Density matrix expansion based semi-local exchange hole applied to range separated density functional theory

Bikash Patra, a Subrata Jana, b and Prasanjit Samal c

School of Physical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India.

(Dated: 3 April 2018)

Exchange hole is the principle constituent in density functional theory, which can be used to accurately design exchange energy functional and range separated hybrid functionals coupled with some appropriate correlation. Recently, density matrix expansion (DME) based semi-local exchange hole proposed by Tao-Mo gained attention due to its fulfillment of some exact constraints. We propose a new long-range corrected (LC) scheme that combines meta-generalized gradient approximation (meta-GGA) exchange functionals designed from DME exchange hole coupled with the ab-initio Hartree-Fock (HF) exchange integral by separating the Coulomb interaction operator using standard error function. Associate with Lee-Yang-Parr (LYP) correlation functional, assessment and bench-marking of our functional using well-known test set shows that it performs remarkably well for a broad range of molecular properties, such as thermochemistry, noncovalent interaction and barrier height of chemical reactions.

I. INTRODUCTION

Since its advent, the Hohenberg-Kohn-Sham density functional theory (DFT) has become one of the most sophisticated and widely used computational tools in studying the electronic structure of atoms, molecules and solids for its reliable accuracy and computational affordability. Although the formulation is exact, the only unknown part of the total energy is exchange-correlation (XC) functional, which needed to be approximate. Designing accurately the XC functional is an active and intriguing research field with several new perspectives. Several approximations of the XC functional has been reported for past couple of decades with continuous increasing accuracy. These proposed density functionals are distinguished through the Jacob’s ladder of density functional approximations according to their accuracy and ingredients they used. On the lowest rung of the Jacob’s ladder, there are local density approximations (LDA) which uses electron density only. One rung higher than the LDA, the generalized gradient approximation (GGAs) are designed using reduced density gradient as its ingredients. Next, meta-generalized gradient approximation (meta-GGAs) are proposed using the Kohn-Sham kinetic energy density (KEKS) along with the reduced density gradient. All these semi-local functionals are very successful in describing atomicization energies, equilibrium lattice constant, equilibrium bond lengths, surface properties, cohesive energies and many others.

Even if these functionals enjoy early success, but fail badly to explain Rydberg excitation energy, charge transfer excitation, reaction barrier height and oscillator strength. Missing non-locality and absence of many electron self-interaction errors (MESI) are the two major drawbacks of semi-local formalism. Another serious difficulty is that XC potential of the corresponding semi-local functional shows incorrect asymptotic behavior and decays faster than $-1/r$, where $r$ is the distance of the electron from the nuclei. Non-locality of exchange functional, which is missing in semi-local functional is essential to describe long-range charge transfer, barrier height and dissociation limit of a molecule. Though, the most popular hybrid B3LYP and others resolve these problems to some extent but it is far from accuracy in several cases. Especially, in describing dissociation limit, barrier height, phenomena related to the fractional occupation number, dramatic failures of the hybrid functionals are observed. Not only that, in hybrid functional, the XC potential decays like $-c/r$, where $c$ is the fraction of mixed Hartree-Fock exchange. One of the interesting findings is to mix Hartree-Fock (HF) with that of semi-local functional by using range separation of coulomb interaction operator (may be long range or short range). This range separation technique also enable us to change the range of semi-local and HF part. Using this method one can mix semi-local form of DFT in long range or short range depending on its requirement. It has been shown that for molecules the long range corrected HF is more effective and for solid state calculation short range HF exchange is superior from computational point of view. All these ideas are used to design the long range corrected LC-$\omega$PBE, LC-BLYP, which reproduces intriguing result and establish superiority over B3LYP in many cases and HSE06, which uses short range HF and mainly applied for the solid state system. In some functionals like CAM-B3LYP, LC-$\omega$PBe both the HF exchange and DFT counterpart are incorporated over the whole range by using generalize parametrization of coulomb interaction operator.

The range separated functionals are designed using the semi-local exchange hole constructed from spherical averaged exchange hole or using reverse engineering.
technique. The CAM-B3LYP functional is designed using LDA exchange hole by passing in-homogeneity through Thomas-Fermi wave-vector. Later, LC-ωPBE, LC-ωPBEh and HSE06 are designed using PBE exchange hole. Though spherical averaged exchange hole is not available for PBE exchange, the way it is designed using system averaged exchange hole. The present aim of this paper is to design a long range corrected meta-GGA level exchange energy functional using recently developed density matrix expansion (DME) based exchange hole. The density matrix expansion based exchange hole has unique properties like correct uniform density limit, correct small $u$ expansion etc., which were previously lack in the exchange hole expansion proposed by Becke and Scuseria and its coworker. The most successful meta-GGA exchange hole proposed by Tao-Mo using DME satisfy the above mentioned properties with addition its large $u$ limit also converges. With all these exact criteria it is always interesting to design a range separated functional using this exchange hole. The present attempt of this paper is in that direction. We use the semi-local exchange hole in short range limit and long range is fixed with HF exchange. The exchange energy proposed here is tested with LYP and next our functional is bench-marked with PBE functionals because they are the commonly used functionals.

II. THEORETICAL BACKGROUND

Let the Hamiltonian for $N$ electron system,

$$
\mathcal{H} = \sum_i h(i) + \sum_{i>j} \frac{1}{r_{ij}}.
$$

where $h$ represents the one electron part of the Hamiltonian which includes kinetic energy of the electrons and electron-nuclei interaction and $r_{ij} = |r_i - r_j|$. Now in range separated functionals the electron-electron coulomb interaction $V_{ee}(r_{ij}) = \frac{1}{|r_i - r_j|}$ between an electron at $r_i$ and another at $r_j$ can be separated into a long range (LR) and a short range part (SR) as,

$$
\frac{1}{r_{ij}} = \frac{1 - g(r_{ij})}{r_{ij}} + \frac{g(r_{ij})}{r_{ij}}.
$$

From various possible choices of the function $g$, the most suitable from both physical and computational point of view is, $g = \text{erf}(\mu r_{ij})$, where $\mu$ is a parameter. For this choice, the first term of Eq.(2) approaches to 0 as $r_{ij} \to \infty$ and second term goes to $2\mu/\sqrt{\pi}$ when $r_{ij} \to 0$. The parameter $\mu$ can be treated as a cutoff between SR and LR part as shown in Fig.1.

In the range separated Kohn Sham scheme the ground state energy of an electronic system is expressed as

$$
E = \min_{\psi} \{ \langle \psi | \hat{T} + \hat{V}_{nc} + \hat{V}^{LR}_{ee} | \psi \rangle + E^{SR}_{Hxc}[\rho_\psi] \}
$$

where $\hat{T}$ is the kinetic energy operator, $\hat{V}_{nc}$ is the electron-nuclei interaction operator, $\hat{V}^{LR}_{ee}$ is the operator for long range part of electron-electron interaction, $E^{SR}_{Hxc}$ is an energy functional, which include short range Hartree, exchange and correlation energy, and $\psi$ is a multi-determinant wave function. The minimizing wave function $\psi^{LR}_{min}$ simultaneously minimizes the long range interacting effective Hamiltonian and give the exact density of the interacting many body system. For $\mu = 0$ as the long range interaction vanishes, we get back the standard Kohn-Sham system, and on the other hand for $\mu = \infty$ the wave function based formulation of electronic structure is recovered. Up to this, the above theory is exact. Now if we replace the multi-determinant wave function in Eq.(3) by a single Slater determinant wave function $\phi$ then the ground state energy of range separated hybrid scheme becomes

$$
E_{RSH}^0 = \langle \phi_0 | \hat{T} + \hat{V}_{nc} | \phi_0 \rangle + E_{H}[\rho_0] + E^{LR}_{x,HF}[\phi_0] + E^{SR}_{x,HF}[\rho_0],
$$

where $\phi_0$ is the Slater determinant which minimizes energy functional and $\rho_0$ is the associated density.

If the range separation is applied only on exchange part then it is called long range corrected functional (LC) and the above expression can be written as,

$$
E_{RSH}^0 = \langle \phi_0 | \hat{T} + \hat{V}_{nc} | \phi_0 \rangle + E_{H}[\rho_0] + E^{LR}_{x,HF}[\phi_0] + E^{SR}_{x,HF}[\rho_0] + E_c[\rho_0]
$$

In the above expression the long range part of the ex-
change interaction can be written as,
\[ E_{x,HF}^{LR}[\phi_0] = -\frac{1}{2} \sum_{\sigma} \sum_{i,j} \int \phi^*_i(r_i) \phi_j(r_j) \frac{erf(\mu(r_{ij}))}{r_{ij}} \phi_j(r_i) \phi_i(r_j) dr_i dr_j \]
where \( \phi_{i\sigma} \) is the ith \( \sigma \)-spin molecular orbital. The short range exchange functional is defined by,
\[ E_x^{SR}[\rho] = \frac{1}{2} \int \int \frac{\rho(r_i)(1 - erf(\mu(r_{ij})))\rho_x(r_i, r_j)}{r_{ij}} dr_i dr_j \]
where \( \rho_x \) is the exchange hole and conventionally defined as \( \rho_x(r_i, r_j) = -|\rho_1(r_i, r_j)|^2/2\rho(r_i) \), with \( \rho_1(r_i, r_j) \) is the first-order reduced density matrix. Spin polarized form of the equation (7) can be written using spin scaling relationship
\[ E_x^{SR}[\rho \uparrow, \rho \downarrow] = (E_x^{SR}[2\rho \uparrow] + E_x^{SR}[2\rho \downarrow])/2 \]

III. PRESENT LONG RANGE CORRECTED HYBRID FUNCTIONAL

Now, we will propose range separated hybrid functional based on recently developed DME exchange hole of Tao-Mo\(^{20}\). The DME exchange hole of Tao-Mo has following semi-local form
\[ \rho_x(r, u) = \frac{-9\rho_j^2(ku)}{2k^2u^2} - \frac{105j_1(ku)j_2(ku)}{k^4u^2} \mathcal{G} - \frac{3675j_3^2(ku)}{8k^6u^2} \mathcal{H} \]
where \( \mathcal{G} = 3(\lambda^2 - \lambda + \frac{1}{2})(\tau - \tau^{unif}) - (\tau - \tau^{unif}) + 7(2\tau - 1)^2|\nabla \rho|/\rho^2 \) and \( \mathcal{H} = (2\tau - 1)^2|\nabla \rho|/\rho^2 \). Tao-Mo proposed exchange hole uniquely recovers (i) correct uniform density limit, (ii) correct small \( u \) expansion proposed be Becke\(^{5} \), and (iii) its large \( u \) limit also converges. To take care the in-homogeneity of the system the parameter \( k \) is set to be \( k =_fk_F \), where \( k_F \) is the Fermi momentum for homogeneous electron gas and \( f \) is fixed from sum rule of exchange hole by extrapolating its low gradient limit and large gradient limit. The obtained form is \( f = 1 + 10(70y/27) + 3y^2 \)\(^{1/10} \), where \( y = (2\tau - 1)^2 \rho \), \( p = |\nabla \rho|^2/(2k_F^2\rho) \) and \( \beta \) is a parameter. We take the value of \( \lambda = 0.6866 \) and \( \beta = 79.873 \), as prescribed in the Tao-Mo paper\(^{20} \). Using this exchange hole in equation (7) we get
\[ E_x^{SR}[\rho] = \frac{1}{2} \int \rho(r)(\mathcal{M} + \mathcal{N} + \mathcal{Q}) d^3r \]
where,
\[ \mathcal{M} = -\frac{9\pi\rho}{2k^2} \left[ 1 - \frac{8}{3} a \left\{ \sqrt{\pi} erf\left(\frac{1}{2a}\right) + \left(2a - 4a^3\right) exp\left(-\frac{1}{4a^2}\right) - 3a + 4a^3 \right\} \right] \]
\[ \mathcal{N} = -\frac{35\pi}{3k^4}\mathcal{G} \left[ 1 + 24a^2 \left\{ (20a^2 - 64a^4) exp\left(-\frac{1}{4a^2}\right) - 3 - 36a^2 + 64a^4 + 10\sqrt{\pi} erf\left(\frac{1}{2a}\right) \right\} \right] \]
\[ \mathcal{Q} = -\frac{245\pi}{48k^4}\mathcal{H} \left[ 1 + \frac{8}{7} a \left\{ -8a + 256a^3 - 576a^5 + 3849a^7 - 122880a^9 \right. \right. \times exp\left(-\frac{1}{4a^2}\right) + \left. \right. \]
\[ 24a^3(-35 + 224a^2 - 1440a^4 + 5120a^6) + 2\sqrt{\pi} (-2 + 60a^2) erf\left(\frac{1}{2a}\right) \] \]

IV. COMPUTATIONAL DETAILS

We have implemented Eq. (10) by locally modifying the NWChem-6.6\(^{59} \) program. We use the same value of \( \mu = 0.33 \) in all parts of the code. Medium grid is used for the evaluation of the exchange-correlation contribution to the density functional. All the results of benchmark calculations reported in this article are obtained self-consistently using NWChem program. Spin unrestricted calculation have been done for open shell system. Deviations are defined as theory - experiment and reported as mean errors (ME) and mean absolute errors (MAE) and in some cases maximum deviation from
standard value. For all the cases under study we compare the results of our range separated functional (DME-RS) with four others popularly known range separated functional CAM-B3LYP, HSE06, LC-ωPBE and LC-ωPBEh.

V. RESULTS

For bench-marking our functional the following databases have been used- i) AE17 for atomic energy, ii) G2/97 for atomization energy, iii) IP13/03 for ionization potential, iv) EA13/03 for electron affinity, v) PA8/06 for proton affinity, vi) NCCE31/05 for noncovalent interaction, vii) HTBH38/08 for hydrogen transfer barrier height, viii) NHTBH38/08 for non-hydrogen transfer barrier height, complexes, ix) πTC13 for the thermochemistry of π system, x) ABDE12 for alkyl bond dissociation energy, x) HC7/11 for Hydrocarbon chemistry, xi) ISOL6/11 for Isomerization energies of large molecules, xii) DC7/11 for Difficult cases.

A. Atomic energy

For the functionals under study, we have calculated the total energies of atoms from H to Cl (AE17). For all atoms, we have used the 6-311++G(3df,3pd) basis set except for Helium, for which aug-cc-pVQZ basis set is used. We compared the calculated total energies with the accurate non-relativistic values. CAM-B3LYP has the smaller MAE among the tested functionals. DME-RS gives comparable results with CAM-B3LYP and LC-ωPBEh has the largest MAE in this case.

| Functional  | ME   | MAE  | Max (+) | Min (-) |
|-------------|------|------|---------|---------|
| DME-RS      | -0.341 | 0.382 | 0.887 (Al) | -0.217 (Be) |
| CAM-B3LYP   | -0.140 | 0.322 | 0.615 (Al) | -0.487 (Be) |
| HSE06       | 1.322  | 1.334 | 0.099 (H) | -3.172 (Cl) |
| LC-ωPBEh    | 1.735  | 1.745 | 0.078 (H) | -3.871 (Cl) |
| LC-ωPBE     | 1.564  | 1.584 | 0.169 (H) | -3.837 (Cl) |

B. Thermochemistry

We have calculated atomization energies (AE) of 148 molecules for the G2/97 test set using MP2(full)/6-31G* optimized geometry. The atomization energy of a molecule is defined as the energy difference between the total energy of a molecule and the sum of energy of its constituent free atoms, all at 0 K. We have compared our calculated atomization energy with the result of CCSD(T), which is gold-standard in quantum chemistry. Table (II) shows, CAM-B3LYP gives the smallest error in AEs, followed by DME-RS. LC-ωPBEh is the least accurate for AEs among the tested functionals.

Ionization potential (IP) and electron affinity (EA) is the amount of total energy difference between the ion and corresponding neutral atom or molecule, all at 0 K. We have calculated IP for IP13 database and EA for EA13/03 data base and QCISD/MG3 level optimized geometry have been taken for both cases. For IP, HSE06 performs best with smallest MAE of 0.139 eV. For both IP and EA, DME-RS is comparable in accuracy with the other range separated functionals.

Proton affinity (PA) is the amount of energy released when a proton is added to a species at its ground state. We have calculated PA of PA8 data-set with MP2/6-31G(2df,p) level optimized geometry. All calculation. From Table (V) DME-RS gives the smallest mean absolute error which is 0.051 eV. All the investigating functionals overestimate PA except for CAM-B3LYP.

| Functional  | ME   | MAE  | Max (+) | Min (-) |
|-------------|------|------|---------|---------|
| DME-RS      | -4.494 | 5.099 | 8.253 (BeH) | -25.876 (C₂Cl₄) |
| CAM-B3LYP   | 1.199  | 4.329 | 15.748 (C₂NH₇) | -20.276 (SiCl₄) |
| HSE06       | -4.610 | 5.195 | 6.133 (C₅H₅N) | -35.505 (SiF₄) |
| LC-ωPBEh    | 2.276  | 5.735 | 22.317 (C₅H₅N) | -24.908 (SiF₄) |
| LC-ωPBE     | 1.746  | 5.362 | 21.765 (C₅H₈) | -18.140 (P₂) |

C. Binding energy of weakly interacting system

We have calculated atomization energies (AE) of 148 molecules for the G2/97 test set using MP2(full)/6-31G* optimized geometry. The atomization energy of a molecule is defined as the energy difference between the total energy of a molecule and the sum of energy of its constituent free atoms, all at 0 K. We have compared our calculated atomization energy with the result of CCSD(T), which is gold-standard in quantum chemistry. Table (II) shows, CAM-B3LYP gives the smallest error in AEs, followed by DME-RS. LC-ωPBEh is the least accurate for AEs among the tested functionals.

Ionization potential (IP) and electron affinity (EA) is the amount of total energy difference between the ion and corresponding neutral atom or molecule, all at 0 K. We have calculated IP for IP13 database and EA for EA13/03 data base and QCISD/MG3 level optimized geometry have been taken for both cases. For IP, HSE06 performs best with smallest MAE of 0.139 eV. For both IP and EA, DME-RS is comparable in accuracy with the other range separated functionals.

Proton affinity (PA) is the amount of energy released when a proton is added to a species at its ground state. We have calculated PA of PA8 data-set with MP2/6-31G(2df,p) level optimized geometry. All calculation. From Table (V) DME-RS gives the smallest mean absolute error which is 0.051 eV. All the investigating functionals overestimate PA except for CAM-B3LYP.
TABLE IV. Deviation of the calculated electron affinity from reference value. All quantities are in eV.

| Functional  | ME    | MAE   | Max (+)     | Min (-)     |
|-------------|-------|-------|-------------|-------------|
| DME-RS      | -0.077| 0.128 | 0.251 (Cl2) | -0.238 (Si) |
| CAM-B3LYP   | 0.022 | 0.084 | 0.304 (Cl2) | -0.141 (Si) |
| HSE06       | -0.068| 0.123 | 0.186 (Cl2) | -0.307 (OH) |
| LC-ωPBEh    | -0.052| 0.105 | 0.166 (C)   | -0.242 (OH) |
| LC-ωPBE     | -0.027| 0.089 | 0.180 (C)   | -0.165 (PH2) |

TABLE V. Summary of deviation of the calculated proton affinity from reference value. All quantities are in eV.

| Functional  | ME    | MAE   | Max (+)     | Min (-)     |
|-------------|-------|-------|-------------|-------------|
| DME-RS      | 0.012 | 0.051 | 0.099 (PH3)| -0.084 (H2) |
| CAM-B3LYP   | -0.047| 0.084 | 0.048 (C2H2)| -0.117 (H2) |
| HSE06       | 0.077 | 0.077 | 0.211 (C2H2)| -           |
| LC-ωPBEh    | 0.470 | 0.470 | 0.642 (PH3)| -           |
| LC-ωPBE     | 0.086 | 0.086 | 0.243 (C2H2)| -           |

introducing kinetic energy in the density functional can substantially reduce the error of LSDA and GGA functional for predicting the binding energy of weakly interacting system.26 We have tested our meta-GGA range separated functional for NCCE31/05 database. We have taken the equilibrium geometries for single point calculation from Ref. 21. 6-311++G (3df,3pd) basis set is used for all the molecules except for the inert gas related molecules for which we have used aug-cc-pVQZ. The summary of the performances of the tested functionals are listed in Table (VI). All the investigating LC functionals performing very well. From Table (VI) we can say DME-RS is the best choice in this case.

TABLE VI. Mean Absolute error (MAE) for the noncovalent complexation energies database (NCCE31/05) and its secondary databases for the functionals shown in each row. All values are in kcal/mol.

| Functional  | ME    | MAE   | ME    | MAE   |
|-------------|-------|-------|-------|-------|
| DME-RS      | -0.27 | -0.24 | -0.46 | -0.45 |
| CAM-B3LYP   |       |       | -0.45 | -0.70 |
| HSE06       |       |       |       |       |
| LC-ωPBEh    |       |       |       |       |
| LC-ωPBE     |       |       |       |       |

D. Thermochemistry of π system

The molecules with π bond are largely dominated by multi configurational state functions than σ-bonded molecules due to their small HOMO-LUMO gap. We are investigating the performance of the range separated functionals to explain the properties of π system. The database (πTC13) of π system contains three secondary database - i) πIE3/06- isomeric energy differences between allene and propyne and higher homologs. ii) PA-CP5/06- Proton affinities of five conjugated polyenes. iii) PA-CP5/06- Proton affinities of five conjugated Schiff bases.74 We have taken MP2/6-31+G(d,p) level optimized geometries from Minessota database64 and 6-311++G(3df,3pd) basis set is used for all the geometries. CAM-B3LYP gives the smallest MAE with 3.41 kcal/mol, followed by DME-RS with MAE of 4.19 kcal/mol.

TABLE VII. Mean Absolute error (MAE) for the πTC13 and its secondary databases for the functionals shown in each row. All values are in kcal/mol.

| Functional  | πTC13 | πIE3/06 | PA-CP5/06 | PA-SB5/06 |
|-------------|-------|---------|-----------|-----------|
| DME-RS      | 4.19  | 0.99    | 5.19      | 5.12      |
| CAM-B3LYP   | 3.41  | 2.37    | 3.61      | 3.82      |
| HSE06       | 6.54  | 4.94    | 6.96      | 7.09      |
| LC-ωPBEh    | 4.79  | 2.39    | 5.45      | 5.58      |
| LC-ωPBE     | 4.24  | 0.98    | 4.92      | 5.51      |

E. Barrier heights of chemical reactions

Semi-local density functionals very often fail to describe the reaction barrier height. Most of the time it gives the transition state to a lower energy state than reactants or products, giving rise to negative barrier height. We can associate this problem of semi-local functionals with self interaction error, because the transition states have stretched bonds and as a result, SIE may be large. We have calculated forward and reverse barrier height of 19 hydrogen transfer reaction from HTBH38/04 data-set and same for 19 non-hydrogen-transfer reaction from HTBH38/0472,73 data set. Further, the set NHTBH38/04 is subdivided into the set of six heavy-atom transfer reactions, eight nucleophilic substitution reaction, five association and unimolecular reactions. For all the calculation 6-311++G(3df,3pd) basis set is used. Equilibrium geometries and reference values are taken from Minessota database64. From table (VIII), LC-ωPBE gives the lowest MAE for hydrogen transfer reaction, and DME-RS gives the minimum MAE for non-hydrogen transfer reaction. Overall DME-RS and LC-ωPBE gives comparable result for barrier height.

F. Alkyl bond dissociation energies, Hydrocarbon chemistry, Isomerization energies of large molecules and Difficult cases

Alkyl bond dissociation energy database (ABDE12)64 contains two subsets ABDE4/05 and ABDEL867.
TABLE VIII. Deviations from experiment of barrier heights of chemical reactions computed using the 6-311++G (3df,3pd) basis set. All values are in kcal/mol.

| Functional  | Hydrogen transfer (38) | HTBH38 | Heavy-atom transfer (12) | Heavy-atom nucleophilic substitution (16) | Unimolecular and association (10) | Full NHTBH38 |
|-------------|------------------------|--------|--------------------------|-----------------------------------------|----------------------------------|--------------|
| Functional  | ME         | MAE    | ME         | MAE    | ME         | MAE    | ME         | MAE    | ME         | MAE    |
| DME-RS      | -0.88      | 2.17   | -2.49      | 2.63   | 0.05       | 1.17   | 0.64       | 2.04   | -0.59      | 1.86   |
| CAM-B3LYP   | -3.00      | 3.29   | -5.47      | 5.47   | -0.88      | 1.19   | -0.54      | 1.76   | -2.24      | 2.69   |
| HSE06       | -3.45      | 3.48   | 2.68       | 12.37  | -1.34      | 1.53   | -0.55      | 1.83   | 0.14       | 5.04   |
| LC-ωPBEh    | -3.28      | 3.31   | -4.45      | 4.45   | 0.08       | 0.95   | -0.10      | 2.26   | -1.39      | 2.40   |
| LC-ωPBE     | -0.57      | 1.26   | -0.19      | 2.11   | 2.95       | 2.95   | 1.41       | 2.34   | 1.55       | 2.52   |

TABLE IX. Summary of deviations of alkyl bond dissociation energy, hydrocarbon chemistry, isomerization energies and difficult cases. All values are in kcal/mol.

| Alkyl bond dissociation energy | Hydrocarbon chemistry | Isomerization energies | Difficult cases |
|-------------------------------|-----------------------|------------------------|-----------------|
| Functional                    | ME        | MAE        | ME        | MAE        | ME        | MAE        | ME        | MAE        |
| DME-RS                        | -9.08     | 9.08       | -5.37     | 5.37       | -1.96     | 1.96       | -15.69    | 15.69      |
| CAM-B3LYP                     | -6.63     | 6.63       | -5.35     | 5.35       | -1.80     | 2.03       | -4.40     | 9.53       |
| HSE06                         | -9.38     | 9.38       | 0.14      | 5.92       | -1.12     | 1.42       | -21.21    | 23.07      |
| LC-ωPBEh                      | -6.42     | 6.42       | 9.22      | 13.65      | -0.65     | 1.67       | -1.15     | 17.54      |
| LC-ωPBE                       | -5.52     | 5.52       | 16.05     | 20.07      | -1.05     | 1.57       | 4.43      | 15.44      |

ABDE4 includes four bond dissociation energies of R-X organic molecules, where R = methyl and isopropyl, and X = CH₃ and OCH₃. For subset ABDEL8 contains eight molecules, with R = ethyl and tert-butyl and X = H, CH₃, OCH₃, OH. B3LYP/6-31G(d) level optimized geometries are taken from Minessota database. For Hydrocarbon chemistry, isomerization energy and difficult cases, we have used respectively HC7, ISOL6 and DC7 databases. For all these cases 6-311++G (3df,3pd) basis set is used. For alkyl bond dissociation energy LC-ωPBE performs best with MAE 5.52 kcal/mol. In case of hydrocarbon chemistry DME-RS, CAM-B3LYP and HSE06 has the comparable result, while all the other functionals deviate too much from HF result and HSE06 gives the worst performance.

We have also considered the dissociation nature of NaCl molecule, which is an ionic pair when the inter-atomic separation R is not very far from equilibrium distance and because of IP_Na > EA_Cl, it dissociates into neutral Na and Cl atom at infinite inter-molecular separation. The critical length R_c at which sudden charge transfer occurs is given by R_c = 1/(IP_Na - EA_Cl). From experimental value of IP_Na and EA_Cl we get R_c ≈ 9.4 Å. HF underestimated the critical length R_c = 5.72 Å due to overestimation of IP_Na - EA_Cl difference. DME-RS and LC-ωPBEh almost overlap and gives R_c = 8.51 Å. From LC-ωPBE and CAM-B3LYP we obtain R_c equal to 8.93 Å and 9.7 Å respectively. HSE06 completely fails in this case and calculation does not converge for inter-atomic separation greater than 9.4 Å.

G. Dissociation energy

Dissociation energy is the amount of energy needed to break every chemical bond in a molecule by separating all of its' constituent atoms. Local or semi-local density functional fail to describe the dissociative nature of symmetrical radical cation like H⁺₂, He⁺₂ etc. The failure of conventional density functional to explain the dissociative nature of one electron molecule H⁺₂ is an indication of self-interaction error. This is due to the fact that traditional density functionals suffer from delocalization error. In figure we have compared the dissociation curve of H⁺₂ from range separated functional with the Hartree-Fock result, which is exact in this case. Albeit all the functionals give same equilibrium bond length, the error increases as we increase the bond length away from equilibrium bond length. LC-ωPBE and DME-RS present almost same result, while all the other functionals deviate too much from HF result and HSE06 gives the worst performance.
In this paper, we have developed a new long range correction scheme for meta-gga exchange functionals in density-functional theory. The new scheme is based on Savin’s long-range correction scheme using Tao-Mo exchange hole at the short range and Hartree-Fock exchange integral at the long range by separating electron-electron interaction operator $1/r_{ij}$ into short and long range by introducing standard error function. We compare our results with four other popularly known LC functionals like CAM-B3LYP, HSE06, LC-ωPBE, LC-ωPBEh. Among these functionals, CAM-B3LYP and LC-ωPBEh mix both SR and LR Hartree-Fock exchange. In HSE06, a finite amount of HF exchange is used at SR but none in the LR limit, in order to scale down the computational cost of the non-local exchange integral for the extended system. Our DME-RS functional is of LC-ωPBE type, where we have only one empirically fitted parameter $\mu$. On the other hand both CAM-B3LYP and LC-ωPBEh has two extra parameters except $\mu$, which determine how much HF exchange is mixed at SR and LR. This functional gives comparable result with other heavily parametrized range separated functionals like $\omega B97X$ (14 parameters), M11 (40 parameters).

In solid state physics as the density tail is not that much important due to screened coulomb interaction, TM hole can be used at long range keeping HF treatment at short range. This approach is also computationally advantageous for extended system applications.

VI. CONCLUSION

In this paper, we have developed a new long range correction scheme for meta-gga exchange functionals in density-functional theory. The new scheme is based on Savin’s long-range correction scheme using Tao-Mo exchange hole at the short range and Hartree-Fock exchange integral at the long range by separating electron-electron interaction operator $1/r_{ij}$ into short and long range by introducing standard error function. We compare our results with four other popularly known LC functionals like CAM-B3LYP, HSE06, LC-ωPBE, LC-ωPBEh. Among these functionals, CAM-B3LYP and LC-ωPBEh mix both SR and LR Hartree-Fock exchange. In HSE06, a finite amount of HF exchange is used at SR but none in the LR limit, in order to scale down the computational cost of the non-local exchange integral for the extended system. Our DME-RS functional is of LC-ωPBE type, where we have only one empirically fitted parameter $\mu$. On the other hand both CAM-B3LYP and LC-ωPBEh has two extra parameters except $\mu$, which determine how much HF exchange is mixed at SR and LR. This functional gives comparable result with other heavily parametrized range separated functionals like $\omega B97X$ (14 parameters), M11 (40 parameters).

In solid state physics as the density tail is not that much important due to screened coulomb interaction, TM hole can be used at long range keeping HF treatment at short range. This approach is also computationally advantageous for extended system applications.

VII. SUPPLEMENTARY MATERIAL

See supplementary material for result of the individual species for each cases.

VIII. ACKNOWLEDGMENT

The authors would like to acknowledge the financial support from the Department of Atomic Energy, Government of India.

1W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
2J. P. Perdew and Y. Wang, Phys. Rev. B 33, 8800 (1986).
3A. D. Becke, Phys. Rev. A 38, 3098 (1988).
4C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).
5A. D. Becke and M. R. Roussel, Phys. Rev. A 39, 3761 (1989).
6A. D. Becke, J. Chem. Phys. 104, 1040 (1996).
7P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. 98, 11623 (1994).
8J. P. Perdew, K. Burke, and M. Ernzerhol, Phys. Rev. Lett. 77, 3865 (1996).
9T. V. Voorhis and G. E. Scuseria, J. Chem. Phys. 109, 400 (1998).
10P. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, J. Chem. Phys. 109, 6264 (1998).
11M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. 110, 5029 (1999).
12J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003). A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. 125, 224106 (2006).
13R. Armiento and A. E. Mattsson, Phys. Rev. B 72, 085108 (2005).
14Y. Zhao and D. G. Truhlar, J. Chem. Phys. 125, 194101 (2006).
15J. I. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003).
16J. P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin, and J. Sun, Phys. Rev. Lett. 103, 026403 (2009).
17J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
18J. I. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. 115, 036402 (2015).
19A. V. Arbuznikov and M. Kaupp, J. Chem. Phys. 141, 204101 (2014).
20J. I. Tao and Y. Mo, Phys. Rev. Lett. 117, 073001 (2016).
21J. P. Perdew, and K. Schmidt AIP Conference Proceedings 577, 1 (2001); doi: 10.1063/1.1300175.
22H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
23J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
24J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
25Z. Wu and R. E. Cohen, Phys. Rev. B 73, 235116 (2006).

FIG. 2. Dissociation curves of $H^+_2$ (upper panel) and NaCl (lower panel) obtained using 6-311++G (3df,3pd) basis set. Zero level is set to be E(H) and E(Na)+E(Cl) respectively for both the cases.
26. R. Peverati, D. G. Truhlar, Phil. Trans. R. Soc. A, 372, 20120476, (2014).
27. V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P. Perdew, J. Chem. Phys. 119, 12129 (2003); 121, 11507(E) (2004).
28. P. Hao, J. Sun, B. Xiao, A. Ruzsinszky, G.I. Csonka, J. Tao, S. Grimme, and J.P. Perdew, J. Chem. Theory Comput. 9, 355 (2013).
29. L. Goerigk and S. Grimme, J. Chem. Theory Comput. 6, 107 (2010).
30. L. Goerigk and S. Grimme, J. Chem. Theory Comput. 7, 291 (2011).
31. D. Jacquemin and C. Adamo, J. Chem. Theory Comput. 7, 369 (2011).
32. Y. Mo, G. Tian, R. Car, V.N. Staroverov, G.E. Scuseria, and J. Tao, Phys. Rev. B 95, 035118 (2017).
33. V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P. Perdew, Phys. Rev. B 69, 075102 (2004).
34. J. Tozer, N. C. Handy, J. Chem. Phys. 109, 10180 (1998).
35. A. Dreuw, J. L. Weisman, M. Head-Gordon, J. Chem. Phys. 119, 2943 (2003).
36. J.P. Perdew, V.N. Staroverov, J. Tao, and G.E. Scuseria, Phys. Rev. A 78, 052513 (2008).
37. J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
38. C.-O. Almbladh and U. V. Barth, Phys. Rev. B 89, 033003 (2002).
39. T. Yanai, D. P. Tew, N. C. Handy, Chem. Phys. Lett. 393, 51-57, (2004).
40. O. A. Vydrov and G.E.Scuseria, J. Chem. Phys. 125, 234109 (2006).
41. M. A. Rohrdanz, K. M. Martins, and J. M. Herbert, J. Chem. Phys. 130, 054112 (2009).
42. H. Baer, E. Livshits, U. Salzner, Annu. Rev. Phys. Chem. 61, 85 (2010).
43. J. Tao, Density Functional Theory of Atoms, Molecules, and Solids (VDM Verlag, Germany, 2010).
44. M. Ernzerhof and J.P. Perdew J. Chem. Phys. 109, 3313 (1998).
45. L.A. Constantin, J.P. Perdew, and J. Tao, Phys. Rev. B 73, 205104 (2006).
46. L.A. Constantin, E. Fabiano, and F. Della Sala Phys. Rev. B 88, 125112 (2013).
47. H. Likura, T. Tsuneda, T. Yanai, and K. Hirao, J. Chem. Phys. 115, 3540 (2001).
48. T. Leininger, H. Stoll, H.-J Werner, and A. Savin, Chem. Phys. Lett. 275, 151 (1997).
49. R. Pollet, A. Savin, T. Leininger, and H. Stoll, J. Chem. Phys. 116, 1250 (2002).-J. Flad, I
50. A. Savin and H.-J. Flad, Int. J. Quantum. Chem., 56(1995) 327.
51. Y. Akinaga and S. Ten-no, Chem. Phys. Lett., 462 (2008) 348.
52. J.-W. Song, M. A. Watson, A. Nakata, and K. Hirao, J. Chem. Phys. 129, 184113 (2008).
53. T. Loute, F. Colonna, A. Savin, Phys. Rev. A 70, 062505 (2004).
54. T. Loute, I. C. Gerber, G. Jansen, A. Savin, and J. G. Angyan, Phys. Rev. Lett. 102, 096404 (2009).
55. J. G. Angyan, I. C. Gerber, A. Savin and J. Toulouse, Phys. Rev. A 72, 012510 (2005).
56. G. E. Oliver and J. P. Perdew, Phys. Rev. A 20, 397 (1979).
57. A. V. Kruskau, G. E. Scuseria, J. P. Perdew, A. Savin, J. Chem. Phys. 129, 124103 (2008).
58. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37, 785 (1988).
59. M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H. J. J. van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, W.A. de Jong, Comput. Phys. Commun. 181, 1477 (2010).
60. S. J. Chakrvorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A 47, 3649 (1993).
61. L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. 106, 1063 (1997).
62. R. Haunschild and W. klopper, J. Chem. Phys. 136, 164102 (2012).
63. B. J. Lynch, Y. Zhao, and D. G. Truhlar, J. Phys. Chem. A. 107, 1384 (2003).
64. B. J. Lynch, Y. Zhao, and D. G. Truhlar, see http://t1.chem.umn.edu/db/ for the Minnesota databases for chemistry and solid state physics.
65. Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Theory Comput. 2, 364 (2006).
66. S. Parthiban and J. M. L. Martin, J. Chem. Phys. 114, 6014 (2001).
67. Y. Zhao and D. G. Truhlar, J. Phys. Chem. A. 110, 10478 (2006).
68. A. J. Cohen, P. Mori-Sanchez, and W. Yang, Science 321, 792 (2008).
69. J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. 49, 1691 (1982).
70. CRC Handbook of Chemistry and Physics, 85th ed., edited by D. R. Lide (CRC, Boca Raton, 2004)
71. Y. Zhang and W. Yang, J. Chem. Phys. 109, 2604 (1998).
72. Y. Zhao, B. J. Lynch, and D. G. Truhlar, J. Phys. Chem. A. 108, 2715 (2004).
73. Y. Zhao, N. Gonzalez-Garca, and D. G. Truhlar, J. Phys. Chem. A. 109, 2012 (2005).
74. Y. Zhao, D. G. Truhlar, J. Chem. Phys. 125, 194101 (2006).
75. -D. Chai, M. Head-Gordon, J. Chem. Phys. 128, 084106 (2008).-R. Peverati, D. G. Truhlar, J. Phys. Chem. Lett. 2, 2810-2817 (2011).-D. Pines, Elementary Excitations in Solids (Perseus Books, Reading, MA, 1999).