

Dynamical Electron Correlation Within Hartree-Fock Limitation

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RESEARCH ARTICLE

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Abstract

Aim: Calculation of dynamical electron correlation energy within Hartree Fock formalism to achieve post Hartree Fock accuracy.

Achievement: Using intermediate Hamiltonian technique and perturbation methodology we can construct a wave equation which on projection gives very simple equation for correlation energy. Correlation energy only depends on the amount of perturbation. This method is applied for few small molecules. It is found that this method produces very accurate results which is comparable to CCSD method.

Conclusion: The present method which is termed as Extended Hartree Fock (EHF) method is proved to be a very good tool for electronic structure theory as its computational requirement is equivalent to HF method but its accuracy is comparable to Coupled Cluster based methods.

Keywords: Dynamical Electron Correlation; Extended Hartree Fock; CCSD

1 Introduction

Development of quantum methodology has immense importance in theoretical physics and chemistry research. At present, computational chemistry is widely used for in silico drug designing, [1, 2, 3] molecular modeling, [4] studying reaction mechanism, theoretical calculation of thermodynamical properties of a chemical system, etc. In computational chemistry there are mainly two different methodologies which are commonly used; Quantum computation *e.g.* Hartree Fock method (HF), [5, 6, 7] Coupled Cluster (CC) based method, [8, 9, 10] Perturbation Theory,

[11, 12, 13] Configuration Interaction (CI) based method, [14, 15] Density functional theory (DFT) [16, 17, 18] etc. and Classical simulation *e.g.* Monte Carlo (MC) simulation, [19, 20] Molecular dynamics (MD) simulation [21, 22] etc. These two methods are also important in theoretical physics research. Quantum computation produces very accurate results but it requires sophisticated computation facilities compare to classical simulations. Thus for larger systems, say for studying protein folding, dynamical properties of a system, etc. we can't use quantum calculations due to computational limitations, though we wish to use.

In quantum computation, there are lots of sophisticated, powerful and accurate methods. These methods may be classified into two distinct classes; traditional wave function based methods *e.g.* HF, CCSD, CISD, etc. and electron density based methods *e.g.* DFT. Wave function based methods are more organized and consistent methods. These methods fulfill desire level of accuracy but computationally costly and not easy to implement. On the other hand, density based methods, like Density functional theory, is easy to implement with loss of acceptable amount of accuracy and applicable for comparatively larger systems.

Hartree Fock (HF) approximation is the most important advancement in wave function based methods. Calculation of ground state electronic energy of any molecular system using HF method yields 98% to 99% accurate results. Still the search for efficient quantum computation methods is going on for more than 80 years after the invention of HF method because for chemical reactions, molecular properties like dipole moment, quadrupole moment, polarizability, gradient, hessian, etc., we need measurement of energy difference or energy response. The error in energy for HF method is due to the dynamical electron correlation which arises due to the use of closed shell Slater determinant as ground state electronic configuration where electrons are forced to confined in particular orbitals. Thus, to calculate the dynamical electron correlation energy, three different classes of methodology have been developed and still developing by several researchers and used to solve chemical problems like excitation energy calculation, transition state prediction, spectroscopic properties prediction, calculation of thermodynamical properties of chemical systems, etc. In all these three methods HF electronic configuration is taken as starting point. In Coupled Cluster (CC)

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and Configuration Interaction (CI) methods excited determinants are generated from HF determinant and added to the Slater determinant with appropriate coefficients to improve the wave function keeping the Hamiltonian fixed. In CC methods excitation operator (T) is taken as an exponential function which makes it size consistent even after the truncation of the cluster operator at T_2 or T_3 level of approximation. On the other hand, in CI method excited determinants are added as a linear combination and hence truncated CI is not size consistent while Full CI is size consistent. Full CI and Full CC are equivalent and exact but not applicable for any moderate systems due to the computational barrier. Even, truncated CI and CC methods need huge amount of computation facilities compare to HF or DFT for same numbers of electrons. Thus, these two methods are not useful for larger systems.

The other class of post HF method is many body perturbation theory (MPT) which is also known as Møller Plasset (MP) theory. Møller Plasset (MP) theory is a special case of Rayleigh-Schrödinger perturbation theory [23] where unperturbed Hamiltonian is replaced by a perturbed Hamiltonian with the constraint that perturbation must be very small and the eigen functions of unperturbed Hamiltonian should also be the eigen function of perturbed Hamiltonian though eigen values are different. As, in this method, only the Hamiltonian is modified not the wave function, we may have the energy corrections only. It is not a variational method. Calculation of molecular properties using this method is not trivial, needs extensive modifications. But MP methods require less computational facilities compare to CC and CI based methods for the same study.

To quantum chemists development of a method which would take care of dynamical electron correlation as good as CI or CC methods but for the computation cost of HF method, is still challenging and beyond our imagination. Till date it is believed that we can't improve dynamical electron correlation doing only HF calculation with out expansion of wave function (as done in CI and CC methods) or solving the perturbed Hamiltonian. In this article I have shown that we can really break this myth. It is possible to calculate electron correlation energy as good as CCSD method with out doing any physical evaluation of expanded wave function or solving perturbed Hamiltonian. We can construct wave function of any system which includes the effects of dynamical electron correlation from Hartree Fock wave function correspond to that system with known values of expansion coefficients. In this method, it is considered that electron correlation arises due to the extra boundary condition to keep all electrons in the lowest energy states. It is obvious that even at ground state there is significant probability of finding an electron above the Fermi level. Hence to put all electrons below the Fermi level we have to perturb the system. Thus, in some sense, present method has similarities with perturbation theory. But, here

perturbation is strictly considered as electric field perturbation as electron correlation arises due to the detention of electrons in Fermi levels only in HF approximation. Not only that, in this method concepts of intermediate Hamiltonian [24, 25, 26] is used to form wave equation of the perturbed system. In this way, we get modeled Hamiltonian with modified wave function but exact energy of that state. As we have considered the perturbation as an electric field perturbation, we may have the coefficients of perturbed wave function. Thus, using the perturbed wave function we may get all information of the system which is related to wave function of that system. In MP methods, we need further quantum computation for correlation energy calculation for the different orders of perturbation. But in the present formalism, I have used the left projection technique to solve the perturbed equation and found that at least for energy calculation we don't need more quantum computation as correlation energy (E_{corr}) only depends on the numerical value of the perturbation (λ), HF energy of the unperturbed system (E_{HF}) and first derivative of the unperturbed HF energy with respect to the electric field perturbation, *i.e.* electric dipole moment of that system. As in this method only HF calculation is required to get correlation energy beyond the HF level, we may name this method as **Extended Hartree Fock (EHF)** method.

2 Theory

Schrödinger wave equation for many electron system may be given as

$$H|\Psi\rangle = E|\Psi\rangle \quad (1)$$

where H is the Hamiltonian of the system, E is the energy of the system and Ψ is the wave function. For Hartree Fock method we can write

$$H_{HF}|\Psi_{HF}\rangle = E_{HF}|\Psi_{HF}\rangle \quad (2)$$

where H_{HF} is Hartree Fock Hamiltonian, Ψ_{HF} is Hartree Fock wave function and E_{HF} is ground state Hartree Fock energy.

As mentioned in the introduction section that the dynamical electron correlation is due to the use of Slater determinant where electrons are forced to confined to the lowest energy states only, we need extra term in the Hamiltonian to do so. Or, in the other way, we can say that Hartree Fock Hamiltonian is perturbed by the electronic pressure which arises due to the addition of electrons one by one to the confined Slater determinant. Thus, we can model our Hamiltonian by adding perturbation term to the unperturbed Hartree Fock Hamiltonian. The Hartree Fock wave function, Ψ_{HF} , may or may not be the eigen function of

our modeled Hamiltonian for finite amount of perturbation. Thus, we may model our wave function by including the effect of perturbation to the Hartree Fock wave function. Here we may use the idea of intermediate Hamiltonian. [24, 25] In intermediate Hamiltonian approach, model Hamiltonian is operated on trial wave function to get exact energy. Thus, we may make an approximation that our modeled wave function is an eigen function of our modeled Hamiltonian and the eigen value is the exact ground state energy. In this approximation our present wave equation is as follows -

$$H_{mod} |\Psi_{mod}\rangle = E_{exact} |\Psi_{mod}\rangle \quad (3)$$

where

$$H_{mod} = H_{HF} + \lambda V$$

and

$$|\Psi_{mod}\rangle = |\Psi_{HF}\rangle + \lambda |\Psi'_{HF}\rangle + \lambda^2 |\Psi''_{HF}\rangle + \dots \quad (4)$$

In equation 4, λ is the amount of perturbation and v is correction term to the Hamiltonian due to perturbation. v must be a Hermitian operator. As we have considered that our perturbation is due to electronic pressure, v must be the first order derivative of H_{HF} with respect to the electric field. Hence, v is the electric dipole operator. To construct the perturbed wave function we may use the Taylor series of expansion of Ψ_{HF} around λ . $|\Psi'_{HF}\rangle$, $|\Psi''_{HF}\rangle$, etc., in equation 4 are different order derivatives of Ψ_{HF} with respect to the electric field. Incorporating the values of H_{mod} and $|\Psi_{mod}\rangle$ in equation 3 we get

$$\begin{aligned} & (H_{HF} + \lambda V) \left(|\Psi_{HF}\rangle + \lambda |\Psi'_{HF}\rangle + \lambda^2 |\Psi''_{HF}\rangle + \dots \right) \\ & = E_{exact} \left(|\Psi_{HF}\rangle + \lambda |\Psi'_{HF}\rangle + \lambda^2 |\Psi''_{HF}\rangle + \dots \right) \end{aligned} \quad (5)$$

In perturbation theory, perturbed equations are solved by comparing different order of λ of left and right side of the perturbed equation. In that process we get different order energy corrections to the ground state Hartree Fock energy. To do so we need further computations which need good computational facilities. Not only that, we do not get perturbed wave function directly. Instead of comparison method, left projection technique is used here to solve equation 5. Projecting $\langle \Psi_{HF} |$ from the left on equation 5 we get

$$\begin{aligned} & E_{HF} + \lambda \langle \Psi_{HF} | H_{HF} | \Psi'_{HF} \rangle + \lambda \langle \Psi_{HF} | v | \Psi_{HF} \rangle \\ & = E_{exact} + \lambda E_{exact} \langle \Psi_{HF} | \Psi'_{HF} \rangle \end{aligned} \quad (6)$$

As λ is small we can ignore the higher terms of λ *i.e.* λ^2 , λ^3 , etc. For very small value of λ *i.e.* when $\lambda \rightarrow 0$

$\langle \Psi_{HF} | \Psi'_{HF} \rangle \rightarrow 1$. Thus, equation 6 becomes

$$\begin{aligned} & E_{HF} + \lambda \langle \Psi_{HF} | H_{HF} | \Psi'_{HF} \rangle + \lambda \langle \Psi_{HF} | v | \Psi_{HF} \rangle \\ & = E_{exact} (1 + \lambda) \\ & = E_{exact} \end{aligned} \quad (7)$$

[as λ is very small $(1 + \lambda) \approx 1$]

Equation 7 is the expression for total energy of a system. For calculation of dynamical electron correlation energy we can rearrange equation 7 to get

$$\begin{aligned} & E_{corr} = E_{exact} - E_{HF} \\ & = \lambda \langle \Psi_{HF} | H_{HF} | \Psi'_{HF} \rangle + \lambda \langle \Psi_{HF} | v | \Psi_{HF} \rangle \end{aligned} \quad (8)$$

We know from Rayleigh-Schrödinger perturbation theory that

$$H_{HF} |\Psi'_{HF}\rangle = E_{HF} |\Psi'_{HF}\rangle + E'_{HF} |\Psi_{HF}\rangle - V |\Psi_{HF}\rangle \quad (9)$$

Putting the value of $H_{HF} |\Psi'_{HF}\rangle$ from equation 9 in equation 8 we get

$$E_{corr} = \lambda (E_{HF} + E'_{HF}) \quad (10)$$

Equation 10 is our working formula for calculation of dynamical electron correlation energy. To calculate correlation energy we need to know the value of λ . In our approximation perturbation is due to the gradual addition of electrons to the lowest electronic states. Thus, we may consider that the value of λ would be inversely proportional to $(N - 1)$ where N is the number of electrons of the system and $(N - 1)$ number of electrons are responsible for the perturbation of that system. So we can write λ as

$$\lambda = \frac{B}{(N - 1)} \quad (11)$$

where B is a constant. We can evaluate B from known value of E_{corr} of any system. If λ is known to us, we can calculate ground state energy of any system by knowing Hartree Fock energy and the dipole moment of that system calculated at the Hartree Fock level.

Still it is not known whether B is an universal constant or it depends upon the nature of the system *i.e.* polar or non-polar. In either case, value of B and hence λ is easy to evaluate. Knowing the value of λ we should get the modeled wave function from equation 4. Using this wave function it would be easy to calculate other molecular properties which depends upon the electronic configuration of a system.

3 Computational Details

To implement the above mentioned method, at first B is calculated for non-polar molecule using H_2 molecule at the Coupled Cluster Singles and Doubles (CCSD) level and then for polar molecule using HF molecule at the same level of theory. Using known values of B , correlation energies and ground state electronic energies of different homo-nuclear and hetero-nuclear molecules are calculated. All Hartree Fock calculations and CCSD calculations for closed shell molecules are performed by using Gaussian 09 package.[27] The structures are optimized without any symmetry constraints. All the minimum energy structures are confirmed by the harmonic vibrational frequency without any imaginary mode. The convergence thresholds are set to 0.000015 Hartree/Bohr for the forces, 0.00006 Å for the displacement and 10^6 Hartree for the energy change. For open shell molecule (NO_2), CCSD calculation is not possible as it has multi-reference character. Thus, Fock-Space Multi-reference Coupled Cluster Singles and Doubles (FSMRCCSD)[28, 29, 30] method is used for comparison. FSMRCCSD calculation is done using standardized[28] in home program. STO-3G, [31] 6-31G [32] and cc-pVDZ [33] basis sets are used for different molecules.

4 Results and Discussions

4.1 Evaluation of B

Table 1 Calculation of B

Mole- cule	E_{HF} (a.u.)	E_{CCSD} (a.u.)	E_{corr} (a.u.)	B
H_2	-1.12675	-1.15167	-0.024917	0.02211
HF	-99.98342	-100.1148	-0.13141	0.01156

Table 2 Correlation energies of few diatomic gases

Mole- cule	E_{HF} (a.u.)	E_{corr} [CCSD] (a.u.)	E_{corr} [EHF] (a.u.)	% error w.r.to E_{corr}^{CCSD}	% error w.r.to E_{CCSD}
N_2	-108.867	-0.2283	-0.1852	18.87	0.038
O_2	-149.461	-0.2663	-0.2203	17.25	0.029
F_2	-198.646	-0.2710	-0.2584	4.66	0.006
Cl_2	-918.862	-0.5758	-0.5567	3.32	0.002
Br_2	-5139.490	-1.5023	-1.4897	0.84	0.000

First, the proportionality constant B is evaluated for both homogeneous and heterogeneous molecules. For homogeneous molecule H_2 and for heterogeneous molecule HF

molecule is chosen. 6-31G basis is used for these calculations. B values are calculated with respect to CCSD correlation energies of these two molecules. Calculated results are presented in Table 1. We observed that B values are not same for polar and non-polar molecules. In fact, B value for polar molecule is nearly half of B value for non-polar molecule. This suggests that in polar molecule electrons are defused and hence perturbation is less compare to the non-polar molecule where electrons are uniformly clouded.

4.2 Correlation energies of homogeneous diatomic molecules

Few diatomic homo-nuclear gasses, N_2 , O_2 , F_2 , Cl_2 and Br_2 , are chosen for validation of extended Hartree Fock (EHF) method *i.e.* method presented here. 6-31G basis is used for all molecules and value of B is taken from Table 1. Calculated results are presented in Table 2. It is observed that for N_2 and O_2 % errors in correlation energies with respect to CCSD correlation energies are more than 10%, 18.87% and 17.25% respectively. But % errors with respect to total CCSD energies are only 0.038% and 0.029% for those two molecules. For other three molecules presented here, % errors in correlation energies as well as in total energies are very small. It is also observed that with increase of number of electrons EHF correlation energies approaches to CCSD correlation energies. Thus, we may conclude that for larger systems EHF and CCSD would be equivalent.

4.3 Electron correlation energy of hetero-nuclear diatomic molecule

Table 3 Electron correlation energy of BH , NH , BF and NF

Mole- cule	E_{HF} (a.u.)	μ (Cal) (D)	E_{corr} [CCSD] (a.u.)	E_{corr} [EHF] (a.u.)	% error w.r.to E_{CCSD}
BH	-25.1079	1.66	-0.0614	-0.0592	0.009
NH	-54.8350	2.01	-0.0942	-0.0898	0.008
BF	-124.048	0.72	-0.1876	-0.1110	0.062
NF	-153.626	0.20	-0.2201	-0.1186	0.066

Electron correlation energy of BH , NH , BF and NF are calculated and presented in Table 3. It is observed that for BH and NH EHF produces very good results with respect to CCSD but for BF and NF EHF correlation energies are far away from CCSD correlation energies. For these two systems dipole moment is less than 1Debye. Thus, we can conclude that B value for these two systems are higher than what is used for these calculations. Small values of dipole

moments indicate that charge polarization is very less and hence perturbation is high. This, in fact, justifies the approximation made in EHF method *i.e.* electron correlation is due to the over clouding of electrons. Thus, for exact calculation of any polar system B value should be evaluated properly. One can scale B according to the dipole moment value of the system.

4.4 Ploy atomic molecules

Table 4 Ground state electronic energies of few poly atomic molecules

Mole- cule	E_{EHF} (a.u.)	μ (Cal) (D)	E_{CCSD} (a.u.)	E_{EHF} (a.u.)	% error w.r.to E_{CCSD}
H_2O	-75.9854	2.50	-76.1196	-76.0818	0.049
H_2S	-398.627	1.87	-398.904	-398.888	0.004
NH_3	-56.1655	1.38	-56.2921	-56.2362	0.099
CH_4	-40.1806	0.00	-40.2988	-40.2793	0.048
CO_2	-187.482	0.00	-187.842	-187.679	0.086

For diatomic molecules or systems EHF works very fine. Thus, I have extended my study for few poly atomic molecules. H_2O , H_2S , NH_3 , CH_4 and CO_2 are chosen for this purpose. All these molecules have closed shell electronic configuration. Calculated results are presented in Table 4. 6-31G basis is used for these calculations. As CH_4 and CO_2 have zero dipole moment, B_{H_2} is used for calculation of these molecules. For other three molecules B_{HF} is used. In all cases EHF energies are very close to CCSD energies but less. Thus, it is expected that if we be able to evaluate λ exactly we should get exact electronic energy of any system.

4.5 Ground state electronic energies of NO_2

Table 5 Ground state electronic energies of NO_2 at two different basis sets

Basis	E_{EHF} (a.u.)	E_{FSMRCC} (a.u.)	E_{EHF} (a.u.)	% error w.r.to E_{CCSD}
STO-3G	-201.2692	-201.4622	201.4518	0.005
cc-pVDZ	-204.0402	-204.5967	-204.2453	0.171

Ground state electronic energies of NO_2 is calculated using EHF method. I have chosen this molecule because it has open shell electronic configuration and multi-reference character at ground state. Thus single reference CCSD calculation is not possible for this molecule. We need

Multi-reference CCSD [34, 35, 36, 37, 38] method for this molecule. Due to multi-reference description more computational complexities arises. Both time and computer space requirement increase for multi-reference methods. This study shows that EHF method is also applicable for such open shell systems with very good accuracy. Fock-space Multi-reference Coupled Cluster (FSMRCC) with singles and doubles approximation is used for this calculation. Two different basis sets are used for this study; STO-3G and cc-pVDZ. Calculated results are presented in Table 5. EHF energy is very close to FSMRCCSD energy value for STO-3G basis but marginally differs for cc-pVDZ basis.[33] This is because B value is not standardized for this basis.

5 Conclusions

The present method which is termed as Extended Hartree Fock (EHF) method is proved to be a very good tool for electronic structure theory as its computational requirement is equivalent to HF method but its accuracy is comparable to CC based methods. It is also shown that there is no need for multi-reference descriptions for degenerate states. In principle it is an exact theory provided we have the exact value of perturbation parameter (λ). A very good guess of perturbation parameter would yield very good result. This method would be applicable for larger systems also.

6 Declarations

6.1 Ethics approval and consent to participate

Not applicable

6.2 Consent for publication

Not applicable

6.3 Availability of data and material

Not applicable

6.4 Competing interests

The author declares that he has no competing interests.

6.5 Funding

This project is not funded. It is done as a part time work.

6.6 Authors' contributions

Not applicable

6.7 List of abbreviations

CCSD = Coupled Cluster singles and Double
 EHF = Extended Hartree Fock
 HF = Hartree Fock
 DFT = Density Functional Theory
 MPT = Many-body Perturbation Theory
 FSMRCC = Fock Space Multi-reference Coupled Cluster

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