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BOUMEFTAH Mohamed El Amine

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President	Kadari Rekia	*Dr*	*University of Saida*
Supervisor	Reinhold Fink	*Prof*	*University of Tübingen*
Supervisor	Rahmouni Ali	*Prof*	*University of Saida*
Examiner	Mostefai Asmaa	*Prof*	*University of Saida*

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Abstract

To directly assess the accuracy of modern hybrid perturbation theory for calculating dipole moments, the perturbation theory wavefunction methods REMP, and OO-REMP are benchmarked by computing the dipole moments of 19 small molecules compared to CCSD(T) method. REMP is constructed by choosing the zeroth-order Hamiltonian $\hat{H}^{(0)}$ as (1–A)-times the retaining the excitation degree (RE) $\hat{H}^{(0)}$ plus A-times the Møller Plesset (MP) $\hat{H}^{(0)}$. While OO-REMP is an orbital optimized variant of REMP.
Evaluating the dipole moments using 40 values of A for REMP and OO REMP, optimal A-parameters could be suggested as confined $A_{opt}(REMP) \in [0.15, 0.35]$ and $A_{opt}(OO-REMP) \in [0.13, 0.25]$. For these A-parameters REMP and OO-REMP performed similarly to CCSD(T), "the gold standard" of computational chemistry. Hereby OO-REMP outperforms REMP in most cases. When comparing REMP and OO-REMP, OO-REMP performs only a cut above REMP but is computationally significantly more expensive. Thus analytical gradients for REMP would lower run times while retaining almost the same quality as OO-REMP.

résumé

Pour évaluer directement la précision de la théorie des perturbations hybride moderne pour le calcul des moments dipolaires, les méthodes de fonction d'onde de la théorie des perturbations REMP et OO-REMP sont comparées en calculant les moments dipolaires de 19 petites molécules par rapport à la méthode CCSD(T). REMP est construit en choisissant l'hamiltonien d'ordre zéro $\hat{H}^{(0)}$ comme (1–A) fois degré d'excitation retenu (RE) $\hat{H}^{(0)}$ plus A-fois Møller Plesset (MP) $\hat{H}^{(0)}$. Alors que OO-REMP est une variante orbitale optimisée de REMP.
En évaluant les moments dipolaires pour 40 valeurs de A pour REMP et OO REMP, les paramètres A optimaux pourraient être suggérés comme confinés $A_{opt}(REMP) \in [0,15, 0,35]$ et $A_{opt}(OO–REMP) \in [0.13, 0.25]$. Pour ces paramètres A, REMP et OO-REMP ont fonctionné de la même manière que CCSD(T), « l'étalon-or » de la chimie computationnelle. Par la présente, OO-REMP surpasse REMP dans la plupart des cas. Lorsque l'on compare REMP et OO-REMP, OO-REMP n'exécute qu'une coupe au-dessus de REMP mais est beaucoup plus coûteux en termes de calcul. Ainsi, les gradients analytiques pour REMP réduiraient les temps d'exécution tout en conservant presque la même qualité que OO-REMP.

ملخص

لتقييم دقة نظرية الاضطراب الهجينة الحديثة REMP في التنبؤ بالخصائص الكهربائية للجزيئات ، تم اختبار دالة الموجة لنظرية الاضطراب REMP و OO-REMP عن طريق حساب العزوم ثنائية القطب و التي تعد من الخصاص الكهربائية الاكثر سهولة من الناحية الحسابية و لها علاقة مباشرة بالكثافة الالكترونية و من خلالها يتم حساب هذه العزوم.

ترتكز REMP اساسا على اختيار الهاميلتوني ذو الترتيب الصفري $\widehat{H}^{(0)}$ كـ (A – 1) - مرات الاحتفاظ بدرجة الإثارة (RE) و A-مرات من Møller Plesset (MP). بينما OO-REMP هو التحسين المداري الأمثل لـ REMP.

قمنا بحساب العزوم ثنائية القطب لـ 19 جزيء صغير بواسطة REMP و 10 بواسطة OO-REMP باستعمال القاعدة aug-cc-pCVQZ و 40 قيمة من المعلمة A لكلتى الطريقتين و تمت مقارنة النتائج المحصل عليها بالنتائج المحصل عليها بطريقة CCSD(T).

تم تقييم العزوم ثنائية القطب باستخدام 40 قيمة من A لـ REMP و OO-REMP ، يمكن اقتراح معلمات A المثلى على أنها محصورة [0.35 ، 0.15]∈ A(REMP) و [0.25 ،0.13]∈ A(OO-REMP). بالنسبة لهذه القيم من المعلمات A ، كانت نتائج REMP و OO-REMP تقريبا مشابهة لنتائج CCSD (T)، "المعيار الذهبي" للكيمياء الحسابية. و ايضا يمكننا ملاحظة تفوق OO-REMP على REMP في معظم الحالات. عند مقارنة REMP و OO-REMP ، فرغم تفوق OO-REMP على REMP من ناحية الدقة بمقدار ضئيل ولكنه أكثر تكلفة من الناحية الحسابية. وبالتالي ، فإن التدرجات الحسابية لـ REMP ستقلل من أوقات التشغيل مع الاحتفاظ تقريبًا بنفس جودة OO-REMP.

Contents

List of Figures

List of Tables

Abbreviations

The next list describes several abbreviations that will be later used within the body of the document

Aug-cc-pCVQZ Augmented Correlation-Consistent Polarized Core Valence-only Quadruple Zeta

CCSD(T) Coupled Cluster Singles Doubles with many body perturbation theory Triples

CI Configuration Interaction

CSFs Configuration State Functions

DFT Density Functional Theory

HF Hartree-Fock

MB-PT Many-Body Perturbation Theory

MP-PT Moller-Plesset Perturbation Theory

MP2 second-order Moller-Plesset

OCEPA(0) Optimized Coupled Electron Pair Approximation variant 0

OO-MP2 Orbital Optimized second-order Møller Plesset

OO-REMP Orbital Optimized Retaining the Excitation degree and Møller Plesset

Post-HF Post-Hartree-Fock

RE-PT Retaining the Excitation degree Perturbation Theory

REMP Retaining the Excitation degree and Møller Plesset

RMSE Root Mean Square Error

RS-PT Reyleigh-Schrodinger Perturbation Theory

SCF Self Consistent Field

SCS-MP2 Spin Component Scaled second order Møller Plesset

SDE Singlet-coupled Double Excitation

TDE Triplet-coupled Double Excitation

Introduction

One of the most widely exercised applications in quantum chemistry is the calculation of molecular electric moments, polarization, and electrostatic potentials [1]. The electric properties of molecules have importance across all the branches of chemistry. The electric moments are essential to provide simple ways to figure out the electric field behavior of complex molecules. These electrical properties provide also information about molecular symmetry since the electric moments depend on the geometry and charge distribution of the molecule [2]. The molecular dipole polarizability is in turn related to the transition moment from the electronic ground state to the excited states. This quantity reflects how easily the excited states can be mixed into the ground state when the system is perturbed by an external electric field.
Dipole moments can be measured precisely by a variety of experimental methods, and are available for many molecules [3, 4, 5]. Also, the theoretical approaches give a good prediction for dipole moments of any molecule synthetic or not. Among these methods, there are post-Hartree-Fock methods [5]. There are different types of post-Hartree-Fock methods and the common ones are the Møller-Plesset perturbation theory (MP-PT) and the coupled-cluster method [6]. Møller-Plesset perturbation theory (MP-PT) also known as many-body perturbation theory (MB-PT) [7]. In MP theory the Hamiltonian is partitioned so that the Zeroth-order part (unperturbed Hamiltonian) is defined as the Fock-operator [8, 9, 10]. Advantages of the MP perturbation theory are the size consistency and the property of being invariant in respect to unitary orbital transformation. Various modifications of MP, such as the spin-component-scaled SCS-MP2 [7, 11, 12] and the orbital optimised second-order Møller Plesset theory (OO-MP2)[13, 14, 15, 16], have been devloped to resolve the flaws of this perturbation theory, in which difficulty has been found in manipulating systems with crowded electron pairs such as late transition metals as well as in the discrete example of the new atom, where the disordered chain diverges [17].
There is also another post-Hartree-Fock method called Retaining The Excitation Degree perturbation theory (RE-PT). The complete Hamiltonian contains terms that maintain the degree of excitation which modifies it, in this theory the $\hat{H}^{(0)}$ contains all the terms of the complete hamiltonian which preserves the degree of excitation [18]. Contrary to MP theory, RE is composed of non-

diagonal elements within the base of the exciting slater determinants. A linear combination between these two methods MP and RE gives a new theoretical approach which is called REMP developed by Behnle and Fink [19], where $\hat{H}^{(0)}$ consists of $(1-A)\hat{H}^{(0)}_{RE}$ and $A\hat{H}^{(0)}_{MP}$ with A is the mixing parameter $A \in [0.1]$. To go further in the approximation of the correlation energy the two authors developed the orbital optimized variant of REMP (OO-REMP) method, where it is an improvement of the REMP2, which was implemented as described for the parent's methods OO-MP2 and OCEPA(0) by Bozkaya [20, 14].
In order to verify the performance of these two approaches to predict the electrical properties of molecules, we calculated the dipole moment with two methods, numerical and analytical of a set of 19 molecules with the two methods REMP and OO-REMP respectively, using the same basis set and the geometries of the molecules which were used by Diptarka Hait and Martin Head-Gordon [21]. We compared our results with their results evaluated by the method CCSD(T).

Chapter I

Theoretical Approaches

I.1 Post-Hartree_Fock methods

In computational chemistry [22, 23] quantum mechanics is the main method for modeling a physical system. Thus to resolve Schrodinger equation of a many-body system there are several methods at different approximation levels, Hartree-Fock, post-Hartree-Fock methods, Density Fonctional Theory (DFT).
The post-Hartree_Fock methods (Post-HF) are improvements of the Hartree-fock (HF) method, or Self Consistent Field (SCF) which does not take into account the total electron-electron repulsion [24, 25], therfore the repulsions between the electrons are completed by including an electronic correlation which may be a more accurate way, than within the Hartree_Fock method where repulsions are only averaged.
The correlation energy is defined as the difference between the true energy and the Hartree_Fock energy in a complete basis "Hartree_Fock limit" .

$$E_{corr} = E_{exact} - E_{HF}^{\infty} \tag{I.1}$$

There are different types of post-Hartree_Fock methods and the common ones are Møller-Plesset perturbation theory (MP) and coupled-cluster method. These two methods have become the most used ones in quantum chemistry.

I.1.1 Moller-Plesset Perturbation Theory

Moller-Plesset Perturbation theory (MP-PT), also called many-body perturbation theory [26] could be a widely used method for approximating the correlation energy of molecules especially the second-order Moller-Plesset perturbation theory (MP2) which is one among the most useful levels of theory beyond the Hartree_Fock approximation [27]. The MP2 improves on the HF method by adding electron correlation effects through Rayleigh_Schrodinger perturbation theory (RS-PT) [8].
The MP perturbation theory is based on Rayleigh_Schrodinger perturbation theory (RS-PT). In MP theory the Hameltonian is partitioned so that the Zeroth-order part $\hat{H}^{(0)}$ is the sum of one electron Fock operators (unperturbed part) [9], to which a small often externel perturbation V is added , which is the correlation potential.

$$\hat{H} = \hat{H}^{(0)} + \lambda V \tag{I.2}$$

where λ is an arbitrary real parameter that controls the size of the perturbation.

$$\hat{H}_{MP}^{(0)} = \hat{F} = \hat{h} + \hat{J} - \hat{K} = \sum_{p,q} F_{p,q} \hat{a}_p^{\dagger} \hat{a}_q \tag{I.3}$$

Expanding the exact wave function and the energy as

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + ... \tag{I.4}$$

and

$$\Psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \lambda^3\psi^{(3)} + ... \tag{I.5}$$

Substituting these expansions into the Schrodinger equation and collecting terms according to power of λ yields

$$H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \tag{I.6}$$

$$H^{(0)}\psi^{(0)} + V\psi^{(0)} = E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)} \tag{I.7}$$

$$H^{(0)}\psi^{(2)} + V\psi^{(1)} = E^{(0)}\psi^{(2)} + E^{(1)}\psi^{(1)} + E^{(2)}\psi^{(0)} \tag{I.8}$$

Multiplying each of the above equations by $\Psi^{(0)}$ and integrating over all space yields the following expression for the nth-order (MPn) energy:

$$E^{(0)} = \langle\psi^{(0)}|H^{(0)}|\psi^{(0)}\rangle \tag{I.9}$$

$$E^{(1)} = \langle\psi^{(0)}|V|\psi^{(0)}\rangle \tag{I.10}$$

$$E^{(2)} = \langle\psi^{(0)}|V|\psi^{(1)}\rangle \tag{I.11}$$

Thus, the Hartree-Fock energy

$$E_0 = \langle\psi^{(0)}|H^{(0)} + V|\psi^{(0)}\rangle \tag{I.12}$$

E_0 is simply the sum of the zeroth- and first-order energies

$$E_0 = E^{(0)} + E^{(1)} \tag{I.13}$$

The correlation energy can then be written as follow:

$$E_{corr} = E_0^{(2)} + E_0^{(3)} + E_0^{(4)} + ... \tag{I.14}$$

where the first term is the MP2 energy [10].
It can be shown that the MP2 energy can be written (in terms of spin-orbitals) as

$$E_0^{(2)} = -\frac{1}{4}\sum_{ab}^{vert}\sum_{ij}^{occ}\frac{|\langle ab||ij\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \tag{I.15}$$

where

$$\langle ab||ij\rangle = \langle ab|ij\rangle - \langle ab|ji\rangle \tag{I.16}$$

and

$$\langle ab|cd\rangle = \int \psi_a^*(r_1)\psi_b^*(r_2)[\frac{1}{r_{12}}]\psi_c(r_1)\psi_d(r_2)dr_1dr_2 \tag{I.17}$$

The second-order Moller-Plesset (MP2) energy is an effective correction of the hartree-Fock ground state energy that take account in to electron correlation effects, and it's the simplest and least expensive way of incorporating electron correlation effects in ab-initio electronic structure calculation [28].Typically accounts for 80%-90% of the correlation energy [7].

I.1.2 Retaining the Excitation Degree Perturbation theory (RE)

In this theory ,the electronic Hamiltonian is considered in its second quantization representation [29].

$$\hat{H} = \sum_{ab} h_{ab}\hat{a}_a^\dagger\hat{a}_b + \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_d\hat{a}_c \tag{I.18}$$

This full Hamiltonian contains some terms that maintain the Excitation Degree that change it, e.g the one particle contribution $h_{ab}\hat{a}_a^\dagger\hat{a}_b$ with the spin-orbitals a and b belonging both to the occupied and to the virtual orbitals maintaining n_{ex}. The author [18] propose in this theory named Retaining the Excitation degree perturbation theory (RE-PT) to set $\hat{H}^{(0)}$ to all terms of the full Hamiltonian which retain the excitation degree [18].

$$\hat{H}_{RE}^{(0)} = \sum_{ab,\Delta n_{ex}=0} h_{ab}\hat{a}_a^\dagger\hat{a}_b + \frac{1}{2}\sum_{abcd,\Delta n_{ex}=0}\langle ab|cd\rangle\hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_d\hat{a}_c \tag{I.19}$$

where h_{ab} is a matrix element of the one-particle operator.
Differently with MP theory $\hat{H}_{RE}^{(0)}$ consiste non-diagonal elements within the basis of the excited Slater determinants [19].
The second-order RE2 provides excelent correlation energies, and it's scales as N^6.

I.1.3 REMP Perturbation Theory

REMP is a new hybrid perturbation theory, it's an approach to the electron correlation energy by choosing the Zeroth-order Hamiltonian as a linear combination of the corresponding RE and MP operators [19], with both contributions adding up to unity in order to fulfill the electron-electron Kato cusp conditions [30].

It's possible to combine MP and RE, since both are variants of the Rayleigh-Schrodinger perturbation theory where the electronic Hamiltonian in perturbation theory is partitioned into an unperturbed part and a perturbation [27]. The unperturbed Hamiltonian $\hat{H}^{(0)}_{REMP}$ is defined as a constrained mixture of $\hat{H}_{MP}$ and $\hat{H}_{RE}$

$$\hat{H}^{(0)}_{REMP} = (1-A)\hat{H}^{(0)}_{RE} + A\hat{H}^{(0)}_{MP} \tag{I.20}$$

where A is the mixing parameter, and $A \in [0,1]$
The REMP is considered with second-order perturbations energies MP2 and RE2, where RE2 has a best overestimate the correlation energy of singlet-coupled doubly excited (SDE) type due to configuration state functions (CSFs). Concurrently, it underestemates correlation contributions form triplet-coupled doubly excited (CSFs) (TDE) to a somewhat larger degree, at variance, the MP2 overestimate the contribution of the TDEs and underestimates those of SDEs.
Then the implementaion of REMP without having to store the non-Zero matrix elements of $\hat{H}^{(0)}$ and $\hat{H}$ of the CI-matrix [20].
Instead, by projection the first-order perturbation equation:

$$0 = (\hat{H}^{(0)} - E^{(0)})|\psi^{(1)}\rangle + (\hat{H}^{(1)} - E^{(1)})|\psi^{(0)}\rangle \tag{I.21}$$

the RE part of the REMP residuals obtaining as follow:

$$\begin{aligned}
\sigma^{ij}_{ab;RE2} &= \langle \psi^{ab}_{ij} | \hat{H} - E_0 | \psi \rangle \\
&= K^{ij}_{ab} + K(C^{ij})_{ab} + \{F^V C^{ij} + C^{ij} F^V\}_{ab} \\
&- \sum_{K=1}^{n_{occ}} \left(F_{jk} C^{ik}_{ab} + F_{ik} C^{kj}_{ab} \right) + \sum_{k,l=1}^{n_{occ}} K^{ij}_{kl} C^{kl}_{ab} \\
&+ \sum_{k=1}^{n_{occ}} \{ (2C^{ik} - C^{ik+}) \left(K^{kj} - \frac{1}{2} J^{kj} \right) + \left(K^{ik} - \frac{1}{2} J^{ik} \right) \left(2C^{kj} - C^{kj+} \right) \}_{ab} \\
&- \sum_{k=1}^{n_{occ}} \{ \frac{1}{2} C^{ik+} J^{jk+} + \frac{1}{2} J^{ik} C^{kj+} + J^{jk} C^{ik} + C^{kj} J^{ik} \}_{ab}
\end{aligned} \tag{I.22}$$

the similar resuduum equation for MP2 has been derived by "Pulay" and "Saebø" as:

$$\sigma^{ij}_{a,b,MP2} = K^{ij}_{ab} + F^V C^{ij} + C^{ij} F^V - \sum_k \left(F_{ik} C^{kj}_{ab} + F_{kj} C^{ik}_{ab} \right) \tag{I.23}$$

As the terms in the MP2 residuum are identical to the first three terms in the RE2 residuum:

$$\sigma^{ij}_{a,b,REMP} = (1-A)\,\sigma^{ij}_{a,b,RE2} + A\sigma^{ij}_{a,b,MP2} \tag{I.24}$$

To obtain the amplitudes $(C^{ij})_{ab}$, they are iteratively modified such $\sigma^{ij}_{ab,REMP2}$ becomes Zero, with the amplitudes the first-order perturbed wave function are often calculated, and consequently the second-order perturbation energy.

I.1.4 OO-REMP Perturbation Theory

OO-REMP Perturbation Theory is devloped by Fink and Behnle, the objective of this method is to make the energy of the correlated method is minimal by adjusting the orbitals of the reference determinant [31].
Orbital Optimization for REMP2 was implemented as described for the parent methods OO-MP2 and OCEPA(0) by Bozkaya [20, 14, 16].
The OO-REMP energy and wavefunction are obtained by minimizing the second-order REMP energy functional:

$$\begin{aligned}\hat{E}^{(2)}_{REMP} = &\langle\phi^{(0)}|\hat{H}|\phi^{(0)}\rangle + \langle\phi^{(0)}|\{\hat{W}_N\hat{T}^{(1)}_2\}_c|\phi^{(0)}\rangle \\ &+ \langle\phi^{(0)}|[\hat{\Lambda}^{(1)}_2\{\hat{W}_N + \hat{F}_N\hat{T}^{(1)}_2 + (1-A)\hat{W}_N\hat{T}^{(1)}_2\}_c]_c|\phi^{(0)}\rangle\end{aligned} \tag{I.25}$$

where:

$$\hat{T}^{(1)}_2 = \frac{1}{4}\sum_{i,j}^{occ}\sum_{a,b}^{virt} t^{i,j(1)}_{a,b}\hat{a}^\dagger_a\hat{a}^\dagger_b\hat{a}_j\hat{a}_i \tag{I.26}$$

$$\hat{\Lambda}^{(1)}_2 = \frac{1}{4}\sum_{i,j}^{occ}\sum_{a,b}^{virt} \lambda^{a,b(1)}_{i,j}\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}_b\hat{a}_a \tag{I.27}$$

To parameterize the orbital change the methodology of Bozkaya et al [32, 33, 34] is used. The unitary orbital rotation operator $e^{\hat{K}}$ allows to rotate orbitals. In consequence operators can be expressed as follows:

$$|\widetilde{P}\rangle = e^{\hat{K}}|P\rangle \tag{I.28}$$

$$\widetilde{\hat{a}}^\dagger_p = e^{\hat{K}}\hat{a}^\dagger_p e^{-\hat{K}} \tag{I.29}$$

$$\widetilde{\hat{a}}_p = e^{\hat{K}}\hat{a}_p e^{-\hat{K}} \tag{I.30}$$

$$\widehat{H}^k = e^{-\hat{K}}\widehat{H}e^{\hat{K}} \tag{I.31}$$

$$\widehat{H}^k_N = e^{-\hat{K}}\widehat{H}_N e^{\hat{K}} \tag{I.32}$$

$$\widehat{f}^k_N = e^{-\hat{K}}\widehat{f}_N e^{\hat{K}} \tag{I.33}$$

$$\widehat{W}_N^k = e^{-\hat{K}} \widehat{W}_N e^{\hat{K}} \tag{I.34}$$

The orbital rotation operator for orbitals p and q reads:

$$\hat{K} = \sum_{p,q} K_{p,q} \hat{a}_p^\dagger \hat{a}_q \tag{I.35}$$

Eq.I.25 can now be written implying the rotated orbitals:

$$\begin{aligned} \hat{E}^{(2)}_{REMP}(k) = &\langle \phi^{(0)} | \hat{H}^k | \phi^{(0)} \rangle + \langle \phi^{(0)} | \{ \hat{W}_N^k \hat{T}_2^{(1)} \}_c | \phi^{(0)} \rangle \\ &+ \langle \phi^{(0)} | [\hat{\Lambda}_2^{(1)} \{ \hat{W}_N^k + \hat{F}_N^k \hat{T}_2^{(1)} + (1-A) \hat{W}_N^k \hat{T}_2^{(1)} \}_c]_c | \phi^{(0)} \rangle \end{aligned} \tag{I.36}$$

The orbital gradient, which is minimized is calculated by:

$$W_{p,q} = \frac{\widetilde{E}^{(2)}_{REMP}(k)}{\partial k_{p,q}} \Big|_{k=0} = 2(F_{pq} - F_{qp}) \tag{I.37}$$

Hereby F_{pq} is the generalized Fock matrix:

$$F_{pq} = \sum_r h_{pr} \gamma_{rq} + 2 \sum_{rst} \langle rs \| tp \rangle \Gamma_{rstq} \tag{I.38}$$

With each orbital gradient w_{pq} new orbital rotation operator factors k_{pq} are calculated, until w_{pq} converges to zero:

$$k_{pq}^{(n+1)} = -\frac{w_{pq}^n}{2(f_{pp} - f_{qq})} \tag{I.39}$$

where $k_{pq}^{(n+1)}$ is damped by the diagnonal Fock matrix elements f_{pp} and f_{qq} .

I.2 Dipole Moment

The multipoles moments "dipole, quadrupole, octapole moments ... " have importance in studies of matter in chemistry. These are the basis for comprehension and interpretation of intermolecular interactions [35].
Further, these properties give one of the most direct relations between the electronic structure of molecules and spectroscopically observable quantities, and are a method to evaluating the accuracy of a quantum chemical method [36, 5].
Two separated charges of opposite sign, $q_1 = -q$ and $q_2 = +q$ form an electric dipole. The dipole moment is defined by:

$$\vec{\mu} = q(\vec{r_2} - \vec{r_1}) = q\vec{r} \tag{I.40}$$

where $\vec{r_1}$ and $\vec{r_2}$ are the vectors that define the position of the two charges in space [35].
The dipole moment is thus a vector quantity for distribution of negative and positive point charges q_i the dipole moment is [37]:

$$\vec{\mu} = \sum_i q_i \vec{r_i} \tag{I.41}$$

Dipole moments are simple and accurate measures of the electron density of a polar molecule. The latter also affects the interactions of a molecule with other molecules in addition to electric fields [21].
The dipole moments is the simplest multipolar molecular moments to describe the spatial moments of electron density, and the accuracy of their calculation is a comprehensive measure of the quality of the corresponding density [38, 39, 40].

$$\vec{\mu} = \int \vec{r}\rho(\vec{r})d\vec{r} \tag{I.42}$$

where $\rho(\vec{r})$ is the charge density, obtained by the sum of the first spatial moment of the electron density and a nuclear charge contribution.
Dipole moment can be evaluated numericaly or analyticaly.

I.2.1 Analytical Method

The analytical dipole moment calculations is given by the following equation:

$$\mu_\alpha^{(0)} = \langle \psi_i | \hat{\mu}_\alpha | \psi_j \rangle \tag{I.43}$$

$$\hat{\mu}_\alpha = \sum_i e_i r_{i\alpha} \tag{I.44}$$

with $\alpha \equiv x, y$ or z. It might be useful to mention that , when actually calculating expectation values, the sum over charge elements e_i be decomposed into a partial sum corresponding to nuclear centers I and a bare electron related continous integration over the entire space of electron charge density $\rho(r)$ [41] such is:

$$\mu_\alpha^{(0)} = \sum_I Z_I r_{I\alpha} - \int \rho(r) r_\alpha dr \tag{I.45}$$

and accordingly the dipole vectors have been also reduced:

$$\mu_{eff} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \tag{I.46}$$

I.2.2 Numerical Method

The energy contribution resulting from the interaction of an electronic charge distribution $\rho(r)$ with an electronic potencial $\phi(r)$ is given by the expansion [12]

$$E = \int \rho(r)\phi(r) dr \tag{I.47}$$

in view of the fact that the electric field ($F = -\frac{\partial \phi}{\partial r}$) is normally fairly uniform at the molecular level.
It is pratical to write E as a multipole expansion

$$E = q\phi - \mu F - \frac{1}{2} Q F' - ... \tag{I.48}$$

here q is the net charge (monopole), μ is the (electric) dipole moment, Q is the quadrupole moment, and F and F' are the field and field gradient ($\frac{\partial F}{\partial r}$),

respectively.The dipole moment and electric field are vectors, and the μF term should be interpreted as the dot product ($\mu F = \mu_x F_x + \mu_y F_y + \mu_z F_z$)
The presence of a field influences the wave function and results in induced dipole, quadrupole,..., moments [36]. For the dipole moment, this might be written as:

$$\mu = \mu_0 + \alpha F + \frac{1}{2}\beta F^2 + \frac{1}{6}\gamma F^3 + ... \tag{I.49}$$

for a homogeneous field, were ($F = 0$) may be written as the total energy of a neutral molecule as a Taylor expansion [23]

$$E(F) = E(0) + \frac{\partial E}{\partial F}\Big|_{F=0} F + \frac{1}{2}\frac{\partial^2 E}{\partial F^2}\Big|_{F=0} F^2 + \frac{1}{6}\frac{\partial^3 E}{\partial F^3}\Big|_{F=0} F^3 + \frac{1}{24}\frac{\partial^4 E}{\partial F^4}\Big|_{F=0} F^4 + ... \tag{I.50}$$

According to eq.I.48 we also have that ($\frac{\partial E}{\partial F} = -\mu$), where μ is given by the expression in eq.I.49. Differentiation of eq.I.50 with respect to F gives:

$$\mu = -\frac{\partial E}{\partial F}\Big|_{F=0} - \frac{\partial^2 E}{\partial F^2}\Big|_{F=0} F - \frac{1}{2}\frac{\partial^3 E}{\partial F^3}\Big|_{F=0} F^2 - \frac{1}{6}\frac{\partial^4 E}{\partial F^4}\Big|_{F=0} F^3 + ... \tag{I.51}$$

Comparing eqs.I.49 and I.51 shows that the first derivative is the (permanent) dipole moment μ_0

$$\mu_0 = -\frac{\partial E}{\partial F}\Big|_{F=0} \tag{I.52}$$

where F is the external field applied [42].
Numericaly the dipole moment is evaluated using:

$$\mu_\alpha = -\frac{E(F_{2\alpha}) - E(F_{1\alpha})}{F_{2\alpha} - F_{1\alpha}} \qquad \alpha(x, y, z) \tag{I.53}$$

with $F_{1\alpha}$ and $F_{1\alpha}$ are electric field in direction α with amplitude close to zero [43, 44].

Chapter II

Dipole moment of some small molecules: Comparison between REMP and CCSD(T) methods

II.1 Introduction

In order to test the quality of the wave function obtained by the new perturbation method REMP, as is generally the case, it is necessary to verify its validity in the calculation of molecular properties.
Among these properties, we have the electrical properties, which are the main properties that are in direct relation with the electronic density.
Thus, among these electrical properties, we cite the simplest way to describe the spatial polarization of the electron density, the dipole moment which is expressed from the electronic density using the expression eq.I.42. The precision of their calculations is a measure full of the quality of the corresponding density.
So the dipole moment can be calculated directly by the OO-REMP method which gives their analytical value. It can also be calculated by the REMP method which gives values of the energy of the system under externel electrical field used in numerical differentiation of the energy.
In this work, the quality of REMP wave function is compared to CCSD(T) one. REMP dipole moment is compared to CCSD(T) ones published by Diptarka Hait and Martin Head-Gordon et al [21].

II.2 Computational Details

In this work, we calculated the dipole moment of nineteen small molecules, which are: CO, CS, ClF, SH_2, PH_3, BH_2Cl, SO_2, ClCN, BH_2F, CSO, CH_3Cl, $BHCl_2$, CH_3F, HCOOH, N_2H_4, P_2H_4, NH_2OH, CH_2NH, and CH_3SH. They are a part of benchemark set used by Diptarka Hait and Martin Head-Gordon et al [21].
The authors published a CCSD(T) dipole moment of large set of molecules using Aug-cc-pCVQZ basis set.
To calculate REMP and OO-REMP dipole moment of our molecules we used the same basis set and molecules geometries obtained from the supplementary data of the cited paper.
The REMP and OO-REMP calculations were carried out for fourty mixing parameter values [A = 0.0, .01, .02, .03, .04, .05, .06, .07, .08, .09, .1, .11, .12, .13, .14, .15, .16, .17, .18, .19, .2, .21, .22, .23, .24, .25, .26, .27, .28, .29, .3, .35, .4, .45, .5, .6, .7, .8, .9, 1.0].
In the REMP method, for calculating dipole moments from numerically differentiated energies, one needs to run calculations including external electric fields. A field increment of $10^{-4} a.u.$ is usually adequate.
The addition of the field will be in all directions with the highest and lowest values, one with an external field of $10^{-4} a.u.$ (highest) and one with an external field of $-10^{-4} a.u.$ (lowest) in x y and z directions.
The REMP and OO-REMP calculations were carried out with the WAVELS code, Statistical calculations were carried out using LibreOfficeCalc 6.4.7.2. All plots were constructed using Gnuplot 5.2.

II.3 Comparison between REMP and CCSD(T) dipole moments

We start the results analysis by collecting the optimal value of the mixing parameter A which correspond to minimum in regularized error against CCSD(T) ones.
The regularized error metric was used to assess the performance of REMP and OO-REMP against the CCSD(T) benchmark.
The REMP dipole moments results are compared to CCSD(T) one published by Hait et al [21]. to mesuare the destance of REMP results from CCSD(T), a regularized error is calculated as defined by Hait et al by: $\frac{\mu_{REMP}-\mu_{CCSD(T)}}{max(\mu_{CCSD(T)},1D)} \times 100\%$.
This regularized model is adopted to ensure that errors are relative to μ_{ref} large (to prevent relatively small perturbations of density from dominating) but are absolute for small μ_{ref} (to prevent a too small denominator from skewing the analysis) [21].

These values are shown in the second column of table II.1. The first column of this table present the molecules while the third and the fort ones present the dipole moment and regularized error values respectively.

Table II.1: The minimum errors of REMP compared to CCSD(T) with their corresponding values of A and μ_{REMP}

molecules	A	$\mu_{REMP}(D)$	Min ERR REMP/CCSD(T)(%)
CH_3Cl	0	1,871	0,010
CH_3SH	0	1,575	0,108
PH_3	0	0,594	0,138
SH_2	0	0,985	0,299
CS	0	1,983	0,314
N_2H_4	0	2,727	0,664
P_2H_4	0	0,987	0,670
CSO	0,08	0,740	0,007
ClCN	0,1	2,868	0,017
CO	0,25	0,120	0,035
HCOOH	0,26	1,381	0,001
NH_2OH	0,3	0,699	0,024
SO_2	0,5	1,629	0,020
ClF	0,7	0,878	0,321
CH_2NH	0,8	2,060	0,038
$BHCl_2$	0,9	0,645	0,028
BH_2F	0,9	0,816	0,037
CH_3F	1	1,799	0,128
BH_2Cl	1	0,669	1,703

In table II.1, we see that most of the values of A which give a good prediction and smaller error values are confined in the interval $A \in [0, 0.5]$, as well as the best approach of the REMP method for this set of molecules is for the HCOOH molecule with a minimum error of 0.001% which is corresponding to the value of the mixing parameter $A = 0.26$. We can also note that the value of $A = 0$ so REMP becomes 100% RE gives a good approach for seven molecules, then we can say that Retaining the Excitation degree method gives good contributions to the dipole moment prediction for the REMP method.

It is noted that the polar molecules CH_3F and CH_3Cl which have comparable dipole moments have completely different optimal A parameters. The preferred method for evaluating the dipole moment of CH_3Cl is RE2 while that of CH_3F is MP2. This constataion can be explained by F and Cl electronic structures differences.

The evolution of the error according to the parameter can be followed for the two molecules on the graph of the figure II.1.

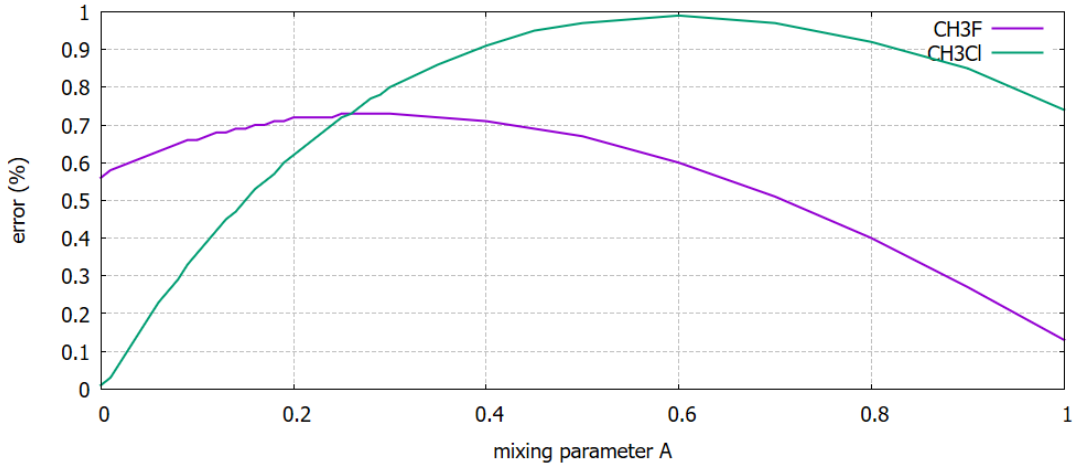

Figure II.1: Regularized error of REMP for CH_3Cl and CH_3F plotted against A

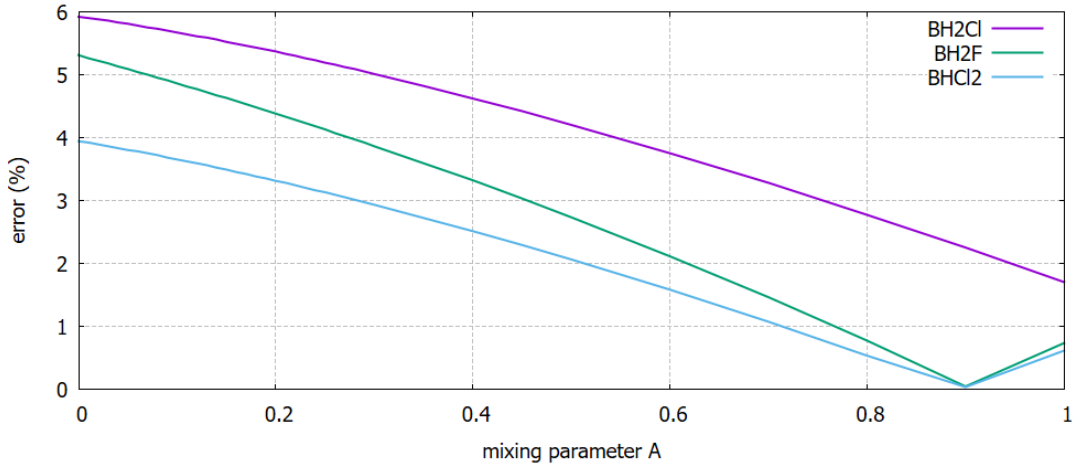

Figure II.2: Regularized error of REMP for $BHCl_2$, BH_2Cl and BH_2F plotted against A

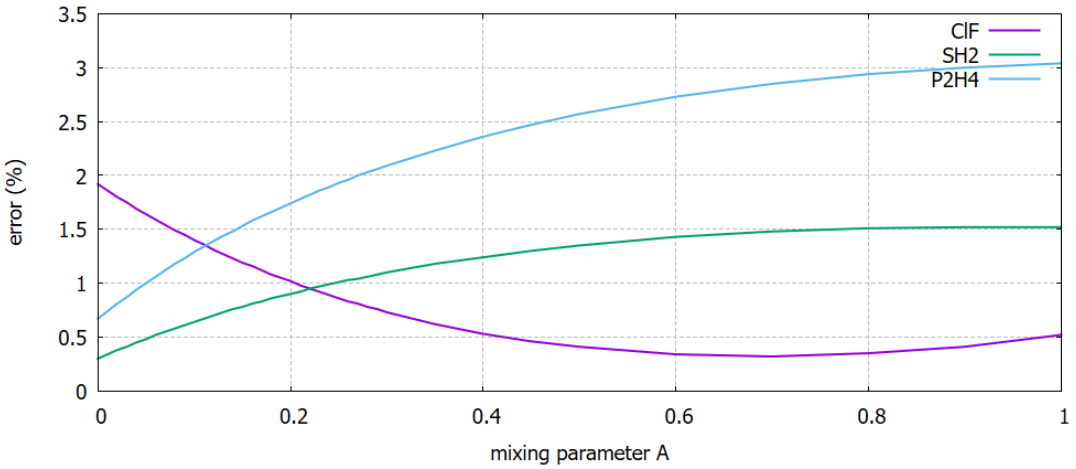

Figure II.3: Regularized error of REMP for ClF, SH_2 and P_2H_4 plotted against A

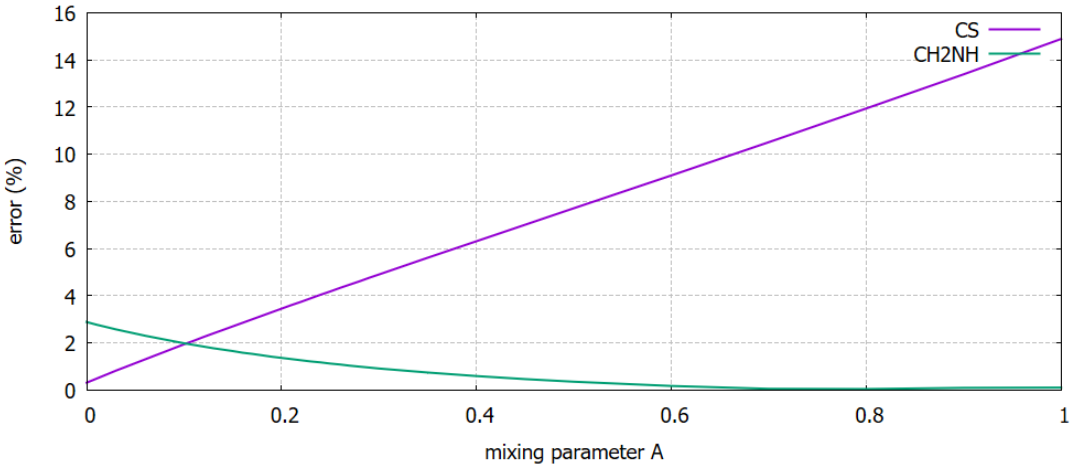

Figure II.4: Regularized error of REMP for CS and CH_2NH plotted against A

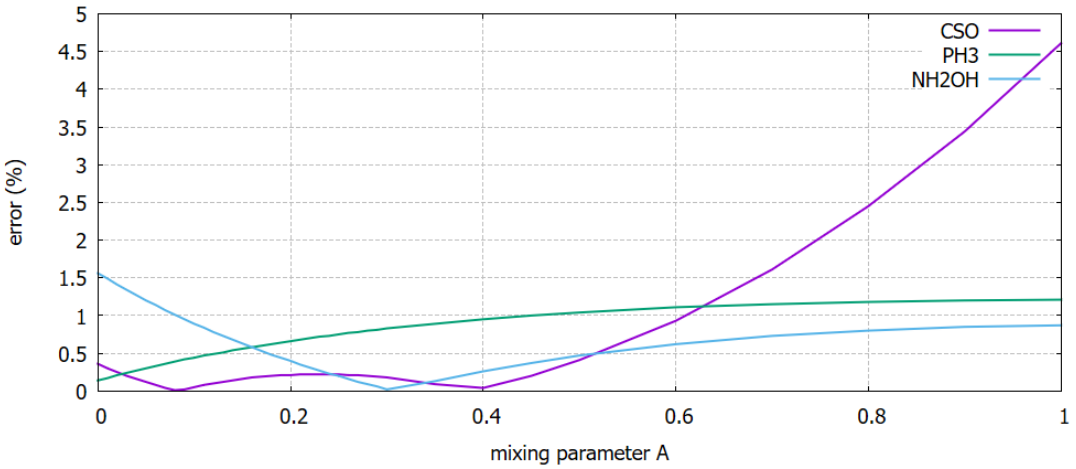

Figure II.5: Regularized error of REMP for CSO, PH_3 and NH_2OH plotted against A

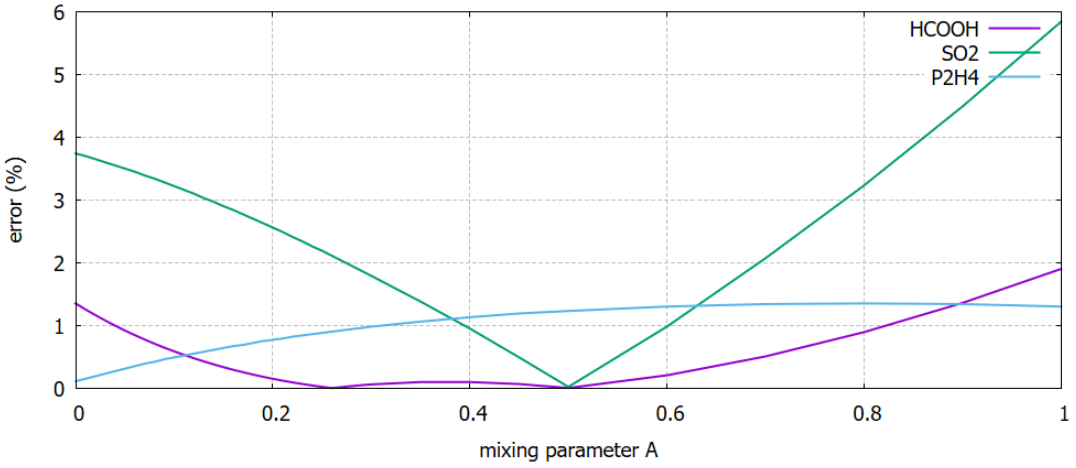

Figure II.6: Regularized error of REMP for $HCOOH$, SO_2 and CH_3SH plotted against A

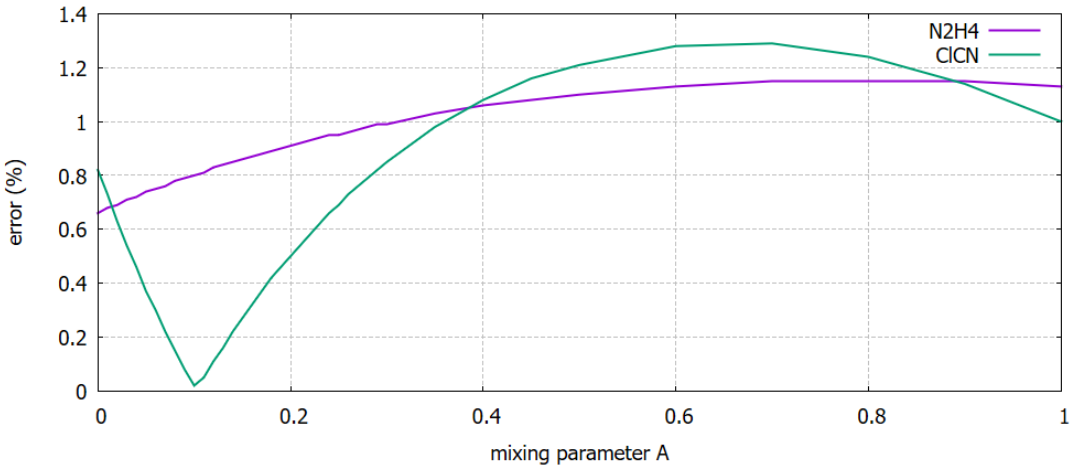

Figure II.7: Regularized error of REMP for N_2H_4 and $ClCN$ plotted against A

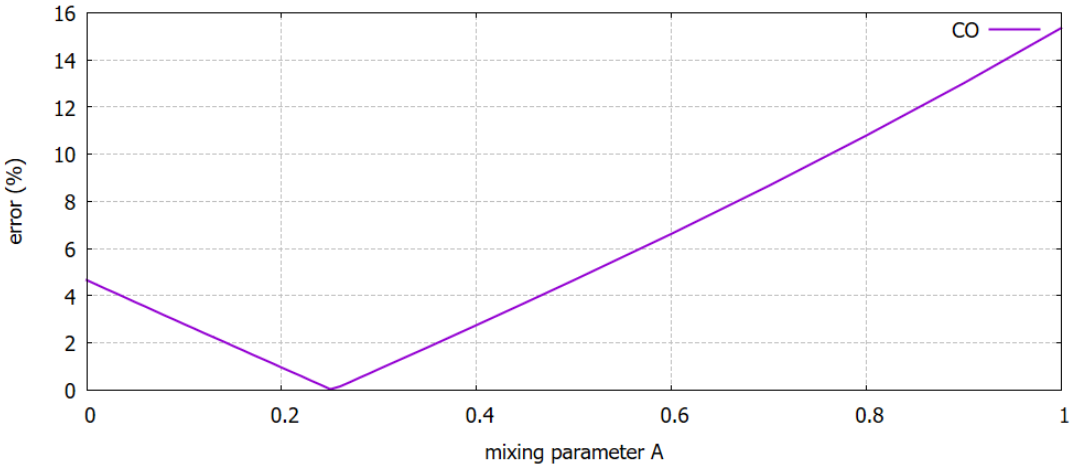

Figure II.8: Regularized error of REMP for CO plotted against A

The graphs above show the variation of the errors as a function of the A values for all the molecules. We can determine different ways of variation, for them: the direct decrease from 5.8% corresponding to $A = 0$ when $REMP = 100\%RE$ to a minimum error of 1.7% Compatible to $A = 1$ with a dipole moment $\mu_{REMP} = 0.6694(D)$, we can also see that there are molecules which that shape two minimums of error II.1 like the error variance of the CSO molecule with a minimum 0.01% corresponds to $A = 0.08$ and a minimum error of 0.04% agree with a mixing parameter value $A = 0.4$ with $\mu_{REMP} = 0.7393(D)$.
The results of HCOOH molecule gives the lowest error of 0.001% corresponds

to
μ_{REMP} = 1.38068(D) with a value of $A = 0.26$ and in II.3 and II.8 the two molecules in each graph evaluated in an inverse manner, the error for CH_3SH increases when A increases on the other hand for the molecule CH_2NH the error decreases by 2.88% ($A = 0$) has 0.04% when $A = 0.8$.

Each statistical value of dipole moments describes an aspect of the quality of REMP.

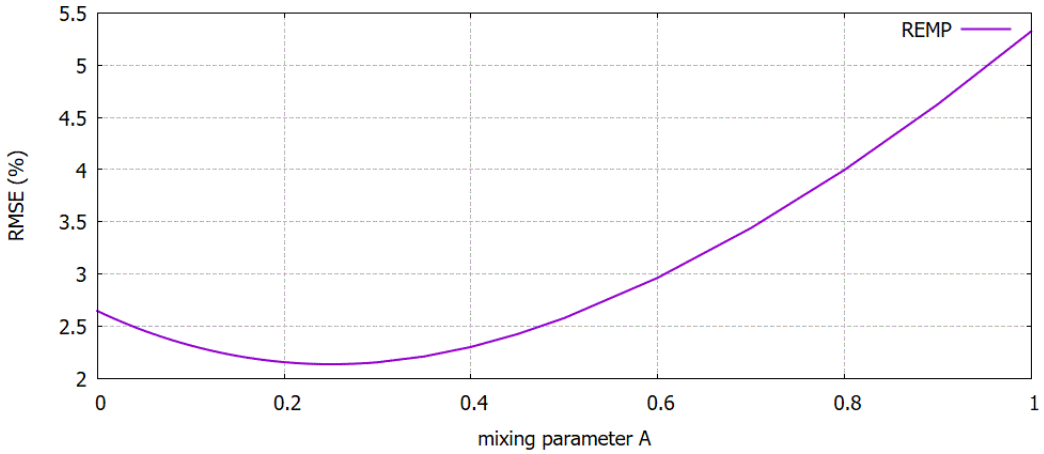

Figure II.9: RMSE(%) of REMP plotted against A

We calculate the Root Main Square Regularized Errors (RMSE) and we extract the maximum values of the regularized errors by values of A for all the molecules. The graph II.9 shows the variation of RMSE for the REMP method according to the mixing parameter A. From this figure II.9, we can quote that the smallest deviations are located in the interval $A \in [0.15, 0.35]$ where the values of the errors are confined from 2.14 to 2.21, also, in this interval, we can see that the maximums regularized errors are small compared to the extremity. Whereas, when we approach towards $A = 0$ the value of RMSE notices a slight increase compared to the other direction where RMSE tends towards 5.32 when ($A \longrightarrow 1$). Therefore, the prediction of dipole moments with REMP is efficient for small molecules, with a mixing parameter value from the interval $A \in [0.15, 0.35]$.

II.4 Comparison between OO-REMP and CCSD(T) dipole moments

With the same parameters of table II.1, the second table II.2 also gives the minimums of the errors of the OO-REMP method compared with CCSD(T) for 10 molecules.

Table II.2: The minimum errors of OO-REMP compared to CCSD(T) with their corresponding values of A and $\mu_{OO-REMP}$

molecules	A	$\mu_{OO-REMP}(D)$	Min ERR OO-REMP/CCSD(T) (%)
SH_2	0,01	0,982	0,003
CS	0,04	1,977	0,023
CSO	0,08	0,740	0,009
CO	0,16	0,120	0,044
PH_3	0,35	0,591	0,119
ClF	0,35	0,868	1,348
BH_2F	0,5	0,815	0,117
CH_3Cl	1	1,874	0,129
CH_3F	0,7	1,795	0,066
ClCN	0,2	2,868	0,002

In this table, we also not that the values of A are mostly confined to the interval $A \in [0, 0.5]$.
For all the molecules indicated in the table, we see that the closest value to the CCSD (T) ones (the lowest minimum OO-REMP error compared to CCSD(T)) is for the SH_2 molecule with a value of 0.003% corresponding to the parameter $A = 0.01$ (very close to the RE2 method).

There is also a minimum value of the error coinciding with a total contribution of the MP2 method for the CH_3Cl molecule where the dipole moment value is 1.874 (D) with an error of 0.13 compared to CCSD(T).

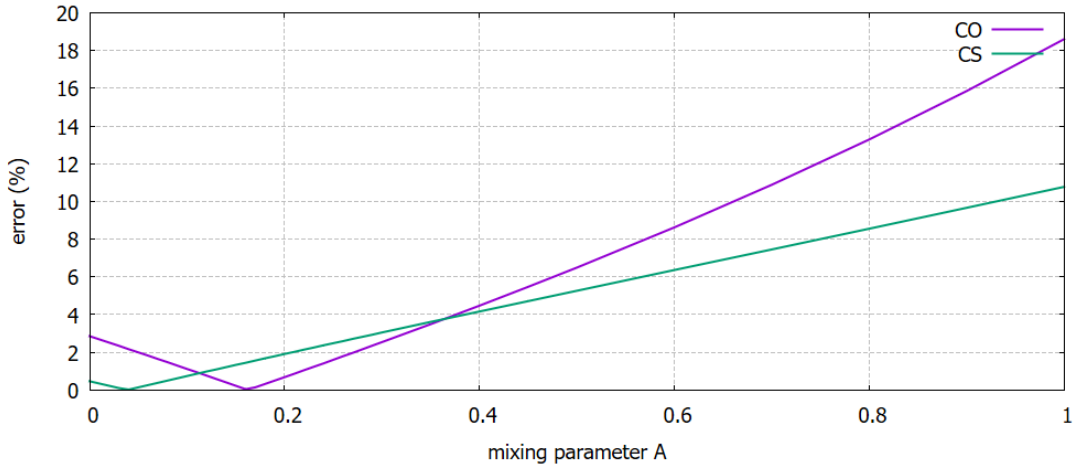

Figure II.10: Regularized error of OO-REMP for CO and CS plotted against A

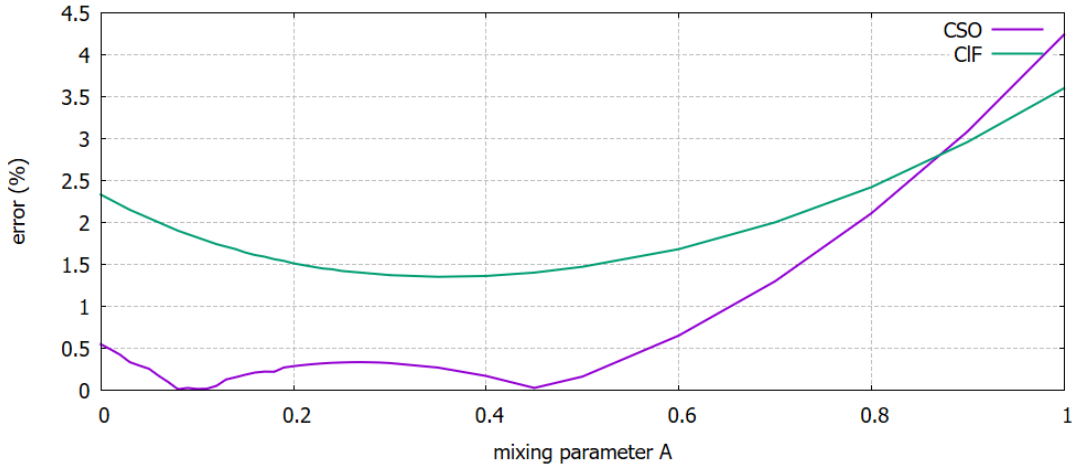

Figure II.11: Regularized error of OO-REMP for CSO and ClF plotted against A

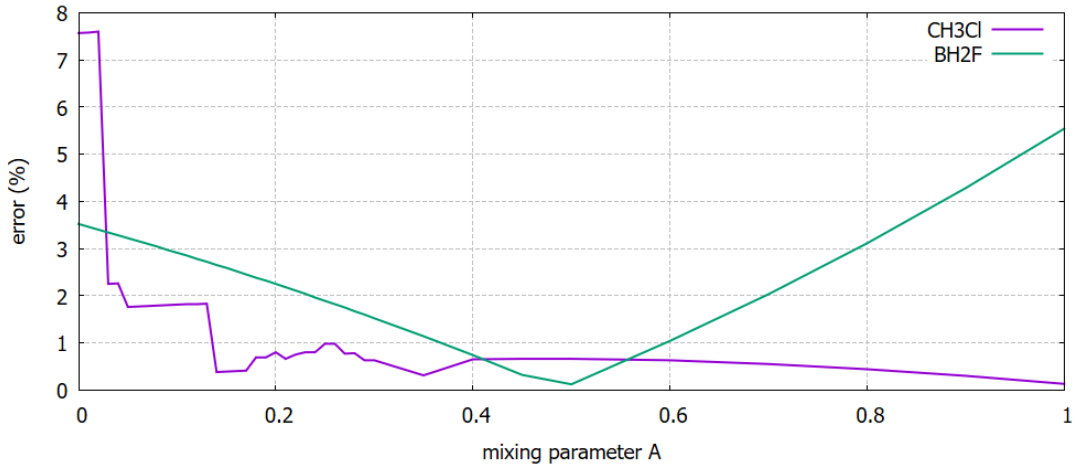

Figure II.12: Regularized error of OO-REMP for CH_3Cl and BH_2F plotted against A

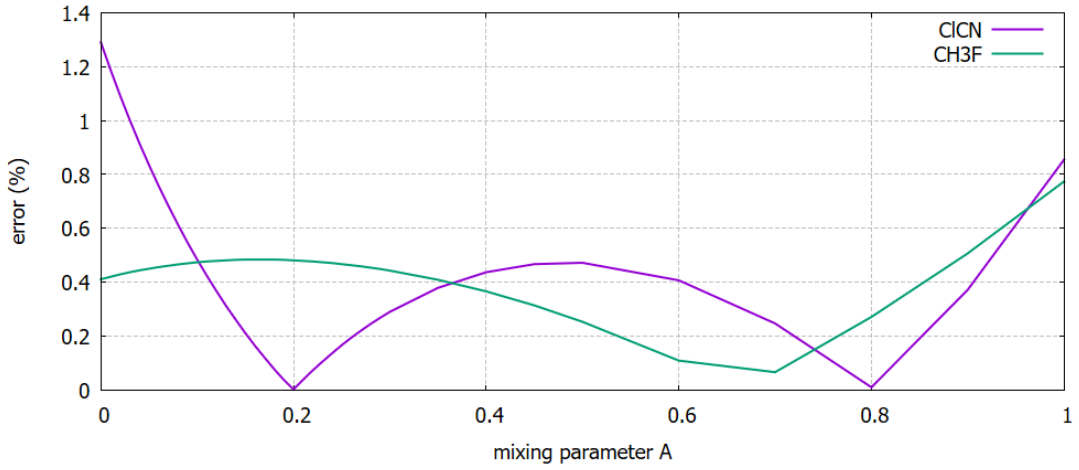

Figure II.13: Regularized error of OO-REMP for $ClCN$ and CH_3F plotted against A

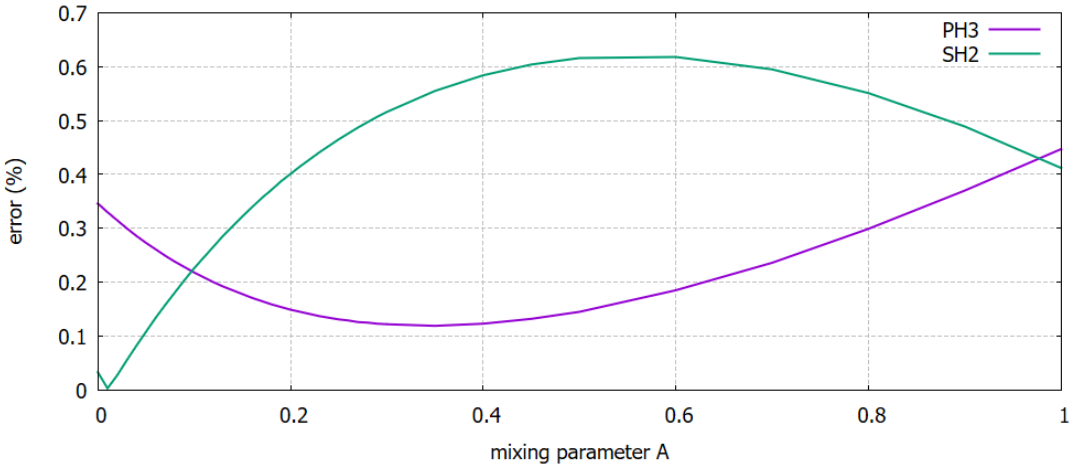

Figure II.14: Regularized error of OO-REMP for $PH3$ and SH_2 plotted against A

The same for the OO-REMP results, the graphs above show the variation of regularized errors as a function of the values of A for the 10 molecules indicated before. We can extract different ways of variation of these errors, from them: that there are molecules which shape two minimums II.12 like the error variance of the CSO molecule with a minimum of 0.009% with $\mu_{OO-REMP} = 0.739612(D)$, this molecule gives the lowest error corresponds to $A = 0.08$ and the second minimum of 0.024% agree with a mixing parameter value $A = 0.45$ corresponds to $\mu_{OO-REMP} = 0.739945(D)$

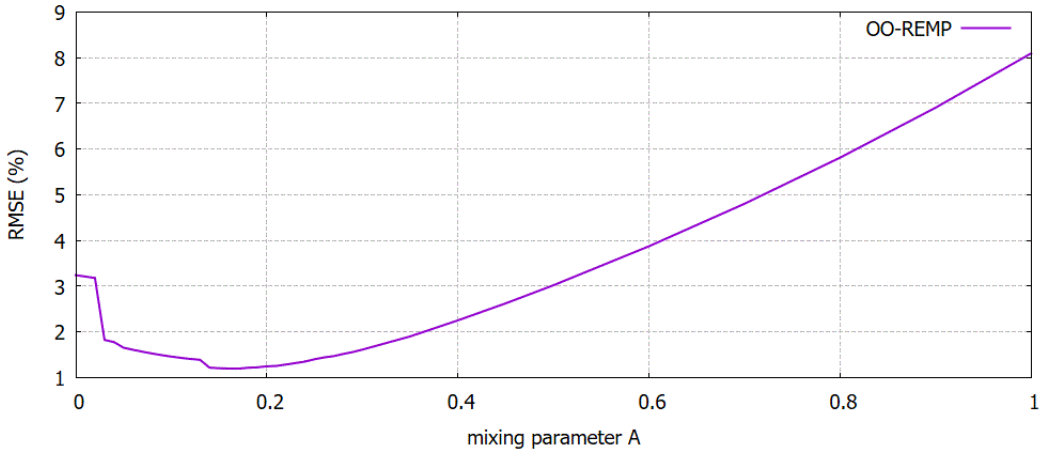

Figure II.15: RMSE(%) of OO-REMP plotted against A

In the same way, We calculated RMSE for OO-REMP. When we look at the

graph II.15 which shows the variation of RMSE as a function of A for the OO-REMP method the observed results are good, the best (small) deviations agree with a mixing parameter from the interval $A \in [0.13, 0.25]$ with a minimum error value of 1.19 is suitable with two values of A $A = 0.16$ and 0.17. We see an increase in the value of RMSE when it is head for from these two values either towards the left ($A \longrightarrow 0$) the RMSE tends towards 3.24 as a maximum value, or towards the right ($A \longrightarrow 1$) the RMSE tends to 8.09. So the prediction of dipole moments for small molecules with the OO-REMP approach is efficient with values of A from the interval $A \in [0.13, 0.25]$

II.5 Comparison between REMP and OO-REMP

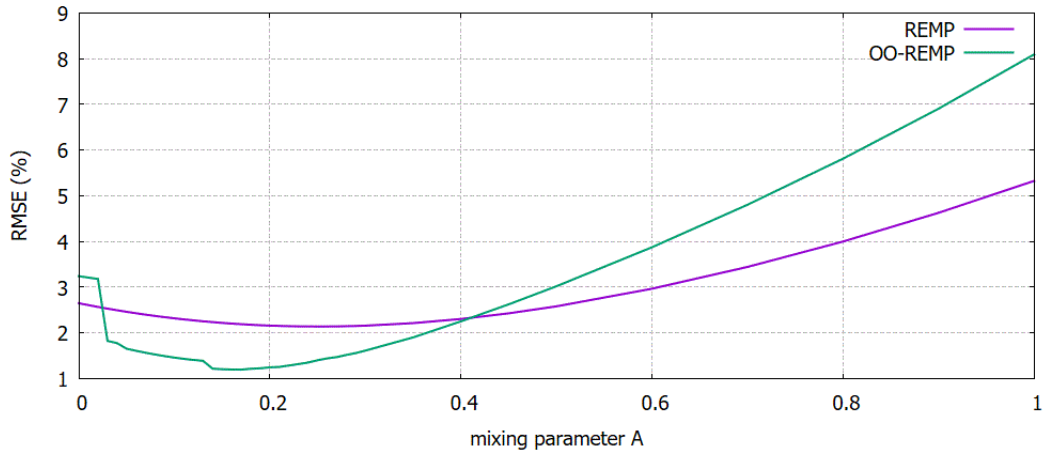

Figure II.16: RMSE(%) of OO-REMP and REMP plotted against A

We compare the results of REMP and OO-REMP, the two methods give slightly the same value of dipole moment. In comparison to CCSD(T), they gave small errors with different mixing parameter values. In some cases, the A value is conserved for both methods for example in the CSO molecule where the minimum error is 0.01% corresponding to a value of $A = 0.08$ in REMP calculation by against in the OO-REMP calculation we see an improvement with a minimum error of 0.009% agrees with the same value of A, we can also see that there is a good improvement for the CS molecule where the minimum error decreases from 0.31% in calculation REMP to 0.02% in OO-REMP calculation for a small increment of A, from $A = 0$ to 0.04
From both tables II.1 and II.2, there is a variation in the values of A parameter which suits the minimum values of the errors from REMP method to OO-REMP method. We can extract values where there is this difference for example for PH_3 molecule the minimum error is suitable with $A = 0$ for REMP method

on the other hand in the OO-REMP calculations is suitable with $A = 0.35$, this difference can improve or reduce prediction accuracy. In this case, it improves the error value from 0.14% to 0.119%, as well as the reduction in the precision of the REMP method to OO-REMP is very clear in the values obtained for the CH_3Cl molecule with a large difference in the value of the mixing parameter A where the minimum error increases from 0.01% to 0.13% for the REMP and OO-REMP methods respectively.

Table II.3: REMP and OO-REMP dipole moments of ClF molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	0.8579	0.8620
0.01	0.8585	0.8626
0.02	0.8591	0.8632
0.03	0.8597	0.8637
0.04	0.8602	0.8643
0.05	0.8607	0.8648
0.06	0.8612	0.8653
0.07	0.8617	0.8658
0.08	0.8622	0.8663
0.09	0.8626	0.8667
0.1	0.8630	0.8672
0.11	0.8634	0.8676
0.12	0.8638	0.8681
0.13	0.8641	0.8685
0.14	0.8644	0.8689
0.15	0.8648	0.8693
0.16	0.8651	0.8696
0.17	0.8653	0.8700
0.18	0.8656	0.8704
0.19	0.8658	0.8707
0.2	0.8661	0.8710
0.21	0.8663	0.8714
0.22	0.8665	0.8717
0.23	0.8667	0.8720
0.24	0.8668	0.8723
0.25	0.8670	0.8726
0.26	0.8671	0.8729
0.27	0.8672	0.8731
0.28	0.8673	0.8734
0.29	0.8674	0.8736
0.3	0.8675	0.8739
0.35	0.8677	0.8750
0.4	0.8676	0.8759
0.45	0.8672	0.8766
0.5	0.8665	0.8771
0.6	0.8644	0.8778
0.7	0.8612	0.8780
0.8	0.8570	0.8777
0.9	0.8517	0.8771
1	0.8452	0.8760

Table II.4: REMP and OO-REMP dipole moments of CSO molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	0.73425	0.73614
0.01	0.73485	0.73668
0.02	0.73550	0.73719
0.03	0.73638	0.73767
0.04	0.73679	0.73812
0.05	0.73718	0.73854
0.06	0.73801	0.73893
0.07	0.73876	0.73930
0.08	0.73961	0.73963
0.09	0.73946	0.73995
0.1	0.73982	0.74023
0.11	0.73985	0.74049
0.12	0.74020	0.74073
0.13	0.74095	0.74095
0.14	0.74122	0.74114
0.15	0.74152	0.74131
0.16	0.74178	0.74146
0.17	0.74189	0.74159
0.18	0.74187	0.74169
0.19	0.74238	0.74178
0.2	0.74254	0.74184
0.21	0.74267	0.74189
0.22	0.74278	0.74191
0.23	0.74287	0.74192
0.24	0.74294	0.74191
0.25	0.74299	0.74188
0.26	0.74301	0.74183
0.27	0.74302	0.74176
0.28	0.74300	0.74167
0.29	0.74297	0.74157
0.3	0.74291	0.74145
0.35	0.74237	0.74059
0.4	0.74137	0.73933
0.45	0.73995	0.73766
0.5	0.73811	0.73561
0.6	0.73322	0.73036
0.7	0.72673	0.72359
0.8	0.71862	0.71525
0.9	0.70884	0.70528
1	0.69730	0.69360

Table II.5: REMP and OO-REMP dipole moments of CS molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	1.96747	1.9827
0.01	1.96984	1.9860
0.02	1.97221	1.9893
0.03	1.97459	1.9926
0.04	1.97696	1.9959
0.05	1.97933	1.9991
0.06	1.98170	2.0023
0.07	1.98406	2.0054
0.08	1.98642	2.0086
0.09	1.98877	2.0117
0.1	1.99112	2.0148
0.11	1.99346	2.0178
0.12	1.99579	2.0209
0.13	1.99812	2.0239
0.14	2.00044	2.0269
0.15	2.00275	2.0299
0.16	2.00506	2.0329
0.17	2.00736	2.0359
0.18	2.00965	2.0388
0.19	2.01194	2.0418
0.2	2.01422	2.0447
0.21	2.01649	2.0476
0.22	2.01876	2.0505
0.23	2.02102	2.0534
0.24	2.02328	2.0563
0.25	2.02553	2.0591
0.26	2.02778	2.0620
0.27	2.03002	2.0648
0.28	2.03225	2.0677
0.29	2.03448	2.0705
0.3	2.03670	2.0733
0.35	2.04776	2.0873
0.4	2.05874	2.1012
0.45	2.06964	2.1151
0.5	2.08050	2.1288
0.6	2.10216	2.1564
0.7	2.12382	2.1842
0.8	2.14556	2.2125
0.9	2.16739	2.2412
1	2.18930	2.2707

Table II.6: REMP and OO-REMP dipole moments of SH_2 molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	0.9816	0.98489
0.01	0.9819	0.98529
0.02	0.9822	0.98567
0.03	0.9825	0.98604
0.04	0.9827	0.98639
0.05	0.9830	0.98674
0.06	0.9832	0.98708
0.07	0.9835	0.98741
0.08	0.9837	0.98773
0.09	0.9839	0.98804
0.1	0.9842	0.98834
0.11	0.9844	0.98863
0.12	0.9846	0.98892
0.13	0.9848	0.98919
0.14	0.9849	0.98946
0.15	0.9851	0.98972
0.16	0.9853	0.98997
0.17	0.9855	0.99022
0.18	0.9856	0.99046
0.19	0.9858	0.99069
0.2	0.9859	0.99092
0.21	0.9861	0.99114
0.22	0.9862	0.99136
0.23	0.9863	0.99156
0.24	0.9864	0.99177
0.25	0.9866	0.99196
0.26	0.9867	0.99216
0.27	0.9868	0.99234
0.28	0.9869	0.99252
0.29	0.9870	0.99270
0.3	0.9871	0.99287
0.35	0.9875	0.99365
0.4	0.9877	0.99433
0.45	0.9879	0.99491
0.5	0.9881	0.99541
0.6	0.9881	0.99618
0.7	0.9878	0.99669
0.8	0.9874	0.99700
0.9	0.9868	0.99713
1	0.9860	0.99711

Table II.7: REMP and OO-REMP dipole moments of CO molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	0.09210	0.0740
0.01	0.09381	0.0759
0.02	0.09552	0.0778
0.03	0.09724	0.0796
0.04	0.09897	0.0815
0.05	0.10071	0.0834
0.06	0.10245	0.0852
0.07	0.10419	0.0871
0.08	0.10594	0.0890
0.09	0.10770	0.0908
0.1	0.10946	0.0927
0.11	0.11123	0.0945
0.12	0.11301	0.0964
0.13	0.11479	0.0982
0.14	0.11657	0.1000
0.15	0.11836	0.1019
0.16	0.12016	0.1037
0.17	0.12196	0.1056
0.18	0.12377	0.1074
0.19	0.12558	0.1092
0.2	0.12740	0.1111
0.21	0.12923	0.1129
0.22	0.13106	0.1147
0.23	0.13290	0.1166
0.24	0.13475	0.1184
0.25	0.13660	0.1203
0.26	0.13846	0.1221
0.27	0.14032	0.1239
0.28	0.14220	0.1258
0.29	0.14408	0.1276
0.3	0.14596	0.1295
0.35	0.15552	0.1387
0.4	0.16528	0.1481
0.45	0.17527	0.1576
0.5	0.18550	0.1672
0.6	0.20682	0.1868
0.7	0.22939	0.2072
0.8	0.25340	0.2285
0.9	0.27908	0.2507
1	0.30663	0.2741

Table II.8: REMP and OO-REMP dipole moments of PH_3 molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	0.58874	0.5936
0.01	0.58890	0.5939
0.02	0.58905	0.5943
0.03	0.58920	0.5946
0.04	0.58934	0.5949
0.05	0.58947	0.5952
0.06	0.58959	0.5955
0.07	0.58971	0.5958
0.08	0.58982	0.5961
0.09	0.58992	0.5964
0.1	0.59002	0.5966
0.11	0.59011	0.5969
0.12	0.59020	0.5971
0.13	0.59028	0.5973
0.14	0.59035	0.5976
0.15	0.59042	0.5978
0.16	0.59049	0.5980
0.17	0.59055	0.5982
0.18	0.59061	0.5984
0.19	0.59066	0.5986
0.2	0.59071	0.5988
0.21	0.59075	0.5990
0.22	0.59079	0.5992
0.23	0.59083	0.5994
0.24	0.59086	0.5995
0.25	0.59089	0.5997
0.26	0.59091	0.5999
0.27	0.59094	0.6000
0.28	0.59096	0.6002
0.29	0.59097	0.6003
0.3	0.59099	0.6005
0.35	0.59101	0.6011
0.4	0.59097	0.6017
0.45	0.59088	0.6022
0.5	0.59075	0.6026
0.6	0.59036	0.6033
0.7	0.58984	0.6037
0.8	0.58921	0.6040
0.9	0.58851	0.6042
1	0.58773	0.6043

Table II.9: REMP and OO-REMP dipole moments of BH_2F molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	0.8510	0.8689
0.01	0.8504	0.8684
0.02	0.8498	0.8680
0.03	0.8492	0.8676
0.04	0.8486	0.8671
0.05	0.8480	0.8667
0.06	0.8474	0.8662
0.07	0.8468	0.8658
0.08	0.8462	0.8653
0.09	0.8455	0.8649
0.1	0.8449	0.8644
0.11	0.8443	0.8639
0.12	0.8436	0.8635
0.13	0.8430	0.8630
0.14	0.8423	0.8625
0.15	0.8417	0.8621
0.16	0.8410	0.8616
0.17	0.8403	0.8611
0.18	0.8396	0.8606
0.19	0.8390	0.8601
0.2	0.8383	0.8596
0.21	0.8376	0.8591
0.22	0.8369	0.8586
0.23	0.8362	0.8581
0.24	0.8354	0.8576
0.25	0.8347	0.8571
0.26	0.8340	0.8565
0.27	0.8333	0.8560
0.28	0.8325	0.8555
0.29	0.8318	0.8550
0.3	0.8310	0.8544
0.35	0.8272	0.8517
0.4	0.8232	0.8490
0.45	0.8190	0.8461
0.5	0.8146	0.8431
0.6	0.8054	0.8369
0.7	0.7955	0.8304
0.8	0.7847	0.8235
0.9	0.7730	0.8162
1	0.7604	0.8085

Table II.10: REMP and OO-REMP dipole moments of CH_3Cl molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	2.0128	1.8709
0.01	2.0130	1.8717
0.02	2.0132	1.8725
0.03	1.9132	1.8732
0.04	1.9134	1.8740
0.05	1.9040	1.8746
0.06	1.9042	1.8753
0.07	1.9044	1.8760
0.08	1.9045	1.8766
0.09	1.9047	1.8772
0.1	1.9049	1.8778
0.11	1.9051	1.8784
0.12	1.9052	1.8789
0.13	1.9054	1.8794
0.14	1.8783	1.8800
0.15	1.8784	1.8804
0.16	1.8785	1.8809
0.17	1.8787	1.8814
0.18	1.8839	1.8818
0.19	1.8841	1.8823
0.2	1.8860	1.8827
0.21	1.8835	1.8831
0.22	1.8852	1.8834
0.23	1.8860	1.8838
0.24	1.8861	1.8842
0.25	1.8894	1.8845
0.26	1.8894	1.8848
0.27	1.8855	1.8851
0.28	1.8856	1.8854
0.29	1.8829	1.8857
0.3	1.8830	1.8860
0.35	1.8768	1.8872
0.4	1.8832	1.8881
0.45	1.8834	1.8888
0.5	1.8834	1.8893
0.6	1.8828	1.8896
0.7	1.8814	1.8893
0.8	1.8794	1.8884
0.9	1.8767	1.8869
1	1.8735	1.8850

Table II.11: REMP and OO-REMP dipole moments of ClCN molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	2,831	2,845
0,01	2,834	2,847
0,02	2,837	2,850
0,03	2,839	2,853
0,04	2,842	2,855
0,05	2,844	2,857
0,06	2,846	2,860
0,07	2,849	2,862
0,08	2,851	2,864
0,09	2,853	2,866
0,1	2,854	2,868
0,11	2,856	2,870
0,12	2,858	2,871
0,13	2,859	2,873
0,14	2,861	2,874
0,15	2,862	2,876
0,16	2,863	2,877
0,17	2,865	2,879
0,18	2,866	2,880
0,19	2,867	2,881
0,2	2,868	2,883
0,21	2,869	2,884
0,22	2,870	2,885
0,23	2,871	2,886
0,24	2,872	2,887
0,25	2,873	2,888
0,26	2,874	2,889
0,27	2,875	2,890
0,28	2,875	2,891
0,29	2,876	2,892
0,3	2,877	2,893
0,35	2,879	2,896
0,4	2,881	2,899
0,45	2,882	2,901
0,5	2,882	2,903
0,6	2,880	2,905
0,7	2,875	2,905
0,8	2,868	2,904
0,9	2,858	2,901
1	2,844	2,897

Table II.12: REMP and OO-REMP dipole moments of CH_3F molecule

A	$\mu_{OO-REMP}$	μ_{REMP}
0	1,80399	1,80673
0,01	1,80415	1,80695
0,02	1,80430	1,80717
0,03	1,80444	1,80737
0,04	1,80457	1,80757
0,05	1,80469	1,80775
0,06	1,80480	1,80792
0,07	1,80489	1,80808
0,08	1,80498	1,80824
0,09	1,80505	1,80838
0,1	1,80511	1,80852
0,11	1,80517	1,80865
0,12	1,80521	1,80877
0,13	1,80525	1,80888
0,14	1,80527	1,80898
0,15	1,80529	1,80908
0,16	1,80530	1,80917
0,17	1,80530	1,80925
0,18	1,80529	1,80932
0,19	1,80527	1,80939
0,2	1,80524	1,80945
0,21	1,80521	1,80950
0,22	1,80517	1,80955
0,23	1,80512	1,80959
0,24	1,80506	1,80962
0,25	1,80499	1,80965
0,26	1,80492	1,80967
0,27	1,80484	1,80969
0,28	1,80475	1,80970
0,29	1,80466	1,80970
0,3	1,80456	1,80970
0,35	1,80394	1,80960
0,4	1,80317	1,80938
0,45	1,80224	1,80904
0,5	1,80115	1,80858
0,6	1,79856	1,80735
0,7	1,79542	1,80575
0,8	1,79173	1,80379
0,9	1,78749	1,80150
1	1,78269	1,79890

The results of the dipole moments indicated in the tables [II.3 - II.12] above obtained after the calculations with the two methods are good. When we compare the values of the two methods we see that there is a small difference from $0.001(D)$ to $0.05(D)$ at most, we take whatever examples, the calculations on the ClF molecule give a difference between the dipole moment predicted by REMP and that of OO-REMP of $0.005(D)$ pretty much. Therefore, they give almost the same values of the dipole moments for the different values of the mixing parameter.
For the calculation time, the OO-REMP method takes more time for calculation than REMP for this molecule.

Conclusion

The quality of REMP and OO-REMP, was explored for a variation of A parameters with the Aug-cc-pCVQZ base set. Both REMP and OO-REMP provide very good results for dipole moments.
The study of dipole moments showed the dissimilarity of the quality alternation between REMP and OO-REMP. OO-REMP surpasses REMP for the majority of calculated dipole moments.
Otherwise, the results of the dipole moments of the two methods REMP and OO-REMP correspond to the dipole moments evaluated by the method CCSD(T). The comparison of the dipole moments calculated with REMP and OO-REMP at CCSD(T) for cc-pCVQZ provides a benchmark for REMP and OO-REMP. CCSD(T), which is called the "gold standard" of computational chemistry gives results similar to REMP and OO-REMP. Each of the three works similarly for different statistical values. Therefore, REMP and OO-REMP are very promising, because they scale as N^6, while CCSD(T) scale as N^7.
The dipole moments of the 19 small molecules were examined in this work. REMP and OO-REMP described this property accurately when we compare it with CCSD(T). when using the aforementioned optimal A parameters (REMP:$A \in [0.15, 0.35]$; OO-REMP: $A \in [0.13, 0.25]$), a relatively.
With these results in mind, the question arises, if it would be worth formulating analytical gradients for REMP, since this would increase the computational speed, especially for larger molecules. When comparing REMP and OO-REMP, OO-REMP performs only a cut above REMP but is computationally significantly more expensive.

Finally, since REMP is a variant of the Rayleigh-Schrödinger perturbation theory, it could be possible to predict the dipole moments with the REMP method with an accuracy of CCSD(T) method.
As perspective of this work, it is important to complete the calculation using REMP and OO-REMP to all molecules studied by Hait et al. It will provide more and sufficient data for statistical analysis. The behavior of REMP wave function in dipole moment evaluation accordingly to molecule nature will be better analyzed.

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