



Impact of electron exchange and correlation to simulate the structure, electronic and nonlinear optical properties of urea

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Abstract: In the present investigation, the efficiency of different quantum chemical methods including a range of electron exchange and correlation has been checked to simulate the molecular structure, electronic and nonlinear optical properties of urea. Different quantum chemical methods including semi-empirical with no exchange and correlation (AM1 and PM3), *ab initio* with static and dynamic correlation (HF, MP2 and CCSD) and density functional theory (B3LYP and PBE0) methods having exchange and correlation effects, have been applied to calculate geometrical, electronic and nonlinear optical properties of urea. The obtained results at different methods have been compared with highly accurate and correlated CCSD method to check the effect of electron correlation. The results show that for molecular geometry optimization, B3LYP functional (with 15 % of HF exchange) is found to be computationally 25 times less expensive and shows good agreement with CCSD geometrical parameters. For polarizability properties including dipole moment (μ_z), polarizability (α_{zz}), and first hyperpolarizability (β_{zzz}), MP2 and B3LYP methods have reproduced the CCSD values, which indicates that exchange and correlation effects are important to accurately model the electronic and nonlinear optical properties of small organic molecules like urea. While for vertical ionization potential (VIP), vertical electron affinity (VEA), and chemical hardness (η), HF and MP2 results are close to highly correlated CCSD results. Thus the present study provides the fundamental insights into the parent organic molecule of urea by spotlighting the impact of exchange and correlation effect on the modeling of its structure-property relationship.

Keywords: urea, electron exchange and correlation; polarizability; hyperpolarizability

1. INTRODUCTION

In the modern era science, the quantum chemical methods are becoming very popular in material designing because the computers are getting faster and algorithms are growing mature. There is a range of computational methods in quantum chemistry.¹ In present study, our focus will be only three main classes of quantum chemical methods with different ranges of exchange and correlation in these methods that are used in modern material science. These quantum chemical methods include semi-empirical without any exchange and correlation effects,² *ab initio* methods with different amounts of electron correlation effects³ and density functional theory methods having both exchange and correlation effects which is a very effective quantum chemical approach now day.⁴ Semi-empirical methods use experimental data to avoid the solution of complex terms that involved in the *ab initio* methods and some examples

are Austin Model 1 (AM1), Parametric Method 3 (PM3), and Modified Neglect of Diatomic Overlap (MNDO) etc.⁵ Theoretically, several contemporary semi-empirical models are based on the neglect of diatomic differential overlap approach in which the unit matrix replaces the overlap matrix S by replacing the Hartree-Fock equation $|\text{H-ES}| = 0$ into a simple equation $|\text{H-E}| = 0$. Existing semi-empirical models differ by the further approximations that are made when evaluating one- and two-electron integrals and by the parameterization philosophy. Semi-empirical methods are computationally less expensive but have poor accuracy especially if parameterization is not available for atoms involved in semi-empirical study.⁶ The second class is *ab initio* methods that are based on the Schrödinger wave equation, which is solved by using quantum mechanics and basic physical constants. Among *ab initio* methods,⁷ Hartree Fock (HF),⁸ Configuration Interaction Singles (CIS),⁹ Møller-Plesset perturbation theory (MP2),¹⁰ and highly Correlated Coupled-cluster Singles and Doubles

(CCSD)¹¹ methods. The CCSD method is based on couple cluster theory, which treats the dynamical electron correlation problem in terms of interacting clusters of electrons. The term "Electron correlation" is used to refer to any electronic many-body effect, which cannot be described by Hartree-Fock theory. That means, which requires a wave function more complicated than a single determinant (or configuration state function) to be described adequately. According to the Schrodinger wave equation for one electron:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi \quad (1)$$

Putting this equation in Born-Oppenheimer approximation, which for an N -electrons with atomic number Z is:

$$\sum_{i=1}^N \left[-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \sum_{j=i+1}^N \frac{1}{|r_i+r_j|} \right] \psi[(r_1, r_2, \dots, r_N) = E\psi(r_1, r_2, \dots, r_N) \quad (2)$$

Here first term is kinetic energy of electron i , the second term is the potential of electron-nuclear attraction while the third term is electron-electron repulsion between electron i and other electrons in the system related with electron correlation. Usually the electron correlation is described as electrons avoiding each other. Generally, the correlation is required to get the accurate energetics of a system, but not for the coarse of electronic structure. The MP2 and CCSD methods based on HF reference, includes both dynamic and static correlation. In recent era of computational science, the CCSD method has emerged as the most powerful, accurate and practical approach to make accurate quantum chemical predictions. Definitely, many scientists consider CCSD method as a "gold standard" in *ab initio* quantum chemistry. The major drawback of CCSD method is that it is computationally very expensive (computing CPU time is very large) method. The third class is density functional theory (DFT) methods.¹² The density functional theory (DFT) methods involve the study of the properties of a chemical system through its electronic density. Unlike the wave functional in *ab initio* methods that is not a physical reality, but a mathematical construct, the electronic density is physical characteristic of all the atoms and their molecules. According to Hohenberg-Kohn Theorem:

$$n(r) = N \int d^3 r_2 \int d^3 r_3 \dots \int d^3 r_N \psi^*(r_1, r_2, \dots, r_N) \psi(r_1, r_2, \dots, r_N) \quad (3)$$

The ground state function is based on ground state electron density with $n(r)$, and $\psi(r)$ as observable properties. The above Hohenberg-Kohn Theorem provides foundations to construct a verity of good density functionals. Exchange effects are included in many DFT functionals. Exchange effects are due Paul exclusion principal and it can be written exactly as a function of single particle orbitals:

$$E_x = -\frac{q^2}{2} \sum_{jk} \int d^3 r \int d^3 r' \frac{\phi_j^*(r)\phi_k^*(r)\phi_j(r)\phi_k(r)}{|r-r'|} \quad (4)$$

Interestingly, the exchange effects are significantly larger than correlation effect, which due to the lowering of Coulomb repulsion energy. Broadly speaking there are three types of methods in DFT. *Local density approximation (LDA)* methods¹³ that are typically not a very popular or useful method. This method assumes a uniform electron density throughout the molecule.

Gradient-corrected (GC) methods¹⁴ look to account for the non-uniformity of the electron density. *Hybrid* methods,¹⁵ as the name suggests, attempt to incorporate some of the more useful features from *ab initio* methods (specifically Hartree-Fock methods) with some of the improvements of DFT mathematics. Hybrid methods, such as B3LYP,¹⁶ tend to be the most commonly used methods for computational chemistry practitioners.

Thus the aims of present investigation are multifold. Firstly, it will be interesting to perform a comparative study of quantum chemical methods with different values of exchange and correlation effects to simulate the structure, electronic and nonlinear optical properties of urea molecule, which will provide a good accurate method with comparatively low computational costs. The urea was the first organic compound to be artificially synthesized and is considered a prototype molecule to understand the basic structure-property relationship in different organic molecules. Secondly, as different electronic properties are usually method dependent, it will be useful to compare the dipole moments, polarizability and first hyperpolarizability of urea at different adopted methods to found the impact of exchange and correlation effects. Thirdly, the global reactivity descriptor properties like VIP, EA and chemical hardness that are the basic characteristics of a chemical system will be also calculated and compared to get a structure-property relation. Last but not least, based on our previous research results on electro-optical properties of different materials,¹⁷ it will be interesting to check the effect of electron correlation and to provide some standard references values for dipole moment, polarizability, first hyperpolarizability, VIP, EA and chemical hardness values at a range of quantum chemical methods so that these reference values will help in future research of small molecules like urea.

2. COMPUTATIONAL DETAILS

In present study, three main classes of quantum chemical methods including semi-empirical, *ab initio* and DFT methods have been used. The AM1, PM3 methods have been adopted from semi-empirical class.⁵ Similarly, the HF, MP2 and CCSD methods^{9-11, 13-14} from *ab initio* class while B3LYP and PBE0 methods have been chosen from DFT class.¹⁵⁻¹⁶ The molecular geometry of urea has been explicitly optimized with all methods. The 6-31G* basis set has been used for geometry optimization and electronic property calculations with all adopted methods (except semi-empirical methods). The Gaussian 09¹⁸ program package has been used to perform all the calculations in present study.

For electronic polarizability and first hyperpolarizability calculation, a finite field (FF) methodology has been used in present investigation. In several previous calculations for electronic polarizability and first hyperpolarizability,¹⁹ the FF methodology has successfully reproduced the results obtained by experimental²⁰ and two-level approaches.²¹ The FF method has been also used in concert with electronic structure calculations. In FF method, a molecule is subjected to a static electric field F and its energy can be expressed by following Eq. 5:

$$E = E^{(0)} - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (5)$$

Where $E^{(0)}$ is the energy of molecule in the absence of an electronic field, μ is the components of the dipole moment vector, β , and γ are the *first and second hyperpolarizability* tensors, respectively, while i, j and k are x, y and z components, respectively. It is clear from Eq.5 that the values of μ, α, β , and γ can be obtained by differentiating E with respect to F . Similarly, Koopman's theorem has been used to calculate ionization potential (IP) and adiabatic electron affinity (EA) of urea molecule.²² According to Koopman's theorem, the IP is equal to $-\epsilon_{\text{HOMO}}$ of the uncharged molecule while the adiabatic EA is equal to $-\epsilon_{\text{HOMO}}$ of the singly charged molecule. Mathematically, it can be written as under:

$$\begin{aligned} \text{IP} &\approx -\epsilon_i, \quad 1 \leq i \leq N \\ \text{EA} &\approx -\epsilon_a, \quad N+1 \leq a \end{aligned}$$

Where N is the number of electrons in a molecule.

The chemical hardness (η) is approximated using following relationship based on HOMO and LUMO energies of urea molecule at all adopted methods.²³

$$\eta = \frac{\epsilon(\text{LUMO}) - \epsilon(\text{HOMO})}{2} \quad (6)$$

Geometry Parameters	Methods						
	No Exchange-Correlation			Correlated		Exchange-Correlation	
	AM1	PM3	HF	MP2	CCSD	B3LYP	PBE0
R C ₁ -N ₃ (Å)	1.402	1.430	1.373	1.391	1.391	1.391	1.383
R C ₁ -O ₂ (Å)	1.255	1.226	1.197	1.197	1.220	1.220	1.216
A N ₃ -C ₁ -N ₄ (°)	120.1	118.7	113.9	113.0	113.2	113.6	113.6
CPU time	16S	10S	22.7S	52.7S	1020S	7S	38S

Table 1. The geometrical parameters at different computational methods with 6-31G* bases set according to the numbering as in Figure 1

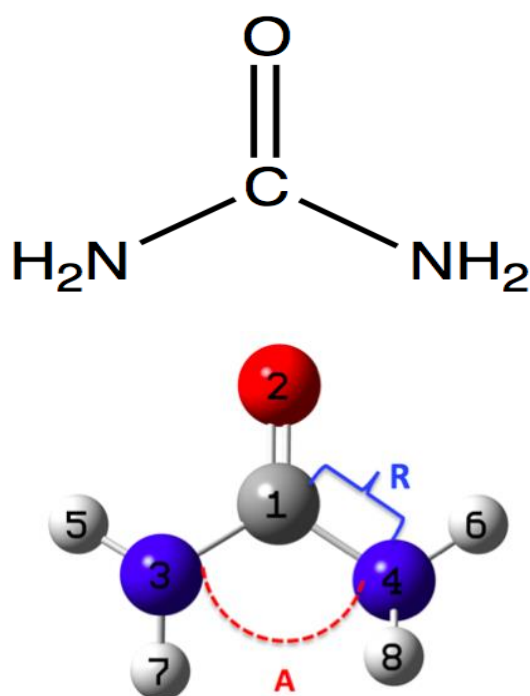


Figure 1. The chemical representative structure and 3D optimized structure of urea molecule in C_2 point group symmetry at CCSD/6-31G* level of theory where R is bond length and A is bond angle.

3. RESULTS AND DISCUSSION

Molecular Geometries

Inline with previous investigation about urea molecular structure, it has been found that urea molecule has two stable structural configurations with point groups C_2 and C_s .²⁴ The molecular structure with C_2 point group has been found to slightly lower in energy than C_s structure. Both the structures have a floppy pyramidal structure of their amino groups. Thus, in present study, the urea molecular structure of C_2 point group with a floppy pyramidal structure of their amino groups has been used (see Figure 1). The C_2 molecular geometry has been further confirmed by frequency calculation as a global minimum structure while a planer molecular geometry with C_{2v} point group has not been found as a global minimum structure due to imaginary frequency in it. The Table 1 shows the two main geometrical parameters including bond lengths (R) and triangle (A) of urea molecule calculated at all adopted methods. The total CPU time to complete optimization has also represented in Table 1.

To make a comparative analysis, the optimized bond lengths at all adopted methods have been compared among each other and with CPU time as illustrated in Figure 2. It can be seen that MP2 and B3LYP methods has successfully reproduced the results of CCSD method while semi-empirical and HF methods have over and under estimated the bond lengths of urea molecule, respectively. It is interesting to note that the B3LYP method that has successfully reproduced the CCSD results has CPU time of 7 seconds that is 25 times less than that of CCSD method. Thus the B3LYP method that is computationally not expensive can be used to get semi-quantitatively accurate results even for larger size molecules where CCSD is not a good choice due to it high computational cost.

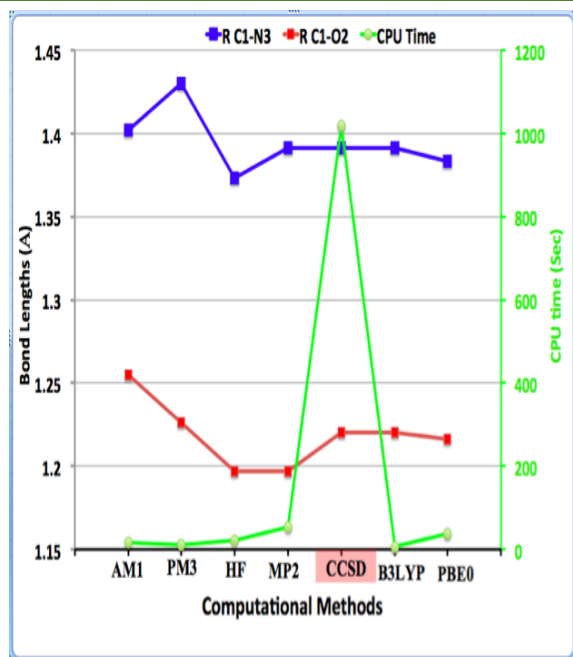


Figure 2. The plot of optimized bond lengths of urea molecule with different adopted methods and their total CPU times

Polarizability and First Hyperpolarizability

Three fundamental electronic properties of urea molecule including dipole moment, polarizability and first hyperpolarizability have been calculated using a range of different method. The electric dipole moment can be defined for two point charges on a molecule as the product of the charge times the distance between them. The direction of dipole moment vector is towards the positive point charge. The concept of dipole moment is very useful to explain the structure of molecules where it is possible to measure charge separation but not the distances between charges. In urea molecule, the carbon atom and oxygen atom form a dipole because oxygen atom is more electronegative element and attracts the bond pair of electrons (hence negative charge) towards itself their by creating a positive point charge of same magnitude at carbon atom. Furthermore, polarizability and first hyperpolarizability of urea molecule have been calculated with all adopted methods. Polarizability represents the relative tendency of a charge distribution over a molecule when an external electric field is applied to it. Polarizability provides several insights into the geometry of molecule by providing a dynamic response to external fields applied on the system. First hyperpolarizability (β) is the microscopic nonlinear optical response to a high intensity beam of laser light. The nonlinear optical materials with significant amplitudes of first hyperpolarizability have several applications in frequency doubling, optical data storage and telecommunications etc.²⁵ For a molecule with C_2 symmetry, its total dipole moment is equal to the C_2 axis as given by following simple relation.

$$\mu_0 = \mu_z$$

Similarly, we have also calculated the only α_{zz} and β_{zzz} , which are the dominant components of polarizability (α_0) and hyperpolarizability (β_0) of urea, respectively.

For the average polarizability, we have

$$\alpha_{zz} \cong \alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (7)$$

The amplitude of first hyperpolarizability is defined as

$$\beta_{zzz} \cong \beta_0 = (\beta_x + \beta_y + \beta_z)^{\frac{1}{2}}, \quad (8)$$

where

$$\beta_i = \frac{3}{5} \sum_j \beta_{ijj} \quad (j = x, y, z) \quad (9)$$

Due to the presence of C_2 symmetry in urea molecular geometry, the α_{zz} and β_{zzz} components are significant in average values of polarizability and first hyperpolarizability, respectively. The Table 2, shows the results of dipole moment, polarizability and first hyperpolarizability calculated using all adopted methods. A plot of calculated dipole moment (μ_z), polarizability (α_{zz}), first hyperpolarizability (β_{zzz}) with all seven adopted methods has been shown in Figure 3. It is important to note that deviation of first hyperpolarizability is more as compared to that of dipole moment and polarizability values. It might be concluded that the higher order energy derivatives are more sensitive to the amount of exchange and correlation effects.

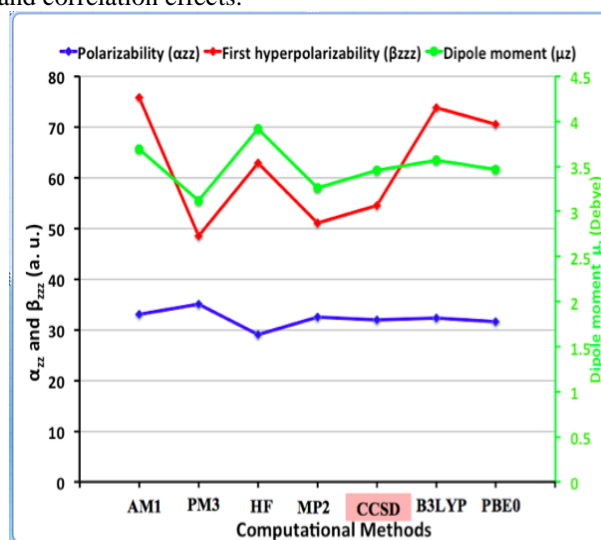


Figure 3. The plot of dipole moment (μ_z), polarizability (α_{zz}), and first hyperpolarizability (β_{zzz}) at all adopted methods

It can be seen from Figure 3 that the PBE0 method has reproduced the dipole value that is very close to highly correlated CCSD method. While for polarizability and first hyperpolarizability, the results of B3LYP and MP2 methods are in good agreement with CCSD results, respectively. Thus it is important to note that significant part of electron correlation can be taken into account using hybrid exchange-correlation B3LYP functional for calculation of electronic properties of molecules like urea.

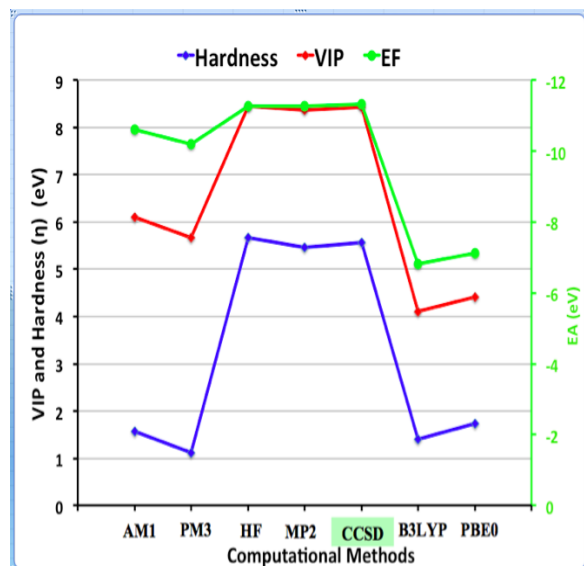


Figure 4. The plot of the global descriptor parameters including vertical ionization (VIP), electron affinity (EA) and chemical hardness (η)

Global Descriptor Properties

In present study, some global reactivity descriptor properties including vertical ionization potential (VIP), vertical electron affinity (VEA), and chemical hardness (η) have been also calculated with all adopted method.²⁶ VIP is the amount of energy that is needed to remove the electron from a molecule. VIP is a very good approximation about the stability of a chemical compound. Larger the value of VIP, higher will be its stability. Another electronic property is VEA, which is the amount of change in energy when a neutral molecule picks up one electron to form an anion. The larger amount of VAE shows that the molecular species.

Electronic Properties	Adopted Methods						
	No Exchange-Correlation			Correlated		Exchange-Correlation	
	AM1	PM3	HF	MP2	CCSD	B3LYP	PBE0
μ_z (Debye)	3.69	3.12	3.92	3.26	3.45	3.57	3.46
α_{zz} (a. u.)	33.07	34.96	28.98	32.52	32.03	32.36	31.58
β_{zzz} (a. u.)	75.72	48.50	62.91	51.05	54.56	73.71	70.53
VIP (eV)	1.57	1.12	5.67	5.47	5.56	1.40	1.73
VEA (eV)	-10.62	-10.20	-11.26	-11.27	-11.31	-6.82	-7.11
η (eV)	6.10	5.66	8.46	8.37	8.44	4.11	4.42

Table 2. The electro-optical properties of urea molecule including dipole moment (μ_z), polarizability (α_{zz}), first hyperpolarizability (β_{zzz}), vertical ionization potential (VIP), vertical electron affinity (VEA), and chemical hardness (η) with all adopted method not represent good result for all three global descriptor parameters.

(VEA) of urea, HF and MP2 showed good agreement with highly accurate CCSD result.

- As the successful methods like CCSD and MP2 are presently not applicable for larger molecules, such investigations as above can help the improvement of methods having lower computational cost as well as good accuracies for larger molecules or basis sets.

6. CONCLUSION

Thus in the light of present quantum chemical investigation, the following concluding points can be drawn as follow:

- It is clear that the effect of electron exchange and correlation has remarkable impact on the calculation of electronic structure and properties for small molecules like urea.
- For geometry optimization, B3LYP results showed good agreement with highly correlated CCSD results and recommended to obtained reliable geometries at low computational costs. The B3LYP not yield the electronic geometry comparable with highly correlated methods but also reduces the computational costs.
- For dipole moment, polarizability, and first hyperpolarizability of urea molecule at MP2 and B3LYP methods showed good agreement with CCSD results, which indicates that the effect of exchange and correlation is important to calculate accurate polarizability, and first hyperpolarizability of urea. For global descriptive parameters like vertical ionization potential (VIP), chemical hardness, and electron affinity

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