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Impact of Non-Empirically Tuning the Range-Separation Parameter of Long-Range Corrected Hybrid Functionals on Ionization Potentials, Electron Affinities, and Fundamental Gaps

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Non-empirically tuning the range-separation parameter (ω) of long-range corrected (LC) hybrid functionals in improving the accuracy of vertical ionization potentials (IPs), vertical electron affinities (EAs), and fundamental gaps (FGs) is investigated. Use of default ω values gives the best overall property predictions employing the Δ self-consistent field (ΔSCF) approach, if sufficiently large basis set is used. Upon tuning, IP (HOMO) (i.e., the IP estimated from the negative of HOMO energy via DFT Koopmans' theorem) with the IP (ΔSCF) (i.e., the IP obtained from the ΔSCF approach) the accuracy of IP (HOMO) significantly improves however a reciprocal phenomenon is not observed. An interesting observation is that EA (LUMO) (i.e., the EA estimated from the negative of LUMO energy) is more accurate than EA (ΔSCF), if the ω value is in the range of 0.30 to 0.50 bohr^{-1}. © 2018 Wiley Periodicals, Inc.

Introduction

Organic materials are making inroads in our day-to-day life in the form of smart phones, computer displays, lightening devices, and so forth. These materials are gradually replacing the traditional materials (e.g., their inorganic counterparts) in different fields that have been dominating the markets over the past few decades. The function and performance of these materials depends heavily on their optoelectronic properties, including the vertical ionization potentials (IPs), vertical electron affinities (EAs), fundamental gaps (FGs), optical gaps, and so forth.[1–3] For example, organic light emitting diodes contain several layers of different stacked organic films, and there exists an energy barrier to the flow of charge between these layers[1], therefore, the knowledge of transport energy levels is required along with IPs, EAs, and FGs that can help in optimizing and designing the devices with higher efficiencies. However, the prediction of IPs, EAs, and FGs with reasonable and consistent accuracy has been a long standing challenge for computational material science.[4]

Accurate IPs, EAs, and FGs can be obtained from the CCSD(T)[5,6] (coupled-cluster theory with iterative singles and doubles and perturbative treatment of triple substitutions) calculations. However, owing to the very high computational cost involved, CCSD(T) is applicable only to small molecules, prohibiting its usage in studying medium- to large-sized molecules that may possess interesting practical applications. On the other hand, density functional theory[7] (DFT) based on the Kohn–Sham approach can serve as an alternative in this regard, as it provides reasonable accuracy with feasible computational cost. The routinely followed procedure to evaluate the IP (EA) of a neutral molecule is the Δ self-consistent field (ΔSCF) approach, where the IP (EA) is determined by the total energy difference of cation and neutral (neutral and anion) molecules at the optimized neutral geometry, and the FG is calculated as the difference between the IP and EA. According to the

Koopmans IP-theorem[8–10], for the exact Kohn–Sham theory, the negative of the highest occupied molecular orbital (HOMO) energy of a neutral molecule is the same as the IP of the neutral molecule. Unfortunately, there is no known exact exchange-correlation (XC) functional, and the commonly used semilocal and hybrid XC functionals do not obey the IP-theorem. Therefore, the negative of HOMO energy obtained from a conventional XC functional can be a poor approximation to IP.[11] Hence, in DFT, the conventional ΔSCF approach is widely used to evaluate the IPs, EAs, and FGs of neutral molecules.

Hybrid functionals generally outperform pure density functionals (e.g., those based on the local density approximation and generalized gradient approximations [GGAs]) in evaluating IPs, EAs, and FGs.[11–13] Our recent investigations concluded that among the various types of XC functionals available (e.g., global hybrid, long-range corrected (LC) hybrid, and double-hybrid functionals), the performance of LC hybrid functionals[14] is superior and consistent for the IPs, EAs, and FGs of neutral molecules.[2] Similar conclusions were also made in earlier studies.[11–13] Baer et al.[15–17] proposed a scheme that restores the IP-theorem by non-empirically tuning the range-separation parameter (ω) of LC

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hybrid functionals, yielding accurate results for various properties, including IPs, FGs, charge-transfer excitations, and so forth. Wong et al.[18] employed the tuning scheme to evaluate quasiparticle properties (HOMO-LUMO gaps) and excitation energies of five DNA and RNA nucleobases. They[18] observed that the non-empirically tuned LC-BLYP functional[19] accurately reproduces experimental IPs, FGs, and excitation energies. In addition, they compared the tuned HOMO energies, tuned LUMO energies, and their energy gaps with the benchmark CASPT2[20] (complete-active-space second-order perturbation theory) results, where the mean absolute errors (MAEs) are 0.12, 0.18, and 0.06 eV, respectively, which are on par with the computationally expensive many-body GW results. Recently, Gallandi et al.[4] have performed benchmarking studies on a set of 24 organic acceptor molecules with respect to the CCSD(T) results, and observed that the non-empirically tuned LC-ωPBE functional outperforms the default LC-ωPBE functional[21,22] (which employs a constant range-separation parameter). The MAEs of HOMO energies were found to decrease from 0.41 to 0.24 eV after tuning. For the LUMO energies, the MAEs remained constant at 0.16 eV, and the MAEs of FGs decreased from 0.54 to 0.38 eV after tuning.[4]

For semilocal and global hybrid functionals, the negative of HOMO energy is a poor approximation to IP due to the self-interaction errors associated with the functionals.[23] In general, to avoid this problem, the IPs and EAs of neutral molecules are routinely calculated employing the ΔSCF procedure, rather than considering the frontier orbital energies. Although tuning the range-separation parameter of LC hybrid functionals and enforcing the IP-theorem has led to improvement in the accuracy of HOMO energies for some cases,[15,16] it is not clear how well this methodology is superior to the conventional ΔSCF approach for obtaining IPs and EAs. In addition, there is also no clarity on the improvement of LUMO energies with the tuning scheme. More importantly, it is not clear whether the conclusion is of general validity for different LC hybrid functionals. Most of the previous studies focused on comparing the HOMO and LUMO energies obtained from the default and tuned LC hybrid functionals.[4,17,18,24] Hence, we perform a benchmarking study to evaluate the significance of tuning scheme in improving the accuracy of IPs, EAs, and FGs. We mainly adopt LC-ωPBE (i.e., a popular LC hybrid functional) to evaluate the IPs, EAs, and FGs of 30 organic molecules of different types, employing both the default and tuned range-separation parameters, where the reference data were obtained from the highly accurate CCSD(T) calculations in our previous study.[2] In this manuscript, we also examine the reliability of tuning scheme with two other popular LC hybrid functionals, LC-BLYP and ωB97X-D[25], for comparisons.

Computational Methodology

A major drawback associated with a global hybrid functional (i.e., a functional with a fixed percentage of Hartree–Fock [HF] exchange) is that the functional needs to find a good balance between the fraction of semilocal exchange and the fraction of HF exchange[26]. For example, the B3LYP[27,28] functional employs 20% HF exchange and 80% semilocal exchange. However, the use of 100% HF exchange is required

for a complete correction of self-interaction and the correct XC potential in the asymptotic region of any atom or molecule.[29] However, a semilocal exchange functional is found to mimic short-range correlation effects, well describing the chemical bond.[26]

Accordingly, a LC hybrid functional can combine both these advantages with the range-separation scheme, allowing for a self-interaction-free description at the long range (based on the full HF exchange), whereas maintaining a balanced description of XC effects at the short range (based on a semilocal XC functional).[30] The basic principle on which a LC hybrid functional relies upon is the splitting of Coulomb operator into the short-range (SR) and long-range (LR) components, which is attained with the help of the standard error function (erf).

$$\left(\frac{1}{r_{12}}\right) = \frac{\text{erfc}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}} \tag{1}$$

Here, erfc is the complementary error function, r_{12} is the interelectronic distance, and ω is the range-separation parameter. Note that 1/ω is the characteristic distance for the transition between the SR ($r_{12} \lesssim 1/\omega$) and LR ($r_{12} \gtrsim 1/\omega$) regimes. The first term on the right-hand side of eq. (1) corresponds to the SR operator, and the second term to the LR operator. Treating the SR and LR electron–electron interactions on a different note, a LC hybrid functional employs the full HF exchange associated with the LR operator, a semilocal exchange functional associated with the SR operator, and a semilocal correlation functional associated with the entire Coulomb operator. Alternatively, the above equation can also be generalized using one extra parameter α as[31]

$$\left(\frac{1}{r_{12}}\right) = \frac{(1-\alpha)\,\text{erfc}(\omega r_{12})}{r_{12}} + \frac{\alpha\,\text{erfc}(\omega r_{12}) + \text{erf}(\omega r_{12})}{r_{12}} \tag{2}$$

The modification of eq. (1) into eq. (2) with the inclusion of α makes the SR electron–electron interactions a hybrid of HF and semilocal exchange, with α quantifying the fraction of HF exchange and (1−α) the fraction of semilocal exchange at the SR limit ($r_{12} = 0$), whereas retraining the full HF exchange at the LR limit ($r_{12} \rightarrow \infty$). When α = 0, eq. (2) reduces to eq. (1). In the current article, we consider three popular LC hybrid functionals: LC-ωPBE, LC-BLYP, and ωB97X-D. Note that LC-ωPBE and LC-BLYP are built upon eq. (1) with the default range-separation parameters ω = 0.40 and 0.47 bohr^{-1}, respectively. On the other hand, ωB97X-D is based on eq. (2) with the default ω = 0.20 bohr^{-1} and α = 0.222036. Note also that LC-ωPBE has one empirical parameter ω, LC-BLYP has a few (i.e., less than 10) empirical parameters, and ωB97X-D has 15 empirical parameters. However, in contrast to LC-ωPBE and LC-BLYP, the GGA expansion coefficients adopted in ωB97X-D are fixed (i.e., ω-independent), and hence, they are optimized *only* for the default range-separation parameter (ω = 0.20 bohr^{-1}). In addition, as discussed by Chai and Head-Gordon[32], the ω values of ωB97X-D and related LC hybrid functionals (ωB97X[31] and ωB97X-D3[33]) are also correlated with the α values. However, in this work, we fix the α value in the tuning scheme just for simplicity. Therefore, if the tuned ω values of ωB97X-D are very different from the default ω value, our results and conclusion

for ωB97X-D can be biased and should be taken with caution, partly due to the fact that the GGA parts and the α values of ωB97X-D are not consistently optimized with the tuned ω values. Nonetheless, as our emphasis is mainly on the non-empirical tuning scheme, LC-ωPBE is favorable (as its sole parameter ω can be non-empirically determined by the tuning scheme!). Therefore, our discussions and conclusion are mainly based on the results of LC-ωPBE, and hence the results presented are mainly obtained from LC-ωPBE, unless noted otherwise.

Tuning Procedure

To obtain an accurate range-separation parameter for a LC hybrid functional, a prerequisite condition, which needs to be obeyed, is the satisfaction of Koopmans theorem. Livshits and Baer suggested[15] an approach to obtain an accurate range-separation parameter for each system non-empirically. In this approach, the IP of a neutral molecule is evaluated at the range-separation parameter ω, where Δ_{IP} (see eq. (3)), the difference between IP (HOMO) (i.e., the IP determined by the negative of the HOMO energy of the neutral molecule) and IP (ΔSCF) (i.e., the IP determined by the total energy difference of cation and neutral molecules at the optimized neutral geometry), is minimal.

$$\Delta_{IP} = \left| \left[-E_{HOMO\,Neutral}^{\omega} \right] - \left[E_{Cation}^{\omega} - E_{Neutral}^{\omega} \right] \right| \quad (3)$$

Similarly, the EA of a neutral molecule is evaluated at the range-separation parameter ω, where Δ_{EA} (see eq. (4)), the difference between EA (LUMO) (i.e., the EA determined by the negative of the LUMO energy of the neutral molecule) and EA (ΔSCF) (i.e., the EA determined by the total energy difference of neutral and anion molecules at the optimized neutral geometry), is minimal.

$$\Delta_{EA} = \left| \left[-E_{LUMO\,Neutral}^{\omega} \right] - \left[E_{Neutral}^{\omega} - E_{Anion}^{\omega} \right] \right| \quad (4)$$

The FG of a neutral molecule is evaluated at the range-separation parameter ω, where Δ_{FG} (see eq. (5)) is minimal. In eq. (5), Δ_{IP} and Δ_{EA} are defined in eqs. (3) and (4), respectively. Note that the FG of the neutral molecule can be calculated as either FG (ΔSCF) = IP (ΔSCF)−EA (ΔSCF) or FG (LUMO–HOMO) = IP (HOMO)−EA (LUMO).

$$\Delta_{FG} = \sqrt{\Delta_{IP}^2 + \Delta_{EA}^2} \quad (5)$$

Results and Discussion

For 30 organic molecules of different types (e.g., electron donors, acceptors, and linkers), the IPs, EAs, and FGs were obtained from the highly accurate CCSD(T) calculations in our earlier studies,[2] which are used in the current study as reference to benchmark the tuning approach. Our benchmarking CCSD(T) results employing the aug-cc-pVTZ basis set (aTZ) are in good accordance with the NIST (National Institute of Standards and Technology) data.[2] All the molecular structures are optimized with LC-ωPBE using the aTZ basis set (i.e., LC-ωPBE//aTZ). All calculations are performed with the Gaussian 09 package[34] using the default SCF
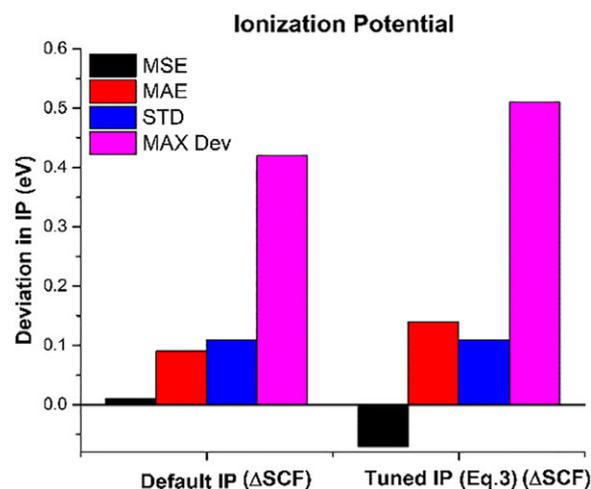
Figure 1. Deviation with respect to CCSD(T)//aTZ in IP (ΔSCF), calculated employing the default and tuning (eq. (3)) schemes based on 30 compounds using LC-ωPBE//aTZ. [Color figure can be viewed at wileyonlinelibrary.com]

convergence criteria (density matrix converged to at least 10^{-8}) and the default numerical integration grid (i.e., grid = fine, for 75 radial and 302 angular points). During the process of tuning, the neutral molecular geometries are optimized at the corresponding range-separation parameter ω. Single-point energies are performed for the respective cation and anion molecules at the optimized neutral molecular geometries to evaluate IP (ΔSCF) and EA (ΔSCF), respectively, and FG (ΔSCF) = IP (ΔSCF)−EA (ΔSCF). In addition, at the optimized neutral molecular geometries, the negative of the HOMO and LUMO energies of the neutral molecules are IP (HOMO) and EA (LUMO), respectively, and FG (LUMO-HOMO) = IP (HOMO)−EA (LUMO). We present the results of tuning approach employing LC-ωPBE, using eqs. (3), (4), and (5), respectively, and the value of ω is varied at an increment of 0.01 bohr^{-1} to meet the proposed criteria (as shown in eqs. (3), (4), and (5)).

Statistical errors for the default IP (ΔSCF) and tuned IP (ΔSCF) (eq. (3)) are shown in Figure 1. The mean sign errors (MSEs) are found to change slightly from 0.01 to −0.07 eV upon tuning, yielding an increasing underestimation of IP (ΔSCF) with tuning. In addition, the MAEs increase from 0.09 to 0.14 eV, the standard deviations (STDs) remain unchanged (0.11 eV), and the maximum deviations (Max DEVs) increase from 0.42 to 0.51 eV upon tuning.

To tune EA, eq. (4) is employed. However, even for the exact DFT, a difference exists between the negative of LUMO energy and EA due to the derivative discontinuity (DD) of the XC functional. Note that a hybrid functional, which contains a fraction of the nonlocal HF exchange, belongs to the generalized Kohn–Sham (GKS) method, the corresponding GKS orbital energies incorporate part of the DD. A recent study[18] shows that DD is close to zero for LC hybrid functionals, and hence the negative of LUMO energy calculated by LC hybrid functionals should be close to EA. Alternatively, on the basis of the definitions of IP and EA, the EA of a neutral molecule is identical to the IP of the anion molecule, and hence identical to the negative of the HOMO energy of the anion molecule (based on the IP-theorem). Consequently, eq. (4) can also be slightly modified as eq. (6).

$$\Delta_{EA2} = \left| \left[-E^{\omega}_{HOMO\ Anion} \right] - \left[E^{\omega}_{Neutral} - E^{\omega}_{Anion} \right] \right| \qquad (6)$$

Here, the EA of a neutral molecule is evaluated at the range-separation parameter ω, where Δ_{EA2} (see eq. (6)), the difference between the negative of the HOMO energy of the anion molecule (which is the same as the IP of the anion molecule for the exact Kohn–Sham theory based on the IP-theorem) and EA (ΔSCF) (which is the same as the IP of the anion molecule based on the definitions of IP and EA), is minimal. Note that the anion molecule is at the optimized neutral molecular geometry.

We observe that the tuned EA (ΔSCF) values obtained with eq. (4) and eq. (6) are very similar or the same in most of the cases. This finding is consistent with the recent finding[35] that the LUMO energy of a neutral molecule is close to the HOMO energy of the anion molecule for LC hybrid functionals. However, in very few cases, different results are found. For example, in the case of Furan, the tuned EA (ΔSCF) is −0.79 eV at a very large ω = 0.90 bohr^{-1} using eq. (4), and is −0.71 eV at a very small ω = 0.14 bohr^{-1} using eq. (6). We present the data of 26 molecules out of 30, where the tuned EA (ΔSCF) values obtained with eq. (4) and eq. (6) are the same.

Statistical errors for the default EA (ΔSCF) values are also shown in Figure 2. No significant change in accuracy is observed upon tuning, and we observe that the deviations slightly increase upon tuning; the MSEs, MAEs, and Max DEVs are found to increase from 0.17 to 0.21 eV, 0.17 to 0.22 eV, and 0.57 to 0.64 eV, respectively, upon tuning. The STDs slightly decrease from 0.16 to 0.14 eV upon tuning.

We also evaluate IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) employing the tuning approach with eq. (5), that is, the FG-tuned equation. Statistical errors for the default and tuned IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) are shown in Figure 3.

No significant improvement is observed after tuning in evaluating IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) from the histogram shown in Figure 3. For IP (ΔSCF), the MAEs increase from 0.09 to 0.14 eV, the Max DEVs increase from 0.42 to 0.51 eV, and the STDs remain unchanged (0.11 eV) upon tuning. Compared to IP
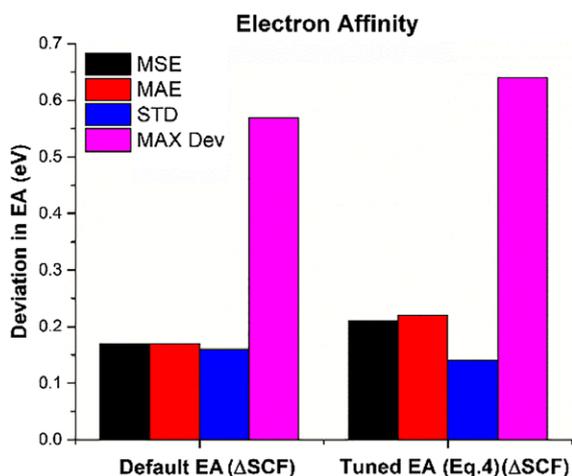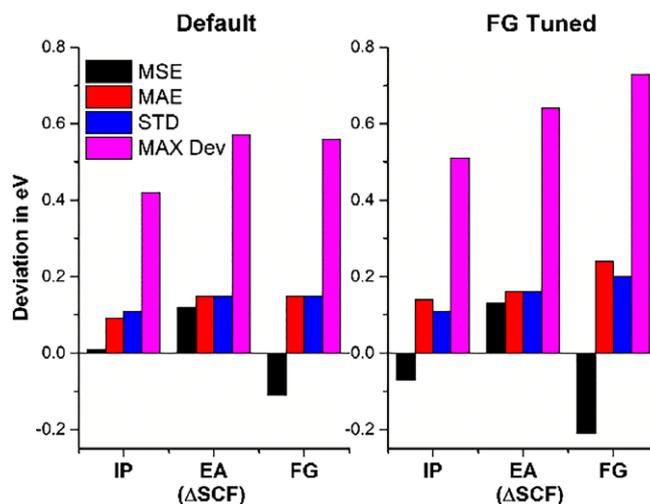
Figure 3. Deviation with respect to CCSD(T)//aTZ in IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF), calculated employing the default and tuning (eq. (5)) schemes based on 30 compounds using LC-ωPBE//aTZ. [Color figure can be viewed at wileyonlinelibrary.com]

(ΔSCF), the changes of EA (ΔSCF) are minimal upon tuning, with the MAEs slightly increasing from 0.15 to 0.16 eV, the STDs from 0.15 to 0.16 eV, and the Max DEVs from 0.57 to 0.64 eV upon tuning. The trend of FG (ΔSCF) is similar to that of IP (ΔSCF) upon tuning, with the MAEs increasing from 0.15 to 0.24 eV, the STDs from 0.15 to 0.20 eV, and the Max DEVs from 0.56 to 0.73 eV upon tuning. We also observe that the MSEs of FG (ΔSCF) decrease from −0.11 to −0.21 eV, yielding an increasing underestimation of FG (ΔSCF).

Tuning either with the IP (using eq. (3)) or FG (using eq. (5)) equation yields similar or the same results (see the supporting information). From Figure 3, it is obvious that the conventional approach of calculating IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) using LC-ωPBE with the default range-separation parameter (ω = 0.40 bohr^{-1}) is still superior to the tuning scheme, and can provide reasonably accurate results with the MAEs ranging from 0.10 to 0.15 eV, which are on par with the computationally more demanding GW calculations.[4] However, it has to be noted that a sufficiently large basis set (aTZ or the larger basis set) is required for the accurate results, especially for EA (ΔSCF).

To investigate the impact of basis set on the tuning approach, we also adopt the aug-cc-pVDZ basis set (aDZ) (i.e., a smaller basis set) to evaluate IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) employing the tuning approach with eq. (5). Statistical errors for the default and tuned IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) are shown in Figure 4.

From Figures 3 and 4, it is evident that the accuracy of IP (ΔSCF) remains passive with respect to the basis sets adopted and the tuning scheme. The MAEs of default IP (ΔSCF) with aDZ and aTZ remain unchanged (0.09 eV), indicating that the impact of basis set on IP (ΔSCF) is minimal, and accurate IP (ΔSCF) can be obtained with the smaller basis set (i.e., aDZ). The MAEs of IP (ΔSCF) increase from 0.09 to about 0.15 eV upon tuning (with either aDZ or aTZ), showing that the tuning scheme deteriorates the accuracy of IP (ΔSCF). In contrast to default IP (ΔSCF), the accuracy of default EA (ΔSCF) decrease with the smaller basis set,

Figure 2. Deviation with respect to CCSD(T)//aTZ in EA (ΔSCF), calculated employing the default and tuning (eq. (4)) schemes based on 26 compounds using LC-ωPBE//aTZ. [Color figure can be viewed at wileyonlinelibrary.com]
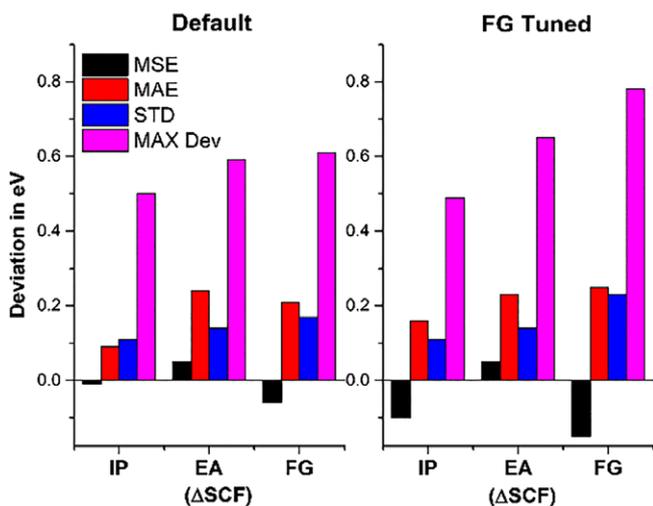
Figure 4. Deviation with respect to CCSD(T)//aTZ in IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF), calculated employing the default and tuning (eq. (5)) schemes based on 30 compounds using LC-ωPBE//aDZ. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 5. Deviation with respect to CCSD(T)//aTZ in IP(HOMO), EA (LUMO), and FG (LUMO-HOMO) (L-H Gap), calculated employing the default and tuning (eq. (5)) schemes based on 30 compounds using LC-ωPBE//aTZ. [Color figure can be viewed at wileyonlinelibrary.com]

with the MAE of 0.24 eV (with aDZ). Relative to the default EA (ΔSCF), the impact of tuning scheme is minimal on EA (ΔSCF) with a marginal change of MAE to 0.23 eV (with aDZ). The trend of FG (ΔSCF) is similar to that of IP (ΔSCF) with respect to the basis sets adopted and the tuning scheme.

From the above findings, it is clear that the default scheme of calculating IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) is still an efficient and accurate scheme, compared to the tuning scheme. If the negative of HOMO and LUMO energies are approximated as IP and EA, respectively, the tuning scheme can indeed improve the accuracy of IP (HOMO); however, the accuracy of tuned IP (HOMO) is found to be lower than that of default IP (ΔSCF). To see this, statistical errors for IP (HOMO), EA (LUMO), and FG (LUMO-HOMO), calculated employing the default and tuning (eq. (5)) schemes, are presented in Figure 5. As shown, the tuning scheme indeed improves the accuracy of IP (HOMO) in all the four parameters (MSE, MAE, STD, and MAX DEV); the MAEs decrease from 0.35 to 0.15 eV, and the STDs decrease from 0.14 to 0.12 eV upon tuning. This is in accordance with the earlier findings, where the tuned IP (HOMO) is a very good approximation to IP, compared to the default IP (HOMO).[4,16–18] In addition, it has been reported that the accuracy of orbital energies becomes worse as the system size increases and this also causes the increasing deviations of the excitation energies when using conventional LC hybrid functionals with a fixed range-separation parameter.[36] Accordingly, the tuning scheme is expected to reduce the errors of orbital energies, for example, IP (HOMO) as evident from Figure 5.

Unlike IP (HOMO), we do not observe an improvement in the trend of EA (LUMO). The tuning scheme yields the slight deterioration of accuracy of EA (LUMO) with the MAEs increasing from 0.12 to 0.16 eV, the STDs from 0.09 to 0.13 eV, and the MAX DEVs from 0.29 to 0.59 eV upon tuning. We notice that the default IP (HOMO) is a poor approximation to IP, and the tuning approach significantly improves the accuracy of IP (HOMO). However, the accuracy of tuned IP (HOMO) is still
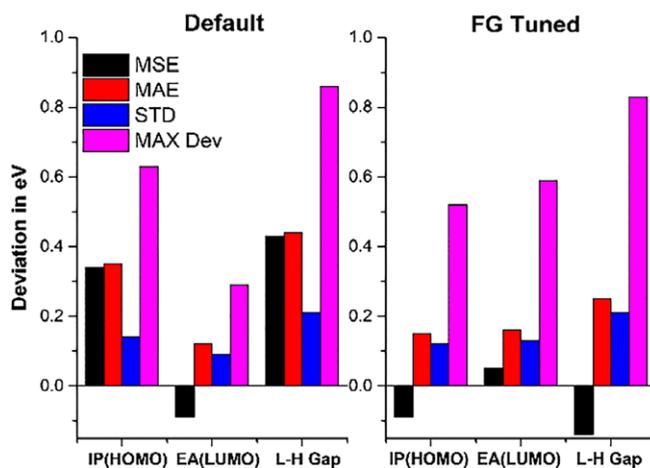
lower than that of default IP (ΔSCF). On the other hand, contrast conclusions are observed in the case of EA (LUMO), compared to IP (HOMO). Interestingly, the default EA (LUMO) is found to be a very good approximation to EA. In fact, the accuracy of default EA (LUMO) is better than the accuracy of tuned EA (LUMO) and default EA (ΔSCF). Similar to IP (HOMO), we also observe an improvement in the accuracy of FG (LUMO-HOMO) upon tuning, which can be mainly attributed to the improvement in the accuracy of IP (HOMO) upon tuning. Therefore, the tuning approach may accurately predict optical gaps and charge-transfer excitations, as these excitations predominantly occur between the frontier molecular orbitals.

To have a deeper insight into the accuracy of EA (LUMO), we have evaluated the values of EA (LUMO) of the dataset molecules at various range-separation parameters (ω): 0.20, 0.30, 0.40, 0.50, and 0.60 bohr^{-1}, respectively. The ω corresponding to zero makes the LC hybrid functional a pure density functional, and increasing the ω value indicates the inclusion of higher fraction of HF exchange. Figure 6 depicts the accuracy of EA (LUMO) obtained at various range-separation parameters of LC-ωPBE.

As the ω value increases, we observe an increasing underestimation of EA (LUMO), with the MSEs decreasing from 0.31 to −0.19 eV. EA (LUMO) evaluated with the range-separation parameter ω = 0.40 bohr^{-1} (i.e., the default ω value) is found to be the most accurate, with the MSE, MAE, STD, and MAX DEV being −0.09, 0.12, 0.09, and 0.29 eV, respectively, whereas the MSE, MAE, STD, and MAX DEV of EA (ΔSCF) at the same ω are 0.12, 0.15, 0.15, and 0.57 eV, respectively. From the MAEs and STDs, it is evident that EA (LUMO) is a very good approximation to EA, when the range-separation parameter is between 0.30 and 0.50 bohr^{-1}. Therefore, when the range-separation parameter is within the above range, the EA of a neutral molecule can be evaluated accurately from the negative of the LUMO energy of the neutral molecule, avoiding the computationally expensive single-point energy calculations of the anion molecule.

From the above findings, it is clear that the tuning scheme is prerequisite condition for improving the accuracy of IP (HOMO); however, the same is not true with respect to EA (LUMO). It is
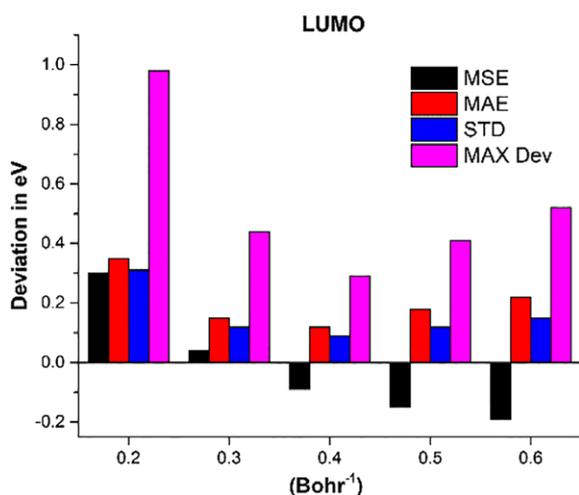
Figure 6. Deviation with respect to CCSD(T)//aTZ in EA (LUMO), calculated employing various range-separation parameters (0.20 to 0.60 bohr^{-1}) based on 30 compounds using LC-ωPBE//aTZ. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 8. MAEs of IP (ΔSCF), EA (ΔSCF), FG (ΔSCF), IP (HOMO), EA (LUMO), and L-H (LUMO-HOMO), calculated employing the default and tuning (eq. (5)) schemes based on 30 compounds using LC-BLYP//aTZ and ωB97X-D//aTZ. [Color figure can be viewed at wileyonlinelibrary.com]

also evident that the tuning scheme does not improve the accuracy of IP (ΔSCF).

To see this, we plot a scattered graph for the deviation with respect to CCSD(T)//aTZ in IP (ΔSCF) versus the difference between IP (ΔSCF) and the corresponding IP (HOMO), calculated using LC-ωPBE//aTZ with the default ω = 0.40 bohr^{-1}. As shown in Figure 7, the accuracy of IP (ΔSCF) is independent of that of IP (HOMO). In few cases, we notice there is negligible difference between IP (ΔSCF) and IP (HOMO), however, the deviation in IP (ΔSCF) is still larger and in the cases where there is appreciable energy difference between IP (ΔSCF) and IP (HOMO), the deviation is still not so large. Therefore, while the tuning scheme improves the accuracy of IP (HOMO), there may not exist any correlation between the tuning scheme and the accuracy of IP (ΔSCF). Hence, it may be stated that the accuracy of IP (ΔSCF) is transferred to that of IP (HOMO) upon tuning, however a vice versa phenomenon is not observed. The impact of tuning scheme on IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF) is marginal, and hence it

can be concluded that the accuracy of ΔSCF procedure is independent of the tuning scheme. IP (HOMO) is quite sensitive to the tuning scheme, and the accuracy of IP (HOMO) improves significantly after tuning, however the same is not true for EA (LUMO).

Similar conclusions are drawn for two other LC hybrid functionals, LC-BLYP and ωB97X-D, employing the default and tuning (eq. (5)) schemes. The MAEs of IP (ΔSCF), EA (ΔSCF), FG (ΔSCF), IP (HOMO), EA (LUMO), and FG (LUMO-HOMO) for LC-BLYP and ωB97X-D are shown in Figure 8.

The default ΔSCF results are generally more accurate than the tuned results, and the accuracy of HOMO energies improves significantly upon tuning. We find that the accuracy of default EA (LUMO) obtained from ωB97X-D is worse than the accuracy of LC-ωPBE and LC-BLYP, which should be related to the fact that the default ω value of ωB97X-D is smaller than those of LC-ωPBE and LC-BLYP. This is also supported by the previous study,[13] where LC-ωPBE (with ω = 0.40 bohr^{-1}) was shown to outperform ωB97X-D (with ω = 0.20 bohr^{-1}) for EA (LUMO) (see Table VIII of Ref. 13).

Conclusion

We have investigated the impact of tuning the range-separation parameter of LC hybrid functionals on the accuracy of IPs, EAs, and FGs. We observe that the tuning scheme improves the accuracy of IP (HOMO), whereas its accuracy is still lower than that of IP (ΔSCF) obtained with the default scheme. On the other hand, the default IP (HOMO) is a poor approximation to IP, and the tuning scheme improves the accuracy of IP (HOMO) significantly. However, we do not observe any improvement in IP (ΔSCF) upon tuning. Tuning IP (HOMO) with IP (ΔSCF) improves the accuracy of IP (HOMO), whereas a reciprocal phenomenon is not observed. Unlike IP (HOMO), the impact of tuning scheme on EA (LUMO) is not profound, and the change in accuracy is negligible. Compared to EA (LUMO), the magnitude of change in IP (HOMO) is larger, indicating that the impact of HF exchange is predominantly high on HOMO energies, and marginal on LUMO energies. EA (LUMO) obtained from LC hybrid functionals with a range-separation

Figure 7. Deviation with respect to CCSD(T)//aTZ in IP (ΔSCF) versus [IP (ΔSCF) - IP (HOMO)], calculated employing the default range-separation parameter (ω = 0.40 bohr^{-1}) based on 30 compounds using LC-ωPBE//aTZ.

parameter of 0.30–0.50 bohr^{-1} is a very good approximation to EA, and its accuracy is even better than the accuracy of EA (ΔSCF). Thus, reliable prediction of EA from the negative of LUMO energy of a LC hybrid functional thus helps in avoiding the computationally expensive anion energy calculations. The LR region of Coulomb operators contributes insignificantly to relative energies, such as IP (ΔSCF), EA (ΔSCF), and FG (ΔSCF), and hence, the details of HF exchange mixing in the LR region are expected to be unimportant.[32] Accordingly, the ΔSCF approach of calculating IPs, EAs, and FGs is found to be independent of tuning scheme. By contrast, as the HOMO and LUMO energies of a molecule are rather sensitive to the asymptotic behavior of XC potential (which is closely related to the range-separation parameter ω), IP (HOMO) can be greatly improved by the tuning scheme; tuned EA (LUMO) is generally less accurate than the tuned IP (HOMO) due to the fact that for a molecule, IP (HOMO) is larger than EA (LUMO) in magnitude, and hence, the tuning scheme naturally takes better care of IP (HOMO) in order to minimize Δ_{FG} (see eq. (5)). The default IP (ΔSCF), and FG (ΔSCF) are found to be better than the tuned IP (HOMO), and FG (LUMO-HOMO), respectively. The accuracy of IP (ΔSCF) remains passive with respect to basis set, whereas a sufficiently large basis set (e.g., aTZ) is required for EA (ΔSCF). Among the different types of hybrid functionals tested from our earlier[2] and current studies, we have found that LC hybrid functionals are consistent and efficient in calculating IPs, EAs, and FGs via the ΔSCF approach. Wong and Hsieh[37] observed similar findings where LC hybrid functionals with a default range-separation parameter also yielded reasonably accurate IPs and FGs in the series of acenes. Among the three LC hybrid functionals examined, LC-ωPBE (with default ω) is found to be efficient, and its accuracy in IP (ΔSCF), EA (ΔSCF), FG (ΔSCF), and EA (LUMO) is found to be on par with the computationally demanding GW approach.

Acknowledgments

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