Employing semilocal exchange hole with an application to meta-GGA level screened range separated hybrid functional: A conventional wisdom method

Subrata Jana$^1$[a] and Prasantj Samal$^1$[b]

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

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Range separated hybrid functional schemes are very successful in describing a wide range of molecular and solid state properties accurately. Range separated hybrid functionals are designed from a combination of short range (SR) and long range (LR) parts. The SR part is known as hybrid exchange, whereas the LR part is known as semilocal exchange. Construction of RS functionals are based on the local density approximation (LDA) based exchange hole coupled with the slowly varying Tao-Mo enhancement factor through the conventional wisdom technique. Comprehensive performance and testing of the present functional shows, it accurately describes several molecular properties.

The most appealing feature of this present screened hybrid functional is that it will be practically very useful in describing solid state properties in meta-GGA level.

Kohn-Sham variant of density functional theory (DFT) is one of the most accurate and widely used many body frameworks for electronic structure calculation. The theoretical framework of KS DFT is exact, only if the exact form of exchange-correlation (XC) is known. The accuracy of DFT depends upon the accuracy of XC functional, which contains all the many electron effects. Therefore, development of accurate XC functional is an intriguing research topic with different new prospects. A large number of approximations based on different global models have been developed in recent decades[2–26]. All these approximations are classified through Jacobs Ladder approximations, which add an extra ingredient in each of its rung starting from the local density approximation (LDA). The generalized gradient approximations (GGAs)[6–9,15] and meta-generalized gradient approximation (meta-GGA)[16–20,22] are the next two higher rungs of Jacob’s ladder. LDA, GGA and meta-GGA are enormously used due to their low computational cost and accuracy in chemistry[28–35] and condensed matter physics[36–41]. All these approximations are known as semilocal formalism because they are constructed from semilocal quantities i.e., density ($\rho$), gradient of density ($\nabla \rho$) and Kohn-Sham kinetic energy density ($\tau$). In spite of its success of describing several thermochemistry test[38–39], equilibrium lattice constants[37–39], bulk modulus[39], bond lengths[36,40], cohesive energy[41] and solid state surface properties[36], semilocal approximations often fail to predict phenomena like solid state band gap, thermochemical reaction barrier heights[42–44], excitation energies, Rydberg excitation and dissociation curves[43,44], because of the inherent absence of “non-locality” and "many electron self interaction (MESI)"[42–51]. Non-locality and MESI information are induced inside the semilocal formalism by suitably mixing Hartree-Fock (HF) exact exchange globally or in range separated scheme[7,8,12,13,32,43,51–59]. The former is known as hybrid[8,12,32], whereas the later is known as range separated hybrid schemes[43,51–52,54,55,59,62–64]. Construction of RS functionals are based on the semilocal exchange hole. The exchange hole can be construed either in Taylor series expansion[52] or density matrix expansion (DME) technique[55] or reversed engineering way[52,55,59,61]. Recently, Tao-Mo[22] developed a full semilocal exchange hole based on DME technique having all desired properties together.

Inspired by TM functional[22] and its underlying exchange hole, in this present paper we have constructed a screened RS hybrid functional using HF in its short range part. The present proposition is the same direction as the RS hybrid functional was proposed by Heyd-Scuseria-Ernzerhof (HSE)[52], but in the meta-GGA rung. The DME based exchange hole is used for constructing the full short or long range part of semilocal exchange functional. For slowly varying density correction we impose the range separated scheme only through the LDA exchange hole. The motivation of inclusion only LDA exchange hole in the present construction is rooted in the construction of coulomb attenuated B88 family long range corrected RS functional[34]. More details and physical inside behind our functional construction is discussed in the construction section. To check the accuracy and performance of the present proposition we applied our scheme to the well-known test set. Performance of the present functional is compared with three very popular hybrids B3LYP, PBE0, TPSSh and one RS hybrid HSE06. All these functionals are designed from their popular parent semilocal functionals B88, PBE and TPSS by suitably mixing exact HF exchange. Special attention has been paid to the performance of present proposition with that of HSE06 functional for thermochemistry and fractional occupation number because both the functionals are de-

[a]Electronic mail: subrata.jana@niser.ac.in
[b]Electronic mail: psamal@niser.ac.in
signed using HF in its short range.

The present paper is organized as follows. In the following, we will discuss the role of exchange hole in designing the RS hybrids. Next, we will propose our formalism in designing a new meta-GGA level range separated functional. The differences and similarities with other RS functionals are also discussed. Lastly, we compare present proposition with that of popular hybrids and RS hybrid functional for different thermochemistry test cases.

The exchange hole $\rho_x$ is the principle constituent of exchange energy functional. It is used for constructing the semilocal exchange energy functional or range separation hybrid functional. The exchange energy functional constructed from exchange hole is given by,

$$E_x[n] = \frac{1}{2} \int d^3 r \ \rho(r) \int d^3 u \ \frac{\rho_x(r, r + u)}{u}. \quad (1)$$

On the other hand, the range separated density functional theory is developed by separating the Coulomb interaction i.e., $v_{xc}(r, r') = \frac{1}{|r - r'|}$ into short and long range part as,

$$\frac{1}{|r - r'|} = \frac{erf(\mu |r - r'|)}{|r - r'|} + \frac{1 - erf(\mu |r - r'|)}{|r - r'|} \quad (2)$$

By replacing $r' = r + u$, and using the exchange hole, the short range and long range part of exchange functional becomes,

$$E^{SR}_x = -\frac{1}{2} \int d^3 r \ \rho(r) \int \frac{1 - erf(\mu u)}{u} \rho_x(r, r + u) \ d^3 u, \quad (3)$$

and

$$E^{LR}_x = -\frac{1}{2} \int d^3 r \ \rho(r) \int \frac{erf(\mu u)}{u} \rho_x(r, r + u) \ d^3 u, \quad (4)$$

In the construction of exchange hole, one needs to formulate only the spin-unpolarized exchange hole. Using the spin density scaling relation the spin-unpolarized exchange hole can be transformed into spin-polarized form as,

$$\rho_x[\rho_{\uparrow}, \rho_{\downarrow}] = \frac{\rho_0}{\rho} \rho_x[2\rho_{\uparrow}] + \frac{\rho_0}{\rho} \rho_x[2\rho_{\downarrow}] . \quad (5)$$

It is noteworthy to mention that exchange energy depends on the spherical average the exchange hole over separation vector $u$. Hence, Eq.(1) can be rewritten as,

$$E_x[n] = \frac{1}{2} \int d^3 r \ \rho(r) \int d^3 u \ \frac{\rho_x(r, r + u)}{u} . \quad (6)$$

In range separated DFT also the semilocal LR or SR part is constructed from spherical averaged semilocal exchange hole. Not only that, the semilocal SR and LR part can also be constructed from reversed engineered system averaged exchange hole. The screened hybrid functional HSE$_{22}$, long range corrected LC-$\omega$PBE$_{55}$ are designed from reversed engineered exchange hole. Also, very recently TPSS exchange energy functional is reversed engineered to construct meta-GGA level screened hybrid functional$_{32}$.

The general scheme of hybrid functional$_8$ is,

$$E_{xc}^{\text{hybrid}} = aE_x^{HF} + (1-a)E_x^{SL} + E_c^{SL} , \quad (7)$$

where $E_x^{HF}$ is the Hartree-Fock exact exchange, $E_x^{SL}$ is the semilocal exchange functional and $E_c^{SL}$ is the semilocal correlation functional. Here, $a$ controls the amount of HF to be mixed with the semilocal exchange functional. However, there is no mixing parameter associated with correlation because it is essential for both the HF and semilocal exchange.

The RS scheme proposed by Heyd, Scuseria, and Ernzerhof (HSE) has the following general form,

$$E_{xc} = aE_x^{HF-SR} + (1-a)E_x^{SL-SR} + E_x^{SL-LR} + E_c^{SL} . \quad (8)$$

Alternatively this can be written as,

$$E_{xc} = aE_x^{HF-SR} - aE_x^{SL-SR} + E_x^{SL} + E_c^{SL} \quad (9)$$

This is particularly useful in implementation point of view as one has to construct only the short range part of semilocal exchange functional. The last two part added to the semilocal XC functional, which in the present case is the TM functional$_{22}$. Thus knowing the exchange energy functional form, the main aim is only to construct the semilocal short range part.

Here, we propose following short range semilocal part of the full range separated hybrid functional scheme,

$$E_x^{SL-SR} = -\int n(r) c^{unif}_x \left[ wF_x^{DME-SR} + \left\{ 1 - \frac{8}{3} \tilde{A} \left( \sqrt{\pi} erf \left( \frac{1}{2\tilde{A}} \right) + (2\tilde{A} - 4\tilde{A}^3)e^{-\frac{1}{2\tilde{A}^2}} - 3\tilde{A} + 4\tilde{A}^3 \right) \right\} (1-w)F_x^{TM-sc} \right] d^3 r , \quad (10)$$
where

$$F_{x}^{DME-SR} = \frac{1}{f^2} \left\{ 1 - \frac{8}{3} A \left( \sqrt{\pi} \text{erf} \left( \frac{1}{2A} \right) + (2A - 4A^3)e^{-\frac{1}{8A}} - 3A + 4A^4 \right) \right\} + \frac{7\lambda}{9f^4} \left\{ 1 + 24A^2 \left( (20A^2 - 64A^4)e^{-\frac{1}{8A}} - 3 - 36A^2 \right) + 64A^4 + 10\sqrt{\pi} \text{erf} \left( \frac{1}{2A} \right) \right\} + \frac{245M}{54f^4} \left\{ 1 + \frac{8}{7} A \left( (8A - 256A^3 - 576A^5 + 384A^7 - 122880A^9)e^{-\frac{1}{8A}} + 24A^3(-35 + 224A^2 - 1440A^4 + 5120A^6) + 2\sqrt{\pi}(-2 + 60A^2)\text{erf} \left( \frac{1}{2A} \right) \right\}$$

(11)

is the short range enhancement factor based on density matrix expansion based semilocal exchange hole and

$$F_{x}^{TM-sc} = \left\{ 1 + 10 \left( \frac{10}{81} + \frac{50p}{729} \right) p + \frac{146}{2025} q^2 - \left( \frac{73q}{405} \right) \left[ \frac{3\tau w}{5\tau} \right] (1 - \frac{\tau w}{\tau}) \right\}^{1/2},$$

(12)

is the slowly varying density correction of TM exchange energy functional, $c_{x}^{\text{unif}} = 3k_f/\pi$ is the exchange energy per electron of the uniform electron gas and the terms associated with the exchange functional factor are $f = [1 + 10(70q/27 + \beta q^2)]^{1/10}$, $L = [3(\lambda^2 - \lambda + 1/2)(\tau - \tau_{\text{unif}} - |\nabla n|/24n) - (\tau - \tau_{\text{unif}})] + \frac{\tau^2}{(2\lambda - 1)^2}(\tau_{\text{unif}} - 1/2)/\tau_{\text{unif}}$, $M = (2A - 1)^2 p$, with $A = 2/k_f^2$, $k_f = (3\pi^2 p)^{1/3}$ (uniform Thomas-Fermi wave vector), $\tau_{\text{unif}} = \frac{1}{3} k_f^2 p$ (uniform KE density), $p = \left( \frac{\nabla n}{(2k_f p)} \right)^2$ (square of the reduced density gradient), $s = \left( \frac{\nabla n}{(2k_f p)} \right)$, $y = (2A - 1)^2 p$, $\tilde{\lambda} = d/d\tau$, $\tilde{q} = 3\tilde{\tau} - 2\tilde{\lambda} + \frac{1}{2}$, $\tau_{\text{unif}} = |\nabla n|^2/8\rho$ and $w = [(\tau' / \tau)^2 + 3(\tau' / \tau)^3]/[1 + (\tau' / \tau)^3]^{1/2}$ (weight factor between DME exchange energy and slowly varying density correction of TM functional). $E_{x}^{TM}$ is the full TM exchange energy functional defined in ref. The correlation part we used one electron self-interaction free TPSS $\Delta$ correlation. The parameter $\mu$ is fixed as the same value is used as in CAM-B3LYP functional, i.e., 0.33. The mixing parameter $a$ is chosen to be 0.10, which gives very good agreement to the atomization energy of G2/148 molecular test set. It is noteworthy to mention that in the TPSSh functional, $a = 0.10$ is obtained by fitting it with molecular properties. As, our present construction is in the meta-GGA level, we stick with that value. Recently, proposed TPSS based RS functional by Tao et. al[23] and HSE06[24] used different values of $\mu$ and $a$. Because those have different nature of construction compared to the present proposition. More realistic explanation of smaller mixing parameter in hybrid meta-GGA functional than GGA is also given in ref. The values of $\lambda$ and $\beta$ are the same as suggested in TM functional, i.e., 0.6866 and 79.873.

Clearly, here we employ the full range separation scheme in the SR part of DME based exchange. For slowly varying density correction we employ the range separation only through the LDA exchange hole. The main motivation of employing the range separation only through the LDA exchange hole is rooted in the construction of the CAM-B3LYP family range separated functional, where the range separation is involved only through the LDA exchange hole coupled with the modified $k_f$. But in the present situation, we consider only $k = k_f$ in the short range semilocal part of exchange hole. Because in the solid state system, where slowly density varying density correction dominates, $k = k_f$ seems to be a good approximation. This is a simplified conventional way to include the slowly varying density scheme within the DME range separation scheme bypassing the reversed engineered exchange hole of the full TM exchange energy functional. Recently, the reversed engineered exchange hole for TPSS functional has been derived by Tao et. al[20] But the enhancement factor form of TPSS and TM functional are quite different. TPSS functional is derived from the enhancement factor of linear response theory. Whereas, part of TM functional is derived form spherically averaged semilocal exchange hole. This completes the construction of our functional.

The self-consistency benchmark calculation of the newly constructed range separated functional is performed using the NWChem-6.0 code. The data set we used in our calculation is summarized in Table. We compared our results with that of three popular hybrid functional B3LYP, PBE0 and TPSSh and one RS functional HSE06. We choose only one RS functional i.e., HSE06 in our comparison because both formalism are constructed using short range HF. Table. We reported the mean absolute error (MAE) and mean absolute error (MAE) for all the test cases except atomization energy, where only MAE is reported. The MAE and ME of our proposed functional are given at the last row of Table - . We called it PW-TPSSc (where PW stands for present work and it is coupled with TPSS correlation).

**Atomization energy:** The atomization energy is defined as the energy required to isolate the constituent atoms from its molecular structure. For atomization energy benchmark we used G2 set, which consists of 148 molecules and the geometries are optimized in MP2/6-31G* level[25,26]. We used aug-cc-pVQZ basis set in
our calculation. The reference values are taken from CCSD(T) calculation given in ref. Table (I) implies that, B3LYP gives the smallest MAE both for AE6 and G2 set and it is not surprising because B3LYP is designed to minimize the atomization error. PW-TPSSc is the second best with an MAE 4.88 Kcal/mol. Whereas, largest MAE is 5.64 Kcal/mol. In case of hydrocarbon chemistry, PW-TPSSc outperformed all other functionals at least MAE 3.55 Kcal/mol.

Isomerization potential (IP), electron affinity (EA) and Proton affinity (PA) are calculated using Minnesota 2.0 data set with QCISD/MG3 level optimized geometries. For IP, PW-TPSSc performs best with smallest MAE of 0.098 eV. For the EA13 test set performance of B3LYP is superior to other functionals under consideration. Other functionals perform almost equivalently in this case. Proton affinity (PA) is the amount of energy released when a proton is added to a species at its ground state. PA are calculated using MP2/6-311+G(2df,p) level optimized geometry. Among all the functionals, reported here, B3LYP is the best with MAE 0.098 eV. In this case, the performance of HSE06 is better than the present proposition.

Alkyl bond dissociation energies, Hydrocarbon chemistry, Isomerization energies of large molecules and Thermochemistry of π systems: Alkyl bond dissociation energy database (ABDE12) contains 12 molecules that include four bond dissociation energies of methyl, isopropyl, CH3 and OCH3 and another eight molecules formed from ethyl, tert-butyl, H, CH3, OCH3 and OH. The performance of B3LYP is best with MAE 7.268 Kcal/mol compared to others. Next, best performance is observed for PW-TPSSc with MAE 7.932 Kcal/mol. In case of hydrocarbon chemistry, PW-TPSSc performed all functionals at least MAE 3.217 Kcal/mol. For IsoL6 data set, HSE06 achieves smallest MAE, while the performance of PW-TPSSc is better than TPSSh meta-GGA functional. For π system we have considered MP2/6-31+G(d,p) level optimized geometries taken from the Minnesota 2.0 database. The B3LYP gives the smallest MAE with 5.776 Kcal/mol. Whereas, largest MAE is obtained from PW-TPSSc with MAE 8.177 Kcal/mol.

**Barrier heights of chemical reactions:** Due to the transition states with stretched bonds the reaction barrier heights of chemical reactions are related to the many electron self interaction error. Therefore, functional with least MESI always perform well for barrier heights. Semilocal functionals with long range correction always perform well in predicting barrier heights. Geometries and the corresponding reference values are again taken from the Minnesota 2.0 database. The data set consists of forward and reverse barrier heights of 19 hydrogen and 19 non-hydrogen transfer reactions. aug-cc-pVQZ basis set has been used for all our functionals calculations. From Table - (II), HSE06 performs
FIG. 1. (a) Shown is the energy difference of C atom with respect to fractional electron occupation number for HSE06 and present case. The exact line is obtained using experimental -IP and -EA. (b) The deviation of HSE06 and present proposition from the piece-wise linear extrapolation with respect to fractional electron occupation number. The 6-311++(3df,3pd) basis set is used for all the calculations.

gives the lowest MAE for the 76 test set with MAE 4.084 Kcal/mol. Performance of PW-TPSSc is better than TPSSh. The reason behind the performance of HSE06 is better than PW-TPSSc is due to the fact that HSE06 have 1/4 fraction exact exchange with its semilocal form, therefore, more MESI free. B3LYP and PBE0 perform equivalently for the BH76 test set with MAE 5.083 Kcal/mol and 4.709 Kcal/mol.

Lastly, we want to draw a comparison of the behavior of HSE06 and PW-TPSSc in case of fractional electron occupation number of C atom. this phenomenon is directly related to the semiconductor band gap. We give special interest to these two functionals because both are designed considering HF in its short range part. Comparison from Fig-(1) clearly indicated that both perform equivalently. HSE06 have 1/4 HF mixing in its SR part compared to the PW-TPSSc, that’s why it behaves slightly better. This difference is only evident when we plot them in Kcal/mol scale as it is shown in Fig-(1) (b).

A meta-GGA level range separated hybrid functional is proposed using exact HF exchange in its short range. The RS functional proposed here utilizes the full DME based exchange hole coupled with the slowly varying density correction of the enhancement factor included through the LDA exchange hole. This is the first ever attempt to utilize the TM functional in RS perspective. Comprehensive assessment of present functional with B3LYP, PBE0, TPSSh and HSE06 shows it performs promisingly in several cases. Specially, G2/148, ABDE12, HC7 and IP13 test cases performance of PW-TPSSc is quite impressive. Performance of HSE06 and PW-TPSSc for the fractional occupation number perspective has also been discussed because both are designed using HF in short range. It has been observed that both perform almost similarly in fractional change prospective. Lastly, we conclude that, the functional we developed here can be used further in solid state calculations. Further extensions and performance to the solid state system of the proposed functional will be reported in future.

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