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Ab initio relativistic density functional theoretical calculations have been carried out on π-conjugated oligomers of increasing length with S, Se, and Te as heteroatoms. The band gap of the corresponding polymers has been obtained by plotting lowest unoccupied molecular orbital (LUMO)-highest occupied molecular orbital (HOMO)gap against the reciprocal of the number of monomer units (1/N) and extrapolating the curve to 1/N = 0. With B3LYP functional, we predict that role of relativistic correction terms is not very significant in the determination of final band gap of thiophene, selenophene, and tellurophene polymer. The origin of this observation is provided through the density of states (DOS) analysis which manifests that DOS contribution across the Fermi level of these polymers is mostly governed by C atoms and as a consequence relativistic correction terms due to heavy heteroatom remain insignificant to the band gap modification. We also inspected the role of inter-chain interaction in determining the net LUMO-HOMO gap of π-stacked double chain oligomers of increasing length. We have found that due to the exciton splitting in the stacked configurations, the LUMO-HOMO gap decreases steadily. Furthermore, we have noticed that dispersion force has important role in the reduction of the LUMO-HOMO gap of the oligomers studied. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3689860]

I. INTRODUCTION

Conjugated oligomers and polymers have attracted a great deal of research interest in recent years due to their potential application in future generation electronic and optical devices.[1] Specially, low band gap conjugated polymers are in focus of fast-growing field of condensed matter physics and chemistry[2] due to their unique electronic properties and ability to absorb solar light.[3,4] Some exemplary polymeric systems, such as polythiophene, polyphenylene, and polyaniline find remarkable device application in photovoltaic cells,[5] low voltage electrochromic windows,[6] polymer light emitting diodes,[7] photodiodes, organic transistors,[8] microelectronic actuators,[9] and nonlinear optics (NLO). A variety of theoretical as well as experimental studies[10–12] have been carried out on short chain oligomers too and the major objectives of most of these earlier investigations were based on the evaluation of electronic structure property relationship, role of electron correlation upon band gap,[13] and so forth.

Amongst these wide variety of polymeric systems, polythiophene takes a very special place owing to its unusual chemical stability, high conductivity upon doping, and remarkable nonlinear optical properties.[14,15] Consequently, from the chemistry perspective, polymers containing next two members of group VI of the periodic table namely, selenium and tellurium as heteroatoms instead of S are also very important, though a very limited number of works have been

done to characterize them. Lack of well-defined structure and insoluble nature make these polymers a difficult subject for extensive experimental investigation. In spite of these limitations, it is already predicted in a number of research works that selenium analogues of polythiophenes are electronically and optically more advantageous.[16] This superiority of polyselenophene is attributed to the various interesting features, such as larger quinoid character of polyselenophene compared to thiophene analogue, lower band gap, higher polarizability, intermolecular Se-Se interaction leading to wide band width and stronger inter-chain charge transfer in organic semiconductors, lower oxidation, and reduction potential as well as higher charge accumulation probability in polyselenophene due to large size of the selenium atoms.[16,17] Though, sulphur and selenium atoms have similar properties, the other member of group VI, i.e., tellurium possesses different features.[16,18] The synthesis and certain properties of tellurophene oligomers have been highlighted in some recent works.[19,20] However, correct description of electronic structure – properties of polytellurophene – is still a challenge for both the experimentalists as well as theoretician and there is enough scope of carrying out further investigations in this field.

Because of the difficulties involved in the experimental characterization of physical properties of polyselenophene and polytellurophene, an alternative theoretical approach has been proposed. Generally, the band gap of a polymer could be measured by extrapolating the linear curve of the LUMO-HOMO gap against the reciprocal of the number of monomer units (1/N).[21] Kuhn's equation provides a parallel route to

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analyze the dependence of band gap of a conjugated polymer upon the length of the conjugated backbone.[22,23] The extrapolation method at B3LYP/6-31G(d) level of theory predicts the band gap of conjugated polymers (polythiophene, polypyrrole, polyfuran, etc.) quite accurately when long conjugated oligomers are used.[24] Earlier, experimental and theoretical studies on polythiophene predicted a non-degenerate ground state with a band gap of 2.1 eV, while the band gap of selenophene polymer is 1.9 eV and this lowering is attributed to the increase of quinoid character in the polymer backbone.[25–27] Albeit, some theoretical predictions are available, estimation of experimental band gap of polytellurophene is still missing. The band gap of polytellurophene is expected to be lower than that of its S and Se counterpart and is reported as 1.48 eV when calculated at the B3LYP/lanl2dz level of theory using extrapolation method.[20,28] Apart from the conjugation length and quinoid character of the hetero cycles, the relativistic effects and inter-chain interactions may have strong influence on the band gap of these polymers. In particular, Davydov's splitting[29] due to inter-chain interaction may play a crucial role in determining the net LUMO-HOMO gap of the oligomers in the solid state. Moreover, the inter-chain interactions in π-stacked organic polymers are controlled by the dispersion force and hence its role on the Davydov's or exciton splitting[29] is needed to be scrutinized for these oligomeric systems at the theoretical level. It is worth recalling that Davydov's splitting[29] and related excitonic effect has already been experimentally verified for thiophene oligomer.[30,31] However, no such experimental and theoretical results are available for selenophene and tellurophene oligomers. This certainly provides us enough motivation to examine the role of inter-chain interaction in stacked selenophene and tellurophene oligomer.

With this background, the present theoretical work is aimed at investigating the role of relativity and dispersion controlled inter-chain interaction vis-a-vis exciton or Davydov's splitting on the LUMO-HOMO gap of thiophene, selenophene, and tellurophene oligomers. The relativistic effects including both the scalar and spin-orbit contributions have been implemented with zero order regular approximation (ZORA) Hamiltonian,[32–35] while the inter-chain interaction has been studied with Grimme's[36,37] semi-empirical dispersion corrected density functional theory (DFT-D) technique considering two oligomer chains up to N = 9. The whole analysis suggests that dispersion controlled exciton splitting plays more prominent role than relativity in determining the net LUMO-HOMO gap of these oligomers.

II. COMPUTATIONAL DETAILS

The geometries of the π-conjugated oligomers of increasing length (N = 1 to 14) with S, Se, and Te as heteroatoms have been optimized using GAUSSIAN03[38] suite of programs employing B3LYP[39,40] hybrid density functional. The basis sets used for all the geometry optimization related calculations are 6-31G(d) for C, H atoms and effective core potential (ECP) corrected lanl2dz for S, Se, and Te atoms. The relevant geometric parameters are analyzed in Figs. 1(a) and 1(b).
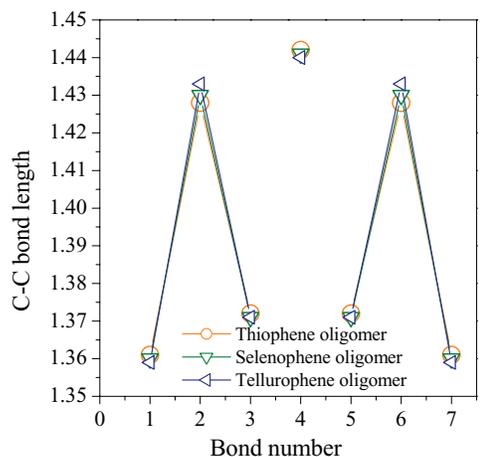
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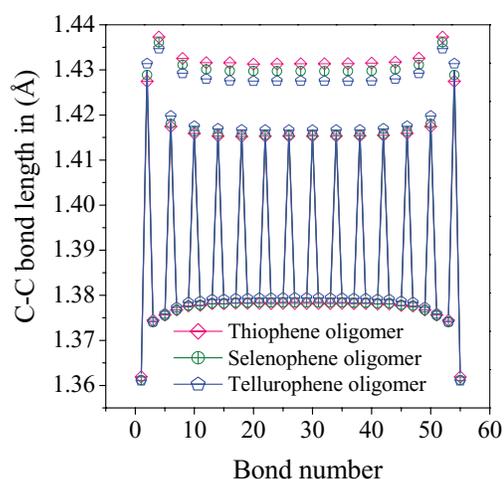
(b)

FIG. 1. Bond length alteration (BLA) for (a) 2 units of thiophene, selenophene, and tellurophene oligomers and (b) 14 units of thiophene, selenophene, and tellurophene oligomers. Repeating set of three linked points corresponds to intra-ring bond length and every 4th point represents inter-ring bond length.

In order to investigate the role of relativity on the LUMO-HOMO gap of the oligomeric systems, we have performed ZORA based scalar relativistic and spin-orbit coupling calculations.[32–35] Entire relativistic calculations have been executed in Amsterdam Density Functional (ADF) 2010.02 (Ref. 41) program employing hybrid B3LYP[39,40] functional. Within ADF 2010.02 (Ref. 41), relativistic core-potential is computed with auxiliary program, DIRAC. The basis set used for the relativistic calculation is of triple zeta polarized (TZP) quality. The LUMO-HOMO energy gaps obtained from scalar ZORA, spin-orbit ZORA, and non-relativistic calculations are plotted against 1/N and the band gap of the system is achieved by extrapolating the curve to 1/N = 0.

To study the role of inter-chain interactions, two oligomer chains up to N = 9 units of thiophene, selenophene, and tellurophene in each chain have been considered. Figure 2 demonstrates representative oligomer system in case of
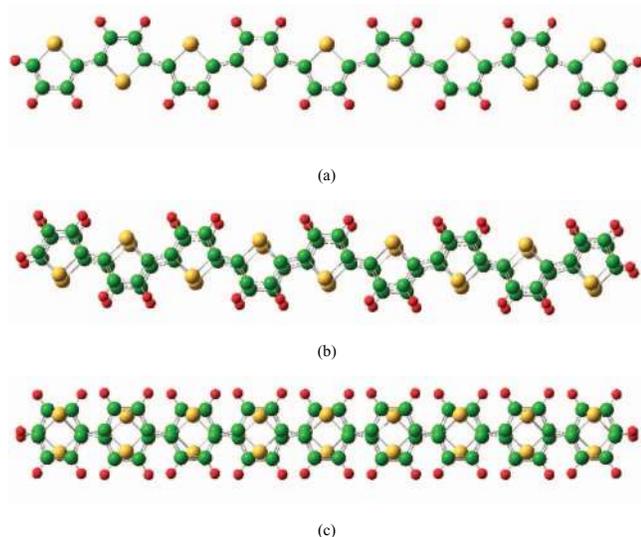
FIG. 2. Representative oligomer system in case of (a) single chain, (b) double-stranded co-facial (heteroatoms in the same direction), and (c) double-stranded antara-facial (heteroatoms in the opposite direction). Green spheres represents C atom, red spheres represents H atom and golden spheres represents S, Se, and Te.

single and double chain of N = 9 units. In the double chain related study, initially we have taken both co- and antara-facial π-stacked configurations. The separation distances between the two oligomer chains have been evaluated from the minima of the potential energy curves (PECs) and for these calculations, we have used both Perdew-Burke-Ernzerhof (PBE) and PBE+D functional which will definitely help us to understand the role of dispersion force in the inter-chain interaction between oligomer chains. The PECs related calculations have been carried out using *double-zeta* plus polarization (DZP) basis set for C, H, and TZP basis for S, Se, and Te with ADF 2010.02 (Ref. 41) suite of programs. It has been observed that the antara-facial arrangement is energetically more stable than that of its co-facial counterpart and hence the Davydov's splitting[29] phenomenon is studied only with the antara-facial configuration. It is worth commenting that PECs related calculations have been performed up to N = 6 units in each chain because we did not find any significant change in the separation distance beyond N = 4 units in each chain and as a consequence, the study of the inter-chain interaction with higher chain length has been done with a separation distance between the chains as obtained with N = 6. After getting the separation distances between the two chains with PBE and PBE+D functional, the LUMO-HOMO gap of all the double chain configurations is re-evaluated with hybrid B3LYP functional in combination with 6-31G(d) basis for C, H atoms and ECP corrected lanl2dz basis for S, Se, and Te.

III. RESULTS AND DISCUSSIONS

A. Role of relativity on the LUMO-HOMO gap of thiophene, selenophene, and tellurophene oligomers

A comparative analysis of the modification in the geometric parameters due to the change in oligomer type from thiophene, selenophene to tellurophene oligomer has been made in Fig. 1. For simplicity, we have presented the results related to the geometric parameters of all the oligomer types with N = 2 and 14 in Figs. 1(a) and 1(b), respectively. Both the figures manifest that albeit intra-ring bond length of each type of oligomer does not differ appreciably, the inter-ring bond length (every fourth point) shows a gradual decrease in its magnitude from thiophene, selenophene to tellurophene. The inter-ring bond distances measured in two units of thiophene, selenophene, and tellurophene oligers are 1.442 Å, 1.441 Å, and 1.440 Å, respectively. The average inter-ring bond distances in 14 units of three different oligomers are 1.432 Å for thiophene, 1.430 Å for selenophene, and 1.428 Å for tellurophene. This gradual shrinking of the inter-ring bond length was also noted in the earlier theoretical work of Zade *et al.*,[17] where they studied up to 50 oligomeric units of thiophene and selenophene. Following their observations, one can surmise that reduction in inter-ring bond length corresponds to a more quinoid character in selenophene and tellurophene rings compared to thiophene analog. As a consequence, the efficiency of conjugation through the backbone enhances gradually from selenophene to tellurophene oligomers. This augmentation in electron delocalization through oligomeric back bone has a direct impact on the band gap of the respective polymer and in fact it has been observed by Zade and co-workers that the HOMO-LUMO gap essentially diminishes from thiophene to selenophene oligomer.[17] The reduction in C-C inter-ring bond length is attributed to various physicochemical properties, such as lower electronegativity and higher electric polarizability of Se and Te with respect to sulphur as well as to the charge accumulation on carbon atoms involved in the inter-ring bond region. It is worth mentioning that primarily both *cis*- and *trans*-geometries with N = 2 of each type of oligomer were optimized using same B3LYP level of theory and 6-31G(d) basis set for C, H atoms and an ecp corrected lanl2dz basis for S, Se, and Te atoms and it was found that in all the cases *trans*-configuration is the more stable one. As a consequence, while investigating the influence of relativistic effect, only *trans*-geometries have been preferred. This instability of *cis* oligomer can be explained by the fact that, particularly in this configuration, all the heteroatoms are oriented towards the +z direction and thus the lone-pair of electrons between two successive heteroatoms faces a syn-interaction which results in the increase of energy of the system as a whole and makes it unstable with respect to the *trans*-configurations. A comparative study of the stability of both *cis*- and *trans*-configurations is presented in Table I.

TABLE I. A comparative study of the stability of *cis*- and *trans*- geometries of two units (N = 2) of thiophene, selenophene, and tellurophene oligomer estimated at B3LYP level of theory and 6-31G(d) basis for C and H atom and ecp corrected lanl2dz basis set for S, Se, and Te atoms.

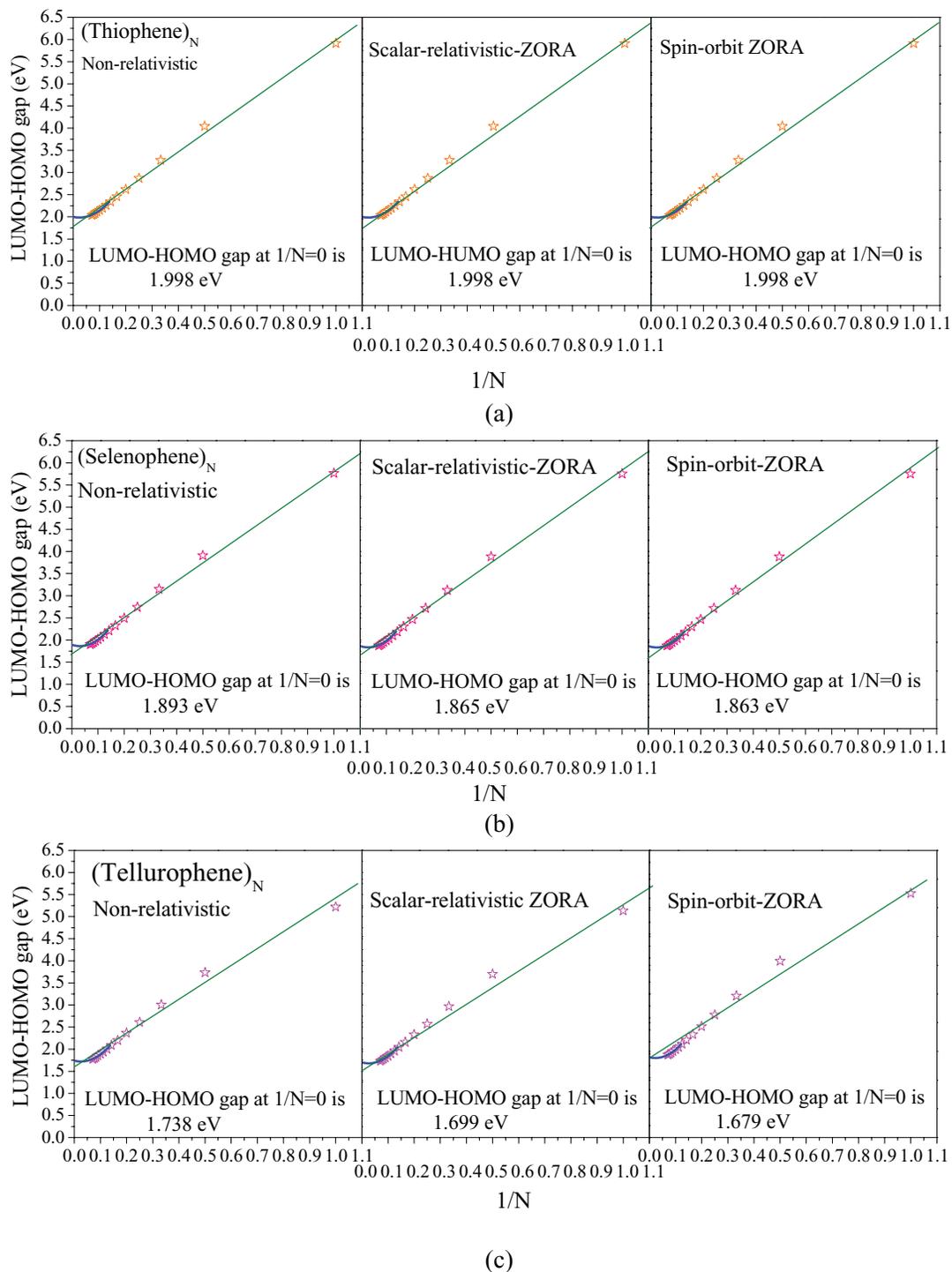| N = 2	E_{OPT} (*cis*-)	E_{OPT} (*trans*-)
Heteroatoms	(hatree)	(hatree)
S	−328.6135	−328.6158
Se	−326.8440	−326.8470
Te	−324.4788	−324.4842

FIG. 3. LUMO-HOMO gap vs 1/N plot for (a) poly thiophene, (b) polyselenophene, and (c) polytellurophene at various levels of relativistic corrections.

In the present study, the role of different types of relativistic effects is described in Figs. 3 and 4. It is worth commenting, that the relativistic effects become significant mostly in heavy elements where the core electrons move with much faster speed around the heavy nucleus and such an effect can be explained by the well known Dirac equation. The relativistic effect is categorized into two parts, scalar-relativistic effect which includes mass-velocity and Darwin corrections and the other one is the spin-orbit interaction. The work of Liu *et al.* provides a comprehensive review of the state of the art applications of relativistic effects in quantum chemistry.[42] Springborg and his group studied relativistic effects on [Pt $(PH_3)_2C_6]_x$ and observed that the band gap actually decreases (about 0.24 eV) due to the spin-orbit coupling.[43] Kisiel *et al.* have shown the influence of the relativistic effect on CdTe and on Hg, where mainly the conduction band is affected due to relativity.[44] In polymer systems, the effect of relativity has been successfully studied by Campbell[45] to describe existence of polarons and solitons in the *trans*-polyacetylene. However, the role of
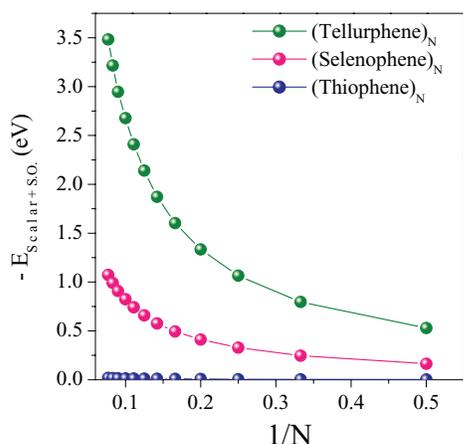
FIG. 4. The stabilization energy contributions due to scalar relativity and spin-orbit interaction in tellurophene, selenophene, and tellurophene oligomer.

relativity in tuning the band gap of thiophene, selenophene, and tellurophene based polymers has only been addressed through the choice of pseudo potential and no attempt has been made yet to separate the effect of scalar- and spin-orbit contributions in modulating the net LUMO-HOMO gap of these polymers.

The variation in LUMO-HOMO gap against the reciprocal of the number of monomer units (1/N) is presented in Fig. 3. It is important to mention here that very recently Zade and co-workers made an excellent review on the theoretical results related to the band gap of polythiophene and polyselenophene.[26] They compared the results with the experimental one and highlighted that when 1/N is small, the correct band gap could be obtained with an asymptotic fit of LUMO-HOMO gap vs 1/N data. Moreover, it is also reported that the linear fit is acceptable for conjugated oligomers up to N = 12 and for higher N values (N > 12), second order polynomials are required to describe the precise relationship between the LUMO-HOMO gap and 1/N. Hence, applying a quadratic fit between the LUMO-HOMO gap and 1/N, the band gap has been estimated at 1/N = 0 for all three types of system. Needless to say, none of the earlier works on thiophene, selenophene, and tellurophene oligomers considered the relativistic effect explicitly and only a part of the relativistic effect was captured through the use of pseudopotential for S, Se, and Te atoms. In our case, the asymptotically extrapolated band gap estimated with all the levels of relativistic corrections for polythiophene, polyselenophene, and polytellurophene are presented in Fig. 3. All the estimated band gaps are well in agreement with the theoretical work of Zade and co-workers[26] and the available experimental results on polythiophene and polyselenophene. The change in LUMO-HOMO gap ($\Delta_{\text{LUMO-HOMO}}$) estimated with scalar ZORA, spin-orbit ZORA, and combined effect of both with respect to nonrelativistic value has been calculated. We have noticed that relativity has no impact on the LUMO-HOMO gap of thiophene oligomer, while the effect is marginal for selenophene oligomers. The lowering of the LUMO-HOMO gap of selenophene due to relativistic effect is less than 0.055 eV, even when the chain length is considerably large (N = 12). In case

of tellurophene oligomer, the decrease in the LUMO-HOMO gap due to relativistic effect is more prominent, although the total change (0.092 eV for N = 12 units) is still not appreciable. Apart from monitoring the LUMO-HOMO gap, we have also evaluated the scalar- and spin-orbit interaction contribution to the net stabilization of all the oligomers of thiophene, selenophene, and tellurophene. The stabilization contributions due to scalar relativity and spin-orbit interaction in these oligomers are presented in Fig. 4. From this figure, it is clearly evident that relativistic effects play insignificant role in the net stabilization of thiophene oligomers, while the stabilization due to scalar relativity and spin-orbit interaction in selenophene oligomers are moderate up to N = 6 and becomes significant in the large N limit (N = 12). In case of tellurophene oligomers, the total relativistic contribution is quite large and reaches a value of 3.5 eV when N is 12. This indicates that both scalar relativity and spin-orbit interaction have profound impact on the stabilization of the tellurophene oligomers. However, the stabilization due to relativistic effect is not at all reflected in the LUMO-HOMO gap, in particular, for selenophene and tellurophene oligomers. To find out the origin of this apparently surprising phenomenon, we have performed calculations with periodic boundary condition (PBC) and evaluated the total density of states (TDOS) of the polymers of thiophene, selenophene, and tellurophene and also extracted the partial density of states (PDOS) of C, S, Se, and Te. The PBC calculations are performed with PBE functional since ADF 2010.02(Ref. 41) does not support Hybrid functionals for such calculations. The results are depicted in Fig. 5. The PDOS of C, S, Se, and Te suggests that the heteroatoms have insignificant role in the construction of the valence and conduction bands of these polymers. In other words, TDOS of these polymers across the Fermi level are mostly governed by the DOS contribution of C and is clearly reflected from its PDOS contribution as shown in Fig. 5. The absence of the DOS contribution of the heteroatoms in the valence and conduction band is probably responsible for the ineffectiveness of the relativistic effects in controlling the band gap of these polymers. It is worth commenting here that we have also considered stacked dimer of thiophene, selenophene, and tellurophene, however, we didn't find any significant relativistic effects on the band gap of these materials. This has happened again due to the absence of the heteroatom DOS associated with the valence and conduction bands of these polymers.

B. Inter-chain interaction controlled modification of the LUMO-HOMO gap of thiophene, selenophene, and tellurophene oligomers

As mentioned earlier, in addition to the relativistic effects, the band gap of these polymers could also be influenced by the inter-chain interactions, specially, in π-stacked multi-chain oligomers. It is a well known fact that, due to inter-chain interaction between oligomer chains, Davydov's splitting or excitonic splitting[29] will occur which eventually will change the band gap in the large N limit. One elegant way to envisage exciton splitting is to consider the interaction potential between two dipoles originated from the two interacting chains, having moments μ_1 and μ_2 can be written as[29]
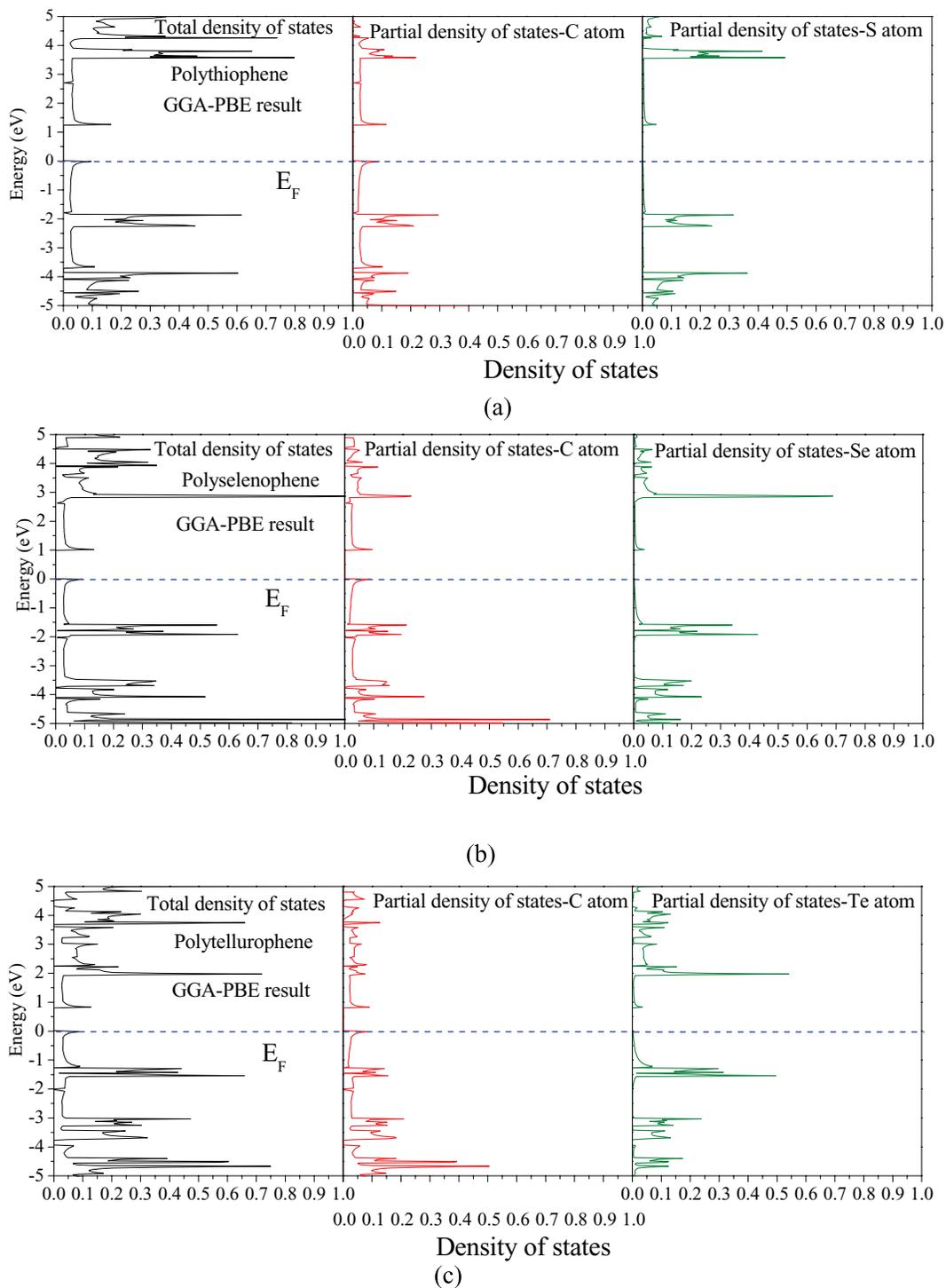
FIG. 5. Total density of states (TDOS) of thiophene, selenophene, and tellurophene polymer along with the partial density of states (PDOS) of C, S, Se, and Te.

$V = (\mu_1 \cdot \mu_2/r^3) - 3((\mu_1 \cdot r)(\mu_2 \cdot r)/r^5)$, where r is the distance vector between the two dipoles. In our case $\mu_1 = \mu_2$, since we are using the identical chains of the oligomers. With this interaction potential, one can express the splitting energy as $\Delta E = 2(\mu^2/r^3)(\cos\phi - 3\cos^2\theta)$, where ϕ is the angle between the dipoles and θ is the angle between the dipole and the r-vector. Depending upon the angle ϕ and θ, the exciton splitting may lead to both red and blue shift of the LUMO-HOMO gap of the oligomer in a double chain configuration. Further-

more, apart from dipolar interaction, the effect of dispersion force in π-stacked oligomer chains is crucial and in fact it can change the extent of exciton splitting vis-à-vis the net LUMO-HOMO gap significantly. However, the major limitation of DFT lies in its inability to capture the dispersion interaction in the framework of local density approximated (LDA) and generalized gradient approximated (GGA), or hybrid functional. One simple yet elegant way to tackle the dispersion force within DFT was prescribed by Grimme.[36,37] Within this

approach, van der Waals (vdW) interaction term is well described by a damped interatomic potential.[37] The interaction potential is applied to account for the long-range dispersion effect in non-bonded systems. For such system, the total density functional energy is written as

$$E_{DFT-D} = E_{DFT} + E_{vdW}, \qquad (1)$$

where E_{DFT} is the normal self-consistent density functional energy and E_{vdW} is the empirical dispersion correction term, which is given by

$$E_{vdW} = -s_6 \sum_{i=i}^{N-1} \sum_{j=i+1}^{N} \frac{C_6^{ij}}{R_6^{ij}} f_{dmp}(R_{ij}). \qquad (2)$$

In Eq. (2) s_6 is a scaling factor, which depends on the density functional used. Grimme determined the scaling factor for BLYP and PBE functional through least-square optimization of the deviations observed in the interaction energy values for the various weakly interacting systems.[37] C_6^{ij} describes the dispersion force between the pair of atoms i and j. R_{ij} is the inter-atomic distance between ith and jth atom and N is total number of atoms present in the system. $f_{dmp}(R_{ij})$ represents the damping function of the system.

To study the excitonic effect in these oligomers, we have initially considered both co- and antara-facial π-stacked double chain configurations up to $N = 9$ monomers in each chain. We have found that antara-facial arrangement is more stable irrespective of the nature of the heteroatoms (S, Se, and Te) and hence we investigated the details of excitonic effect on the antara-facial arrangement of the thiophene, selenophene, and tellurophene oligomers. As mentioned earlier, the equilibrium separation distance between the two oligomeric chains in the anatara-facial arrangement has been evaluated with PBE and PBE+D functionals. The use of PBE+D functional will ensure the capture of dispersion part of the net inter-chain interactions and this ultimately will help us to figure out the role of dispersion force on the exciton splitting and the LUMO-HOMO gap of these materials in the π-stacked antara-facial double chain configurations. All the double chain π-stacked oligomers of thiophene, selenophene, and tellurophene with

minimum separation distance obtained with and without the inclusion of dispersion correction have further been used to re-evaluate the LUMO-HOMO gap at the B3LYP level of theory and the results are presented in Fig. 6. The figure demonstrates that the double chain oligomers have lower LUMO-HOMO gap in comparison to that of the single chain oligomers and is consistent for all three heteroatoms. With PBE separation distance, the LUMO-HOMO gap in the 9th double chain oligomer unit is reduced from the corresponding single chain value by 0.163 eV for thiophene oligomer and for the selenophene and tellurophene oligomers, the related values are 0.207 eV and 0.251 eV, respectively. This lowering of LUMO-HOMO gap is happened due to Davydov's splitting. In the antara-facial arrangement of the π-stacked oligomers, the dipoles are aligned anti-parallel which stabilizes both the ground and the excited states. However, the net decrease in the LUMO-HOMO gap indicates that the stabilization due to dipolar interaction is much higher than that in the ground state and this has been confirmed by our *time-dependent density functional theory* (TDDFT) calculations.

This reduction in LUMO-HOMO gap is further enhanced when the effect of dispersion force is considered. With PBE+D separation distance, Davydov's splitting reduces the LUMO-HOMO gap of the 9th double chain from the single chain analog by 0.330 eV, 0.396 eV, and 0.420 eV in thiophene, selenophene, and tellurophene oligomers, respectively. It indicates that the reduction in the LUMO-HOMO gap with PBE+D separation distance between oligomers is more prominent than that with PBE separation distance. It is worth commenting that dispersion force has no direct bearing with Davydov's splitting. The inclusion of the dispersion correction actually decreases the separation distance between the oligomers and this significantly affects the extent of Davydov's splitting as it has $1/r^3$ distance dependence. With small PBE+D separation distance between the oligomers, the extent of Davydov's splitting between two LUMO states (L1 and L2) will be higher and as a consequence the L1 state with respect to its parent LUMO state will be more stabilized. The greater stabilization of the L1 state at a shorter distance (PBE+D separation distance) between the oligomers
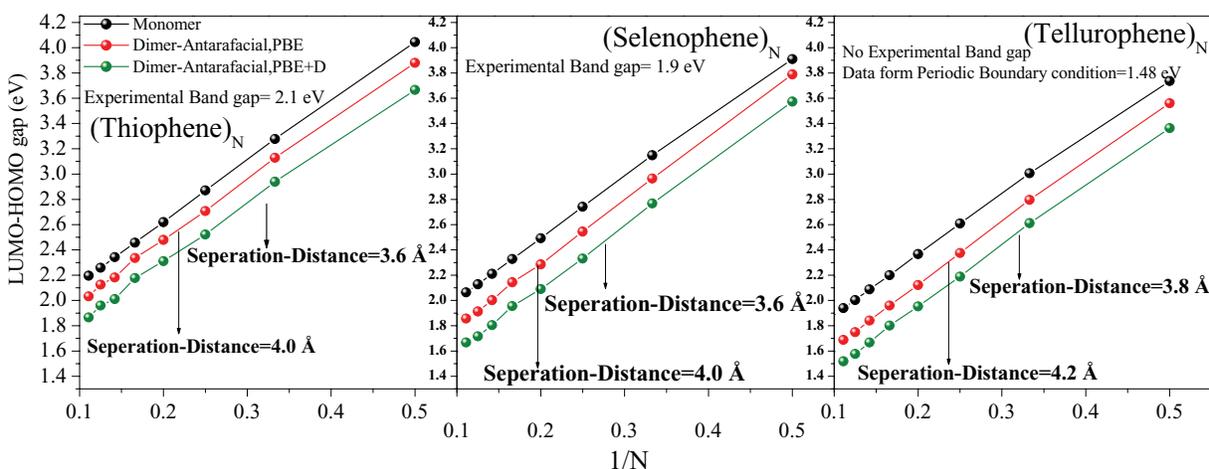

FIG. 6. LUMO-HOMO gap vs. 1/N plot for single chain and antara-facial arrangement of π-stacked double chain (a) thiophene, (b) selenophene, and (c) tellurophene oligomer.

TABLE II. LUMO-HOMO gap measured with BHandHLYP and CAMB3LYP exchange-correlation functionals.

N=9 in each chain (antara-facial π stacked arrangement) PBE+D geometry	LUMO-HOMO gap (eV)		
	BHandHLYP	CAMB3LYP	B3LYP
Thiophene single chain	3.787	4.323	2.452
Thiophene double chain	3.377	3.919	1.865
Selenophene single chain	3.620	4.133	2.093
Selenophene double chain	3.149	3.669	1.667
Tellurophene single chain	3.595	4.103	1.925
Tellurophene double chain	3.091	3.608	1.518

is ultimately responsible for the more effective lowering of the net LUMO-HOMO gap in comparison to that obtained from PBE separation distance. Nevertheless, the whole study indicates that the antara-facial double chain configuration will have lower LUMO-HOMO gap than that of a single chain configuration.

From Fig. 6, it is also worth noting that the band gap of poly-thiophene and poly-selenophene is reached to their experimental value at relatively smaller oligomer length and this attainment is even much quicker in presence of dispersion forces. In fact, the 8th unit of the double chain configurations of polythiophene and poly-selenophene has started underestimating the experimental band gap of these materials. This underestimation of the LUMO-HOMO gap is probably attributed to the use of B3LYP functional. The interaction between two oligomer chains is essentially long range in nature and B3LYP functional is not capable of treating such interaction even it has certain amount of non-local Hartree-Fock (HF) exchange contribution. To overcome the underestimation problem associated with the present LUMO-HOMO gap, one can either use hybrid functional with HF exchange much larger than B3LYP or the state-of-the art available long range corrected hybrid functionals. To check the long range effect on the net Davydov split LUMO-HOMO gap of the double chain configurations, we have performed calculations with BHandHLYP (Ref. 46) and range-separated CAM-B3LYP (Ref. 47) functionals. The LUMO-HOMO gaps obtained with BHandHLYP (Ref. 46) and CAMB3LYP (Ref. 47) functionals for the 9th unit of the double chain configuration are presented in Table II. We have found that the use of these two additional functionals improves the LUMO-HOMO gap significantly. However, in this case too, the dispersion controlled modulation of the LUMO-HOMO gap is quite appreciable which indicates that macroscopic band gap of these polymers will be strongly influenced by the inter-chain interactions.

IV. CONCLUSION

A systematic theoretical analysis has been carried out to explore the role of relativity and inter-chain interactions in controlling the band gap of conjugated polymers based on thiophene, selenophene, and tellurophene. We have noticed that relativity has little impact on the LUMO-HOMO gap of these oligomers although spin-orbit interaction has significant contribution to the net stabilization of selenophene and tellurophene oligomers. Our study reveals that the TDOS of these polymers across the Fermi level are mostly governed by the DOS contribution of C atoms, while the DOS contribution of the heteroatoms are missing in the construction of the valence and conduction band of these materials. As a consequence, the relativistic effects are not at all playing important role in determining the band gap of these systems even in a situation where spin-orbit interaction is very strong. On the other hand, LUMO-HOMO gap of these oligomeric systems are strongly affected by the dipolar interaction dominated exciton splitting. We have further noticed that the addition of dispersion interaction have profound impact on the net LUMO-HOMO gap of these oligomers and has been justified by the use of functionals, such as BHandHLYP (Ref. 46) and CAMB3LYP (Ref. 47). Finally, to the best of our information, this is the first attempt to account the dispersion controlled tuning of the LUMO-HOMO gap of selenophene and tellurophene oligomers.

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