440321	-0.7433353608	1.7401691092
8	H	-1.2605320234	-1.0250895013	2.6462507588
9	H	-0.2872240918	-0.1411913513	1.7881028607
10	O	0.9532888191	0.9339889681	1.6138172130
11	H	1.7305388593	0.4609984978	1.2429026338
12	H	0.6736367805	1.5240168487	0.8894469531
13	O	-2.4746091385	0.6200850714	-0.3097662017
14	H	-2.2190491099	0.2246490307	0.5472463083
15	H	-2.4303290682	-0.1450081882	-0.9046151622
16	O	1.0636229529	-0.2969917597	-1.8057333176
17	H	0.3514180122	-0.9158011395	-1.5528360890
18	H	0.6759818832	0.5808559904	-1.6336642276
19	O	-1.0389409095	-1.9535482592	-0.7473164015
20	H	-0.9814879306	-1.7630484498	0.2135708387
21	H	-0.9569478299	-2.9121581592	-0.8255365921

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 394.5486847962 \text{ hartrees}$$

$$\text{SCF energy} = -532.34533919 \text{ hartrees}$$

$$\text{MP2 energy} = -533.94210320 \text{ hartrees}$$

$$\text{CCSD total energy} = -533.98760671 \text{ hartrees}$$

DNA bases: Geometries and energies

TABLE A.8: Adenine Bases

I	Atom	X	Y	Z
1	C	-0.7095750307	-0.7732187297	0.0000000000
2	N	-2.0742348209	-0.5867034910	0.0000000000
3	C	-2.2879564922	0.7763530787	0.0000000000
4	N	-1.1811502729	1.4731108498	0.0000000000
5	C	-0.1787391419	0.5182944908	0.0000000000
6	N	-0.0215873595	-1.9184432090	-0.0000000000
7	C	1.2938327702	-1.6990140577	-0.0000000000
8	N	1.9447531891	-0.5260724171	-0.0000000000
9	C	1.2275836680	0.6087890422	-0.0000000000
10	N	1.8770717768	1.7950705728	-0.0000000000
11	H	-3.2847450326	1.1922233278	0.0000000000
12	H	1.3613016360	2.6584977023	-0.0000000000
13	H	2.8832905568	1.8019800038	-0.0000000000
14	H	1.9255729511	-2.5821972071	-0.0000000000
15	H	-2.7702623401	-1.3164629117	0.0000000000

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 502.6117247443 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvdz}$$

$$\text{SCF energy} = -464.58737353 \text{ hartrees}$$

$$\text{MP2 energy} = -466.12422322 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvtz}$$

$$\text{SCF energy} = -464.68546833 \text{ hartrees}$$

$$\text{MP2 energy} = -466.66533610 \text{ hartrees}$$

(A.1)

TABLE A.9: Cytosine Bases

I	Atom	X	Y	Z
1	C	1.1302982383	0.2519350032	0.0000000000
2	N	0.0813527373	1.0486913118	0.0000000000
3	C	-1.1858509321	0.5305606802	0.0000000000
4	N	-1.2815694802	-0.8942320599	-0.0000000000
5	C	-0.2021106792	-1.7119611885	-0.0000000000
6	C	1.0478793902	-1.1857630369	-0.0000000000
7	O	-2.2157233229	1.1772192088	0.0000000000
8	N	2.3536047475	0.8418798948	0.0000000000
9	H	3.2045370882	0.3083660659	0.0000000000
10	H	2.3965493562	1.8483693248	0.0000000000
11	H	1.9255160310	-1.8159719058	-0.0000000000
12	H	-0.3942371678	-2.7780940888	-0.0000000000
13	H	-2.2215908597	-1.2634258412	-0.0000000000

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 356.1709957013 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvdz}$$

$$\text{SCF energy} = -392.67756693 \text{ hartrees}$$

$$\text{MP2 energy} = -393.93331980 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvtz}$$

$$\text{SCF energy} = -392.76555579 \text{ hartrees}$$

$$\text{MP2 energy} = -394.38546489 \text{ hartrees}$$

(A.2)

TABLE A.10: Guanine Bases

I	Atom	X	Y	Z
1	O	-0.0659082384	-2.6635640236	-0.0000000000
2	H	-2.2339158799	-1.4842007097	0.0000000000
3	C	-0.1816174968	-1.4459313882	0.0000000000
4	N	-1.4611867005	-0.8307205604	0.0000000000
5	H	-3.7691740023	0.2835169445	0.0000000000
6	C	0.8200505341	-0.4347618437	-0.0000000000
7	N	2.1974739889	-0.5102510995	-0.0000000000
8	C	-1.6924935686	0.5322740727	0.0000000000
9	N	-2.9989636137	0.9275596130	0.0000000000
10	C	0.5167127513	0.9265740431	-0.0000000000
11	H	-3.1817150754	1.9168854621	0.0000000000
12	N	-0.7490287747	1.4319702136	0.0000000000
13	C	2.6445401684	0.7775386509	-0.0000000000
14	H	3.6985592242	1.0141703880	-0.0000000000
15	N	1.6720687776	1.6671067997	-0.0000000000
16	H	2.7478115680	-1.3556758702	-0.0000000000

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 595.2592440969 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvdz}$$

$$\text{SCF energy} = -539.47462058 \text{ hartrees}$$

$$\text{MP2 energy} = -541.20753640 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvtz}$$

$$\text{SCF energy} = -539.59144927 \text{ hartrees}$$

$$\text{MP2 energy} = -541.82412019 \text{ hartrees}$$

(A.3)

TABLE A.11: Thyamine Bases

I	Atom	X	Y	Z
1	C	-0.6723048800	-0.8987539486	0.0000000000
2	C	-1.1561447379	0.4870077421	-0.0000000000
3	C	-0.2413790065	1.4787343208	-0.0000000000
4	N	1.1182551132	1.2417212288	-0.0000000000
5	C	1.6811108613	-0.0262914120	0.0000000000
6	N	0.7281117399	-1.0311223806	0.0000000000
7	C	-2.6381666576	0.7185294443	-0.0000000000
8	O	2.8783603010	-0.2238232538	0.0000000000
9	O	-1.3822353414	-1.8872278675	0.0000000000
10	H	-3.1033195483	0.2602835250	0.8768310000
11	H	-3.1033195483	0.2602835250	-0.8768310000
12	H	-2.8685201660	1.7857491947	-0.0000000000
13	H	-0.5229422149	2.5248131912	-0.0000000000
14	H	1.7775364443	2.0052412079	-0.0000000000
15	H	1.0883039085	-1.9775104911	0.0000000000

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 438.8181253833 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvdz}$$

$$\text{SCF energy} = -451.57286797 \text{ hartrees}$$

$$\text{MP2 energy} = -452.99902890 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvtz}$$

$$\text{SCF energy} = -451.67611316 \text{ hartrees}$$

$$\text{MP2 energy} = -453.51695208 \text{ hartrees}$$

(A.4)

TABLE A.12: Uracil Bases

I	Atom	X	Y	Z
1	N	1.1731449921	0.9873449768	-0.0000000000
2	C	0.0016184038	1.7073256197	-0.0000000000
3	H	0.1185297664	2.7838522294	-0.0000000000
4	C	-1.2043114477	1.1064575126	-0.0000000000
5	H	-2.1235595863	1.6719869448	-0.0000000000
6	C	-1.2905475412	-0.3490012972	-0.0000000000
7	O	-2.3126825128	-1.0064481147	-0.0000000000
8	N	-0.0318083527	-0.9887855803	0.0000000000
9	H	-0.0432756652	-2.0015364902	0.0000000000
10	C	1.2224746287	-0.4048949133	0.0000000000
11	O	2.2643008072	-1.0250807858	0.0000000000
12	H	2.0705983932	1.4486912146	-0.0000000000

Standard Nuclear Orientation (Angstroms)

$$\text{Nuclear Repulsion Energy} = 356.2534815774 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvdz}$$

$$\text{SCF energy} = -76.04139352 \text{ hartrees}$$

$$\text{MP2 energy} = -413.82428239 \text{ hartrees}$$

$$\text{Basis set} : \text{aug} - \text{cc} - \text{pvtz}$$

$$\text{SCF energy} = -412.62444245 \text{ hartrees}$$

$$\text{MP2 energy} = -414.26494971 \text{ hartrees}$$

(A.5)

Appendix B

List of publications

Thesis work

1. **Analytical dipole moments and dipole polarizabilities of doublet radicals using Cholesky representation of constrained variational linear response to Fock-space multi-reference coupled-cluster method with single and double substitutions**

D Kumar, PU Manohar

Chemical Physics Letters 730 , 234-238 [2019]

2. **Resolution of the Identity and Cholesky Representation of EOM-MP2 Approximation: Implementation, Accuracy and Efficiency**

D Kumar, AK Dutta, PU Manohar

Journal of Chemical Sciences 129 (10), 1611-1626 [2017]

Collaboration work

1. **Functionalized pyranopyrazole molecules as corrosion inhibitors for mild copper metal in HCl solution: synthesis, theoretical studies, and physical investigations**

A Sharma, **D Kumar**, PU Manohar, S Pande, A Dalvi, P Shukla

Materials Research Express 5 (2), 025101 [2018]

2. **A study of water quality index for the assessment of suitability of water for drinking in rural & urban areas of Mathura Distt. of U.P.**

A Kumar, **D Kumar** and GS Chahar

International Journal of Applied Research 2 (7), 377-379 [2016]

Appendix C

List of presentations

1. **Theoretical Chemistry Symposium (TCS - 2019)**

BITS Pilani, India. Feb. 14 - 16, 2019

“Analytical Dipole Moments and Dipole Polarizabilities of Doublet radicals using Cholesky Representation of Constrained Variational response to Fock-space Multi-reference Coupled Cluster method with Single and Double substitutions”

2. **Asia-Pacific Conference of Theoretical and Computational Chemistry (APCTCC 8)**

IIT Bombay, India. Dec. 15 - 17, 2017

“Keto-enol tautomerism ground and excited-state energy profiles A computational study”

3. **International Conference on Nano- and Functional Materials: Interface between Science & Engineering (NFM - 2017)**

BITS Pilani, India. Nov. 16 - 19, 2017



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

“Resolution-of-identity and Cholesky representations of equation-of-motion coupled-cluster methods with MP2 approximation for water cluster molecule”

4. **North West Meeting On Spectroscopy, Structure & Dynamics (SSD)**

BITS Pilani, India. Mar. 18 - 19, 2017

“RI/CD Scheme For MP2 Approximation”

5. **Theoretical Chemistry Symposium (TCS - 2016)**

University of Hyderabad, India. Dec. 14 - 17, 2016

“Resolution of the Identity and Cholesky Representation of EOM-MP2 Approximation”

6. **National Conference on Organic Chemistry in Sustainable Development: Recent Advances and Future Challenges (OCSD - 2016)**

BITS Pilani, India. Aug. 29 - 30, 2016

“Functionalized Pyranopyrazole Molecules as Corrosion Inhibitors for Mild Copper Metal in HCl Solution: Synthesis, Theoretical Studies, and Physical Investigations”

7. **International Conference on Nascent Developments in Chemical Sciences (NDCS - 2015)**

BITS Pilani, India. Oct. 16 - 18, 2015

“Fock-space multi-reference coupled-cluster with single double substitution: IP and EA code development”

8. **The 14th Theoretical Chemistry Symposium (TCS - 2014)**

CSIR - National Chemical Laboratory, Pune & IISER Pune, India. Dec. 14 - 17, 2016

“Some cost-effective intermediate variants of coupled-cluster based methods for open-shell states of molecules”

Appendix D

List of workshops and courses

List of workshops

1. **Q - Chem User Workshop**

Birla Institute of Science & Technology, Pilani, India. Oct. 19, 2015

2. **National Workshop on LaTeX & MATLAB for Beginners**

Birla Institute of Science & Technology, Pilani, India. Dec. 24 - 28, 2014

3. **Q - Chem User Workshop**

IISER PUNE & CSIR-NCL Pune, India. Dec. 21, 2014

4. **Workshop on Chemo-Informatics**

RASA Life Science Informatics Ltd., Pune & Alard College of Pharmacy, Pune,
India. Mar. 18 - 19, 2012

5. 2nd National Workshop on Chemo-Informatics

Biotechnology & Bioinformatics, Christ College, Rajkot, Gujrat, India. Jan. 7 - 8, 2011

List of courses**1. Computational Electronic Structure Methods For Atomic and Molecular and Solid State Systems**

IIT Bhubaneswar July 07 - 18, 2016

GIAN Scheme Under MHRD, Govt. of India

2. Web Development

BITS Pilani. Aug. - Dec., 2016

Software Development & Educational Technology Unit

Appendix E

List of meetings

1. **A.C.S. Meeting - 2017**

The Westin Mumbai Garden City, Mumbai, India. Dec. 14 - 15, 2017

American Chemical Society Industry Symposium

2. **North West Meeting - 2017**

BITS Pilani, India. Mar. 18 - 19, 2017

North West Meeting on Spectroscopy, Structure and Dynamics

Appendix F

Brief biography of the candidate

Dinesh Kumar was born in Harduaganj, Aligarh (Aka. Hari-garh), Uttar Pradesh, India. He completed his B.Sc.(Hons.) and Master's degree (Organic Chemistry) from Aligarh Muslim University, Aligarh in 2010 and 2012, respectively. In January 2013, he was awarded DST-JRF by DST, Govt. of India and joined the Department of Chemistry, BITS Pilani for Ph.D under the guidance of Dr. Prashant Uday Manohar. In January 2015, he was awarded DST-SRF by DST, Govt. of India. In 2016, he has selected in "Computational Electronic Structure Methods For Atomic and Molecular and Solid State Systems" course by GIAN Scheme Under MHRD, Govt. of India, IIT Bhubaneswar. He has published four research articles in peer reviewed journals and few others are under manuscript preparation. He presented his papers in many national/international conferences/symposiums and also attended a American Chemical Society Industrial Symposium in 2017. His research interest lies in the "Computational development and implementation of some cost-effective variants of coupled-cluster based methods for energies and properties of molecules in near-degenerate electronic states".



Appendix G

Brief biography of the supervisor

Dr. Prashant Uday Manohar is an Assistant Professor at the Department of Chemistry, BITS Pilani, Pilani Campus, since August 2009. He carried out his doctoral research in Chemistry at National Chemical Laboratory (July 2001-July 2007) under the supervision of Dr. Sourav Pal and obtained the Ph.D. degree (University of Pune) in 2007. He was a Postdoctoral Research Associate at Department of Chemistry, University of Southern California, Los Angeles, CA (USA) in Prof. Anna I. Krylov's research group from October 2007 to June 2009. Dr. Manohar has authored 18 research paper in the peerreviewed international journals in the area of Theoretical and Computational Chemistry. His research work has been widely recognized and highly cited in the scientific community. He has participated in several national and international symposia/conferences and delivered invited lectures.



Dr. Manohar is a Theoretical and computational chemist. His research interest lies in theoretical and computer-code development of electronic structure methods for near-degenerate and non-degenerate systems. In particular, he has been working on coupled-cluster approaches for static and dynamic electron correlation in molecules. He has been an active developer of Q-CHEM (a commercial Quantum Chemistry Software) since 2008.

Bibliography

- [1] Puzzarini, Cristina and Stanton, John F and Gauss, Jürgen. “Quantum-chemical calculation of spectroscopic parameters for rotational spectroscopy”. In: *International Reviews in Physical Chemistry* 29.2 (2010), pp. 273–367. ISSN: 0144235X. DOI: 10.1080/01442351003643401.
- [2] Graham R Fleming. “Chemical applications of ultrafast spectroscopy”. In: (1986), p. 280.
- [3] Jaan Laane, Hiroaki Takahashi, and Andre Bandrauk. *Structure and Dynamics of Electronic Excited States*. Springer Science & Business Media, 2011. DOI: 10.1007/978-3-642-59855-5.
- [4] Frank Neese, Andreas Hansen, and Dimitrios G Liakos. “Efficient and accurate approximations to the local coupled cluster singles doubles method using a truncated pair natural orbital basis”. In: *Journal of Chemical Physics* 131.6 (2009), p. 64103. ISSN: 00219606. DOI: 10.1063/1.3173827. URI: <http://scitation.aip.org/content/aip/journal/jcp/131/6/10.1063/1.3173827>.
- [5] Robert W Boyd. *Nonlinear optics*. Elsevier, 2003.
- [6] Shaul Mukamel. *Principles of nonlinear optical spectroscopy*. Vol. 29. Oxford University Press New York, 1995.
- [7] Christiansen, O and Coriani, S and Gauss, J and Hättig, C and Jørgensen, P and Pawłowski, F and Rizzo, A. *Non-linear Optical Properties of Matter: From Molecules to Condensed Phases*. 2006.
- [8] Attila Szabo and Neil S Ostlund. *Modern quantum chemistry: introduction to advanced electronic structure theory*. Courier Corporation, 2012.



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

1.2 Electronic Structure of Atoms and Molecules

Electronic structure theory deals with theoretical and computational study of energies, bonding-patterns, molecular properties and spectroscopic parameters of molecules, collectively termed as “electronic structure” of the molecules. Central to the electronic structure is the time-independent Schrödinger wave equation [8, 72].

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

Here, we consider only non-relativistic Hamiltonian for the system of electrons and nuclei.

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \quad (1.2)$$

where,

$$\hat{T}_n = - \sum_{K=1}^M \frac{1}{2M_K} \nabla_K^2; \quad \leftarrow \text{Nucleus Kinetic Energy operator}$$

$$\hat{T}_e = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2; \quad \leftarrow \text{Electron Kinetic Energy operator}$$

$$\hat{V}_{nn} = + \sum_{K=1}^M \sum_{L=1}^M \frac{Z_K Z_L}{|\vec{R}_K - \vec{R}_L|}; \quad \leftarrow \text{Nucleus-Nucleus repulsion P.E. operator}$$

$$\hat{V}_{ne} = - \sum_{K=1}^M \sum_{i=1}^N \frac{Z_K}{|\vec{r}_i - \vec{R}_K|}; \quad \leftarrow \text{Nucleus-Electron attraction P.E. operator}$$

and

$$\hat{V}_{ee} = + \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad \leftarrow \text{Electron-Electron repulsion P.E. operator}$$

This equation is exactly solvable for one-nucleus one-electron system, that is, hydrogenic atoms. However, for larger systems, the problem becomes untractable and one is bound to go for approximations.

In 1927, Max Born and J. Robert Oppenheimer [73] observed the large difference in the time scales between electron motion and the motion of atomic nuclei due to heavier mass of nuclei in comparison to electron.

They proposed that-

“electron in a molecule to be moving in the field of fixed nuclei.”

In other words, the motion of atomic electrons and nuclei in a molecule can be treated separately. This approximation, known as Born-Oppenheimer approximation (BOA), enables a separation of the Hamiltonian operator into electronic and nuclear terms. Therefore, cross-terms between electrons and nuclei are neglected, so that the two smaller and decoupled systems can be solved more efficiently.

Mathematically, BOA, thus, expresses the total wavefunction of a molecule as the product of a nuclear (vibrational, rotational, translational) and electronic wavefunctions.

$$\Psi_{\text{Total}}(\vec{x}, \vec{R}) = \psi_{\text{nuclear}}(\vec{R}) \times \psi_{\text{electronic}}(\vec{x}, \vec{R}) \quad (1.3)$$

where $\vec{x} = (\vec{r}, s)$ is a composite variable and has information about position and spin angular momentum of the corresponding electron. $\psi_{\text{nuclear}}(\vec{R})$ and $\psi_{\text{electronic}}(\vec{x}, \vec{R})$ are a nuclear wavefunction and an electronic wavefunctions, respectively. The nuclei are considered stationary while solving for the electronic wavefunction and thus, the electronic wavefunction and the total electronic energy are thus, parametrically dependent on the nuclear positions. The electronic Schrödinger equation is thus solved for various fixed nuclear positions and the total electronic energy as a parametric function of nuclear position, then appears as potential energy in the solution of the nuclear Schrödinger equation. The electronic Schrödinger equation can be written as: Since, $\hat{T}_n = 0$, Thus -

$$\hat{H} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \quad (1.4)$$

Of this, the V_{nm} is constant for given geometry, under BOA and does not affect the electronic wavefunction. The terms in Eq. 1.4 are mathematically expressed as under.

$$\hat{H}_{elec} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \quad (1.5)$$

and,

$$\hat{H}_{elec} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{K=1}^M \sum_{i=1}^N \frac{Z_K}{|\vec{r}_i - \vec{R}_K|} + \sum_{i=1}^N \sum_{j=1}^{i-1} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (1.6)$$

or

$$\hat{H}_{elec} = \sum_{i=1}^N \hat{h}(i) + \sum_{i>j}^N V(i, j) \quad (1.7)$$

where, one electron part is

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_{K=1}^M \frac{Z_K}{|\vec{r}_i - \vec{R}_K|}$$

and two electron part is shown by,

$$V(i, j) = \frac{1}{|\vec{r}_i - \vec{r}_j|} - \frac{1}{r_{ij}}$$

Now, the solution to Schrödinger wave equation is given by,

$$\hat{H}_{elec} \psi_{elec} = E_{elec} \psi_{elec} \quad (1.8)$$

where,

$$\psi_{elec} = \psi_{elec}(\{\vec{r}_i\}; \{\vec{R}_K\})$$

and

$$E_{elec} = E_{elec}(\{\vec{R}_K\})$$

Electronic wavefunction depends explicitly on the electronic coordinates and parametrically on the nuclear coordinates. Electronic energy parametrically depends only on nuclear coordinates.

For one electron system, BO approximation can give exact electronic energy for given geometry. However, for many electron system, the Hamiltonian becomes non-separable due to the electron-electron repulsion term $V(i, j)$ in equation 1.7. Thus, one needs to consider further approximations while moving to solution of many-electron Schrödinger equation. However, apart from going for the approximation, one needs to take care of yet another feature of a many-electron feature. For single electron molecule, the spin-angular momentum of electron does not play any significant role in absence of external field as the Hamiltonian is independent of spins of electron/nuclei. However, for atoms and molecules with two or more electrons, the role of the electron-spin becomes crucial and the Pauli principle plays a key role in further solution of electronic Schrödinger equation.

Pauli Principle or Antisymmetry Principle Probability density of a system of indistinguishable particles should remain unaltered due to interchange of any two identical particles. This leads to two possibilities in wavefunction of the particles. Upon interchange of two identical indistinguishable particles, the wavefunction should either remain the same (symmetric) or should change its sign (anti-symmetric). However, whether the wavefunction would be symmetric or antisymmetric is governed solely by the spin angular momentum of the particles as studied by Pauli and based on this, the indistinguishable particles are classified into two classes, namely, the bosons (those which obey the Bose-Einstein statistics) and the fermions (those which obey the Fermi-Dirac statistics). The bosons have integer spin-quantum numbers and consequently, their wavefunction must be symmetric with respect to interchange of any two bosons. On the other hand, the fermions have half-integer spin quantum numbers and their wavefunction must be antisymmetric with respect to interchange of any two fermions. Since electrons have half-integer spins, according to Pauli, a many-electron wavefunction must be antisymmetric with respect to interchange of the co-ordinates \vec{x} of any two electrons. Many electron Hartree product wavefunction does not satisfy the antisymmetry principle. Now, we require another wavefunction form which has to satisfy the SWE and must be antisymmetric.

$$\psi(\vec{x}_1, \dots, \vec{x}_i, \dots, \vec{x}_j, \dots, \vec{x}_N) = -\psi(\vec{x}_1, \dots, \vec{x}_j, \dots, \vec{x}_i, \dots, \vec{x}_N) \quad (1.9)$$

This requirement is easily accomplished by expressing the wavefunction in terms of the Slater determinants of spin-orbitals of electrons. In the limit of complete set of spin-orbitals, the set of resulting Slater determinants would be complete and in principle, one can get exact wavefunction for many electrons in this way. However, practically, it is impossible to use complete set of spin-orbitals and thus, the wavefunction obtained this way cannot be exact.

1.3 Mean Field Approximation and Hartree Fock Method

1.3.1 Mean Field Approximation

The essence of this approximation is to replace extremely complicated many electrons problem into one electron problem. HF approximation proposed that,

“motion of an electron within the molecular system depends only on the average potential of all the remaining electrons.”

In other words, this approximation replace two electron $V(i, j)$ term in 1.7 into one electron problem in which electron-electron repulsion is treated in an average way. Equation 1.7 becomes,

$$\hat{H}_{elec}(i) = \hat{h}(i) + v^{HF}(i) = f(i) \quad (1.10)$$

where, $f(i)$ is an effective one electron operator, called the Fock operator and $v^{HF}(i)$, is the average potential of (N-1) electrons experienced by the i^{th} electron in the molecular system.

Thus, we get another form of Hamiltonian,

$$\hat{H}_{elec} = \sum_{i=1}^N h(i) \quad (1.11)$$

where, $h(i)$ operator contain the kinetic energy, potential energy and average potential energy of i^{th} electron.

The average potential field $v^{HF}(i)$ seen by the i^{th} electron, depends on the spin orbitals of other electrons. thus, $h(i)$ will have set of spin orbitals $\{\chi_j\}$. Equation 1.8 becomes,

$$h(i)\chi_j(x_i) = E_j\chi_j(x_i) \quad (1.12)$$

Since, H is sum of one electron Hamiltonian. Therefore, many electron wavefunction becomes separable or product of spin orbital wavefunctions for each electron which is called ‘‘Hartree Product’’. Eigenfunction of \hat{H}_{elec} ,

$$\begin{aligned} \Psi^{HP}(x_1, x_2, x_3, \dots, x_N) &= \chi_i(x_1)\chi_j(x_2)\chi_k(x_3)\dots\chi_m(x_N) \\ \hat{H}_{elec}\Psi^{HP} &= E\Psi^{HP} \end{aligned} \quad (1.13)$$

where, E is a sum of spin orbital energies,

$$E = E_i + E_j + E_k + \dots + E_m$$

Many electron Hartree product wave function has still a basic deficiency; ‘it takes no account of the indistinguishability of electrons’, but it distinguishes the electron-one as occupying spin orbital χ_i , the electron-two as occupying spin orbital χ_j , ... and so on. This shortcoming is solved by replacing the products of the orbitals by their anti-symmetrized products – by means of the so called, ‘‘Slater determinants’’ and it then leads to the Hartree-Fock method.

1.3.2 Hartree-Fock method

First, we determine set of spin orbitals $\{\chi_i\}$ which construct Slater determinant. For N electron system,

$$|\Psi_0\rangle = |\chi_1\chi_2 \dots \chi_i\chi_j \dots \chi_N\rangle$$

where, Ψ_0 is best possible approximation to the ground state. Assume that we have exact ground state wavefunction $|\Psi_0\rangle$ which gives exact solution for SWE. Since, the Hamiltonian is hermitian, the solution to be orthogonal and normalized.

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}$$

To derive the HF equations, one minimizes the energy functional with respect to the orbitals $\chi_i \rightarrow \chi_i + \delta\chi_i$. We assume that the orbitals χ are orthonormal, and ensure that our variational procedure leaves them orthonormal. We can accomplish this by Lagrange's method of undetermined multipliers, where we employ a functional \mathcal{L} defined as

$$\mathcal{L}[\{\chi_i\}] = E_0[\{\chi_i\}] - \sum_{i=1}^N \sum_{j=1}^N \epsilon_{ij} ([i|j] - \delta_{ij})$$

where ϵ_{ij} are the undetermined Lagrange multipliers and $\langle i|j \rangle$ is the overlap between spin orbitals i and j , that is,

$$\int dx_1 \chi_i^*(\vec{x}_1) \chi_j(\vec{x}_1) = [i|j] = \delta_{ij}$$

Therefore,

$$E_0[\{\chi_i\}] = \sum_i \langle i|h|i \rangle + \frac{1}{2} \sum_i \sum_j \langle ij||ij \rangle$$

or,

$$E_0 - \sum_i [i|h|i] + \frac{1}{2} \sum_{ij} [ii|jj] - [ij|ji]$$

where,

$$[ii|jj] = \int dx_1 dx_2 \chi_i^*(\vec{x}_1) \chi_i(\vec{x}_1) r_{12}^{-1} \chi_j^*(\vec{x}_2) \chi_j(\vec{x}_2) \quad (1.14)$$

and,

$$[ij|ji] = \int dx_1 dx_2 \chi_i^*(\vec{x}_1) \chi_j(\vec{x}_1) r_{12}^{-1} \chi_j^*(\vec{x}_2) \chi_i(\vec{x}_2) \quad (1.15)$$

and, finally we got HF equation [9, 10] in the form of eigenvalue equation -

$$\hat{F}(\vec{x}_1)\chi_i(\vec{x}_1) = \epsilon_i\chi_i(\vec{x}_1) \quad (1.16)$$

$$\text{Where, } \hat{F}(\vec{x}_1) = \hat{T}_e + \hat{V}_{ne} + v(\vec{x}_1) \leftarrow \text{Fock operator} \quad (1.17)$$

$$v(\vec{x}_1) = \sum_{j=1}^N J_j(\vec{x}_1) + \sum_{j=1}^N K_j(\vec{x}_1) \quad (1.18)$$

$$J_j(\vec{x}_1)\chi_i(\vec{x}_1) = \int dx_2 \frac{\chi_j^*(\vec{x}_2)\chi_j(\vec{x}_2)}{|\vec{x}_1 - \vec{x}_2|} \chi_i(\vec{x}_1) \leftarrow \text{Coulomb operator} \quad (1.19)$$

$$K_j(\vec{x}_1)\chi_i(\vec{x}_1) = \int dx_2 \frac{\chi_j^*(\vec{x}_2)\chi_i(\vec{x}_2)}{|\vec{x}_1 - \vec{x}_2|} \chi_j(\vec{x}_1) \leftarrow \text{Exchange operator} \quad (1.20)$$

Fock operator ($\hat{F}(\vec{x}_1)$) [8] and is an effective one-electron operator. Average potential $v(\vec{x}_1)$ is experienced by an electrons due to motions of all other electrons and is called HF potential.

It includes the average Coulomb interaction term which is defined by local operator $J_j(\vec{x}_1)$ and a non-classical potential represented by a exchange potential operator $K_j(\vec{x}_1)$. Exchange operator arises due to anti-symmetric nature of the wavefunction. Equation 1.16 - 1.20 are solved iteratively until some self-consistency is achieved between successive equations. We will have a total energy as a function of a set of nuclear co-ordinates $\{R_A\}$ by adding the nuclei-nuclei repulsion to electronic energy. We can then explore the potential energy surface (PES) for nuclear motion by repeating the calculation for different nuclear co-ordinates.

Koopmans' Theorem HF theory provides best set of orthogonal spin-orbitals which are eigen functions of the Fock operator. In equation 1.16, i^{th} spin-orbital energy represented by ϵ_i . N-electrons are occupied the N spin-orbitals with lowest energies in HF configuration and resultant determinant is the HF wavefunction. The remaining spin-orbitals in HF configuration are termed as virtual orbitals.

Koopmans' theorem provides physical significance of orbital energies. This theorem provides the explanation of total energies which is not equal to the sum of the orbital energies.

The detailed explanation is provided by the action of adding or subtracting an electron to the N-electron state $|\Psi_0\rangle$. Koopmans' observed that,

“the energy of an occupied orbital in HF ground state configuration is negative of the energy required for removing an electron from the orbital without relaxation of the rest of the orbitals.”

The IP calculated according to this theorem are highly accurate because the relaxation and correlation effects in ionized state partially cancel the correlation effects in the ground state. Koopmans' theorem also predicts the first electron affinity for the HF ground state. However, in case of EA, the relaxation and correlation errors add up instead of cancelling each other and thus, the Koopmans' EA's are no way any accurate.

In an exact treatment, the IP exact is the total energy difference between the atom A and the ion A^+ with a separated electron [74]. However, these predictions are found to be quite absurd since, the correlation and relaxation errors add up in this case. While Koopmans' theorem works very well for IP, it turns out to be very bad for EA for obvious reasons. Unlike IP, in case of EA, the relaxation energy and correlation energies both decrease,

Brillouin's Theorem In previous section, we have discussed that HF procedure gives occupied and virtual spin-orbitals in HF ground state. Brillouin's consider, there are many other determinants which can be formed from the set of lowest-energy occupied spin-orbitals $\{\chi_i\}$. The set of singly excited determinants $|\Psi_a^r\rangle$ obtained from $|\Psi_0\rangle$. Brillouin's consider only the singly excited determinants as corrections to exact ground state and results analysed. Brillouin's observed that [8],

“Singly excited determinants $|\Psi_a^r\rangle$ will not interact directly with a ground state Hartree-Fock determinant $|\Psi_0\rangle$.”

or,

$$\langle\Psi_0|\hat{H}|\Psi_a^r\rangle = 0 \quad (1.21)$$

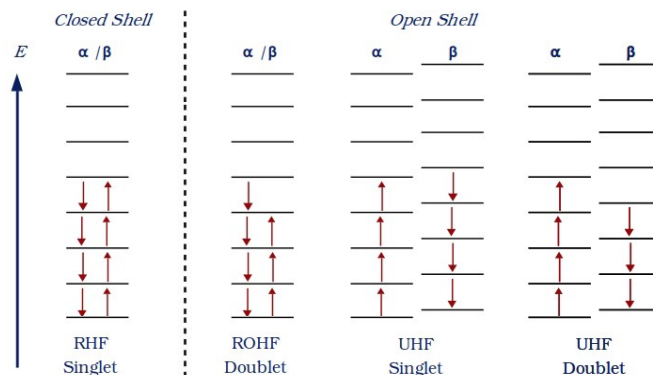


FIGURE 1.1: Restricted and unrestricted electronic system

1.3.2.1 HF approximation to restricted systems & Roothaan Equation

The Hartree-Fock approximation can be applied with or without restrictions on the spins of the MOs. The set of spin-orbital has been presented in form of Slater determinant in which χ_i is a products of a spatial orbital and a spin function) α or β . The trial wavefunction is an *Unrestricted Hartree-Fock* (UHF) wavefunction, if there are no restrictions on the form of spatial orbitals. It is also known as *Different Orbitals for Different Spins* (DODS). If there are restrictions on the form of spatial orbitals, the trial wavefunction is either *Restricted Hartree-Fock* (RHF) or *Restricted Open-shell Hartree-Fock* (ROHF) which depends on the paired or unpaired electron present on the system. RHF has closed shell type system which has an even number of electrons and provide singlet system. ROHF wavefunction has odd number of electron which is not possible to choose a unitary transformation that makes the matrix of Lagrange multipliers diagonal in HF equation.

Therefore, ROHF provided orbitals energies are not uniquely defined and can not be equated to ionization potentials by a Koopmans' theorem. The ROHF or RHF determinant is a pure eigenfunction of total spin operator, UHF determinant, in general, is not.

The Roothaan Equations : Closed Shell RHF

In molecular electronic structure computation, explicit evaluation of two electron terms such as electron repulsion integrals (ERIs) becomes difficult. Hence, Roothaan [75] proposed

that the spin orbitals be expressed in terms of finite set of basis functions.

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu} \quad i = 1, 2, 3, \dots, K \quad (1.22)$$

The problem of calculating the HF molecular orbitals reduces to calculation of the set of expansion coefficients $C_{\mu i}$. Finally, we got *Roothaan Equation 1.23*,

$$\sum_{\nu} F_{\mu,\nu} C_{\nu,i} = \epsilon_i S_{\mu,\nu} C_{\nu,i} \quad (1.23)$$

Where, $\mu, \nu = 1, 2, \dots, K$ and Fock matrix is

$$F_{\mu,\nu} = \int dr_1 \psi_{\mu}^*(\vec{x}_1) h(\vec{x}_1) \psi_{\nu}(\vec{x}_1) + \sum_a^{\frac{N}{2}} \int dr_1 \psi_{\mu}^*(\vec{x}_1) [2J_j(\vec{x}_1) - K_j(\vec{x}_1)] \psi_{\nu}(\vec{x}_1) \quad (1.24)$$

and C is a $K \times K$ square matrix,

$$C_{\nu,i} = \begin{pmatrix} C_{11} & C_{12} & \dots & C_{1K} \\ C_{21} & C_{22} & \dots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \dots & C_{KK} \end{pmatrix}$$

and ϵ is diagonal matrix of the orbital energies ϵ_i .

$$\epsilon = \begin{pmatrix} \epsilon_1 & & & \\ & \epsilon_2 & & 0 \\ & & \ddots & \\ & 0 & & \epsilon_i \end{pmatrix}$$

1.3.2.2 HF approximation to unrestricted systems

The UHF wave function contains a sum of several antisymmetrized products, each of which contains a (doubly occupied) closed-shell Ψ_C , and a partially occupied open shell Ψ_O . In

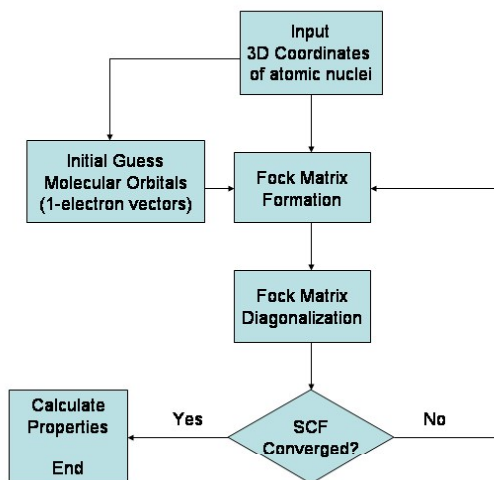


FIGURE 1.2: SCF Procedure

closed shell case Ψ_C , the orbitals can always be subjected to a unitary transformation, which brings the matrix of Lagrange multipliers into diagonal form. When diagonalization has been done, the orbitals all satisfy the pseudo-eigenvalue equation 1.16.

In open shell Ψ_O case, we have available only the transformation which transforms the open and closed shells within themselves. Such a transformation can eliminate only the off-diagonal multipliers but, not the multipliers which couple the closed and open shells. There is one exception, when the closed-shell and open-shell orbitals have no common symmetry. Now, open-shell system equivalent to two pseudo-eigenvalue equation problems of the type 1.16 after vanishing the multipliers which couple the closed and open shells[75].

1.3.2.3 Self Consistent Field Procedure

SCF procedure gives both the occupied and virtual orbitals. Once atomic basis sets 1.22 have been selected for each atom, the **one- and two-electron integrals** appearing in Fock operator 1.24 must be evaluated.

This is a time-consuming process, but nowadays, several highly efficient computer codes are available which allows such integrals to be computed for s, p, d, f, and even higher

basis functions. One-electron part has $\frac{N^2}{2}$ computational cost while $\frac{N^4}{8}$ required by the two-electron integrals. The Factors of $\frac{1}{2}$ and $\frac{1}{8}$ arise from permutational symmetries of the integrals. When chosen extremely large atomic orbital basis sets, modern computer codes calculate the requisite integrals but never store them on the disk.

1.3.3 Second Quantization

Second quantization is the fundamental approach for the development of many particle quantum theory which is the assemblies of indistinguishable particles. It is an essential approach in the non-relativistic systems where the number of particles is fixed, however too large for the use of Schrödinger's wavefunction description. In 1927, Dirac - Field theory of the electromagnetic field using creation and annihilation operators (second quantization approach) after that Jordan & Klein (1927) and Jordan & Wigner (1928) denoted that Dirac's description is also useful for many-particle systems in which particles may interact [76].

This is applicable in quantum field theory (QFT) because a quantized field (CQF) is a quantum mechanics (QM) operator with many degrees of freedom and, in condensed matter theory (CMT) since matter involves many particles. The same algebra, without interrupting the physics of many-electron systems can be more conveniently explained applying the concept of second quantization. In 1932, Fock developed FS by applying this approach. The main advantage of second quantization is replacement of the cumbersome determinant structure by required action of creation and annihilation operators. The resulting developments like diagrammatic techniques [77], normal ordering and Wicks theorem [77–79] more helped in simplification of the tedious algebra and also in understanding the physics more easily.

The second quantization approach has been long back reported in the literature [8, 80]. It is more useful where especially if you want to describe processes in which particles are created and annihilated. consider a complete set of orthonormal spin orbitals $\{\chi_p(x)\}$. For each spin-orbital χ_p , are associated, two operators a_p and a_p^\dagger known as an annihilation

and creation operators respectively. A creation operator a_p^\dagger creates an electron in χ_p if it is empty. Similarly, if χ_p is occupied, the annihilation operator a_p will destroy the electron. The above-mentioned effects are observed when the operators operate on the right-hand side. On the left-hand side, the operations of the creation and annihilation operators are interchanged. A creation operator cannot create an electron in a previously occupied orbital. Similarly, an annihilation operator cannot destroy an electron from an empty orbital. A vacuum ($|>$ or $<|$) is defined as a state with no electrons. These conclusions can be compiled as follows.

$$\begin{aligned}
a_p^\dagger|\chi_q(\vec{x}_1), \chi_r(\vec{x}_2), \dots, \chi_s(\vec{x}_N)> &= |\chi_p(\vec{x}_1), \chi_q(\vec{x}_2)\chi_r(\vec{x}_3), \dots, \chi_s(\vec{x}_{N+1})> \\
a_p|\chi_p(\vec{x}_1), \chi_q(\vec{x}_2), \chi_r(\vec{x}_3), \dots, \chi_s(\vec{x}_N)> &= |\chi_q(\vec{x}_1)\chi_r(\vec{x}_2), \dots, \chi_s(\vec{x}_{N-1})> \\
a_p^\dagger|> &= |\chi_q(\vec{x}_i)> \quad ; \quad <|a_p = <|\chi_p(\vec{x}_p)| \\
a_p|\chi_p(\vec{x}_p)> &= |> \quad ; \quad <|\chi_p(\vec{x}_p)|a_p^\dagger = <| \\
a_p|> &= 0 \quad = <|a_p^\dagger \\
a_p^\dagger|\chi_p(\vec{x}_p)> &= 0 \quad = <|\chi_p(\vec{x}_p)|a_p
\end{aligned} \tag{1.25}$$

One can thus obtain N -electron determinant by operation of N creation operators on vacuum (or, empty space) ($|>$). Similarly, the action of N annihilation operators on vacuum on the left ($<|$) also generates N -electron determinant. The linear vector space spanned by determinants with different number of electrons including the vacuum is known as FS [79]. It can be observed as a direct sum of Hilbert spaces with a different number of electrons. The creation and annihilation operators perform the following anti-commutation relations.

$$\begin{aligned}
\{a_p^\dagger, a_q^\dagger\} &= a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger = 0 \\
\{a_p, a_q\} &= a_p a_q + a_q a_p = 0 \\
\{a_p^\dagger, a_q\} &= a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq}
\end{aligned} \tag{1.26}$$

From the given relations, it can be observed that the interchange between any two creation or annihilation operators will outcome in change of the sign of the resulting

determinant, thereby ensuring the antisymmetry. The electronic Hamiltonian can thus be written in second quantized notation as follows.

$$\hat{H}_{ele} = \sum_{p,q} \langle p|\hat{h}|q \rangle a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s} \langle pq|\hat{g}|rs \rangle a_p^\dagger a_q^\dagger a_r a_s \quad (1.27)$$

where,

$$\begin{aligned} \langle p|\hat{h}|q \rangle &= \int d\vec{x} \chi_p^*(\vec{x}) \hat{h}(\vec{x}) \chi_q(\vec{x}) \\ \langle pq|\hat{g}|rs \rangle &= \int d\vec{x}_1 d\vec{x}_2 \chi_p^*(\vec{x}_1) \chi_q^*(\vec{x}_2) \hat{g}(|\vec{x}_1 - \vec{x}_2|) \chi_r(\vec{x}_1) \chi_s(\vec{x}_2) \end{aligned} \quad (1.28)$$

The given form of electronic Hamiltonian is independent of the number of electrons which can be applied to the full of FS.

1.3.3.1 Normal-Ordered Second Quantized Operators

In the normal-order approach, “all the annihilation operators are shifted to the right-hand side.” [77, 79, 81] As an example, consider an operator,

$$\hat{T} = a_p a_q^\dagger a_r a_s^\dagger$$

Now, we may shift the two annihilation operators to the right-hand side and therefore write the strings in an equivalent form as,

$$\begin{aligned} \hat{T} &= a_p a_q^\dagger a_r a_s^\dagger \\ &= (\delta_{pq} - a_q^\dagger a_p) a_r a_s^\dagger \\ &= (\delta_{pq} - a_q^\dagger a_p) (\delta_{rs} - a_s^\dagger a_r) \\ &= \delta_{pq} \delta_{rs} - \delta_{pq} a_s^\dagger a_r - \delta_{rs} a_q^\dagger a_p + a_q^\dagger a_p a_s^\dagger a_r \\ &= \delta_{pq} \delta_{rs} - \delta_{pq} a_s^\dagger a_r - \delta_{rs} a_q^\dagger a_p + a_q^\dagger (a_p a_s^\dagger) a_r \\ &= \delta_{pq} \delta_{rs} - \delta_{pq} a_s^\dagger a_r - \delta_{rs} a_q^\dagger a_p + a_q^\dagger (\delta_{ps} - a_s^\dagger a_p) a_r \\ &= \delta_{pq} \delta_{rs} - \delta_{pq} a_s^\dagger a_r - \delta_{rs} a_q^\dagger a_p + \delta_{ps} a_q^\dagger a_r - a_q^\dagger a_s^\dagger a_p a_r \end{aligned} \quad (1.29)$$

If we assume that the vacuum state is normalized then we obtain the following equation after evaluating the quantum mechanical expectation value of \hat{T} operator (1.29) in the true vacuum state, $| \rangle$,

$$\begin{aligned} \langle \hat{T} | \rangle &= \langle |\delta_{pq}\delta_{rs}| \rangle - \langle |\delta_{pq}a_s^\dagger a_r| \rangle - \langle |\delta_{rs}a_q^\dagger a_p| \rangle + \langle |\delta_{ps}a_q^\dagger a_r| \rangle - \langle |a_q^\dagger a_s^\dagger a_p a_r| \rangle \\ &= \delta_{pq}\delta_{rs} \end{aligned} \quad (1.30)$$

In above equation 1.30, the only term of \hat{T} , which gives a non-zero result is the one including second quantized operators, all other terms involves uses of an annihilation operator to $| \rangle$ on the right.

If we consider, \hat{T} between the single particle states, $\langle \phi_i |$ and $|\phi_j \rangle$,

$$\langle \phi_i | \hat{T} | \phi_j \rangle = \langle a_i \hat{T} a_j^\dagger \rangle . \quad (1.31)$$

Now, assume that $a_i \hat{T} a_j^\dagger = \hat{A}$, then we get,

$$\begin{aligned} \langle \phi_i | \hat{T} | \phi_j \rangle &= \langle \hat{A} \rangle \\ &= \delta_{ij}\delta_{pq}\delta_{rs} + \delta_{iq}\delta_{ps}\delta_{rj} - \delta_{iq}\delta_{pj}\delta_{rs} - \delta_{is}\delta_{pq}\delta_{rj} \end{aligned} \quad (1.32)$$

1.3.3.2 Wick's Approach for the evaluation the Matrix Elements

According to Wick's theorem,

“an arbitrary string of annihilation and creation operators, ABC ... XYZ, may be written as a linear combination of normal-ordered strings.”

In other words, Wick's theory [77–79] states that any generic operator sequence is equivalent to the sum of its normal-ordered form and the normal-ordered forms of its all possible contractions.

1.3.3.3 Fermions and Particle-Hole Formalism

The second quantization along with diagrammatic technique offers a handy tool to obtain programmable expressions for various many-body methods. The diagrammatic approach is based on Feynman diagrams. The operators are represented by vertices. The operator can be distinguished by introducing different kinds of vertices (e.g. hollow vertices, solid vertices, etc). The creation and annihilation of fermion (electron) is represented by lines segments with outward and inward arrows, respectively, joining the respective vertex. The occupied orbitals are represented by downward arrow, whereas the virtual orbitals are represented by upward arrows.

The algebra of creation and annihilation of fermions is useful for most of the SR methods. In case of MR methods, the configurations in the reference state form the model space (MS) and in general differ in the occupancy of the orbitals and the creation and annihilation of fermions may have different effects in different configurations. It is often more convenient to introduce the so called particle-hole formalism. A suitable configuration of electrons is defined to be a hole-particle vacuum i.e. the configuration with zero holes and zero particles in it. Hole is defined to be created when an electron from one of the occupied orbitals is annihilated, whereas creation of electron in one of the virtual orbitals is equivalent to creation of a particle. Consequently, removal of the electron from the virtual subspace would resemble with annihilation of the particle, and putting the electron back to the occupied subspace would result in annihilation of the hole. The MS configurations in MR methods can thus, be labeled in terms of the number of particles and holes present in them. This part will be further discussed later, in the context of FSMRCC [1.8](#).

1.3.4 Electron Correlation

The HF theory provides approximate solution to SWE where the actual inter-electronic interactions are replaced by average interactions felt by the electrons due to presence of other electrons. If the basis function is sufficiently large, the energy computed by HF is $\sim 99\%$ of the exact energy. However, the remaining $\sim 1\%$ turns out to be very important

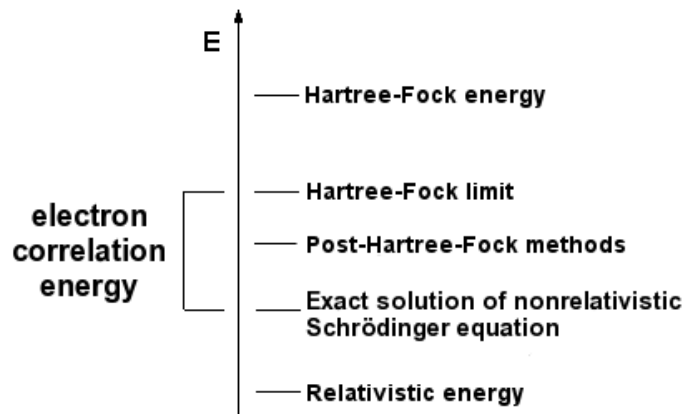


FIGURE 1.3: Electron Correlation Energy

and is the order of few hundreds of Kcal/mole. This $\sim 1\%$ error is called correlation energy. More specifically,

$$\text{correlation energy} = \text{exact energy} - \text{HF energy}$$

and is thus, always negative.

UHF type wavefunction is, to a certain degree, able to include electron correlation energy. In RHF type wavefunction, the two electron in a molecular orbital occupy the same physical spatial space and differ only in spin function (α or β). The spatial overlap between the orbitals of two such **pair** electrons is one while, the overlap between the orbitals of two electrons belonging to **different pairs** is zero, owing to the orthogonality of the molecular orbitals.

In other words, electron-electron repulsion integrals ($\langle \psi_i | \psi_j \rangle = 0$ for $i \neq j$, but $\langle \psi_i \psi_j | A | \psi_i \psi_j \rangle$ and $\langle \psi_i \psi_j | A | \psi_j \psi_i \rangle$ are not necessarily zero. It may be expected that the correlation effect between pairs of electrons associating to the same spatial molecular orbitals would be the major part of the electron correlation. Correlation between the same spin (**Fermi correlation**) is smaller than the correlation between the opposite spins (**Coulomb correlation**) which has both intra- and inter-orbital contributions [82]. Therefore, Coulomb correlation plays major role. The electron correlation is of two types,

namely, the dynamical one and the non-dynamical or static one. The dynamical correlation arises by the virtue of instantaneous repulsion between electrons. The dynamic contribution belongs to the electrons which occupy the same spatial orbital. The non-dynamical or static correlation belongs to the electrons that are avoiding each other on a more “permanent” basis (occupancy in different spatial orbitals). The multi-configurational wavefunction takes account of this static correlation, but not dynamical correlation. This is also called **near-degeneracy** effect. Thus, it is more important for a system where different orbitals have similar energies.

The quality of a computation is described by the level of theory and the size of the basis set (i.e. how much electron correlation is included). J. A. Pople was introduced notation which is denoted as “*level/basis*”. This implies that the geometry is optimized at this level of theory. The relative energy is more sensitive to the theoretical level than the geometry. Therefore, geometries are optimized at low-level theories. This is denoted by the “level2/basis-set-2//level1/basis-set-1” where the notation after the “//” indicates the level at which the geometry is optimized [83].

There are two ways for calculating the correlation energy, firstly variational (e.g. configurational interaction) and secondly, perturbational (e.g. MP2). But, the third approach also uses which is neither variational nor perturbational (e.g. Coupled cluster).

1.4 Configurational Interaction (CI)

Like HF, CI is also the variational method. The CI wavefunction is expressed as linear combination of determinants whose coefficients are varied so as to get energy minimum. The determinants (and hence, the orbitals) are not varied in CI. Thus, unlike HF, it is a linear variation method as only the linear expansion coefficients are the variation parameters. It is worth mentioning here (although we don’t want to discuss in detail) that, if additionally, the orbitals are also varied, it would result in multi-configuration (MC) HF or MCSCF method which is fully variational. In the limit of complete set of basis

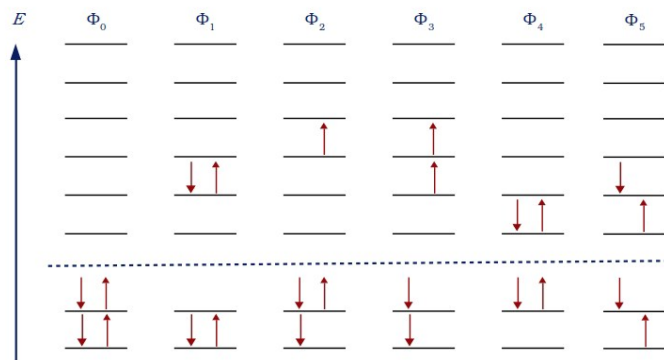


FIGURE 1.4: Electron excited state configuration

functions (and hence, the orbitals and hence, the determinants), CI wavefunction would be exact. However, it is impractical. Finite set of orbitals would result in approximate wavefunction and energy. However, if the orbitals are variationally optimized (like in HF) and if all possible resulting determinants are considered, it results in Full CI wavefunction which is the benchmark of the highest pragmatic accuracy.

The trial wavefunction is expressed as a linear combination of determinants with the expansion coefficients determined by requiring that the energy should be a minimum. This procedure is known as *configuration interaction*. All molecular orbitals are expanded in a basis set of one electron function but, basis set has a finite number of members and consequently, incompleteness of the basis set causes the *basis-set truncation error*.

$$\Psi_{CI} = c_0|\phi_0\rangle + \sum_{ia} c_i^a|\phi_i^a\rangle + \sum_{ijab} c_{ij}^{ab}|\phi_{ij}^{ab}\rangle + \sum_{ijkabc} c_{ijk}^{abc}|\phi_{ijk}^{abc}\rangle + \dots \quad (1.33)$$

Or,

$$\Psi_{CI} = c_0|0\rangle + \sum_S c_S|S\rangle + \sum_D c_D|D\rangle + \sum_T c_T|T\rangle + \dots \quad (1.34)$$

$$\Psi_{CI} = \sum_{i=0} a_i \phi_i \quad (1.35)$$

Variational problems give the CI *secular equations* after introducing the Langrange multipliers.

$$\begin{pmatrix} H_{00} - E & H_{0S} & H_{0D} & \dots \\ H_{S0} & H_{SS} - E & H_{SD} & \dots \\ H_{D0} & H_{DS} & H_{DD} - E & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_0 \\ c_S \\ c_D \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (1.36)$$

or,

$$(H - EI)c = 0 \quad \rightarrow \quad Hc = Ec \quad (1.37)$$

We get eigen values after solving above secular equation. The first excited state corresponds to the second lowest eigenvalue.

For N electron and X basis functions, the total number of singlet determinants (or Configuration state functions, CSFs) that can be produced is given by,

$$\text{Number of singlet CSF} = \frac{X!(X + 1)}{(\frac{N}{2})!(\frac{N}{2} + 1)!(X - \frac{N}{2})!(X - \frac{N}{2} + 1)!}$$

For example, H₂O with the 6-31G(d) basis, there are $\sim 30 \times 10^6$ CSFs(N=10, X=19) and, larger basis function 6-3111G(2d,2p), there are $\sim 106 \times 10^9$ CSFs (N=10, X=41).

TABLE 1.1: Number of singlet CSFs for H₂O with a 6-31G(d) basis set.

Excitation level	Number of n^{th} excited CSFs	total number of CSFs ^a
1	71	71
2	2485	2556
3	40 040	42 596
4	3 48 530	3 91 126
5	17 23 540	21 14 666
6	50 33 210	71 47 876
7	86 88 680	1 58 36 556
8	86 53 645	2 44 90 201
9	45 54 550	2 90 44 751
10	10 02 001	3 00 46 752

^a See Ref. [82].



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

- [9] D. R. Hartree. “The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion”. In: *Mathematical Proceedings of the Cambridge Philosophical Society* 24.1 (1928), pp. 111–132. DOI: 10.1017/S0305004100011920.
- [10] D R Hartree. “The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion”. In: *Mathematical Proceedings of the Cambridge Philosophical Society* 24.1 (1928), pp. 111–132. DOI: 10.1017/S0305004100011920.
- [11] Hylleraas EA. “On the ground state term of the two-electron problem for H^+ , He, Li^+ , Be^{++} , etc.” In: *Z. Phys.* 65 (1930), pp. 209–224.
- [12] C David Sherrill and Henry F Schaefer III. “The configuration interaction method: Advances in highly correlated approaches”. In: *Advances in quantum chemistry*. Vol. 34. Elsevier, 1999, pp. 143–269.
- [13] Chr. Møller and Milton S Plesset. “Note on an approximation treatment for many-electron systems”. In: *Physical Review* 46.7 (1934), p. 618.
- [14] Dieter Cremer. “Møller Plesset perturbation theory: from small molecule methods to methods for thousands of atoms”. In: *Wiley Interdisciplinary Reviews: Computational Molecular Science* 1.4 (2011), pp. 509–530. DOI: 10.1002/wcms.58. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/wcms.58>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/wcms.58>.
- [15] Isaiah Shavitt and Rodney J Bartlett. *Many-body methods in chemistry and physics: MBPT and coupled-cluster theory*. Cambridge university press, 2009.
- [16] Helgaker, Trygve and Jørgensen, Poul and Olsen, Jeppe. *Molecular electronic-structure theory*. John Wiley & Sons, 2014.
- [17] Debashis Mukherjee, Raj Kumar Moitra, and Atri Mukhopadhyay. “Applications of a non-perturbative many-body formalism to general open-shell atomic and molecular problems: calculation of the ground and the lowest π - π^* singlet and triplet energies and the first ionization potential of trans-butadiene”. In: *Molecular Physics* 33.4 (1977), pp. 955–969.

- [18] Ingvar Lindgren. “A coupled-cluster approach to the many-body perturbation theory for open-shell systems”. In: *International Journal of Quantum Chemistry* 14.S12 (1978), pp. 33–58.
- [19] Bogumil Jeziorski and Hendrik J Monkhorst. “Coupled-cluster method for multiterminantal reference states”. In: *Physical Review A* 24.4 (1981), p. 1668.
- [20] William D Laidig and Rodney J Bartlett. “A multi-reference coupled-cluster method for molecular applications”. In: *Chemical Physics Letters* 104.5 (1984), pp. 424–430.
- [21] JP Malrieu, Ph Durand, and JP Daudey. “Intermediate Hamiltonians as a new class of effective Hamiltonians”. In: *Journal of Physics A: Mathematical and General* 18.5 (1985), p. 809.
- [22] Ingvar Lindgren and Debashis Mukherjee. “On the connectivity criteria in the open-shell coupled-cluster theory for general model spaces”. In: *Physics Reports* 151.2 (1987), pp. 93–127.
- [23] Pal, Sourav and Rittby, Magnus and Bartlett, Rodney J and Sinha, Dhiman and Mukherjee, Debashis. “Molecular applications of multireference coupled-cluster methods using an incomplete model space: Direct calculation of excitation energies”. In: *The Journal of Chemical Physics* 88.7 (1988), pp. 4357–4366.
- [24] Leszek Meissner. “Fock-space coupled-cluster method in the intermediate Hamiltonian formulation: Model with singles and doubles”. In: *The Journal of Chemical Physics* 108.22 (1998), pp. 9227–9235.
- [25] John F Stanton, Rodney J Bartlett, and C Magnus L Rittby. “Fock space multireference coupled-cluster theory for general single determinant reference functions”. In: *The Journal of Chemical Physics* 97.8 (1992), pp. 5560–5567.
- [26] Arie Landau, Ephraim Eliav, and Uzi Kaldor. “Intermediate Hamiltonian Fock-space coupled-cluster method”. In: *Chemical Physics Letters* 313.1-2 (1999), pp. 399–403.
- [27] Pittner, Jiří and Nachtigall, Petr and Čárský, Petr and Mášik, Jozef and Hubač, Ivan. “Assessment of the single-root multireference Brillouin–Wigner coupled-cluster method: Test calculations on CH₂, SiH₂, and twisted ethylene”. In: *The Journal of Chemical Physics* 110.21 (1999), pp. 10275–10282.

- [28] Koch, Henrik and Jensen, Hans Jørgen Aa and Jørgensen, Poul and Helgaker, Trygve and Scuseria, Gustavo E and Schaefer III, Henry F. “Coupled cluster energy derivatives. Analytic Hessian for the closed-shell coupled cluster singles and doubles wave function: Theory and applications”. In: *The Journal of Chemical Physics* 92.8 (1990), pp. 4924–4940.
- [29] Prashant Uday Manohar, Nayana Vaval, and Sourav Pal. “Constrained variational response to Fock-space multi-reference coupled-cluster theory: Some pilot applications”. In: *Journal of Molecular Structure: THEOCHEM* 768.1-3 (2006), pp. 91–96.
- [30] Prashant Uday Manohar and Sourav Pal. “Constrained Variational Response to Fock-Space Multi-Reference Coupled-Cluster Theory: Formulation for Excited-State Electronic Structure Calculations and Some Pilot Applications”. In: *AIP conference proceedings*. Vol. 963. AIP. 2007, pp. 337–344.
- [31] Bag, Arijit and Manohar, Prashant Uday and Vaval, Nayana and Pal, Sourav. “First and second-order electrical properties computed at the FSMRCCSD level for excited states of closed-shell molecules using the constrained-variational approach”. In: *The Journal of Chemical Physics* 131.2 (2009), p. 024102.
- [32] Lalitha Ravichandran, Nayana Vaval, and Sourav Pal. “Magnetizability of doublet radicals using Fock space multi-reference coupled cluster method”. In: *International Journal of Quantum Chemistry* 109.10 (2009), pp. 2191–2198. DOI: 10.1002/qua.22093. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/qua.22093>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/qua.22093>.
- [33] D J ROWE. “Equations-of-motion method and the extended shell model”. In: *Reviews of Modern Physics* 40.1 (Jan. 1968), pp. 153–166. ISSN: 0034-6861. DOI: 10.1103/RevModPhys.40.153. URL: <http://link.aps.org/doi/10.1103/RevModPhys.40.153>.
- [34] Geertsen, Jan and Rittby, Magnus and Bartlett, Rodney J. “The equation-of-motion coupled-cluster method: Excitation energies of Be and CO”. In: *Chemical Physics Letters* 164.1 (1989), pp. 57–62.

- [35] John F Stanton and Rodney J Bartlett. “The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties”. In: *The Journal of Chemical Physics* 98.9 (1993), pp. 7029–7039.
- [36] Anna I Krylov. “Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The hitchhiker’s guide to Fock space”. In: *Annu. Rev. Phys. Chem.* 59 (2008), pp. 433–462.
- [37] Marcel Nooijen and Rodney J Bartlett. “Equation of motion coupled cluster method for electron attachment”. In: *The Journal of Chemical Physics* 102.9 (1995), pp. 3629–3647.
- [38] Kowalski, Karol and Piecuch, Piotr. “The active-space equation-of-motion coupled-cluster methods for excited electronic states: The EOMCCSDt approach”. In: *The Journal of Chemical Physics* 113.19 (2000), pp. 8490–8502.
- [39] Rodney J Bartlett. “Coupled-cluster theory and its equation-of-motion extensions”. In: *Wiley Interdisciplinary Reviews: Computational Molecular Science* 2.1 (2012), pp. 126–138.
- [40] Mukhopadhyay, Debasis and Mukhopadhyay, Saroj and Chaudhuri, Rajat and Mukherjee, Debashis. “Aspects of separability in the coupled cluster based direct methods for energy differences”. In: *Theoretica Chimica Acta* 80.6 (Nov. 1991), pp. 441–467. ISSN: 1432-2234. DOI: 10.1007/BF01119665. URL: <https://doi.org/10.1007/BF01119665>.
- [41] H Nakatsuji and K Hirao. “Cluster expansion of the wavefunction. Pseudo-orbital theory based on the SAC expansion and its application to the spin density of open-shell systems”. In: *The Journal of Chemical Physics* 68.9 (1978), pp. 4279–4291.
- [42] Péter G. Szalay and Rodney J. Bartlett. “Approximately extensive modifications of the multireference configuration interaction method: A theoretical and practical analysis”. In: *The Journal of Chemical Physics* 103.9 (1995), pp. 3600–3612. DOI: 10.1063/1.470243. eprint: <https://doi.org/10.1063/1.470243>. URL: <https://doi.org/10.1063/1.470243>.



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>

- [43] Ove Christiansen, Henrik Koch, and Poul Jørgensen. “Response functions in the CC3 iterative triple excitation model”. In: *The Journal of Chemical Physics* 103.17 (1995), pp. 7429–7441. ISSN: 00219606. DOI: 10.1063/1.470315.
- [44] Kiran Bhaskaran-Nair, Karol Kowalski, and William A. Shelton. “Coupled cluster Green function: Model involving single and double excitations”. In: *The Journal of Chemical Physics* 144.14 (2016), p. 144101. DOI: 10.1063/1.4944960. eprint: <https://doi.org/10.1063/1.4944960>. URL: <https://doi.org/10.1063/1.4944960>.
- [45] Celestino Angeli, Mariachiara Pastore, and Renzo Cimiraglia. “New perspectives in multireference perturbation theory: the n-electron valence state approach”. In: *Theoretical Chemistry Accounts* 117.5 (200), pp. 743–754.
- [46] Haruyuki Nakano. “Quasidegenerate perturbation theory with multiconfigurational selfconsistentfield reference functions”. In: *The Journal of Chemical Physics* 99.10 (1993), pp. 7983–7992. DOI: 10.1063/1.465674. eprint: <https://doi.org/10.1063/1.465674>. URL: <https://doi.org/10.1063/1.465674>.
- [47] Prashant U Manohar and Anna I Krylov. “A noniterative perturbative triples correction for the spin-flipping and spin-conserving equation-of-motion coupled-cluster methods with single and double substitutions”. In: *The Journal of Chemical Physics* 129.19 (2008), p. 194105.
- [48] Manohar, Prashant U and Stanton, John F and Krylov, Anna I. “Perturbative triples correction for the equation-of-motion coupled-cluster wave functions with single and double substitutions for ionized states: Theory, implementation, and examples”. In: *The Journal of Chemical Physics* 131.11 (2009), p. 114112.
- [49] Dutta, Achintya Kumar and Pal, Sourav and Ghosh, Debashree. “Perturbative approximations to single and double spin flip equation of motion coupled cluster singles doubles methods”. In: *Journal of Chemical Physics* 139.12 (2013), p. 124116. ISSN: 00219606. DOI: 10.1063/1.4821936. URL: <http://scitation.aip.org/content/aip/journal/jcp/139/12/10.1063/1.4821936>.
- [50] Dutta, Achintya Kumar and Vaval, Nayana and Pal, Sourav. “Performance of the EOMIP-CCSD(2) method for determining the structure and properties of

- doublet radicals: A benchmark investigation”. In: *Journal of Chemical Theory and Computation* 9.10 (2013), pp. 4313–4331. ISSN: 15499618. DOI: 10.1021/ct400316m.
- [51] Achintya Kumar Dutta, Nayana Vaval, and Sourav Pal. “EOMIP-CCSD(2): An Efficient Method for the Calculation of Ionization Potentials”. In: *Journal of Chemical Theory and Computation* 11.6 (2015), pp. 2461–2472. ISSN: 15499626. DOI: 10.1021/ct500927h.
- [52] Achintya Dutta et al. “Partitioned EOMEA-MBPT(2): An efficient N⁵ scaling method for calculation of electron affinities”. In: *Journal of Chemical Theory and Computation* 10 (Apr. 2014). DOI: 10.1021/ct4009409.
- [53] Weigend, Florian and Häser, Marco and Patzelt, Holger and Ahlrichs, Reinhart. “RI-MP2: optimized auxiliary basis sets and demonstration of efficiency”. In: *Chemical Physics Letters* 294.1-3 (1998), pp. 143–152.
- [54] Jerry L Whitten. “Coulombic potential energy integrals and approximations”. In: *The Journal of Chemical Physics* 58.10 (1973), pp. 4496–4501.
- [55] Martin Feyereisen, George Fitzgerald, and Andrew Komornicki. “Use of approximate integrals in ab initio theory. An application in MP2 energy calculations”. In: *Chemical Physics Letters* 208.5-6 (1993), pp. 359–363.
- [56] O Vahtras, J Almlöf, and MW Feyereisen. “Integral approximations for LCAO-SCF calculations”. In: *Chemical Physics Letters* 213.5-6 (1993), pp. 514–518.
- [57] Frank Neese. “An Improvement of the Resolution of the Identity Approximation for the Formation of the Coulomb Matrix”. In: *Journal of Computational Chemistry* 24.14 (2003), pp. 1740–1747. ISSN: 01928651. DOI: 10.1002/jcc.10318. URL: <http://dx.doi.org/10.1002/jcc.10318>.
- [58] Jung, Yousung and Sodt, Alex and Gill, Peter MW and Head-Gordon, Martin. “Auxiliary basis expansions for large-scale electronic structure calculations”. In: *Proceedings of the National Academy of Sciences* 102.19 (2005), pp. 6692–6697.

- [59] Distasio Jr, Robert A and Steele, Ryan P and Rhee, Young Min and Shao, Yi-han and Head-Gordon, Martin. “An improved algorithm for analytical gradient evaluation in resolution-of-the-identity second-order Møller-Plesset perturbation theory: Application to alanine tetrapeptide conformational analysis”. In: *Journal of Computational Chemistry* 28.5 (2007), pp. 839–856.
- [60] Nelson HF Beebe and Jan Linderberg. “Simplifications in the generation and transformation of two-electron integrals in molecular calculations”. In: *International Journal of Quantum Chemistry* 12.4 (1977), pp. 683–705.
- [61] Koch, Henrik and Sánchez de Merás, Alfredo and Pedersen, Thomas Bondo. “Reduced scaling in electronic structure calculations using Cholesky decompositions”. In: *The Journal of Chemical Physics* 118.21 (2003), pp. 9481–9484.
- [62] Aquilante, Francesco and Pedersen, Thomas Bondo and Lindh, Roland. “Low-cost evaluation of the exchange Fock matrix from Cholesky and density fitting representations of the electron repulsion integrals”. In: *The Journal of Chemical Physics* 126.19 (2007), p. 194106.
- [63] Pedersen, Thomas Bondo and Aquilante, Francesco and Lindh, Roland. “Density fitting with auxiliary basis sets from Cholesky decompositions”. In: *Theoretical Chemistry Accounts* 124.1-2 (2009), pp. 1–10.
- [64] Aquilante, Francesco and Gagliardi, Laura and Geneva, Ch- and Pedersen, Thomas Bondo and Lindh, Roland. “Unbiased auxiliary basis sets for density fitting approximation with tunable accuracy and efficiency”. In: *The Journal of Chemical Physics* 130.15 (2009), pp. 1–6.
- [65] Weigend, Florian and Kattannek, Marco and Ahlrichs, Reinhart. “Approximated electron repulsion integrals: Cholesky decomposition versus resolution of the identity methods”. In: *The Journal of Chemical Physics* 130.16 (2009), p. 164106.
- [66] Aquilante, Francesco and Boman, Linus and Boström, Jonas and Koch, Henrik and Lindh, Roland and de Merás, Alfredo Sánchez and Pedersen, Thomas Bondo. “Cholesky Decomposition Techniques in Electronic Structure Theory”. English. In: *Linear-Scaling Techniques in Computational Chemistry and Physics*. Ed. by Zalesny, Robert and Papadopoulos, Manthos G and Mezey, Paul G and Leszczynski,

- Jerzy. Vol. 13. Challenges and Advances in Computational Chemistry and Physics. Springer Netherlands, 2011, pp. 301–343. ISBN: 978-90-481-2852-5. DOI: 10.1007/978-90-481-2853-2_13. URL: http://dx.doi.org/10.1007/978-90-481-2853-2_{_}13.
- [67] Uüür Bozkaya. “Analytic energy gradients and spin multiplicities for orbital-optimized second-order perturbation theory with density-fitting approximation: an efficient implementation”. In: *Journal of Chemical Theory and Computation* 10.10 (2014), pp. 4389–4399.
- [68] Evgeny Epifanovsky and Dmitry Zuev and Xintian Feng and Kirill Khistyayev and Yihan Shao and Anna I. Krylov. “General implementation of the resolution-of-the-identity and Cholesky representations of electron repulsion integrals within coupled-cluster and equation-of-motion methods: theory and benchmarks”. In: *The Journal of Chemical Physics* 139.13 (2013), p. 134105.
- [69] Feng, Xintian and Epifanovsky, Evgeny and Gauss, Jürgen and Krylov, Anna I. “Implementation of analytic gradients for CCSD and EOM-CCSD using Cholesky decomposition of the electron-repulsion integrals and their derivatives: Theory and benchmarks”. In: *The Journal of Chemical Physics* 151.1 (2019), p. 014110. DOI: 10.1063/1.5100022. eprint: <https://doi.org/10.1063/1.5100022>. URL: <https://doi.org/10.1063/1.5100022>.
- [70] Kumar, Dinesh and Dutta, Achintya Kumar and Manohar, Prashant Uday. “Resolution of the Identity and Cholesky Representation of EOM-MP2 Approximation: Implementation, Accuracy and Efficiency”. In: *Journal of Chemical Sciences* 129.10 (2017), pp. 1611–1626.
- [71] Dinesh Kumar and Prashant Uday Manohar. “Analytical dipole moments and dipole polarizabilities of doublet radicals using Cholesky representation of constrained variational linear response to Fock-space multi-reference coupled-cluster method with single and double substitutions”. In: *Chemical Physics Letters* 730 (2019), pp. 234 –238. ISSN: 0009-2614. DOI: <https://doi.org/10.1016/j.cplett.2019.06.004>. URL: <http://www.sciencedirect.com/science/article/pii/S0009261419304671>.

- [72] Mindy Levine, A Heath, et al. “Quantum Chemistry”. In: (1991).
- [73] M Born and R Oppenheimer. “Zur Quantentheorie der Molekeln”. In: *Annalen der Physik* 389.20 (1927), pp. 457–484. DOI: 10.1002/andp.19273892002. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/andp.19273892002>.
- [74] John F. Stanton and Jürgen Gauss. “A simple correction to final state energies of doublet radicals described by equation-of-motion coupled cluster theory in the singles and doubles approximation (Erratum)”. English. In: *Theoretica Chimica Acta* 95.3 (1997), p. 97. ISSN: 00405744. DOI: 10.1007/s002140050186. URL: <http://dx.doi.org/10.1007/BF01127508>.
- [75] C C J Roothaan. “Self-Consistent field theory for open shells of electronic systems”. In: *Reviews of Modern Physics* 32.2 (Apr. 1960), pp. 179–185. ISSN: 00346861. DOI: 10.1103/RevModPhys.32.179. URL: <https://link.aps.org/doi/10.1103/RevModPhys.32.179>.
- [76] Paul Adrien Maurice Dirac. *A new notation for quantum mechanics*. Vol. 35. 3. 1939, pp. 416–418.
- [77] Alexander Fetter and John Dirk Walecka. “Quantum theory of many-particle systems”. In: (1971).
- [78] I. Lindgren and J. Morrison. “Atomic Many-Body Theory”. In: (1982).
- [79] W Kutzelnigg. “Aspects of Many-Body Effects in Molecules and Extended Systems”. In: *Lecture Notes in Chemistry* (1989).
- [80] Poul Jørgensen. *Second quantization-based methods in Quantum Chemistry*. Elsevier, 2012.
- [81] E. Merzbacher. “Quantum Mechanics”. In: *Quantum Mechanics*. John Wiley & Sons, New York, 1970, 2nd Edition.
- [82] Frank Jensen. *Introduction to Computational Chemistry*. John wiley & sons, 2017.
- [83] John A Pople. “Theoretical models for chemistry”. In: *Energy, Structure and Reactivity: Proceedings of the 1972 Boulder Summer Research Conference on Theoretical Chemistry*. 1973, pp. 51–67.

- [84] Hylleraas EA. "On the ground state term of the two-electron problem for H , He, Li⁺ , Be⁺⁺ , etc." In: *Z. Phys.* 65 (1930), pp. 209–224.
- [85] Cremer D. and Schleyer PvR Allinger NL and Clark T, Gasteiger J and Kollman PA, Schaefer III HF and Schreiner PR. "Møller-Plesset Perturbation theory". In: *In Encyclopedia of Computational Chemistry* 3 (1998), pp. 1706–1735.
- [86] Kutzelnigg and Werner. "How Many-Body Perturbation theory (MBPT) has changed Quantum Chemistry". In: *International Journal of Quantum Chemistry* 109.15 (2009), pp. 3858–3884.
- [87] Stanley Raimes. *Many-electron theory*. North-Holland Pub. Co. - Amsterdam, 1972.
- [88] Ingvar Lindgren and John Morrison. *Atomic many-body theory*. Vol. 3. Springer Science & Business Media, 2012.
- [89] Bartlett, Rodney J and Silver, David M. "Correlation energy in LiH, BH, and HF with many-body perturbation theory using slater-type atomic orbitals". In: *International Journal of Quantum Chemistry* 8.S8 (1974), pp. 271–276.
- [90] John A Pople, J Stephen Binkley, and Rolf Seeger. "Theoretical models incorporating electron correlation". In: *International Journal of Quantum Chemistry* 10.S10 (1976), pp. 1–19.
- [91] Rodney J Bartlett and Isaiah Shavitt. "Comparison of high-order many-body perturbation theory and configuration interaction for H₂O". In: *Chemical Physics Letters* 50.2 (1977), pp. 190–198.
- [92] George D Purvis and Rodney J Bartlett. "The potential energy curve for the X 1Σ^{g+} state of Mg₂ calculated with many-body perturbation theory". In: *The Journal of Chemical Physics* 68.5 (1978), pp. 2114–2124.
- [93] RJ Bartlett. "Many-body perturbation theory and coupled cluster theory for electron correlation in molecules". In: *Annual Review of Physical Chemistry* 32 (1981), p. 359.
- [94] Raghavachari, Krishnan and Trucks, Gary W and Pople, John A and Head-Gordon, Martin. "A fifth-order perturbation comparison of electron correlation theories". In: *Chemical Physics Letters* 157.6 (1989), pp. 479–483.

- [95] JS Binkley and JA Pople. “Møller–Plesset theory for atomic ground state energies”. In: *International Journal of Quantum Chemistry* 9.2 (1975), pp. 229–236.
- [96] Krishnan, R and Pople, John A. “Approximate fourth-order perturbation theory of the electron correlation energy”. In: *International Journal of Quantum Chemistry* 14.1 (1978), pp. 91–100.
- [97] R Krishnan, MJ Frisch, and JA Pople. “Contribution of triple substitutions to the electron correlation energy in fourth order perturbation theory”. In: *The Journal of Chemical Physics* 72.7 (1980), pp. 4244–4245.
- [98] Stanislaw A Kucharski and Rodney J Bartlett. “Fifth-order many-body perturbation theory and its relationship to various coupled-cluster approaches”. In: *Advances in quantum chemistry*. Vol. 18. Elsevier, 1986, pp. 281–344.
- [99] Stanislaw A Kucharski, Jozef Noga, and Rodney J Bartlett. “Fifth-order many-body perturbation theory for molecular correlation energies”. In: *The Journal of Chemical Physics* 90.12 (1989), pp. 7282–7290.
- [100] Zhi He and Dieter Cremer. “Sixth-order many-body perturbation theory. I. Basic theory and derivation of the energy formula”. In: *International Journal of Quantum Chemistry* 59.1 (1996), pp. 15–29.
- [101] Zhi He and Dieter Cremer. “Sixth-order many-body perturbation theory. II. Implementation and application”. In: *International Journal of Quantum Chemistry* 59.1 (1996), pp. 31–55.
- [102] Zhi He and Dieter Cremer. “Sixth-order many-body perturbation theory. III. Correlation energies of size-extensive MP6 methods”. In: *International Journal of Quantum Chemistry* 59.1 (1996), pp. 57–69.
- [103] Dieter Cremer and Zhi He. “New developments in many body perturbation theory and coupled cluster theory”. In: *Conceptual Perspectives in Quantum Chemistry*. Springer, 1997, pp. 239–318.
- [104] C Van Alsenoy. “Ab initio calculations on large molecules: The multiplicative integral approximation”. In: *Journal of computational chemistry* 9.6 (1988), pp. 620–626.

- [105] Aquilante, Francesco and Lindh, Roland and Bondo Pedersen, Thomas. “Unbiased auxiliary basis sets for accurate two-electron integral approximations”. In: *The Journal of Chemical Physics* 127.11 (2007), p. 114107.
- [106] Aquilante, Francesco and Lindh, Roland and Pedersen, Thomas Bondo. “Analytic derivatives for the Cholesky representation of the two-electron integrals”. In: *The Journal of Chemical Physics* 129.3 (2008), p. 034106.
- [107] Uūr Bozkaya. “Orbital-optimized second-order perturbation theory with density-fitting and cholesky decomposition approximations: An efficient implementation”. In: *Journal of Chemical Theory and Computation* 10.6 (2014), pp. 2371–2378.
- [108] Crawford, T Daniel and Schaefer, Henry F. “An introduction to coupled cluster theory for Computational Chemists”. In: *Reviews in Computational Chemistry* 14 (2000), pp. 33–136.
- [109] Sven Thorwirth and Michael E Harding. “Coupled-cluster calculations of C(2)H(2)Si and CNHSi structural isomers”. In: *The Journal of Chemical Physics* 130.21 (2009), pp. 214–303.
- [110] Kucharski, Stanisław A and Włoch, Marta and Musiał, Monika and Bartlett, Rodney J. “Coupled-cluster theory for excited electronic states: The full equation-of-motion coupled-cluster single, double, and triple excitation method”. In: *Journal of Chemical Physics* 115.18 (2001), pp. 8263–8266. ISSN: 00219606. DOI: 10.1063/1.1416173.
- [111] Łoch, Marta W and Lodriguito, Maricris D and Piecuch, Piotr and Gour, Jeffrey R. “Two new classes of non-iterative coupled-cluster methods derived from the method of moments of coupled-cluster equations”. In: *Molecular Physics* 104.13-14 (2006), pp. 2149–2172.
- [112] Jeffrey R Gour, Piotr Piecuch, and Marta Włoch. “Active-space equation-of-motion coupled-cluster methods for excited states of radicals and other open-shell systems: EA-EOMCCSDt and IP-EOMCCSDt”. In: *The Journal of Chemical Physics* 123.13 (2005), p. 134113.

- [113] Karol Kowalski and Piotr Piecuch. “Extension of the method of moments of coupled-cluster equations to excited states: The triples and quadruples corrections to the equation-of-motion coupled-cluster singles and doubles energies”. In: *Journal of Chemical Physics* 116.17 (2002), pp. 7411–7423.
- [114] Mihály Kállay and Jürgen Gauss. “Calculation of excited-state properties using general coupled-cluster and configuration-interaction models”. In: *Journal of Chemical Physics* 121.19 (2004), pp. 9257–9269.
- [115] K Hirao and H Nakatsuji. “A generalization of the Davidson’s method to large nonsymmetric eigenvalue problems”. In: *Journal of Computational Physics* 45.2 (Feb. 1982), pp. 246–254. ISSN: 10902716. DOI: 10.1016/0021-9991(82)90119-X. URL: <http://www.sciencedirect.com/science/article/pii/002199918290119X>.
- [116] Hendrik J Monkhorst. “Calculation of properties with the coupled-cluster method”. In: *International Journal of Quantum Chemistry* 12.S11 (1977), pp. 421–432.
- [117] Rodney J Bartlett. “Analytical evaluation of gradients in coupled-cluster and many-body perturbation theory”. In: *Geometrical Derivatives of Energy Surfaces and Molecular Properties*. Springer, 1986, pp. 35–61.
- [118] U Sinha Mahapatra, B Datta, and D Mukherjee. “A state-specific multi-reference coupled cluster formalism with molecular applications”. In: *Molecular Physics* 94.1 (1998), pp. 157–171.
- [119] J Meller, JP Malrieu, and R Caballol. “State-specific coupled cluster-type dressing of multireference singles and doubles configuration interaction matrix”. In: *The Journal of Chemical Physics* 104.11 (1996), pp. 4068–4076.
- [120] Sourav Pal. “Multireference coupled-cluster response approach for the calculation of static properties”. In: *Phys. Rev. A* 39 (1 Jan. 1989), pp. 39–42. DOI: 10.1103/PhysRevA.39.39. URL: <https://link.aps.org/doi/10.1103/PhysRevA.39.39>.
- [121] Sourav Pal. “An open-shell coupled-cluster response method for static properties”. In: *International journal of quantum chemistry* 41.3 (1992), pp. 443–452.
- [122] D Ajitha and Sourav Pal. “Time-dependent multireference coupled-cluster-based response approach for evaluating dynamic properties”. In: *Physical Review A* 56.4 (1997), p. 2658.

- [123] D Ajitha and Sourav Pal. “Dipole moments of open-shell radicals using an analytic linear response approach in the Fock space multi-reference coupled cluster method”. In: *Chemical Physics Letters* 309.5-6 (1999), pp. 457–462.
- [124] D Ajitha and Sourav Pal. “Dipole moments of adiabatic excited states using the Fock space multireference coupled-cluster analytic response approach”. In: *The Journal of Chemical Physics* 114.8 (2001), pp. 3380–3384.
- [125] Ajitha Devarajan and Sourav Pal. “Z-vector formalism for the Fock space multireference coupled cluster method: Elimination of the response of the highest valence sector amplitudes”. In: *The Journal of Chemical Physics* 111 (Sept. 1999), pp. 3832–3836. DOI: 10.1063/1.479686.
- [126] Péter G Szalay. “Analytic energy derivatives for coupled-cluster methods describing excited states: General formulas and comparison of computational costs”. In: *International Journal of Quantum Chemistry* 55.2 (1995), pp. 151–163.
- [127] KR Shamasundar, Subashini Asokan, and Sourav Pal. “A constrained variational approach for energy derivatives in Fock-space multireference coupled-cluster theory”. In: *The Journal of Chemical Physics* 120.14 (2004), pp. 6381–6398.
- [128] Marcel Nooijen and Rodney J Bartlett. “Similarity transformed equation-of-motion coupled-cluster study of ionized, electron attached, and excited states of free base porphyrin”. In: *The Journal of Chemical Physics* 106.15 (1997), pp. 6449–6455.
- [129] Robert G Parr. “Density functional theory of atoms and molecules”. In: *Horizons of Quantum Chemistry*. Springer, 1980, pp. 5–15.
- [130] Erich Runge and Eberhard KU Gross. “Density-functional theory for time-dependent systems”. In: *Physical Review Letters* 52.12 (1984), p. 997.
- [131] John F Stanton and Jurgen Gauss. “A discussion of some problems associated with the quantum mechanical treatment of open-shell molecules”. In: *Advances in Chemical Physics* 125 (2003), pp. 101–146.
- [132] Larsen, Helena and Hald, Kasper and Olsen, Jeppe and Jørgensen, Poul. “Triplet excitation energies in full configuration interaction and coupled-cluster theory”. In: *Journal of Chemical Physics* 115.7 (2001), pp. 3015–3020. ISSN: 0021-9606. DOI: 10.1063/1.1386415.

- [133] John F Stanton, Jürgen Gauss, and John F Stanton. “Perturbative treatment of the similarity transformed Hamiltonian in equation of motion coupled cluster approximations Perturbative treatment of the similarity transformed Hamiltonian in equation-of-motion coupled-cluster approximations”. In: *The Journal of Chemical Physics* 1064.1995 (2015), pp. 1063–1076. DOI: 10.1063/1.469817.
- [134] Per Olov Löwdin. “Studies in perturbation theory. Part I. An elementary iteration-variation procedure for solving the Schrödinger equation by partitioning technique”. In: *Journal of Molecular Spectroscopy* 10.1-6 (Jan. 1963), pp. 12–33. ISSN: 1096083X. DOI: 10.1016/0022-2852(63)90151-6. URL: <http://www.sciencedirect.com/science/article/pii/0022285263901516>.
- [135] Y. Shao and Z. Gan and E. Epifanovsky and A. T. B. Gilbert and M. Wormit and J. Kussmann and A. W. Lange and A. Behn and J. Deng and X. Feng and D. Ghosh and M. Goldey and P. R. Horn and L. D. Jacobson and I. Kaliman and R. Z. Khaliullin and T. Kúš and A. Landau and J. Liu and E. I. Proynov and Y. M. Rhee and R. M. Richard and M. A. Rohrdanz and R. P. Steele and E. J. Sundstrom and H. L. Woodcock III and P. M. Zimmerman and D. Zuev and B. Albrecht and E. Alguire and B. Austin and G. J. O. Beran and Y. A. Bernard and E. Berquist and K. Brandhorst and K. B. Bravaya and S. T. Brown and D. Casanova and C.-M. Chang and Y. Chen and S. H. Chien and K. D. Closser and D. L. Crittenden and M. Diedenhofen and R. A. DiStasio Jr. and H. Dop and A. D. Dutoi and R. G. Edgar and S. Fatehi and L. Fusti-Molnar and A. Ghysels and A. Golubeva-Zadorozhnaya and J. Gomes and M. W. D. Hanson-Heine and P. H. P. Harbach and A. W. Hauser and E. G. Hohenstein and Z. C. Holden and T.-C. Jagau and H. Ji and B. Kaduk and K. Khistyayev and J. Kim and J. Kim and R. A. King and P. Klunzinger and D. Kosenkov and T. Kowalczyk and C. M. Krauter and K. U. Lao and A. Laurent and K. V. Lawler and S. V. Levchenko and C. Y. Lin and F. Liu and E. Livshits and R. C. Lochan and A. Luenser and P. Manohar and S. F. Manzer and S.-P. Mao and N. Mardirossian and A. V. Marenich and S. A. Maurer and N. J. Mayhall and C. M. Oana and R. Olivares-Amaya and D. P. O’Neill and J. A. Parkhill and T. M. Perrine and R. Peverati and P. A. Pieniazek and A. Prociuk and D. R. Rehn and E. Rosta and N. J. Russ and N. Sergueev and

- S. M. Sharada and S. Sharma and D. W. Small and A. Sodt and T. Stein and D. Stück and Y.-C. Su and A. J. W. Thom and T. Tsuchimochi and L. Vogt and O. Vydrov and T. Wang and M. A. Watson and J. Wenzel and A. White and C. F. Williams and V. Vanovschi and S. Yeganeh and S. R. Yost and Z.-Q. You and I. Y. Zhang and X. Zhang and Y. Zhou and B. R. Brooks and G. K. L. Chan and D. M. Chipman and C. J. Cramer and W. A. Goddard III and M. S. Gordon and W. J. Hehre and A. Klamt and H. F. Schaefer III and M. W. Schmidt and C. D. Sherrill and D. G. Truhlar and A. Warshel and X. Xua and A. Aspuru-Guzik and R. Baer and A. T. Bell and N. A. Besley and J.-D. Chai and A. Dreuw and B. D. Dunietz and T. R. Furlani and S. R. Gwaltney and C.-P. Hsu and Y. Jung and J. Kong and D. S. Lambrecht and W. Liang and C. Ochsenfeld and V. A. Rassolov and L. V. Slipchenko and J. E. Subotnik and T. Van Voorhis and J. M. Herbert and A. I. Krylov and P. M. W. Gill and M. Head-Gordon. “Advances in molecular quantum chemistry contained in the Q-Chem 4 program package”. In: *Molecular Physics* 113.2 (2015), pp. 184–215. DOI: 10.1080/00268976.2014.952696. eprint: <https://doi.org/10.1080/00268976.2014.952696>. URL: <https://doi.org/10.1080/00268976.2014.952696>.
- [136] Aidas, Kestutis and Angeli, Celestino and Bak, Keld L and Bakken, Vebjørn and Bast, Radovan and Boman, Linus and Christiansen, Ove and Cimiraglia, Renzo and Coriani, Sonia and Dahle, Pål and Dalskov, Erik K and Ekström, Ulf and Enevoldsen, Thomas and Eriksen, Janus J and Ettenhuber, Patrick and Fernández, Berta and Ferrighi, Lara and Fliegl, Heike and Frediani, Luca and Hald, Kasper and Halkier, Asger and Hättig, Christof and Heiberg, Hanne and Helgaker, Trygve and Hennum, Alf Christian and Hettema, Hinne and Hjertenæs, Eirik and Høst, Stinne and Høyvik, Ida Marie and Iozzi, Maria Francesca and Jansík, Branislav and Jensen, Hans Jørgen Aa and Jonsson, Dan and Jørgensen, Poul and Kauczor, Joanna and Kirpekar, Sheela and Kjærgaard, Thomas and Klopper, Wim and Knecht, Stefan and Kobayashi, Rika and Koch, Henrik and Kongsted, Jacob and Krapp, Andreas and Kristensen, Kasper and Ligabue, Andrea and Lutnæs, Ola B. and Melo, Juan I and Mikkelsen, Kurt V and Myhre, Rolf H and Neiss, Christian and Nielsen, Christian B and Norman, Patrick and Olsen, Jeppe and Olsen, Jógvan

- Magnus H and Osted, Anders and Packer, Martin J and Pawlowski, Filip and Pedersen, Thomas B and Provasi, Patricio F and Reine, Simen and Rinkevicius, Zilvinas and Ruden, Torgeir A and Ruud, Kenneth and Rybkin, Vladimir V and Sałek, Pawel and Samson, Claire C.M. and de Merás, Alfredo Sánchez and Saue, Trond and Sauer, Stephan P.A. and Schimmelpfennig, Bernd and Sneskov, Kristian and Steindal, Arnfinn H and Sylvester-Hvid, Kristian O and Taylor, Peter R and Teale, Andrew M and Tellgren, Erik I and Tew, David P and Thorvaldsen, Andreas J and Thøgersen, Lea and Vahtras, Olav and Watson, Mark A and Wilson, David J.D. and Ziolkowski, Marcin and Ågren, Hans. “The Dalton quantum chemistry program system”. In: *Wiley Interdisciplinary Reviews: Computational Molecular Science* 4.3 (2014), pp. 269–284. ISSN: 17590884. DOI: 10.1002/wcms.1172. URL: <http://dx.doi.org/10.1002/wcms.1172>.
- [137] Furche, Filipp and Ahlrichs, Reinhart and Hättig, Christof and Klopper, Wim and Sierka, Marek and Weigend, Florian. “Turbomole”. In: *Wiley Interdisciplinary Reviews: Computational Molecular Science* 4.2 (2014), pp. 91–100. ISSN: 1759-0884. DOI: 10.1002/wcms.1162. URL: <http://dx.doi.org/10.1002/wcms.1162>.
- [138] Frank Neese. “The ORCA program system”. In: *Wiley Interdisciplinary Reviews: Computational Molecular Science* 2.1 (2012), pp. 73–78. ISSN: 17590876. DOI: 10.1002/wcms.81. URL: <http://dx.doi.org/10.1002/wcms.81>.
- [139] Schreiber, Marko and Silva-Junior, Mario R and Sauer, Stephan P.A. and Thiel, Walter. “Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3”. In: *Journal of Chemical Physics* 128.13 (2008), p. 134110. ISSN: 00219606. DOI: 10.1063/1.2889385. URL: <http://scitation.aip.org/content/aip/journal/jcp/128/13/10.1063/1.2889385>.
- [140] Dutta, Achintya Kumar and Vaval, Nayana and Pal, Sourav. “EOMIP-CCSD (2) : An Efficient N_5 Scaling Method For Structure and Properties of Doublet Radicals”. In: *Journal of Chemical Theory and Computation* 10.2 (2014), pp. 1923–1933. ISSN: 1549-9618.
- [141] Huels, Michael A and Hahndorf, Ina and Illenberger, Eugen and Sanche, Léon. “Resonant dissociation of DNA bases by subionization electrons”. In: *Journal of*

- Chemical Physics* 108.4 (1998), pp. 1309–1312. ISSN: 00219606. DOI: 10.1063/1.475503.
- [142] T E Wheldon. *Radiation physics and genetic targeting: New directions for radiotherapy: The Douglas Lea lecture 1999*. 2000. DOI: 10.1088/0031-9155/45/7/201. URL: <http://stacks.iop.org/0031-9155/45/i=7/a=201>.
- [143] Gary B Schuster. “Long-range charge transfer in DNA: Transient structural distortions control the distance dependence”. In: *Accounts of Chemical Research* 33.4 (2000), pp. 253–260. ISSN: 00014842. DOI: 10.1021/ar980059z. URL: <http://dx.doi.org/10.1021/ar980059z>.
- [144] Holmlin, R Erik and Dandliker, Peter J and Barton, Jacqueline K. *Charge Transfer through the DNA Base Stack*. 1997. DOI: 10.1002/anie.199727141. URL: <http://dx.doi.org/10.1002/anie.199727141>.
- [145] Crespo-Hernández, Carlos E. and Close, David M and Gorb, Leonid and Leszczynski, Jerzy. “Determination of redox potentials for the Watson-crick base pairs, DNA nucleosides, and relevant nucleoside analogues”. In: *Journal of Physical Chemistry B* 111.19 (2007), pp. 5386–5395. ISSN: 15206106. DOI: 10.1021/jp0684224. URL: <http://dx.doi.org/10.1021/jp0684224>.
- [146] Jiande Gu, Yaoming Xie, and Henry F. Schaefer. “Understanding electron attachment to the DNA double helix: The thymidine monophosphate-adenine pair in the gas phase and aqueous solution”. In: *Journal of Physical Chemistry B* 110.39 (2006), pp. 19696–19703. ISSN: 15206106. DOI: 10.1021/jp064852i. URL: <http://dx.doi.org/10.1021/jp064852i>.
- [147] Xifeng Li, Zhongli Cai, and Michael D. Sevilla. “DFT calculations of the electron affinities of nucleic acid bases: Dealing with negative electron affinities”. In: *Journal of Physical Chemistry A* 106.8 (2002), pp. 1596–1603. ISSN: 10895639. DOI: 10.1021/jp013337b. URL: <http://dx.doi.org/10.1021/jp013337b>.
- [148] D Mariano A Vera and Adriana B Pierini. “Species with negative electron affinity and standard DFT methods”. In: *Physical Chemistry Chemical Physics* 6.11 (2004), pp. 2899–2903. ISSN: 14639076. DOI: 10.1039/b403898c. URL: <http://dx.doi.org/10.1039/B403898C>.

- [149] Roca-Sanjuán, Daniel and Merchán, Manuela and Serrano-Andrés, Luis and Rubio, Mercedes. “Ab initio determination of the electron affinities of DNA and RNA nucleobases”. In: *Journal of Chemical Physics* 129.9 (2008), p. 95104. ISSN: 00219606. DOI: 10.1063/1.2958286. URL: <http://scitation.aip.org/content/aip/journal/jcp/129/9/10.1063/1.2958286>.
- [150] Dedíková, Pavlína and Demovič, Lukáš and Pitoňák, Michal and Neogrady, Pavel and Urban, Miroslav. “CCSD(T) calculations of the electron affinity of the uracil molecule”. In: *Chemical Physics Letters* 481.1-3 (Oct. 2009), pp. 107–111.
- [151] Bravaya, Ksenia B and Kostko, Oleg and Dolgikh, Stanislav and Landau, Arie and Ahmed, Musahid and Krylov, Anna I. “Electronic structure and spectroscopy of nucleic acid bases: Ionization energies, ionization-induced structural changes, and photoelectron spectra”. In: *Journal of Physical Chemistry A* 114.46 (2010), pp. 12305–12317. ISSN: 10895639. DOI: 10.1021/jp1063726. URL: <http://dx.doi.org/10.1021/jp1063726>.
- [152] Ksenia B Bravaya, Evgeny Epifanovsky, and Anna I Krylov. “Four bases score a run: Ab initio calculations quantify a cooperative effect of H-bonding and π -stacking on the ionization energy of adenine in the AATT tetramer”. In: *Journal of Physical Chemistry Letters* 3.18 (2012), pp. 2726–2732. ISSN: 19487185. DOI: 10.1021/jz3011139. URL: <http://dx.doi.org/10.1021/jz3011139>.
- [153] Anna A Golubeva and Anna I Krylov. “The effect of π -stacking and H-bonding on ionization energies of a nucleobase: Uracil dimer cation”. In: *Physical Chemistry Chemical Physics* 11.9 (2009), pp. 1303–1311. ISSN: 14639076. DOI: 10.1039/b817284f. URL: <http://dx.doi.org/10.1039/B817284F>.
- [154] Bravaya, Ksenia B and Kostko, Oleg and Ahmed, Musahid and Krylov, Anna I. “The effect of π -stacking, H-bonding, and electrostatic interactions on the ionization energies of nucleic acid bases: Adenine-adenine, thymine-thymine and adenine-thymine dimers”. In: *Physical Chemistry Chemical Physics* 12.10 (2010), pp. 2292–2307. ISSN: 14639076. DOI: 10.1039/b919930f. URL: <http://dx.doi.org/10.1039/B919930F>.

- [155] Dutta, Achintya Kumar and Sengupta, Turbasu and Vaval, Nayana and Pal, Sourav. "Electron attachment to DNA and RNA nucleobases: An EOMCC investigation". In: *International Journal of Quantum Chemistry* 115.12 (2015), pp. 753–764. ISSN: 1097461X. DOI: 10.1002/qua.24892. URL: <http://dx.doi.org/10.1002/qua.24892>.
- [156] K. Aflatooni, G. A. Gallup, and P. D. Burrow. "Electron attachment energies of the DNA bases". In: *Journal of Physical Chemistry A* 102.31 (1998), pp. 6205–6207. ISSN: 10895639. DOI: 10.1021/jp980865n. URL: <http://dx.doi.org/10.1021/jp980865n>.
- [157] Periquet, V and Moreau, A and Carles, S and Schermann, J.P. and Desfrancois, C. "Cluster size effects upon anion solvation of N-heterocyclic molecules and nucleic acid bases". In: *Journal of Electron Spectroscopy and Related Phenomena* 106.2-3 (Feb. 2000), pp. 141–151. ISSN: 03682048. DOI: 10.1016/S0368-2048(99)00072-9. URL: <http://www.sciencedirect.com/science/article/pii/S0368204899000729>.
- [158] S Harinipriya and M V Sangaranarayanan. "Estimation of the electron affinities of nucleobases using thermochemical data and structural considerations". In: *Journal of Molecular Structure* 644.1-3 (Jan. 2003), pp. 133–138. ISSN: 00222860. DOI: 10.1016/S0022-2860(02)00469-6. URL: <http://www.sciencedirect.com/science/article/pii/S0022286002004696>.
- [159] Jiande Gu, Jerzy Leszczynski, and Henry F. Schaefer. *Interactions of electrons with bare and hydrated biomolecules: From nucleic acid bases to DNA segments*. 2012. DOI: 10.1021/cr3000219. URL: <http://dx.doi.org/10.1021/cr3000219>.
- [160] Marcel Nooijen and Rodney J Bartlett. "Description of core-excitation spectra by the open-shell electron-attachment equation-of-motion coupled cluster method". In: *The Journal of Chemical Physics* 102.17 (1995), pp. 6735–6756.
- [161] John F Stanton and Jürgen Gauss. "Analytic energy derivatives for ionized states described by the equation-of-motion coupled cluster method". In: *The Journal of Chemical Physics* 101.10 (1994), pp. 8938–8944.

- [162] D. S. N. Parker, A. M. Mebel, and R. I. Kaiser. “The role of isovalency in the reactions of the cyano (CN), boron monoxide (BO), silicon nitride (SiN), and ethynyl (C₂H) radicals with unsaturated hydrocarbons acetylene (C₂H₂) and ethylene (C₂H₄)”. In: *Chem. Soc. Rev.* 43 (8 2014), pp. 2701–2713. DOI: 10.1039/C3CS60328H. URL: <http://dx.doi.org/10.1039/C3CS60328H>.
- [163] Szalay, Péter G. and Thøgersen, Lea S. and Olsen, Jeppe and Kállay, Mihály and Gauss, Jörgen. “Equilibrium Geometry of the Ethynyl (CCH) Radical”. In: *The Journal of Physical Chemistry A* 108.15 (2004), pp. 3030–3034. DOI: 10.1021/jp036885t. eprint: <https://doi.org/10.1021/jp036885t>. URL: <https://doi.org/10.1021/jp036885t>.
- [164] Thom H. Dunning Jr. “Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen”. In: *The Journal of Chemical Physics* 90 (1989), p. 1007.
- [165] Thom H. Dunning Jr. “Electron affinities of the first row atoms revisited. Systematic basis sets and wave functions”. In: *The Journal of Chemical Physics* 96 (1992), p. 6796.
- [166] David E. Woon and Thom H. Dunning Jr. “Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon”. In: *The Journal of Chemical Physics* 98 (1993), p. 1358.
- [167] Schmidt, Michael W. and Baldridge, Kim K. and Boatz, Jerry A. and Elbert, Steven T. and Gordon, Mark S. and Jensen, Jan H. and Koseki, Shiro and Matsunaga, Nikita and Nguyen, Kiet A. and Su, Shujun and Windus, Theresa L. and Dupuis, Michel and Montgomery Jr, John A. “General atomic and molecular electronic structure system”. In: *Journal of Computational Chemistry* 14.11 (1993), pp. 1347–1363. DOI: 10.1002/jcc.540141112.
- [168] Lim, Ivan S and Pernpointner, Markus and Seth, Michael and Laerdahl, Jon K and Schwerdtfeger, Peter and Neogrady, Pavel and Urban, Miroslav. “Relativistic coupled-cluster static dipole polarizabilities of the alkali metals from Li to element 119”. In: *Physical Review A* 60.4 (1999), p. 2822.

-
- [169] Kállay, Mihály and Gauss, Jürgen. “Calculation of frequency-dependent polarizabilities using general coupled-cluster models”. In: *Journal of Molecular Structure: THEOCHEM* 768.1-3 (2006), pp. 71–77.
- [170] Jørgensen, Poul and Helgaker, Trygve. “Møller–Plesset energy derivatives”. In: *The Journal of Chemical Physics* 89.3 (1988), pp. 1560–1570.



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>