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To cite this article: Bin Zhou *et al* 2018 *J. Phys.: Condens. Matter* **30** 215501

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Benchmark study of ionization potentials and electron affinities of armchair single-walled carbon nanotubes using density functional theory

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Received 8 February 2018, revised 22 March 2018

Accepted for publication 10 April 2018

Published 30 April 2018



Abstract

The intrinsic parameters of carbon nanotubes (CNTs) such as ionization potential (IP) and electron affinity (EA) are closely related to their unique properties and associated applications. In this work, we demonstrated the success of optimal tuning method based on range-separated (RS) density functionals for both accurate and efficient prediction of vertical IPs and electron affinities (EAs) of a series of armchair single-walled carbon nanotubes $C_{20n}H_{20}$ ($n = 2-6$) compared to the high-level IP/EA equation-of-motion coupled-cluster method with single and double substitutions (IP/EA-EOM-CCSD). Notably, the resulting frontier orbital energies ($-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$) from the tuning method exhibit an excellent approximation to the corresponding IPs and EAs, that significantly outperform other conventional density functionals. In addition, it is suggested that the RS density functionals that possess both a fixed amount of exact exchange in the short-range and a correct long-range asymptotic behavior are suitable for calculating electronic structures of finite-sized CNTs. Next the performance of density functionals for description of various molecular properties such as chemical potential, hardness and electrophilicity are assessed as a function of tube length. Thanks to the efficiency and accuracy of this tuning method, the related behaviors of much longer armchair single-walled CNTs until $C_{200}H_{20}$ were studied. Lastly, the present work is proved to provide an efficient theoretical tool for future materials design and reliable characterization of other interesting properties of CNT-based systems.

Keywords: range separated density functional theory, carbon nanotube, ionization potential, electron affinity

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWCNTs), have attracted enormous attention in the past few decades due to their various interesting electronic, mechanical, structural and transport properties [1]. Since the discovery of CNTs in 1991 [2, 3], their highly unique properties render them promising for a great variety of applications, such as organic solar cells [4], electrical energy storage [5], polymer matrix fillers [6], biological imaging and nanomedicinal therapy [7] and etc.

Among numerous intrinsic parameters of properties, the ionization potential (IP) and electron affinity (EA) are well known as critical energy-level parameters governing the various redox, electronic, optical, and transport properties of CNTs-based materials [8–10]. In particular, the accurate measurement or reliable prediction of the IPs/EAs and transport (fundamental) gaps is a key to understand internal mechanisms such as covalently chemical functionalization [11, 12] and carrier injection/transport [13, 14], and further will be in favor of materials design and property optimization. Accordingly, the conjugation of the π orbitals along the CNTs backbone leads to the formation of delocalized π molecular orbitals and of special interest are the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). Typically, the IPs (and EAs) of the material correspond to the HOMOs (and LUMOs) for the isolated finite-size molecular system; and to the hole (and electron) quasiparticle energies, or to the top of the valence band (and the bottom of the conduction band) for the periodic or solid systems [8, 15].

From a theoretical perspective, however, two challenges clearly exist in the field of CNTs: (1) how accurate can the available theoretical methods provide for the prediction of these energy-level parameters and how large the studied system, i.e. length of CNTs, can achieve? (2) to what extent the approximation between the calculated HOMO/LUMO energy levels and the corresponding IPs/EAs reaches, since the former frontier orbital energies were widely used to represent IPs/EAs? For the first question, several methods such as the many-body perturbation theory within the GW approximation [16–21] and IP/EA equation-of-motion coupled-cluster method with single and double substitutions (IP/EA-EOM-CCSD) [22–25] have been demonstrated to provide accurate IPs and EAs values. However, the high computational expense of these so-called high-level methods greatly limits the size of extended systems and it seems to be impossible to deal with an enough long nanotube with these methods. Although the periodic boundary condition (PBC) calculation can be performed for CNTs using GW approach, of specific interests also focus on the gradual behavior of parameters such as orbital energies and chemical reactivities of SWCNTs from short to long, especially as a function of tube length.

For the second one, density functional theory (DFT) [26] is well-known to strike a right balance between the accuracy of the results and the computational cost and thus the predictive power of DFT leaves a lot to be desired for long SWCNTs [27]. However, the DFT-calculated HOMO and LUMO energy

levels, which typically provide an inconsistent approximation to the IPs/EAs, are found to strongly depend on the kernel of the exchange–correlation (XC) functional or the amount of Hartree–Fock exact-exchange (eX%) included [8, 10, 15, 28, 29]. For example, Louie and colleagues concluded that orbital energies from a series of conventional density functionals (PBE [30], B3LYP [31, 32], PBE0 [33, 34], HSE [35]) do not give reliable quasiparticle energies and band gaps of solid silicon and armchair graphene nanoribbons and strong variations are observed from different hybrid functionals. The accuracy of prediction strongly depends on the specific studied system and its structural configurations (e.g. surfaces or bulk) [36]. Furthermore, the pure or hybrid functionals such as PBE, PBE0 and B3LYP with low or no eX% produce significantly overestimated HOMO energies and underestimated LUMO energies, respectively, resulting in much smaller HOMO–LUMO gaps for various finite-sized molecular systems and bulk solids [37, 38]. Unfortunately, previous studies of structures and aromaticities of finite-length CNTs is still limited to the B3LYP functional or even lower semi-empirical PM3 approach that only produce a trustable trend but not in a quantitative way [27]. The Hartree–Fock (HF) method and the default long-range corrected LC- ω PBE [39, 40] functional with high or full eX% yield a much lower HOMO and higher LUMO energy level, and result in an overestimated gap accordingly [15, 24, 36]. In short, the failure of these conventional functionals can be attributed to their inappropriate XC approximations or too high/low eX% included in the functionals, that tend to over-/underestimate the delocalization effect of holes/electrons or wave functions. This phenomenon is also known as the electron self-interaction error (SIE) or delocalization error (DE) [41].

The idea of ‘optimal tuning’ [42, 43] was proposed recently to effectively eliminate the so-called DEs and allow for an improved description of the frontier orbital energies obtained from range-separated (RS) density functionals [44, 45]. The nonempirical tuning procedure is based on a consistency condition: the negative HOMO/LUMO energy ($-\varepsilon_{\text{HOMO}}/-\varepsilon_{\text{LUMO}}$) in exact Kohn–Sham DFT should equal the vertical IP and EA obtained from total energy difference between the neutral and cationic/anionic systems for a fixed geometry. See the Computational Methodology for the details of introduction of optimal tuning approach. It has been further demonstrated that the optimal tuning method can efficiently predict frontier orbital energies with an accuracy comparable to the GW approximation for a set of organic electron-deficient acceptor molecules [46], DNA and RNA nucleobases [47], and organic photovoltaic molecules [48, 49]. In our previous work we also have demonstrated the accuracy and efficiency of this optimal tuning approach served as a reliable theoretical tool for a series of molecular properties. For example, through applying the optimally-tuned long-range corrected functionals, significant improvement is found for the prediction of the IPs, EAs and transport gap of π -conjugated thiophene-based oligomers and polymers [38, 50], nucleobase clusters [28], organic molecular crystals [29, 51]; hyperpolarizabilities of ‘push–pull’ systems [52, 53], and excitation energies of various organic fluorescence molecules

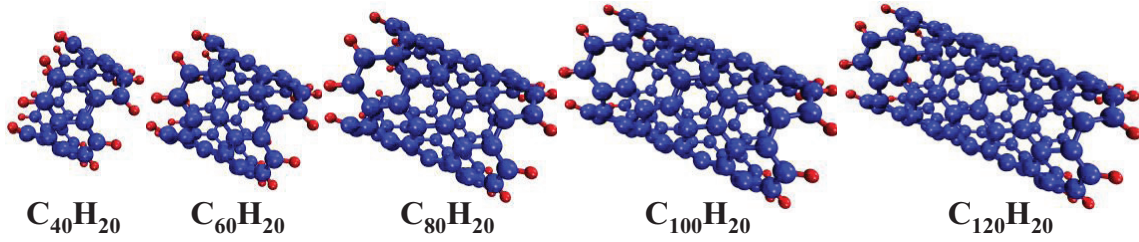


Figure 1. A series of armchair $C_{20n}H_{20}$ SWCNTs models with $n = 2-6$ studied in this work.

[54–57]. Since the research of CNTs has rapidly become a hotspot in both academic and industry, there is still lack of a theoretical method that can provide quantitative prediction of properties of CNTs but with relatively low computational cost. To answer the two questions posted above, in this work we performed DFT benchmark calculations on the IPs/EAs and corresponding HOMO/LUMO energy levels of a series of $C_{20n}H_{20}$ SWCNTs with $n = 2-6$ (as shown in figure 1). The results are compared with the high-level IP/EA-EOM-CCSD data taken from the work of Kowalski and colleagues [24]. The predictive power of optimal tuning method is demonstrated for a series of SWCNTs. Thanks to the insignificant increase of computational cost, this tuning method also allows for the study of longer SWCNTs that hold challenges for the much expensive IP/EA-EOM-CCSD approach.

2. Computational methodology

The optimal tuning method is performed based in the framework of RS density functionals. In the RS functionals, the three-parameter separation was used for the range separation of the interelectronic distance r_{12} in the exchange through the standard error function [58]

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta_{\text{erf}}(\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta_{\text{erf}}(\omega r_{12})}{r_{12}}. \quad (1)$$

The first term on the right side represents the short-range DFT component of the exchange, and the second term is used for the long-range HF (eX) component. The parameter α quantifies the fraction of eX in the short-range beginning, while $\alpha + \beta$ gives the fraction of eX in the long range limit. The range-separation parameter ω determines the inverse of a distance where the exchange of functional switches from DFT-like to HF-like. For example, for the RS ω B97XD functional, $\alpha = 0.22$ and $\alpha + \beta = 1$, indicates a 22% eX at the beginning of short-range and 100% eX in the long-range limit. Its default ω equals 0.20 bohr^{-1} , indicating the type of exchange switches from DFT-like to HF-like at the r_{12} distance of 5 bohr. Thus, a smaller ω indicates such a switching behavior of exchange takes place at a longer interelectronic distance. As introduced previously, the ‘tuning’ concept is to choose an optimal ω to satisfy the following condition: the negative HOMO energy for an N -electron system, $-\epsilon_{\text{HOMO}}(N)$, equals the vertical IP in exact DFT and accordingly the negative LUMO, $-\epsilon_{\text{LUMO}}(N)$, as close as possible to the vertical EA. Thus, the following equation is made by minimizing:

$$J^2 = \sum_{i=0}^1 [\epsilon_H(N+i) + \text{IP}(N+i)]^2 \quad (2)$$

If relaxation effect is ignored here, the IP of $N+1$ anion system is thus approximately considered as the EA of neutral system, and the HOMO energy of $N+1$ anion as the LUMO of neutral system. Finally, an optimal ω for RS functionals is non-empirically determined in this way. All the optimal ω values in this work were thus tuned based on the ω B97XD functional and listed in table S1 (stacks.iop.org/JPhysCM/30/215501/mmedia) in the supporting information (SI).

Ground-state geometries for a series of armchair $C_{20n}H_{20}$ ($n = 2-6$) SWCNTs in this work are taken from the work by Kowalski *et al* [24], and Petrushenko and Ivanov [59], that allow for a consistent comparison with the previously published IP/EA-EOM-CCSD benchmark calculations. Note that the only model of armchair (5,5) SWCNTs was considered in the present work. The IPs and EAs values are obtained by calculating the difference in total energy between the N -electron neutral system and its $N \pm 1$ -electron cationic/anionic state using DFT. Note that the effects of structural relaxation are not considered in the present work and thus these values are referred to vertical IPs/EAs. The HOMOs and LUMOs energy levels are calculated based on the neutral systems.

Nine functionals (eX%), including a pure GGA functional PBE (0%); a hybrid-GGA functional, B3LYP (20%); three Minnesota functionals, MN15 [60] (44%), M062X [61] (54%) and M06HF [62] (100%); three RS functionals, HSE06 [63] (short-range–long-range: 25%–0%), CAM-B3LYP [58] (19%–65%), and ω B97XD [64] (22%–100%); and double-hybrid functional B2PLYP [65], were employed to test the influence of various density functionals and percentages of exact exchange in the functionals.

In the work of Kowalski *et al* [24], the IP/EA-EOM-CCSD benchmark data of the IPs and EAs of $C_{20n}H_{20}$ systems ($n = 2-6$) was performed with the small 6-31G basis set. A larger basis set, aug-cc-pVDZ [66], is only employed for the $C_{40}H_{20}$ system due to the very high numerical cost of IP/EA-EOM-CCSD approach. The calculated IPs and EAs of IP/EA-EOM-CCSD were further demonstrated to be more sensitive to the quality of basis set than those of DFT. For example, the difference between IPs (and EAs) obtained from the IP/EA-EOM-CCSD method with 6-31G and aug-cc-pVDZ basis sets is as large as $\sim 0.5 \text{ eV}$ (and $\sim 1 \text{ eV}$). Such differences from DFT are only $\sim 0.1 \text{ eV}$ for IPs and $\sim 0.5 \text{ eV}$ for EAs, respectively. It can be concluded that the IP/EA-EOM-CCSD data can be safely used to assess DFT result if a larger basis

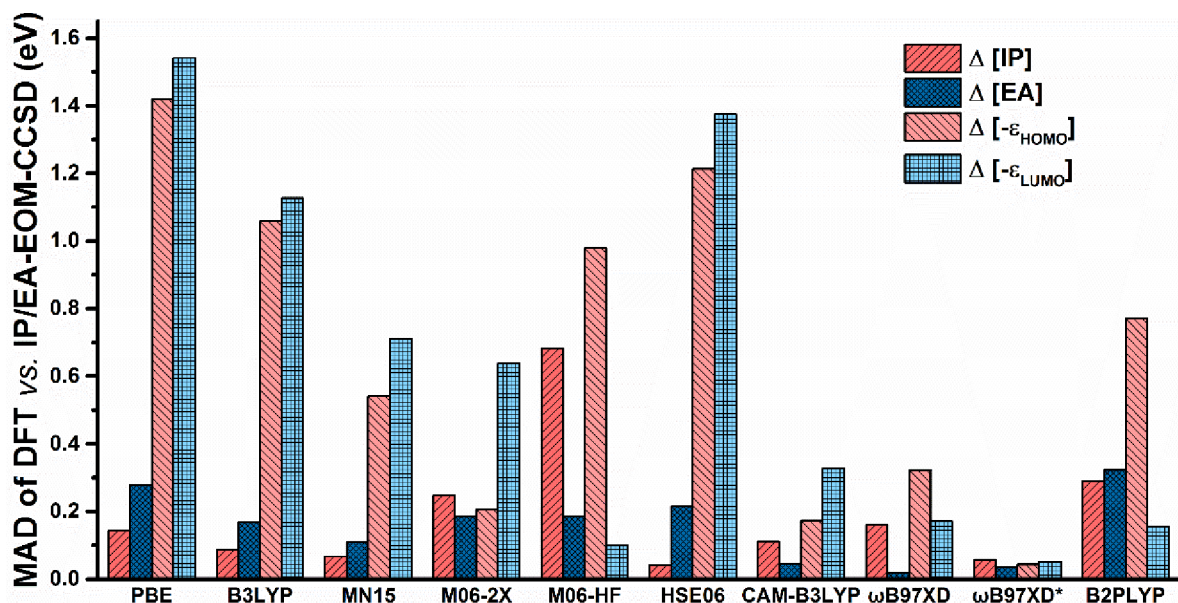


Figure 2. Mean absolute deviation (MAD) (in eV) of the calculated orbital energies ($-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$), vertical ionization energies (IP) and EA using various density functionals compared to the IP/EA-EOM-CCSD data.

set such as aug-cc-pVDZ is used. Second, the EAs values are found to be more sensitive to the diffusion function in the basis set. The basis set effects were thus examined by extending the basis sets from 6-31G to cc-pVDZ, may-cc-pVDZ [67] and aug-cc-pVDZ (see figure S2). The may-cc-pVDZ basis set, also known as one of Truhlar's 'calendar' basis sets, is also considered here because it is proved to significantly reduce the computational cost without loss of accuracy compared to its augmented counterpart aug-cc-pVDZ basis [29]. More importantly, the may-cc-pVDZ basis set is in more favor of SCF convergence compared to the aug-cc-pVDZ basis. To obtain the IP/EA-EOM-CCSD benchmark data with a safe larger basis, the following equation is used through MP2 energy correction (see figure S1 and table S2):

$$\begin{aligned} \text{IP/EA}_{(\text{EOM-CCSD/may-cc-pVDZ})} &= \text{IP/EA}_{(\text{EOM-CCSD/6-31G})} \\ &+ \Delta \text{IP/EA}_{(\text{MP2/may-cc-pVDZ versus 6-31G})}. \end{aligned}$$

The IP/EA-EOM-CCSD/may-cc-pVDZ benchmark data is collected in table S2. If not specified otherwise, the may-cc-pVDZ basis was used throughout this work. In addition, the optimal ω values appear not to be sensitive to extension of the basis set from 6-31G to may-cc-pVDZ, especially for larger $\text{C}_{20n}\text{H}_{20}$ systems when $n \geq 5$ (see table S1).

All the calculations were carried out using Gaussian 09 and Gaussian 16 packages [68, 69]. The contributions for each fragment of SWCNTs in HOMOs and LUMOs were analyzed using Multiwfn program [70] and the corresponding HOMOs and LUMOs were displayed with VMD tool [71].

3. Results and discussion

Numerical data of calculated IPs and EAs, as well as negative frontier orbital energies ($-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$), for a series of armchair $\text{C}_{20n}\text{H}_{20}$ ($n = 2-6$) SWCNT systems are listed

in table S2. The calculated mean absolute deviation (MAD) with respect to the IP/EA-EOM-CCSD data are shown in figure 2. First, for the optimally-tuned ωB97XD^* , the calculated IPs and EAs are in good agreement with IP/EA-EOM-CCSD data with MADs of 0.06 eV and 0.04 eV, respectively. Excellent agreement is also found for the prediction of $-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$ with MADs of 0.04 eV and 0.05 eV, respectively. The results confirm that after tuning the corresponding negative HOMO and LUMO energies agree quite well with the vertical IPs and EAs, respectively, and the success of optimally-tuned ωB97XD^* functionals reproducing the high-level IP/EA-EOM-CCSD results.

Among all the other density functionals, the calculated MADs for $-\epsilon_{\text{HOMO}}$ ranges from 0.21 to 1.42 eV and MADs for $-\epsilon_{\text{LUMO}}$ range from 0.10 to 1.54 eV. The results indicate that the approximation using the HOMO and LUMO energy levels to represent the IPs and EAs strongly depends on the type of density functionals. With respect to the IP/EA-EOM-CCSD data, the MADs for the PBE and B3LYP functionals are unacceptably large and calculated to be 1.42 and 1.06 eV for the $-\epsilon_{\text{HOMO}}$, respectively, and 1.54 eV and 1.13 eV for the $-\epsilon_{\text{LUMO}}$, respectively. The HSE06 functional does not improve the results, with MADs of 1.21 eV for $-\epsilon_{\text{HOMO}}$ and 1.37 eV for $-\epsilon_{\text{LUMO}}$, and performs between PBE and B3LYP as expected. This can be explained by the relatively small eX% included in the functionals: 0% for PBE, 20% for B3LYP, and 25%–0% for HSE06. By including a larger fraction of eX, the MN15 functional with 44% eX and M06-2X functional with 54% can reduce the MADs by about more than half. The MADs for $-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$ are 0.54 and 0.71 eV, respectively, for MN15 and are 0.21 and 0.64 eV, respectively, for M06-2X, indicating the importance of the 'optimal' eX% embedded in the construction of DFT formulism. For the M06-HF functional with full 100% eX, the MAD for $-\epsilon_{\text{HOMO}}$ is obviously large and calculated to be 0.98 eV and

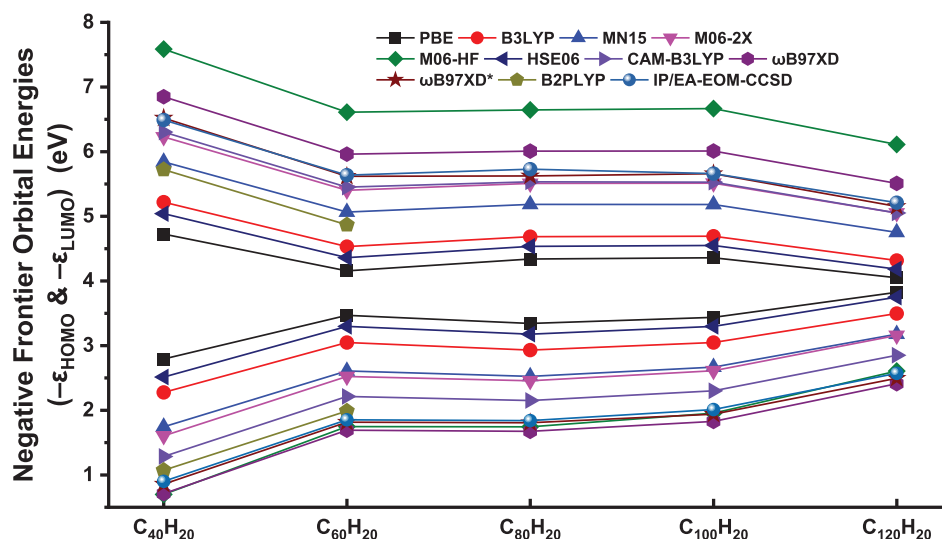


Figure 3. Comparison between negative frontier orbital energies ($-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$) and IP/EA-EOM-CCSD values of a series of SWCNTs from $\text{C}_{40}\text{H}_{20}$ to $\text{C}_{120}\text{H}_{20}$.

the MAD for $-\epsilon_{\text{LUMO}}$ is only 0.10 eV possibly due to the effect of error cancellation. Unexpectedly, the double-hybrid B2PLYP functional does not show an obvious superiority to other functionals and the MADs for $-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$ are calculated to be 0.77 and 0.15 eV, respectively. The RS functionals such as CAM-B3LYP and ωB97XD , which possess a correct asymptotic behavior in the long range limit, produce much improved predictions compared to the above non-RS functionals. The MADs for $-\epsilon_{\text{HOMO}}$ and $-\epsilon_{\text{LUMO}}$ are 0.17 and 0.33 eV, respectively, for CAM-B3LYP and are 0.32 and 0.17 eV, respectively, for ωB97XD . It should be noted that another RS LC- ωPBE functional, which possesses zero short-range $\text{eX}\%$ and 100% in the long-range limit, possesses significantly larger errors with a MAD of ~ 0.5 (~ 0.8) eV for IP ($-\epsilon_{\text{HOMO}}$) by consistently comparing the LC- $\omega\text{PBE}/\text{aug-cc-pVDZ}$ data taken from [24] with the corrected IP-EOM-CCSD data. The results strongly suggest that the inclusion of a certain amount of $\text{eX}\%$ in the short range (19% for CAM-B3LYP and 22% for ωB97XD) may be important to yield reliable orbital energy levels for SWCNTs. This is also in consistent with the finding by Salzner and Aydin for conjugated polymers [72]. In short, with respect to the conventional density functionals, the overall good performance of RS functionals such as CAM-B3LYP and ωB97XD can be attributed to the combination of their short-range $\text{eX}\%$ and long-range correction of asymptotic behavior of electrons. However, there still have space to further improvement for these RS functionals, for instance, through performing ‘tuning’.

As shown in figure 3 and table S2, it should be noted that the PBE functional produces very low (or overestimated) $-\epsilon_{\text{HOMO}}$ and very high (or underestimated) $-\epsilon_{\text{LUMO}}$, resulting a very small HOMO-LUMO gap. On the contrary, the M06-HF functional yields high $-\epsilon_{\text{HOMO}}$, low $-\epsilon_{\text{LUMO}}$, and thus a much larger HOMO-LUMO gap. This phenomenon is closely related to the amount of $\text{eX}\%$ included in the functionals that controls the degree of delocalization or localization effect of wave-functions. In other word, for π -conjugated

systems, the density functionals with low $\text{eX}\%$ tend to over-delocalize the wave functions; and the functionals with high $\text{eX}\%$ oppositely overlocalize the wave functions. To support this point, the HOMOs and LUMOs based on the optimized geometries of $\text{C}_{120}\text{H}_{20}$ using PBE, M06-HF and ωB97XD^* are plotted in figures 4 and S3 and the contributions of each fragment of $\text{C}_{120}\text{H}_{20}$ nanotube in HOMOs and LUMOs are shown in figures 4(a) and (b), respectively. Clearly, the PBE functional displays most delocalized HOMO and LUMO wave functions and the M06-HF functional possesses more localized electronic structures. In addition, along the axis of the extended nanotube as shown in figure 6(c), a symmetric configuration was observed for $\text{C}_{120}\text{H}_{20}$ with bond g as the center of symmetry. Interestingly, the bond length changes periodically and three bonds such as b , c and d behave as a cycle. Clearly, the PBE functional tends to equalize all the bonds showing a delocalized character; and the bond length alternation by the M06-HF functional shows the greatest volatility and confirms its localized nature. Notably, the optimally-tuned ωB97XD^* can achieve a good balance between the delocalization and localization effect and allows for a reasonable description of the electronic structure of SWCNTs.

Next, we investigate the performance of various DFTs in the calculations of IPs and EAs compared to the IP/EA-EOM-CCSD data. Since the IPs and EAs were calculated from total energy differences, they seem to exhibit less functional-dependence with comparison with the HOMO and LUMO energies. The calculated errors for IP range from 0.04 to 0.68 eV and errors for EA range from 0.02 to 0.28 eV. Among various density functionals, the largest error for IP is from M06-HF with a MAD of 0.68 eV and the smallest one is from HSE06 with a MAD of 0.04 eV. The largest error for EA is from PBE with a MAD of 0.28 eV and the smallest one is from ωB97XD with a MAD of 0.02 eV. Compared to the IP/EA-EOM-CCSD benchmark data, the following density functionals can provide a balanced prediction for both IPs and EAs: MN15 with MADs of 0.07 eV for IP and 0.11 for

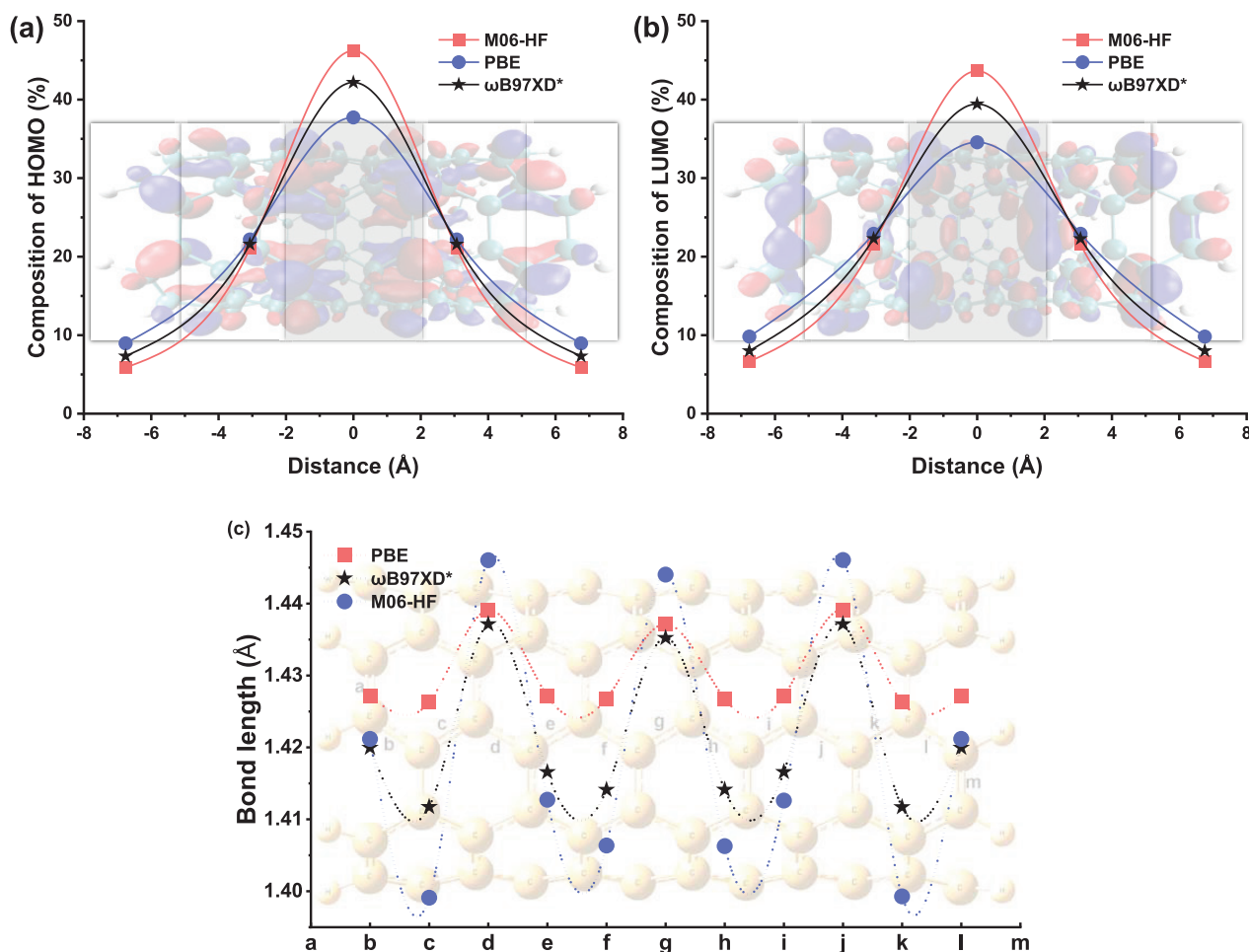


Figure 4. The contribution of fragments of $C_{120}H_{20}$ nanotube in HOMOs (a) and LUMOs (b) based on the optimized geometries of $C_{120}H_{20}$ using PBE, M06-HF and ω B97XD*. The HOMO and LUMO of $C_{120}H_{20}$ using ω B97XD* are also displayed with the isovalue of 0.022 in the figure. (c) bond length (Å) based on the corresponding optimized structures.

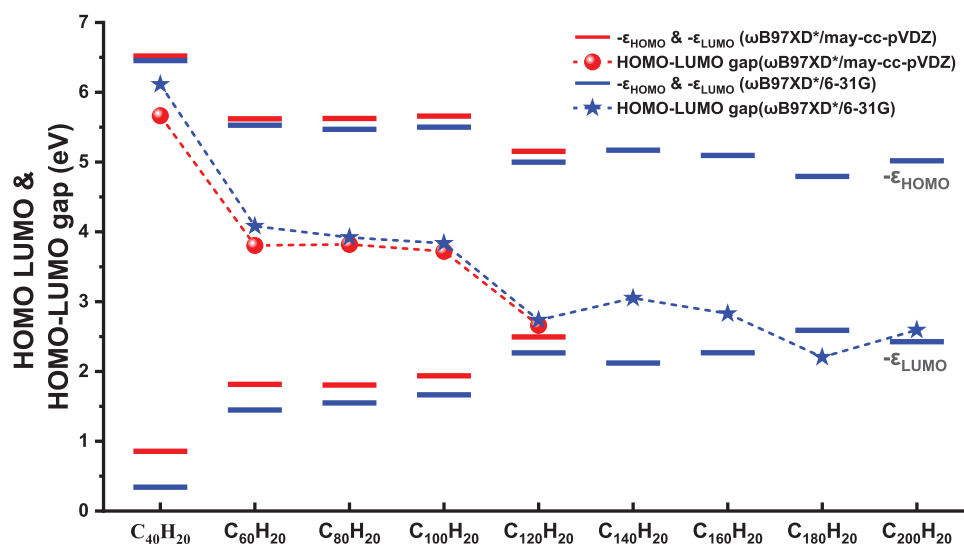


Figure 5. Calculated HOMO, LUMO and HOMO-LUMO gap of $C_{20n}H_{20}$ ($n = 2-10$) at the ω B97XD*/6-31G level and those of $C_{20n}H_{20}$ ($n = 2-6$) at the ω B97XD*/may-cc-pVDZ level.

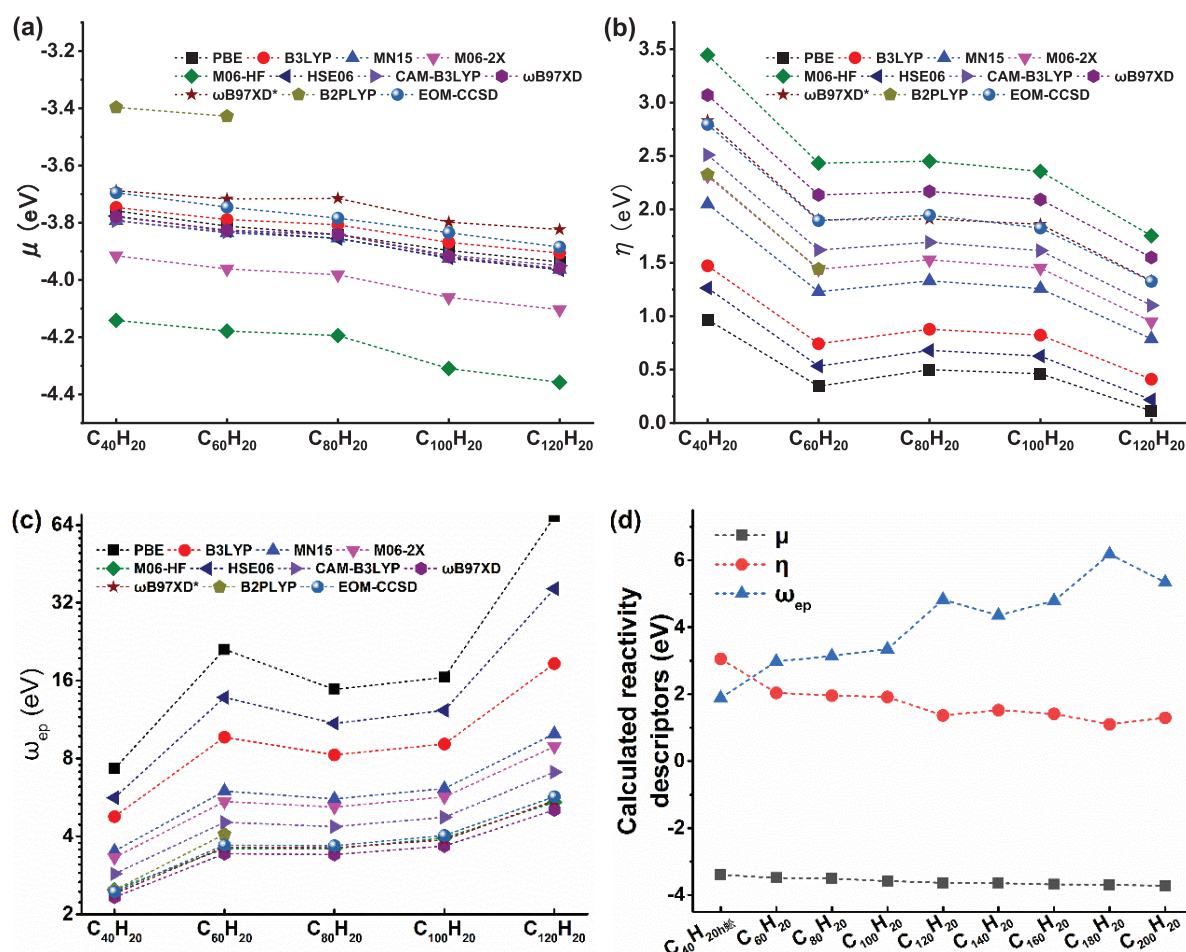


Figure 6. Calculated reactivity descriptors of (a) chemical potential μ , (b) global hardness η , and (c) electrophilicity ω_{ep} as a function of SWCNT length using frontier orbital energies from equations (5) and (4) at different DFT levels. (d) calculated μ , η and ω_{ep} values as a function of tube length from C₄₀H₂₀ to C₂₀₀H₂₀ at the ω B97XD*/6-31G level.

EA, CAM-B3LYP with MADs of 0.11 eV for IP and 0.04 for EA, and ω B97XD with MADs of 0.16 eV for IP and 0.02 for EA. In addition, it should be noted that the good performance of non-tuned ω B97XD functional can be partly attributed to the fact that the optimally tuned ω values from 0.17 bohr⁻¹ to 0.12 bohr⁻¹ (table S1) for the benchmark systems from C₄₀H₂₀ to C₁₂₀H₂₀ are close to the default RS parameter ω (0.20 bohr⁻¹). However, this extension is not guaranteed for longer SWCNTs, i.e. C₂₀₀H₂₀, which possesses a significantly smaller optimal ω value of 0.09 bohr⁻¹ (see table S1).

Overall, the results show the optimally-tuned ω B97XD* can quantitatively predict the IPs and EAs with an accuracy comparable to the high-level IP/EA-EOM-CCSD method. It is important to mention that the computational scaling of EOM-CCSD formalism as N⁶, currently preventing routine calculations on longer SWCNT systems in this work. As shown in figure 5, the behavior of HOMO, LUMO and HOMO-LUMO gap as a function of the length of SWCNT system is studied. Thanks to the efficiency and accuracy of the tuned ω B97XD* functional, the studied SWCNT systems are extended to a much longer C_{20n}H₂₀. The negative HOMO energies decrease and the negative LUMO energies increase as the nanotube length increases. On the whole, the resulting HOMO-LUMO

gaps decrease and show an obviously converged behavior in the extended range. Moreover, the periodicity for the changes of frontier orbital energies and HOMO-LUMO gap is observed from C₄₀H₂₀ to C₂₀₀H₂₀. This can be reasonably explained by the formation of Kekule, partial Clar and complete Clar networks during the growing of SWCNTs [27], that is, for C₆₀H₂₀, C₁₂₀H₂₀ and C₁₈₀H₂₀ SWCNTs where n equals a multiple of 3, they tend to yield a more delocalized complete Clar structure and possess a relatively narrower HOMO-LUMO gap. Notably, the combination of low cost with high accuracy using the optimal ‘tuning’ approach confirms the clear benefit from the perspective of computational cost and it is of great importance for the future investigation of properties of long CNTs.

The chemical modification of SWCNTs remains an important topic of nanoscience so far [27]. The prediction of chemical reactivity and the electron density redistribution during bonds form and break on SWCNTs is of great importance to understand the mechanism such as covalent functionalization of SWCNTs. Three reactivity parameters including chemical potential (μ), global hardness (η), and electrophilicity (ω_{ep}) as a function of nanotube length were thus calculated according to definitions of the valence state parabola model [73, 74]

$$\mu = -\frac{\text{IP} + \text{EA}}{2}, \quad \eta = \frac{\text{IP} - \text{EA}}{2} \quad (3)$$

$$\omega_{\text{ep}} = \frac{\mu^2}{2\eta}. \quad (4)$$

By using the negative frontier orbital energies ($-\varepsilon_{\text{LUMO}}$ and $-\varepsilon_{\text{HOMO}}$) representing the IPs and EAs, we then have

$$\mu = \frac{\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}}{2}, \quad \eta = \frac{\varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}}}{2}. \quad (5)$$

The calculated μ , η and ω_{ep} parameters as a function of SWCNT length using equations (5) and (3) are displayed in figures 6 and S4, respectively. As expected, the optimally-tuned ωB97XD^* can give overall excellent description of all these parameters with respect to IP/EA-EOM-CCSD method. In line with the performance of various density functionals calculating frontier molecular orbital energies, the calculated ω_{ep} and η parameters defined with $-\varepsilon_{\text{LUMO}}$ and $-\varepsilon_{\text{HOMO}}$ are indeed more sensitive to the employed functionals than those defined with IPs and EAs. The chemical potentials μ , also known as negative electronegativity, is found to be insensitive to the definitions using $-\varepsilon_{\text{LUMO}}/-\varepsilon_{\text{HOMO}}$ or IP/EA. The difference of calculated μ values between DFTs and IP/EA-EOM-CCSD is smaller than ~ 0.5 eV, indicating its less density functional-dependence. The calculated μ values is further found to be independent of the nanotube length until $\text{C}_{200}\text{H}_{20}$ as shown in figure 6(d). This is also in agreement with previous studies [75]. The global hardness η that equals half of HOMO-LUMO energy gap can be considered as an important stability criterion. A large η value typically implies high stability and low chemical reactivity. It is clear that the overdelocalized PBE functional tends to produce a much smaller η close to zero and thus an unstable electronic structure especially for the long $\text{C}_{120}\text{H}_{20}$. Last, the electrophilicity ω_{ep} reflects the energy lowering while accepting bonding electrons from the environment for SWCNTs [73]. As the nanotube length increases, the studied SWCNT system shows an increasing ability to accept electrons. The increasing tendency of ω_{ep} is still kept until the longest $\text{C}_{200}\text{H}_{20}$. The result strongly suggests that accepting an electron pair in order to bond is more possible for a longer SWCNT in a functionalization chemical reaction. Unfortunately, such a trend is greatly overestimated by ~ 12 fold for PBE, ~ 6.4 fold for HSE06, and ~ 3.3 fold for B3LYP compared to the IP/EA-EOM-CCSD reference.

4. Conclusions

In conclusion, the vertical IPs and EAs of a series of armchair SWCNTs were investigated using various DFT functionals. Firstly, by enforcing the energy condition in exact DFT, the optimally tuned ωB97XD^* functionals produce the negative frontier orbital energies ($-\varepsilon_{\text{HOMO}}$ and $-\varepsilon_{\text{LUMO}}$) that roughly equal the vertical IPs and EAs, and are further in good agreement with the high-level IP/EA-EOM-CCSD method. The resulting MADs are only 0.06 and 0.04 eV for IP and EA, respectively, and 0.04 and 0.05 eV, respectively, when using $-\varepsilon_{\text{HOMO}}$ and $-\varepsilon_{\text{LUMO}}$. As expected, the conventional

functionals fail to give consistent descriptions of IPs and EAs and the resulting frontier orbital energies are found to be strongly functional-dependent. For example, the PBE, HSE06, B3LYP and M06-HF functionals yield significantly large MADs for the $-\varepsilon_{\text{HOMO}}$ and $-\varepsilon_{\text{LUMO}}$ compared to the IP/EA-EOM-CCSD data. The MN15 and M06-2X functionals possess reduced errors. The RS CAM-B3LYP and ωB97XD functionals produce significantly improved results compared to the conventional functionals. The different performances of density functionals are closely related to their eX% included, e.g. density functionals with low (or high) eX% tend to overdelocalize (or overlocalize) the HOMOs and LUMOs and result in incorrect frontier orbital energy levels. Furthermore, we also demonstrate that for SWCNTs systems, great attentions should be paid to provide a balanced description of delocalization and localization of wave functions of molecular orbitals.

Next the chemical potential (μ), global hardness (η), and electrophilicity (ω_{ep}) were investigated as a function of nanotube length. The results are generally in line with the above trend for the performance of density functionals while predicting frontier orbital energies. Importantly, thanks to the efficiency of this tuning method, it allows for the studied system that can be explored to a much longer length. The calculated μ values is found to be independent of the nanotube length. The calculated ω_{ep} parameter for the SWCNT systems increases as the nanotubes extend until $\text{C}_{200}\text{H}_{20}$, showing an increasing ability to accept bonding electrons and the possibility of functionalization on an enough long SWCNT. Unfortunately, the overdelocalized functionals such as PBE, greatly overestimate the ω_{ep} value and also yield a small η for long SWCNTs.

Finally, we believe the present work can provide an efficient and reliable theoretical tool to describe the electronic structures for a wider range of CNT-based systems. Due to the efficiency and accuracy of this tuning method, our ongoing studies focus on the effects of armchair or zigzag SWCNTs and their spin polarization effects, and exploration of excited-state properties of SWCNTs related to specific optoelectronic applications, for example, the behavior of singlet-triplet energy splitting as a function of CNT length.

Acknowledgments

This work has been supported by National Natural Science Foundation of China (Nos. 21603074 and 11774094), ‘Chenguang Program’ by Shanghai Education Development Foundation and Shanghai Municipal Education Commission (16CG25), Shanghai-International Scientific Cooperation Fund (17ZR146900 and 16520721200) and Program of Introducing Talents of Discipline to Universities 111 project (B12024). We acknowledge the ECNU IT Research Computing Team for providing computational and storage resources.

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