# A Review on DFT- Computational Methods for Solving Research Problems

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***Abstract**:*

*Density functional theory has emerged as the most popular electronic structure method in computational chemistry. To assess the ever-increasing number of approximation exchange-correlation functionals,* ***(1)*** *The evolution of non-empirical and semi-empirical density functional design is reviewed, and guidelines are provided for the proper and effective use of density functionals.(****2****).Today's state-of-the-art functionals are close to achieving the level of accuracy desired for a broad range of chemical applications, and the principal remaining limitations are associated with systems that exhibit significant self-interaction/ delocalistions errors and or strong correlation effects.*

*Applications of DFT computational techniques to studies of the molecular structure and mechanism of the oxygen-evolving water oxidizing Mn4/Ca catalytic site in photosystem II are viewed .* ***(3)****We summarise results from the earlier studies pre-2000 but concentrate mainly on those developments that have occurred since the publication of several PS II crystal structures of progressively increasing resolutions starting in 2003.*

*The work of all computational groups actively involved in PS I I studies is examined in the light of direct PS II structural information from x-ray diffraction crystallography and EXAFS on the metal in the catalytic site.*

*Density Functional Theory (DFT) evaluated in atomic orbital basis sets this work provides best practice guidance on the numerals methodological and Technical aspects of DFT.(****4****) A particular force is on achieving an optimal balance between accuracy robustness and efficiency through multi-level approaches.*

***Keywords:***

*Density Functional Theory, Density functionals , Famous Theorem, Schrödinger equations, DFT computational methods.*

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**Introduction**

DFT is a Quantum mechanical modeling method used in Physics and Chemistry to investigate the electronic structure (principally the ground state) of many body systems ,in particular atoms ,molecules, and the condensed phases. DFT is a computational quantum mechanical modeling to that is used in various fields of research and Engineering, including Material science and drug design processes to study the electronic structure of atoms or molecules(**5**). DFT is a today a very powerful tool in the study of electronic structures of molecules it has made it possible to treat ever larger systems at a reasonable level of accuracy.The basic principle of DFT is that the electronic density of a system affects the ground state energy and other molecular properties.

Hence ,density functional for a system is represented by the ground state energy that is used to map a function to a value. For example" DFT can be used to calculate the electronic and structural properties of atoms and molecules" which are necessary to create and optimize the drug life properties of potential drug candidates.Classical density functional theory DFT calculations are cost-effective statistical methods increasingly used in recent decades to calculate and predict the properties of molecules.

Many chemical investigations are supported by routine calculations of molecular structures, reaction Energies, barrier Heights, and spectroscopic properties .Most of these Quantum chemical calculations apply various combinations of DFT-based methods. Keep in mind that Quantum ATK is more than just a DFT code "It comprises force fields and semiperical models as well and the synergy Obtained by these models" co-existing in the same code environment make it possible to solve unique problems such as combining a classical potential for phonons with a DFT model for the electron Transport simulations or use machine learning to fit accurate force fields for new materials.

Moreover ATK is developed with the ambition to provide as realistic physical results as possible in complex materials and under many different circumstances.This requires a simulation engine that can handle DFT calculations for very large systems and we are constantly adding new models that aim to provide more accurate results faster.(**6**) DFT calculations are used to help understand how materials and devices behave and operate under different conditions.

A Trained DFT user can correlate measurement data with simulation results to draw conclusions about the physical origin of certain effects observed in the material or device, but which cannot readily be explained with simple models.

Such insight is crucial in order to fully exploit the effects and material in question and even more so in order to for instance,scale down device dimensions or optimize material choices or process conditions.

With its predictive capabilities and atomistic quantum-mechanical nature , DFT is a crucial tool for the technology part finding to explore novel material and exotic physical phenomena , years prior to a first test device being manufactured or even before new material has been fully characterized experimentally .DFT density functional theory is a competitional chemistry method that uses Quantum Mechanics to calculate the electronic structure of atoms molecules and solids and is used to study the properties of materials design drugs and more,(**7**)Density functional theory constitutes a family of methodologists for quantum mechanical electronics structure calculations with broad applications to organic and main group molecules as well as more complicated systems.

These methods are of particular value for transition metal complexes where electron correlation effects can be large and for systems of similar complexity like metals solid state compounds and surfaces.

The problems that can be studied effectively include electronic structure charge and Spin distributions molecular geometries and reaction pathway energetics.There are now a variety of applications both to ground state and to excited state energy in properties and Pathways. GST methods for medium and large-size systems combine high computational efficiency with very good physical accuracy

DFT is a today a very powerful tool in the study of Electronics structures of molecules advancements in DFT in particular the development of Beeke's 3- 3-parameter functional (B3LYP) together with the nearly exponential growth of computer power have made it possible to treat our largest systems at a reasonable level of accuracy.

DFT for nano particles(**8**) Classical density functional theory DFT calculations are cost-effective statistical methods, increasingly used in recent decades to calculate and predict properties of molecules with great precision and low processing cost without any experimental input.Quantum Simulation systems allow for the reliable calculation of organic molecule geometric Optimisation, absorption spectra , and lowest energy electronic transition, defining molecule behavior as a nucleophile or electrophile characterized by the binding capacity of a drug and its release from carriers.

**Many-Particle Problems**

Find the ground state for a collection of atoms by solving the Schrödinger equation

$H\Psi(\{ri\}\{Rl\}) = E\Psi\ [\{ri\}\{Rl\}]$

So here we have a bunch of nuclei & bunch of electrons which makes the complicated equation to solve , Let's try to at least a bit simpler .

.If the first thing we do apply B.O. approximation nuclei they are big (heavy),slow & electrons they are small , fast that means

m-nuclei>>me

.That means the dynamics of atomic nuclei & electrons are separated

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Ψ({ri},{Rl})___Ψn(Rl)*Ψe(ri)

So for this calculate ground state energy now

**Solve the Schrödinger equation for electron:**

HΨ(r1r2…..rn) = EΨ(r1r2…….rn)

The electronic Hamiltonian consists of three parts

H = -h2/2me Σ Ni to i Vext(ri) + ΣN to i,j>1U (rirj)

Density functional Theory _from wavefunction to electron density

It defines the electron density

n(r) = Ψ*(r1r2….rn)Ψ(r1r2….rn)

That reduces to 3N dimensional to 3 spatial dimension. So density is only 3 dimensional.

Now make another approximation HARTREE FOCK APPROXIMATION Considering the jth electron is treated as a point charge in the field of all other electrons this simplifies **the many electron problem to many one electron problem.** So we considered a single electron system Ψ(rir2…rn) = Ψ(r1)*Ψ(r2)*Ψ(r3)....Ψn(rn)

We define the electron density in terms of the individual electron wave function.

n(r) = 2Σn to i Ψ*(r)Ψi(r)(**9**)

**Theory**

Density Functional Theory

There are two theorems that form the basis of density function theory.

**Theorem1**

The Total energy of a system is a unique function of the ground state electron density.

**E = E[n(r)]**

The second important Theorem of DFT is the -

**THEOREM-2**

The exact ground state density is minimized.

**E[n(r)]>Eo[no(r)] (10)**

**1.The Hohenberg-Kohn Theorems: Theorem 1:**

The ground state electron density uniquely determines the external potential and, therefore, the ground state properties of the system.

**Theorem 2:**

There exists a function of the electron density that minimizes the total energy.

**2. The Kohn-Sham Equations:**

- DFT uses the Hohenberg-Kohn theorems to derive the Kohn-Sham equations, which are a set of single-particle equations that are analogous to the Hartree equations but include an exchange-correlation energy term.

- These equations allow for calculating the electron density and the energy of the system in a computationally efficient way.

**3. Exchange-Correlation Functional:**

- The exchange-correlation functional ($E_{xc}[n(r)]$) is a crucial part of DFT and represents the energy associated with electron exchange and correlation effects, which are not included in the simplified one-electron model.
- Approximations for the exchange-correlation function are used in practical DFT calculations, such as the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA).

**4. Computational Process:**

- DFT calculations involve iteratively solving the Kohn-Sham equations, using an approximation for the exchange-correlation function, until the electron density and energy converge to a stable solution.
- This iterative process is computationally demanding but allows for the calculation of a wide range of properties, such as electronic structure, molecular geometries, and vibrational frequencies.

**Energy Functional**

Two electrons not only interact via their electronic charge but also by their spins & mutual repulsion & attraction.

Exchange co-relation functional is an approximation that takes care of all the quantum mechanical information.

Energy function consists of two parts one is known & unknown is the exchange co-relation function.

$E[\{\Psi i\}] = Eknown[\{\Psi\}] + Exc[\{\Psi i\}]$ (**11**)

**DFT METHODS**

Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving complex chemical problems. It exploits methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the values, the interactions, and the properties of molecules . (**12**)

There are different methods suitable in computational chemistry, such as ab initio, semiempirical, and density functional theory (DFT) methods. Among these methods, DFT calculations have gained an important role in investigating the interactions between BNNTs and drug molecules: during the past few years many attempts have in fact been performed to investigate the interactions of BNNTs with different molecules by using this approach.

DFT is a widely used formalism for electron structure calculations of atoms, molecules, and solids , based on the earlier fundamental work of Hohenberg and Kohn and Kohn and Sham.

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In the Kohn–Sham DFT formalism , the electron density is decomposed into a set of orbitals, leading to a set of one-electron Schrödinger-like equations to be solved self-consistently.

Solve a set of single electron wave functions that only depend on three spatial variables Ψ(r) and it is non interacting system.(**13**)

The Hamiltonian for single electron system

[-h/2me “2+V(r) +Vh(r) +Vxc(r)] Ψi(r)

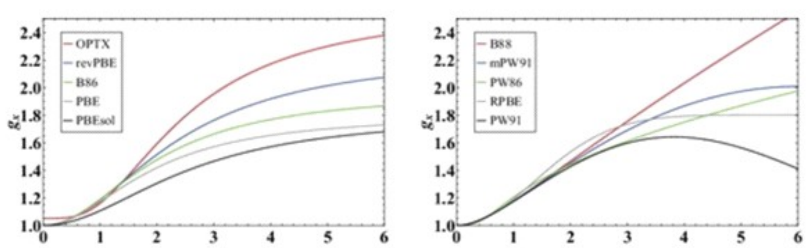
**=Ei(r)Ψi**

The Kohn–Sham equations are structurally similar to the Hartree–Fock equations, but include in principle exactly the many-body effects through a local exchange-correlation (xc) potential. Thus, DFT is computationally much less expensive than the traditional ab initio multiple electron wave function approaches, and this accounts for its great success for large systems. The essential element of DFT is the input of the exchange–correlation (xc) energy functional, the exact form of which is unknown.

The simplest approximation for the xc energy functional is through the local spin-density approximation (LSDA) of homogeneous electronic gas. A deficiency of the LSDA is that the xc potential decays exponentially, and does not follow the correct long-range asymptotic Coulombic (“1/r) behavior(**14**). As a result, “The LSDA electrons are too weakly bound, and for negative ions even unbound”. More accurate forms of the xc energy functionals are available from the generalized gradient approximation (GGA) , which takes into account the gradient of electron density.

**Ex(GGA)= Σ +” e UEG gGGA dr**

However, the xc potentials derived from these GGA energy functionals suffer similar problems as in LSDA, and do not have the proper long-range asymptotic potential behavior either. Notwithstanding, the total energies of the ground states predicted by these GGA density functionals are reasonably accurate. (**15**) Density functional theory calculations, implemented in different computational software such as Gaussian , SIESTA, VASP , and DMOL3 are usually applied to investigate the interactions of drugs with BNNTs.



To help quantify the effect of introducing additional ingredients into the density functional form, Table 1 contains mean signed errors (MSE) and mean absolute deviations (MAD) for Hartree–Fock (HF) and several non-empirical density functionals from various rungs of Jacob's Ladder.(**16**) The statistics are for a set of 124 single-reference atomization energies [Citation46], a set of 12 dispersion-bound alkane dimer binding energies [Citation47], and a set of 38 hydrogen-bonded water cluster binding energies [Citation48], ranging from dimers to decamers. (**17**)To set the stage, HF has an MSE of 112.79 kcal/mol for the atomization energies, while SPW92 has an MSE of -58.11 kcal/mol. Thus, HF systematically underestimates all 124 atomization energies (due to the neglect of electron correlation), while SPW92 systematically overestimates them.(**18**) Remarkably, the PBE GGA functional reduces the overbinding of the LSDA by nearly a factor of 5. For the hydrogen-bonded systems, the reduction is even more pronounced, as PBE reduces the -30.74 kcal/mol MSE of SPW92 by a factor of nearly 25.(**19**) However, since the LSDA overbinds the dispersion-bound systems only slightly, PBE tends to systematically underbind the alkane dimers. Based on the data in Table 1, it is apparent that GGA functionals improve upon the LSDA by reducing its systematic overestimation of interaction energies. (**20**)

Figure 2. Inhomogeneity correction factors (ICF) for a variety of GGA exchange functionals as a function (**21**). The subfigure on the left contains exchange functionals with ICFs that are PBE-like, while the subfigure on the right contains exchange functionals with ICFs that differ substantially from the PBE form. The local density approximation is equivalent to a horizontal line at gx = 1.(**22**) The kinetic energy density is by far the more popular ingredient and has been used in many modern functionals to add flexibility to the functional form with respect to both constraint satisfaction and least-squares fitting.(**23**)From a chemical perspective, the kinetic energy density can be useful for detecting electron delocalization in molecules(**24**)

**DFT RELIES FAMOUS THEOREM**

DFT relies on a famous theorem by Hohenberg and Kohn that states that ground state properties of an interacting many-electron system can be viewed as functionals of the local density only. There is, however, no hope of constructing these functionals explicitly in an exact way, and approximations are the only way to make use of the theory. The most common approximation to the total energy functional is the LDA, which approximates its exchange–correlation part by a construction based on the homogeneous electron gas. (**25**) As a result, the interacting electron system is mapped onto an auxiliary noninteracting system in an effective density-dependent potential. The one-particle eigenstates of this system (the "Kohn–Sham orbitals") parameterize the density and have to be determined self-consistently.

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When using DFT-LDA for calculating spectral properties and interpreting the Kohn–Sham eigenvalues as estimates for the band structure of the system, a second source of error—besides the LDA to the functional—enters: DFT as a ground state theory is not designed to describe excited states. In simple materials, such as sp-metals where the valence electrons are of itinerant character—indeed reminiscent of homogeneous electron gas behavior—the agreement between DFT-LDA and experiments is nevertheless often quite good, but this trend does not carry through to transition metal oxides with partially localized electrons or strongly correlated materials, in general.(**26**) Density functional theory (DFT) provides an exact approach to the problem of electronic structure theory(8). Within the Born-Oppenheimer approximation, the electronic energy,Ee[p(r)],can be written as a functional of the electron density,

Ee[p(r)]=T[p(r)] + Ven [p(r)] + J [p(r)] + Q[p(r)]……1

Where T[p(r)] is the kinetic energy of the electron,Ven[p(r)] is the nuclear- electron attraction energy .(**27**)

J[p(r)] is the classical electron-electron repulsion energy,

and Q[p(r)] is the non-classical (quantum) electron-electron interaction energy

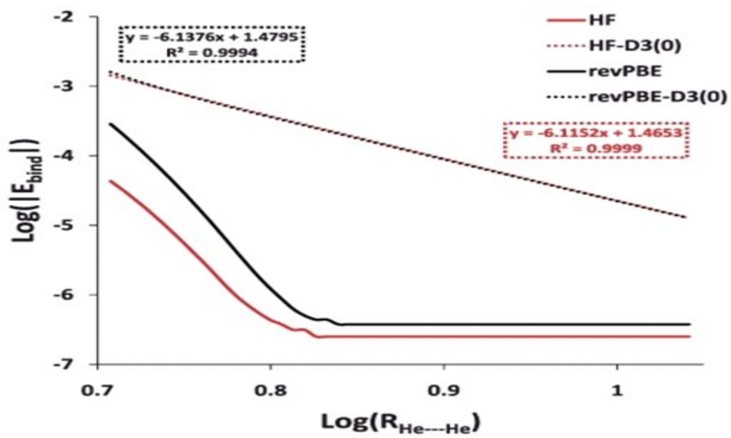
The second and third terms in equation 1 are known and can be computed according to equations 2 and, 3 respectively:(**28**)

Ven[p(r)] = -Σ M to A=1+"Za/[r-Ra]p(r)dr…..2

J[p(r)] = 1/2++" p(r)p(r2)/r12 dr1dr2…..3

Fortunately,Kohn and Sham helped circumvent this obstacle by demonstrating that the kinetic energy could be accurately approximated by a single Slater determinant of orbitals describing a fictitious system of non - non-interacting electrons that has the same density as the exact electronic wave function In principle,Ks - DFT,like is an exact theory. (**29**)

Although the introduction of orbitals-free DFT or OF-DFT By several orders of magnitude,Ks-DFT is by far the more popular flavor, and is widely used today in many areas of chemistry,physics and materials science. (**30**) Grimme's DFT-D method is a damped, atom-atom empirical potential that can be trained as an additive correction for any of the aforementioned functionals. Three generations of DFT-D tails have been developed by Grimme thus far: D1 [Citation110], D2 [Citation111], and D3 [Citation112]. The D3 tail can be used either with the original damping function, D3(0), or the newer Becke-Johnson damping function [Citation113], D3(BJ). Recently, Sherrill and co-workers [Citation117] refit the D3(BJ) parameters for a set of eight density functionals, and these revised parameters are referred to as D3M(BJ). Additionally, Schwabe and co-workers [Citation118] reformulated the D3(BJ) damping function to depend only on C6 dispersion coefficients, defining the D3(CSO) damping function, While it is straightforward to train a dispersion correction onto an existing density functional (and many of the previously mentioned functionals have D2, D3(0), D3(BJ), D3M(BJ), and D3(CSO) parameterizations), simultaneously training a semi-empirical functional with a dispersion correction is more involved. The first successful attempt of the latter was Grimme's B97-D functional [Citation111], a local GGA functional utilizing the D2 tail. Recently, both the D3(0) and D3(BJ) tails have been refitted to the existing local exchange-correlation functional of B97-D to give B97-D3(0) and B97-D3(BJ). Other examples include the ωB97X-D [Citation119] (GGA) and ωM05-D [Citation120] (meta-GGA) RSH functionals by Chai and co-workers, which use a slightly modified(**31**)




In general, dispersion corrections such as DFT-D should be used with functionals that tend to underbind non-covalent interactions (both strong and weak). However, fitting a dispersion correction to a functional like PBE is tricky, (**32**)since PBE is already overbound for the binding energies of the 38 water clusters mentioned earlier.(**33**) Consequently, PBE-D3(BJ) increases the MSE of PBE by a factor of almost 5 for these clusters (-5.86 vs. -1.26 kcal/mol). On the other hand, PBE-D3(BJ) drastically improves upon PBE for the 12 dispersion-bound systems. (**34**)The same circumstances afflict the PBE0 functional, which has a remarkably small MSE of only 0.20 kcal/mol for the water clusters. However, the addition of the D3(BJ) dispersion tail leads to overbinding (-3.86 kcal/mol). Similar to PBE, however, PBE0 systematically underbinds the 12 alkane dimers, and the addition of the dispersion correction reduces the MSE from 3.37 to -0.02 kcal/mol.(**35**)

$$E_{\text{disp}}^{\text{DFT}-D} = -\sum_{A<B} \sum_{n=6,8,\ldots} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{\text{damp},n}\left(R_{AB}\right)$$

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**HOW IT WORKS**

- On the idea that the electronic density of a system affects its ground state energy and other properties
- The energy of a molecule is a function of the electron density.
- DFT calculations can be performed in atomic orbital basis sets.(**36**)

**WHY IT'S POPULAR**

DFT is the first principle method which means it can predict material properties for unknown systems without experimental input. DFT offers and excellent compromise between required computation time and the quality of the results in comparison to the alternative which is less accurate and robust but much faster semi-empirical quantum mechanics.(**37**) DFT can be considered as a robust theory in that a breakdown in the form of entirely wrong results is careful even when applied to challenging molecules or exotic chemistry DFT is in need of new strategies for functional development'. An approach that the present authors have recently developed to avoid the overfitting problem is to use a combinatorial design strategy.(**38**)

**Conclusion**

Density functional theory provides us with a relatively efficient and unbiased tool with which to compute the ground state energy in realistic models of bulk materials and their surfaces. The reliability of such calculations depends on the development of approximations for the exchange-correlation energy function. Significant advances have been made in recent years in the quality of exchange-correlation functionals as dependence on local density gradients, semi-local measures of the density and non-local exchange functionals have been introduced.

The local density approximation is a very simple and remarkably reliable for the structure, elastic moduli, and relative phase stability of many materials but is less accurate for binding energies and details of the energy surface away from equilibrium geometries. There is a distinct tendency for functionals that are highly parameterized and fitted to the properties of molecular systems to perform somewhat better than lightly parameterized functions for molecules but to perform relatively poorly in simulations on periodic materials.

**References:**

1. P.Hohenberg and W.kohn, physics.Rev.136,B864(1964).
2. L.H Thomas, Math.proc. Cambridge Philos soc.23,542
3. 2011,Journal of Photochemistry and Photobiology[Phillip Gatt ,…Ron J.Pau]
4. Fundamentals : Physics Methods ,Theoretical analysis and case studies.
5. 2024, computer in biology and medicine Samson O.Oselusi___Samuel A.Egleyeh
6. W.kohn and L.J Sham, Phys.Rev.140

7. Y.A Wang,N.Govind and E.A.Carter, Phys
8. 2023,Biomedicine and pharmacotherapy Ali Razei ….Amir Hamoyoun Keihan
9. DFT by Dr. Divya Srivastava M.S.C Physics , Central University of Rajasthan
10. 003, Encyclopedia of Materials: Science and Technology O.Eriksson
11. DFT energy function by Dr. Divya Srivastava. M.S.C physics
12. 2016, Boron Nitride Nanotubes in Nanomedicine, Ehsan Shakerzadeh.
13. Hamiltonion for single Electron J.O Lugo and L.I Vergara, P.G Balcatto and E.C.Goldberg
14. N.Mardirossian and M.Head - Gordan, J. Chemii 2016
15. J. Chemistry 2017
16. A.zupan , J.P Perdew,K.Burke and M. causa , Int.J Quantum chem.61,835(1997).
17. A.D.Becke , Int.J. Quantum chem.23,1915(1983).
18. J.P Perdew, K. Burke and M.Ernzerhof.Phep.Rev.lett.77,3865(1996).
19. J.Tao , J.P.Perdew , U.N. Staroverov and G.E. Scuseria phys.
20. H. Schmider and A. Becke, J. Mol. Struct.: THEOCHEM. 527, 51 (2000)
21. K. Raghavachari, G.W. Trucks, J.A. Pople, and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).
22. J.P Perdew.S.kurth,A.Zupan,and P.Blaha, Phys rev. Lett.82,2544(1999)
23. J.Sun, B.Xiao and A.Ruzsinszky, J. Chem. Phys.137 , 051101(2012)
24. A.D. Becke, J. Chem.Phys.112,4020 (2000).
25. J.Grafenstein, D.Izotov and D.cremer,J.chem .Phy 127 ,214103(2007)
26. E.R.Johnson,A.D.Becke, C.D. Sherrill and G.A.DiLabio J.Chem.Phy.131,034116 (2009)
27. S.E Wheeler and K.N.Howk ,J.Chem.Theory comput.6,395(2010)
28. P. Mori. Sanchiz . A.J. Cohin and W.Yang. J.Chem. 125,201102 (2006)
29. J.P.Perdew and A.zunger, Phys. Rev B23,5048 (1981)
30. A.D. Bechke, J.chem. Phy.98,1372 (1993)
31. D.C Langreth and J.P. Perdew , Phys . Rev.B15,2884 (1997)
32. J. Harris , Phys. Rev. A29,1648 (1984)
33. C.Adamo and V.Barone, J.Chem.Phys.110,6158(1999)
34. P.J Wilson, J.J Bradley and D.J.Tozer, J. Chem 115,9233(2001).
35. S.Grimme, J.Comput . Chem.25,1463 (2004)
36. S.Grimme, J.Comput . Chem.25,1787 (2006)
37. S.Grimme, S.Ehrlich and L. Goerigk,J Comput . Chem.32,1456 (2011)
38. H.Schroder , A. Creon and T . Schwabe, J.chem. Theory Comput 11,3163 (2015)
39. J.D. Chai and M. Head-Gordon,Phys. Chem 10,6615 (2008).