VISUAL AND COMPUTATIONAL COMPARISON OF FUNCTIONALS USED IN DENSITY FUNCTIONAL THEORY

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Abstract - This work presents the visual and quantitative comparison of Density Functional Theory (DFT) exchange-correlation energy E_{xc} functionals with Coupled Cluster with Single and Double excitations (CCSD) calculations (and experiment where possible). The E_{xc} functional is an approximate term which is a component of the total energy of a molecule. This comparison is based on visualizing the differences of computed properties, such as the charge density, geometry and other molecular properties between the functional and a CCSD calculation. In this work, this visual comparison for a set of functionals using a set of small molecules is presented to elucidate the method.
Specifically, this visual comparison of the local molecular properties includes the charge density and electron localization function and global molecular properties such as molecular geometry for each DFT functional compared with a CCSD calculation. Note, that the differences of the particular computed properties are computed visually.

Keywords - DFT functionals, Electronic Structure, n-body Schrödinger Equation

1. INTRODUCTION

Density Functional Theory (DFT) [1] is a widely used method of electronic structure theory to solve the n-body Schrödinger equation for gas, solid or solvent phase molecular systems. DFT computes the ground-state energy of molecular systems by approximating the exchange-correlation energy of electrons, expressed in terms of a functional for the electronic energy of the specific system. The core of DFT is the approximate functional describing the exchange-correlation energy, which is constructed from a set of approximations and is increasing in mathematical complexity.

A visual method to display the differences among the numerous (and increasing number of functionals) is discussed which explores the differences in the functionals in computing the charge density and other molecular properties. Scientific visualization is an approach to display the results of using a particular functional and, as such, is a complementary approach to global property parameterization and test suites used to develop functionals.

In this work, an improved method (see [2]) is used to compare density functionals that directly utilizes the local charge density to quantitatively describe differences in computed properties of the molecular systems. The approach for the comparison, utilizes a metric based on the distance from a more accurate but

computationally expensive method called Coupled Cluster (CC) theory [3]. The Coupled Cluster theory is a very accurate method of computing the electronic structure, based on wave function theory that also solves the n-body Schrödinger equation for molecular systems. Coupled Cluster with Single and Double excitations (CCSD) method has been shown to be extremely accurate for small molecules but is often prohibitively expensive (compared with DFT) in its effectiveness.

2. THEORY

The non-relativistic time-independent Schrödinger [4], see Eq. 1, is the starting point for the study of the electronic structure of atoms and molecules.

$$\hat{\mathbf{H}} \mid \Psi \rangle = E \mid \Psi \rangle \tag{1}$$

where $\hat{\mathbf{H}}$ is the Hamiltonian energy function and the Dirac ket vector $\mid \Psi \rangle$ is the wave function describing the molecular system and E is the energy. In this notation, the energy eigenvalue is given as:

$$\langle \Psi \mid \mathbf{H} \mid \Psi \rangle = \int_{-\infty}^{\infty} \overline{\psi} \, \hat{\mathbf{H}} \psi \; d^3 \vec{r} = E \tag{2}$$

Where $\langle \Psi \mid$ is the complex conjugate of $\mid \Psi \rangle$, denoted as $\overline{\psi}$.

A computationally practical implementation of density functional theory has been given by Kohn and Sham (KS) [5]. The Kohn-Sham approach is based on an orbital-density description. The kinetic energy of a non-interacting system of electrons is minimized with respect to a set of single-particle orbitals, $\{\phi_i(\vec{r})\}$, subject to the constraint that the orbitals are orthonormal and that the sum of the squares of the orbitals gives the exact ground state density.

The Kohn-Sham variational principle is expressed as:

$$\delta \left\{ T_s[\phi_i(\vec{r})] + J[\rho(\vec{r})] + V_{ne}[\rho(\vec{r}), v] - \sum_{i=1}^{N} \varepsilon_i (\langle \phi_i(\vec{r}) \mid \phi_i(\vec{r}) \rangle - 1) \right\} = 0 \tag{3}$$

where:

$$T_s[\phi_i(\vec{r})] = -\frac{1}{2} \sum_{k=1}^{N} \langle \phi_i(\vec{r}) \mid \nabla^2 \mid \phi(\vec{r}) \rangle \tag{4}$$

is the kinetic energy for a system of non-interacting electrons,

$$J[\rho(\vec{r})] = \frac{1}{2} \int \int \frac{\rho(\vec{r}) - \rho(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} \; d\tau \, d\tau' \tag{5}$$

where τ is a volume element and $J[\rho(\vec{r})]$ is the Coulomb energy also,

$$V_{ne} = \int \int \rho(\vec{r}) v_{ne}(\vec{r}) d\tau \tag{6}$$

is the nuclear-electron attraction potential energy $E_{xc}[\rho(\vec{r})]$ is the exchange-correlation energy (containing both kinetic and potential contributions to the correlation energy), the ε_i are Lagrange multipliers introduced to ensure that $\{\phi_i(\vec{r})\}$ are orthonormal and

$$\rho(\vec{r}) = \sum_{i=1}^{N} n_i \mid \phi_k(\vec{r}) \mid^2 \qquad (7)$$

is the ground-state electron density. Here n_i is the occupation number of th ith Kohn-Sham orbital $\phi_i(\vec{r})$. The last term in Eq. 3 is the orthonormality constraint for the orbitals $\phi_i(\vec{r})$. The Kohn-Sham variational principle leads to a simple differential equation whose solutions are the Kohn-Sham orbitals:

$$-\frac{1}{2}\nabla^2\phi_i(\vec{r}) + v_{eff}\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}) \qquad (8)$$

where:

$$v_{eff} = \frac{\delta J[\rho(\vec{r})]}{\delta\rho} + \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho} + v_{ne} \qquad (9)$$

is the Kohn-Sham effective potential. This differential equation is reminiscent of the Hartree and Hartree-Fock equations, but it is fundamentally different in that it yields, in principle, the exact ground state density. Although the KS formalism is, in principle, exact. The application of KS is made inexact because the exchange-correlation energy, as a functional of the electron density $E_{xc}[\rho(\vec{r})]$ is not known. Thus, the ability of the KS formalism to yield quantitative results for calculated structures and properties of molecular systems is directly connected to the accuracy of the approximation to $E_{xc}[\rho(\vec{r})]$ used. Fortunately, reasonable approximations to $E_{xc}[\rho(\vec{r})]$ are known.

2.1. Exchange-Correlation Energy

Current strategies for the $E_{xc}[\rho(\vec{r})]$ functional development rely on a process of continuous parameterization in order to capture global properties of sets of well-studied molecules known as test suites and is built upon constituent pieces of previously designed functionals (see Table 1). Thus, the improvement in the ability to compute the electronic structure of molecular systems does not come cheaply, as every step has an associated cost that is a direct consequence of the increased mathematical complexity of the functional.

Table 1. Basic Mathematical Structure of Functionals

Functional	Mathematical Structure [6]
LDA	$E_{xc}^{LDA}[\rho_\alpha,\rho_\beta] = \int d^3r\, \varepsilon_{xc}^{unif}(\rho_\alpha,\rho_\beta)$
GGA	$E_{xc}^{GGA}[\rho_\alpha,\rho_\beta] = \int d^3rf(\rho_\alpha,\rho_\beta,\nabla\rho_\alpha,\nabla\rho_\beta)$
M-GGA	$E_{xc}^{M-GGA}[\rho_\alpha,\rho_\beta] = \int d^3rf(\rho_\alpha,\rho_\beta,\nabla^2\rho_\alpha,\nabla^2\rho_\beta)$

The Local Density Approximation (LDA) is only a functional of the interacting charge densities. The Generalized Gradient Approximations (GGA) are functionals of the interacting charge densities and the gradient of the charge densities. The Meta-Generalized Gradient Approximations (M-GGA) are functionals of the interacting charge densities and the gradient of the charge density plus the kinetic energy. Note that the core foundational components of many modern density functional computations utilize M-GGA functionals.

3. RESULTS

For this study, a small set of carbon and silicon molecules (see Table II) are selected such that single, double, and triple bonded systems are included. Sixteen density functionals (Table 2) selected from the common LDA, GGA and M-GGA functionals are used to compute the approximate ground state energy and geometry for each molecular system. Also, to ensure that the differences are not in fact due to basis set effects, the cc-pvtz basis set is used for all calculations. This basis set is a widely used large basis set for accurate results in both CC and DFT methods.

TABLE 2. The molecules and functionals used in this study.

Sixteen Molecules			Sixteen Functionals			
Single	Double	Triple	LDA	Hybrid	GGA	M-GGA
C_2H_6	C_2H_4	C_2H_2	PWC [7]	B3LYP [8]	BLYP[7, 9]	BMK[10]
Si_2H_6	Si_2H_4	Si_2H_2	—	O3LYP [11, 12]	BPL [7, 13]	M06HF[14]
CNH_5	$HNCH_2$	CNH	—	TPSS5LYP	HTCH [15]	M062X [14]
H_3SiNH_2	H_2SiNH	HSiN	—	X3LYP [16]	PBE [17]	MPW1K[18]
—	COH_2	COH_4	—	—	RPBE [19]	TPSS [20]
—	H_2SiO	H_3SiOH	—	—	—	TPSSh [20]

The results from each functional is then compared with the CCSD results by visually displaying the deviations for every molecular system. Gaussian 09 [21] is used to perform energy and geometry optimizations for every molecular system with each functional and CCSD. To compare each DFT functional for the different molecular systems, the STM [22] modules of the visualization tool AVS/Express [23] are used to visually subtract the ground state charge density computed by each functional from that of CCSD. The energy convergence for the optimization step, performed for the CC calculations, is on the order of 10^{-8} Hartrees which is more accurate than the charge density differences. Note, additional details can be found in [24].

3.1. Electron Charge Density Differences

Minimizing the total energy of the system via geometry optimizations results in a local charge density for each functional. This property along with the molecular geometry (a global property) is then used to evaluate and quantify differences in the functionals. That is, charge densities for each functional are subtracted from those computed with CCSD. The resulting charge density differences are then used to qualitatively describe how the resulting charge density differences contribute to the global properties of each molecule. The quantitative differences of charge density differences for a particular molecular geometry, charge densities computed from DFT are numerically subtracted from CCSD and displayed as a three dimensional function of distance from the geometric center of the molecule. These direct comparisons of DFT and CCSD reveal just how different DFT functionals are relative to each other. Figures 1 and 2 show how quantitative differences in maximum and minimum density values affect the charge distribution for $HNCH_2$.
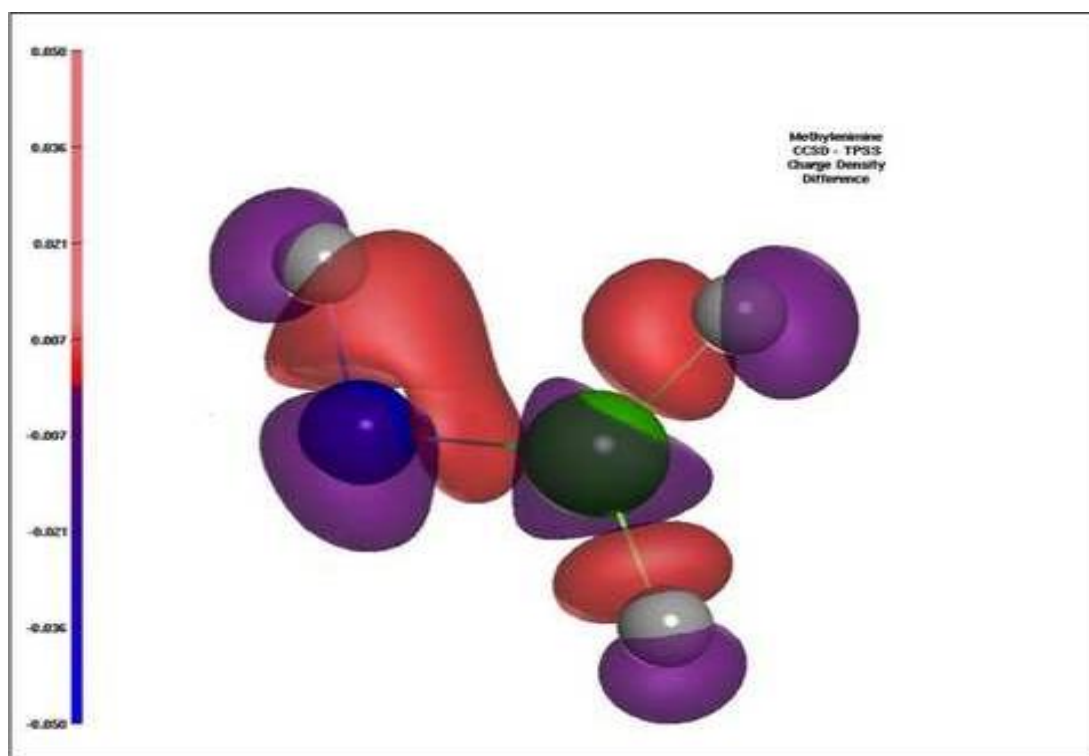

Figure 1. Methylenimine charge density difference between CCSD and TPSS.

Figure 1 shows that the positive change in density difference from CCSD for the TPSS functional results in the three local maxima. These maxima correspond to the three volumes of local positive charge difference seen in Fig. 1. Alternatively the two local maxima and one local minima see in Figure 2 correspond to the relatively large amount of positive charge density between the N-H bond and H-C-H bond angle, as well as the negative charge density difference dominating the C-N bond shown in Figure 2.
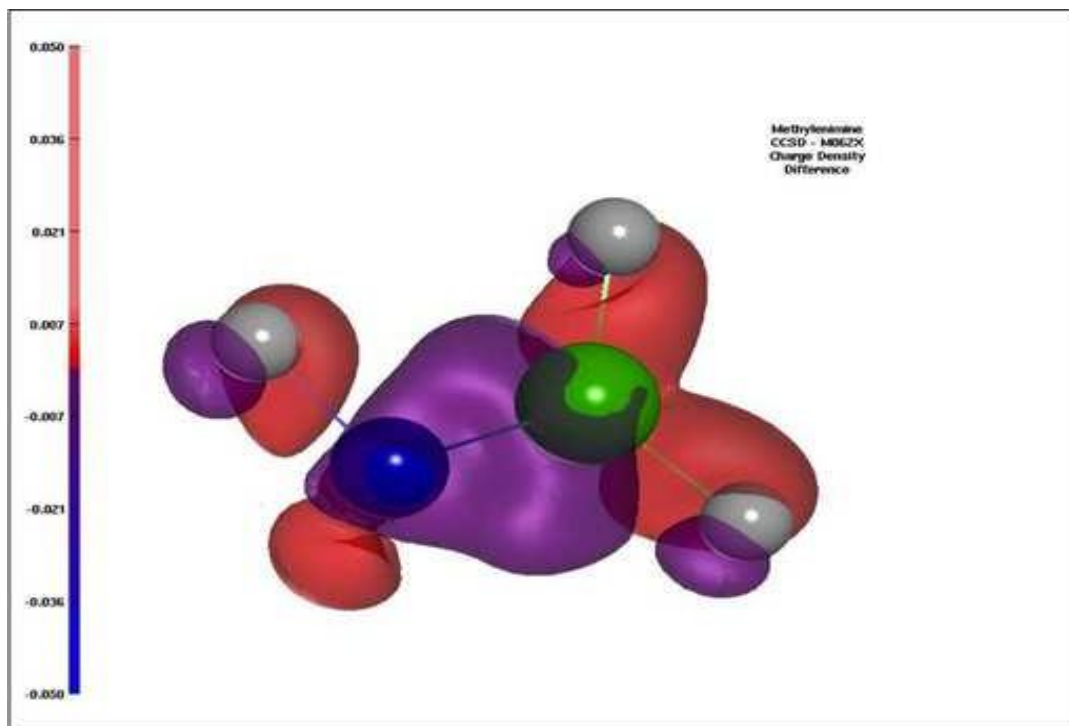
Figure 2. Methylenimine charge density difference between CCSD and M062X.

Figure 3 shows a numerical plot through the center plane of the projection of the 3D charge density differences $\Box\Box$x,y) shown on the left and $\Box\Box$x) as shown n the right.
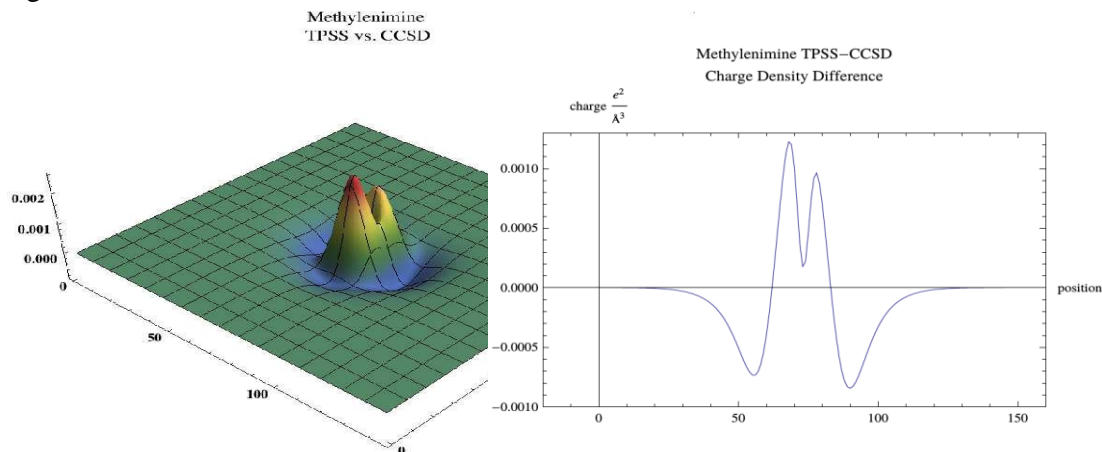

Figure 3. Methylenimine quantitative charge density difference as a function of position (in angstroms) between CCSD and TPSS.

The charge density differences provide an adequate description of the ability of each density functional to account for the external charge density of a molecular system. However, to more completely determine the working mechanism of a functional, one could also investigate its ability to approximate the intra-molecular forces that occur between electrons within a given molecule. This internal picture together with the charge density differences will provide a

complete visual interpretation of a density functional, from which one would be able to better assess the capabilities of each functional for a particular system. For example, Figure 4 depicts the bond length differences with respect to different functionals. Several functionals (namely BPL, PBE and TPSS) closely reproduces the same bond lengths as the CC approach. In addition to an understanding of the structural predictive abilities of density functionals, thermochemical properties such as ionization potential energies must also be accounted for when designing density functionals.

Figure 4. Methylenimine Hydrogen-Carbon bond length difference as a function of the functionals.

3.2. Electron Localization Function (ELF)

Charge density differences allow one to visualize the electron density distribution of a molecule from an outside perspective. However, it becomes difficult to determine how the distribution of electronic charge is related to the atomic centers. That is, where precisely are the atoms of the molecule itself. This can be computed via the electron localization function [25]. The ELF provides a method for the mapping of electron pair probability in multi-electronic systems and as such, provides a description of the chemical bond.

Then the outcome of combining ELF, together with the charge density differences, is a much clearer picture of the localization of electronic charge within a molecule, and its effect on global properties of the molecule. Thus, by utilizing these two methods together one is able to specifically ascertain the differences, in the

density functionals by studying by the localized electron localizations within a molecule and the global properties that result from such localizations.

In Figures 5 and 6, notice the width of the distribution of charge between the three atoms of the molecules. The localization given by B3LYP shows a slight favoring of charge localization tending toward the Si atom from Hydrogen, but localizes charge outside of the N atom. Similarly, the localization of charge for BLYP tends slightly more toward the Si atom, and also slightly more toward the N atom of the molecule. These two slightly different localizations, lead to significant differences in the charge density distribution for the overall molecules.
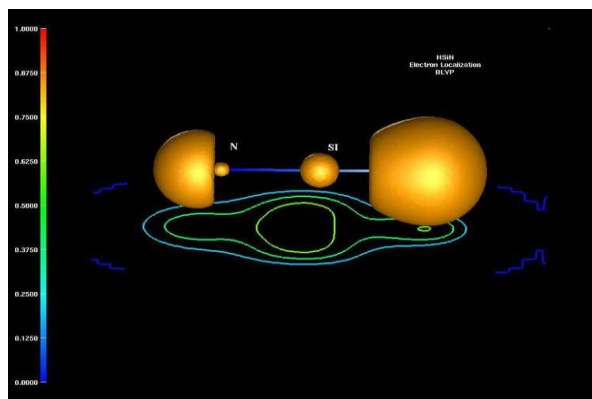
Figure 5. Electron localization for HSiN using the B3LYP functional.
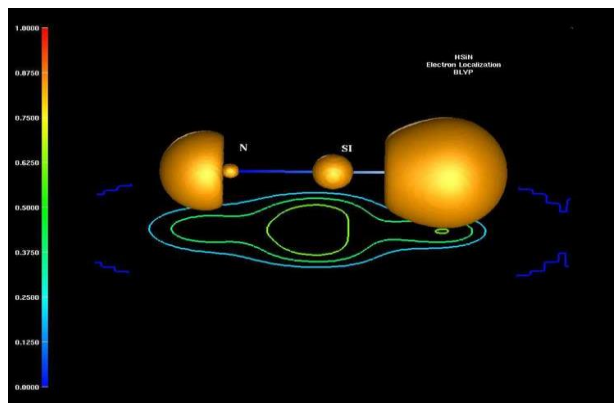
Figure 6. Electron localization for HSiN using the BLYP functional.

4. CONCLUSIONS

Visual interpretation of the resultant charge density differences provides a unique qualitative basis to describe the differences in global molecular properties. In this work a set of molecular visualization techniques have been presented that are shown to elucidate differences in the performance of various density functionals for both homo-nuclear and hetero-nuclear - single, double and triple bonded systems. The selection of both the functionals and the molecular systems reflect the types of electron-electron interaction and the types of functionals available. This work is to provide additional insight for the development of computational solutions of the

n-body Schrödinger equation. The visualization strategies, and the numerical data presented of the charge density differences shows the intermolecular electrostatic potential differences produced solely by the functional applied to the molecular system. This charge density difference is displayed on the surface of the molecule showing local molecular regions of positive, neutral, and negative charge densities to the environment.

The DFT functionals tend to have too much charge between the atomic centers for covalent bonds, in general. While this is in part, compensated by reduced charge for the lighter atoms, the bonds lengths and angles tend to be too short for covalent systems. In addition, the lighter atoms tend to generate bond lengths that are too large. Lastly, the increased charge for the heavier atoms also affects the bond angles, tending to make them too small.

The Electron Localization Function displays intra-molecular electronic potential that dictates the positions of the other intra-molecular atoms of the molecular system. The differences presented here support the charge density arguments for the functional differences.

As the development of the functionals progress, the performance in terms of describing the fundamental properties of the molecular systems can be displayed using these visualization strategies.

Future work will include a visual study of the effects of basis sets in conjunction with CC and DFT models.

5. ACKNOWLEDGEMENTS

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