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Structural and Electronic Properties of Polyacetylene and Polyyne from Hybrid and Coulomb-Attenuated Density Functionals

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The bond length alternation (BLA), the highest-occupied−lowest-unoccupied (HO−LU) orbital energy gap, and the corresponding excitation energy are determined for *trans*-polyacetylene (PA) and polyyne (PY) using density functional theory. Results from the Coulomb-attenuated CAM-B3LYP functional are compared with those from the conventional BHHLYP and B3LYP hybrid functionals. BLA values and HO−LU gaps are determined using both finite oligomer and infinite chain calculations, subject to periodic boundary conditions. TDDFT excitation energies are determined for the oligomers. The oligomer excitation energies and HO−LU gaps are then used, in conjunction with the infinite chain HO−LU gap, to estimate the infinite chain excitation energy. Overall, BHHLYP and CAM-B3LYP give BLA values and excitation energies that are larger and more accurate than those obtained using B3LYP. The results highlight the degree to which excitation energies can be approximated using the HO−LU gaps—at the infinite limit, this approximation works well for B3LYP, but not for the other functionals, where the HO−LU gap is significantly larger. The study provides further evidence for the high-quality theoretical predictions that can be obtained from the CAM-B3LYP functional.

1. Introduction

There has recently been considerable interest in approaches that split the exchange energy of density functional theory (DFT)[1,2] into short- and long-range components, through a partitioning of the $1/r_{12}$ operator. The procedure allows short-range exchange to be treated primarily with a local DFT functional and long-range exchange to be treated primarily with nonlocal, exact orbital exchange, leading to significant improvements in calculated long-range properties. Approaches that achieve this include the schemes of Iikura et al.,[3] Gerber and Ángyán,[4] Vydrov et al.,[5] Baer and Neuhauser,[6] Cohen et al.,[7] and Yanai et al.[8] The last authors proposed the Coulomb-attenuated (CA) CAM-B3LYP functional,[8] which is the focus of the present study. Functionals developed using an exchange partitioning provide improved performance over standard hybrid functionals for a variety of properties,[9−12] such as excited states,[10,13−19] electric-field−induced second harmonic generation,[20] nonlinear optical properties,[21] optical rotation,[22] and reaction barriers.[10,23] Our own work has highlighted that CA functionals offer an improved description of excited states and barriers while maintaining competitive performance for other thermochemical and geometrical properties.[10]

An area that may benefit from the application of CA functionals is the study of polymeric chains; see refs 24−38 for recent relevant studies. In particular, we highlight the work of Jacquemin et al.[32] and Yang and Kertesz.[33] Jacquemin et al. demonstrated that CAM-B3LYP provides an improved description of the bond length alternation (BLA) in short-chain oligomers of *trans*-polyacetylene (PA), although they did not consider the infinite limit nor electronic properties. Yang and Kertesz considered infinite limit BLA and band gaps in PA but did not consider Coulomb-attenuated functionals. Rather than estimating the optical gap using the appropriate time-dependent DFT (TDDFT), Yang and Kertesz calculated the difference between the highest occupied (HO) and lowest unoccupied (LU) Kohn−Sham orbital energies; we denote this quantity the HO−LU gap. The main focus of their study was polyyne (PY), although technical difficulties prevented calculations at the infinite limit in this system.

In the present study we consider the BLA and electronic properties of PA and PY, for both oligomers and the infinite limit, using both conventional and CA functionals. Attention is paid to whether the TDDFT excitation energies can be approximated using HO−LU gaps, and to the convergence of oligomer to infinite chain results. We commence in section 2 by presenting computational details, including a brief summary of the implementation of periodic boundary conditions in the DALTON program.[39] Results for PA and PY are presented in sections 3 and 4, respectively. Conclusions are presented in section 5.

2. Computational Details

To quantify the influence of exchange partitioning, we consider three exchange−correlation functionals. The first two are the conventional hybrid functionals B3LYP[40−44] and BHHLYP,[41,42,45] containing fixed amounts (20% and 50%, respectively) of exact exchange. As noted above, a number of Coulomb-attenuated approximations could be used. We choose the CAM-B3LYP functional, which has attracted significant recent interest and has previously shown promise in the calculation of oligomer BLA.[32] The CAM-B3LYP functional

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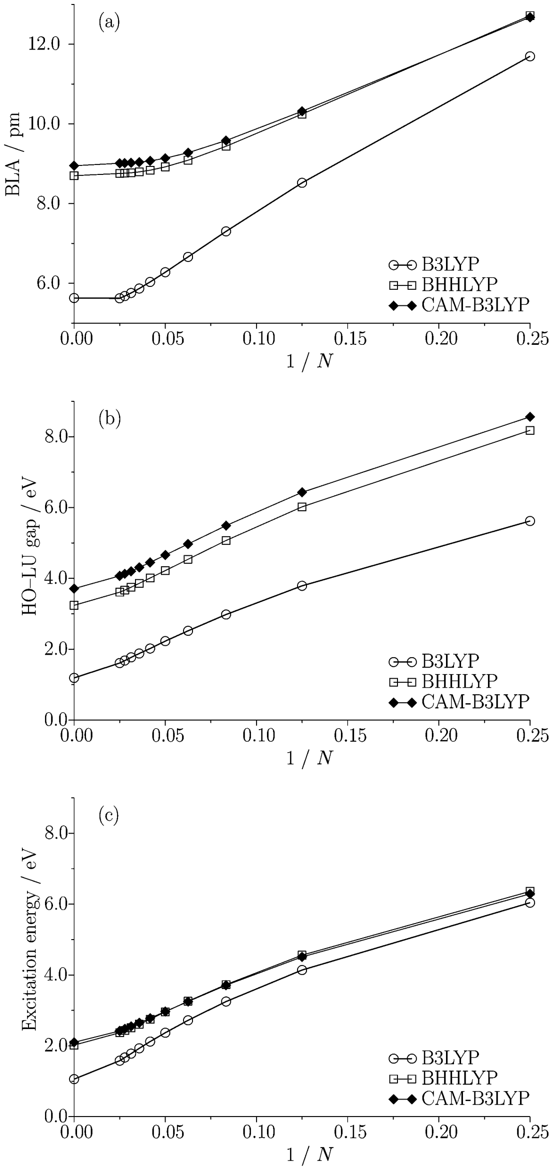

Figure 1. (a) BLA, (b) HO−LU gap, and (c) TDDFT excitation energy in polyacetylene oligomers, as a function of $1/N$.

has 19% exact exchange at short r_{12}, but 65% at large r_{12}. Results using alternative percentages will also be mentioned.

All calculations use the 6-31G* basis set, which has been widely used in studies of BLA,[31−36] with the VWN(III)[43] version of B3LYP. Where comparison can be made, we have confirmed that our results are in very good agreement with those of Jacquemin et al.[31,32] and Yang and Kertesz.[33] Basis set errors become less pronounced as the size of the system increases. Analysis of the PA results in refs 31, 33, and 37 suggests that expanding the basis set would at most increase the BLA values by a few tenths of a picometer (i.e., by a few percent), consistent with the observation in ref 36. For excitation energies and band gaps, our own basis set investigations indicate that for more than 10 carbon atoms, expansion of the basis to 6-31+G* or cc-pVTZ lowers the values by less than a tenth of an electronvolt. As will be seen, such changes would not affect the general conclusions reached regarding functional performance. For PY, it is more difficult to judge the influence of basis set expansion, due to the significant linear dependence.

The oligomer calculations were performed using a development version of the DALTON program.[39] Geometries were optimized using analytic gradients with default DALTON convergence criteria. The reported BLA is the difference between the longest double bond and the shortest single bond, which occurs in the center of the molecule where the effect of chain termination (by H atoms) is minimized. HO−LU gaps and TDDFT excitation energies were determined at the optimized geometries. The excitation energies correspond to the lowest dipole-allowed transitions ($^1\mathrm{B}_\mathrm{u} \leftarrow {}^1\mathrm{A}_\mathrm{g}$ for PA and $^1\Sigma_\mathrm{u}^+ \leftarrow {}^1\Sigma_\mathrm{g}^+$ for PY), characterized by the excitation of a single electron from the HO orbital to the LU orbital.

TABLE 1: TDDFT Excitation Energies and HO−LU Gaps in Polyacetylene Oligomers, as a Function of the Number of Carbon Atoms, *N* (All Values in eV)

N	B3LYP	BHHLYP	CAM- B3LYP	expt[a]
		Excitation Energy		
4	6.04	6.36	6.29	5.92
6	4.87	5.26	5.19	4.95
8	4.14	4.56	4.51	4.41
10	3.63	4.08	4.04	4.02
12	3.25	3.73	3.71	
16	2.72	3.26	3.25	
20	2.37	2.96	2.97	
24	2.12	2.75	2.78	
28	1.93	2.61	2.65	
32	1.78	2.51	2.55	
36	1.67	2.43	2.48	
40	1.58	2.37	2.42	
		HO−LU Gap		
4	5.62	8.18	8.56	
6	4.49	6.84	7.24	
8	3.79	6.02	6.43	
10	3.32	5.46	5.88	
12	2.98	5.07	5.49	
16	2.52	4.54	4.97	
20	2.23	4.22	4.66	
24	2.02	4.01	4.45	
28	1.88	3.86	4.31	
32	1.77	3.75	4.20	
36	1.68	3.67	4.13	
40	1.61	3.61	4.07	
∞	1.19	3.24	3.71	

[a] References 56−59.

The infinite chain calculations, subject to periodic boundary conditions, were performed using a locally modified, development version of DALTON.[39] This code, which will be described in more detail elsewhere,[46] is based on the general approach described in ref 47. A basis set of standard Gaussian-type orbitals $\{|\mu_l\rangle_{\mathrm{GTO}}\}$ is formally associated with each unit cell replica l in the periodic system and is combined with different phase factors to form translation-symmetric Bloch orbitals,

$$|k,\mu\rangle = \frac{1}{\sqrt{N}}\sum_l \mathrm{e}^{ikl}|\mu_l\rangle_{\mathrm{GTO}} \tag{1}$$

Here k is the quasi-momentum in the first Brillouin zone (BZ) and the sum runs over all unit cells. Real-space and k-space matrix elements of any translation-symmetric operator $\hat{A}$ are related via a Fourier transform,

$$A^{0l}_{\mu\nu} = \langle\mu_0|\hat{A}|\nu_l\rangle_{\mathrm{GTO}} \qquad A^{k}_{\mu\nu} = \langle k,\mu|\hat{A}|k,\nu\rangle$$
$$A^{k}_{\mu\nu} = \sum_l \mathrm{e}^{ikl} A^{0l}_{\mu\nu} \tag{2}$$

All matrix elements needed to form the Kohn−Sham matrix are computed in real space and then transformed to k-space where the Roothaan−Hall equations, $\mathbf{F}^k\mathbf{C}^k = \mathbf{S}^k\mathbf{C}^k\epsilon^k$, are solved. The infinite summation of the Coulomb interactions was done

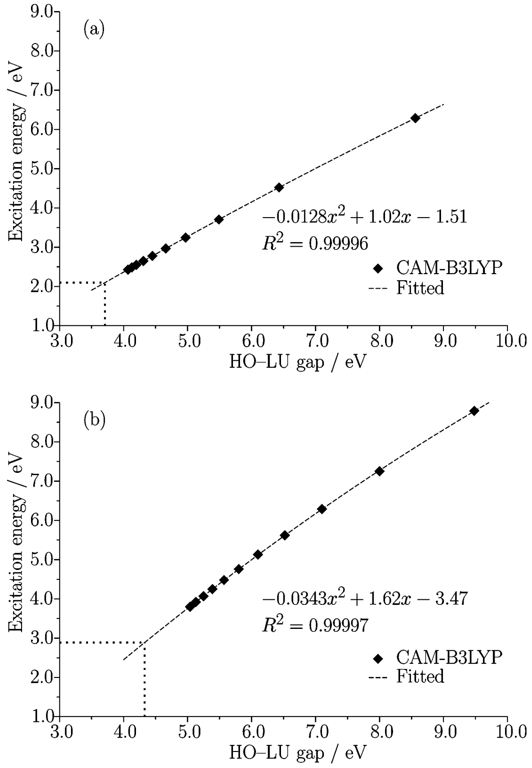

Figure 2. CAM-B3LYP extrapolation of TDDFT excitation energy for (a) polyacetylene and (b) polyyne.

using the multipole method described by Kudin and Scuseria.[48,49] An advantage of the Gaussian approach of ref 47 is that it allows the same basis set to be used for both molecular and periodic calculations, thus facilitating comparisons.

The combination of the geometry of polyyne and the split-valence basis set 6-31G* leads to near-linear-dependence problems. More precisely, the smallest eigenvalue of the *k*-space overlap matrix $\mathbf{S}^k$ varies from the order of 10^{-7} (at $k = 0$) to 10^{-4} (at the BZ boundary). When the Kohn−Sham orbitals are normalized with respect to this near-singular metric, some orbital coefficients (and density matrix elements) can become very large and require extremely precise calculation of the exact orbital exchange, because large density matrix elements are not "damped" by small overlaps in the expression for the exchange (see refs 50 and 51 for similar observations),

$$K^{0l}_{\mu\nu} = \sum_{mj}\sum_{\sigma\lambda} D^{0j}_{\sigma\lambda}(\mu_0\sigma_m|\nu_l\lambda_{m+j}) \qquad (3)$$

Following Ahlenius et al.,[52] we handle this problem by canonical orthonormalisation and projection. At each *k*-point we diagonalize the overlap matrix, transform to the eigenvector basis, and project out eigenvectors corresponding to the smallest eigenvalues. After this procedure, one is left with a transformed Roothaan−Hall equation $\tilde{\mathbf{F}}^k\tilde{\mathbf{C}}^k = \tilde{\mathbf{C}}^k\epsilon^k$ of reduced dimension. To avoid introducing small discontinuities in the potential energy surface for polyyne, we do not base the projection on a fixed threshold but instead project out one eigenvector at each *k*-point.

All calculations use a uniform sampling grid consisting of $N_k = 180$ *k*-points and the density matrix is transformed to real-space using numerical integration,

$$D^{0l}_{\mu\nu} = \frac{1}{N_k}\sum_k \mathrm{e}^{-\mathrm{i}kl} D^k_{\mu\nu} \qquad (4)$$

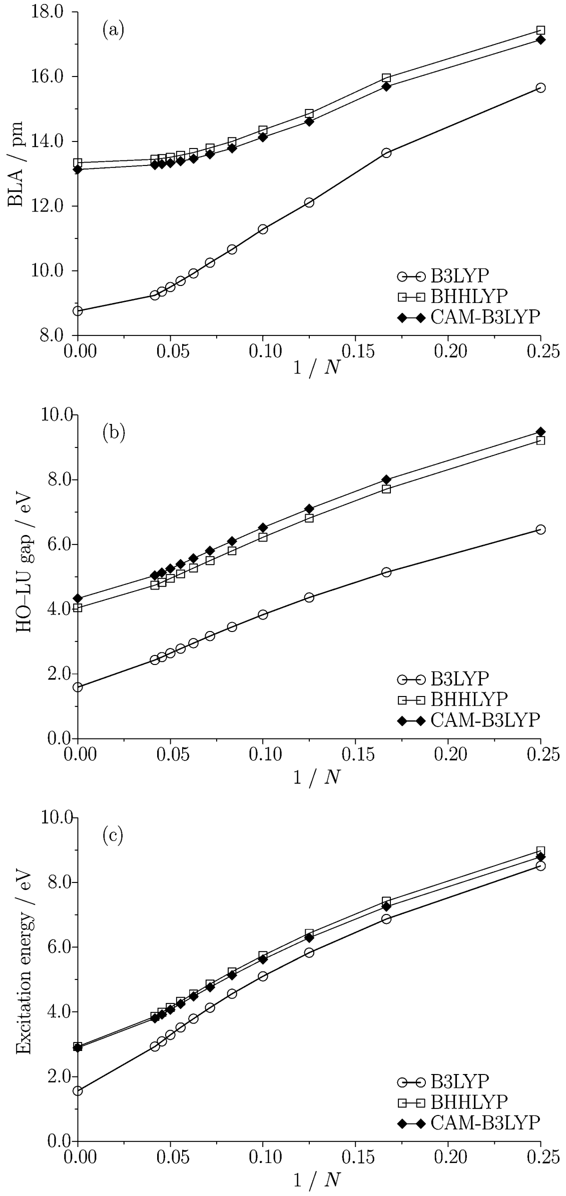

Figure 3. (a) BLA, (b) HO−LU gap, and (c) TDDFT excitation energy in polyyne oligomers, as a function of 1/*N*.

At present, analytic gradients are not implemented and we therefore optimized the geometries by successively varying one parameter and fitting a quadratic curve to the energy as a function of that parameter. We stop the procedure when the energy is minimal with respect to all geometrical parameters. For both PA and PY, all geometrical parameters were optimized. We have confirmed that, to the precision quoted, the geometries are global minima. HO−LU gaps (band gaps) were determined at the optimized geometries. TDDFT excitation energies are not yet available in our program.

3. Polyacetylene (PA)

Figure 1a presents the BLA values for PA oligomers containing *N* carbon atoms, for 4 ⩽ *N* ⩽ 40, as a function of 1/*N*. The BHHLYP and CAM-B3LYP functionals give similar BLA values, which are significantly larger than those of B3LYP. The results clearly highlight the increase in BLA that occurs as the amount of exact orbital exchange is increased, in one case through an increase in the exact exchange prefactor and in the other through Coulomb attenuation. As argued in ref 32, CAM-

B3LYP provides a very good estimate of the BLA in PA oligomers, because the results are bracketed by second-order Møller−Plesset and coupled cluster singles doubles values, which are considered to be lower and upper bounds, respectively. Figure 1a also presents the infinite chain BLA (at $1/N = 0$), determined using periodic boundary conditions. The convergence from oligomers to the infinite chain appears monotonic and slow for BHHLYP and CAM-B3LYP. For B3LYP, it seems likely that there is a minimum in the curve for longer chain lengths; calculations on a 48 carbon chain give a BLA marginally below the infinite chain value, supporting the presence of a minimum. Extrapolation would be problematic for this functional, as is evident in the discrepancy between the extrapolated and periodic BLA values in refs 33 and 36. We reiterate that our B3LYP oligomer results are in good agreement with those in ref 31, and our infinite chain result is in good agreement with the values in refs 33 and 35. Compared to the (solid state) experimental BLA of 7−9 pm,[53−55] the B3LYP value of 5.6 pm is rather short. By contrast, the BHHLYP and CAM-B3LYP values of 8.7 and 8.9 pm do lie within the experimental range.

Table 1 lists excitation energies and HO−LU gaps in PA, as functions of N. For chain lengths $4 \leqslant N \leqslant 10$, experimental excitation energies are also presented. For B3LYP, the excitation energies are rather close to HO−LU gaps, with the agreement improving with increasing chain length. This is consistent with the observations of Ma et al.,[60] demonstrating that HO−LU gaps can be used to estimate PA excitation energies with B3LYP. For BHHLYP and CAM-B3LYP, however, the values are very different, even for the longest chain, indicating that such an approximation is invalid.

Table 1 also presents the HO−LU gap from the infinite chain calculations. The convergence of this quantity from oligomers to the infinite chain is shown in Figure 1b. Given the aforementioned similarity between the B3LYP HO−LU gaps and excitation energies, the infinite chain B3LYP HO−LU gap of 1.2 eV can be assumed to be a reasonable estimate for the B3LYP excitation energy. It is below the experimental optical gap of 1.5−1.8 eV,[61,62] which is consistent with the underestimated BLA. The BHHLYP and CAM-B3LYP infinite chain HO−LU gaps are much larger (3.2 and 3.7 eV, respectively) but, as noted above, will not resemble the excitation energies.

One way to estimate the excitation energy for the infinite chain is to consider the relationship between the excitation energies and the HO−LU gaps in the oligomer calculations and then extrapolate on the basis of the infinite chain HO−LU gap. Investigations revealed that the results are relatively insensitive to the choice of polynomial fit between the two oligomer quantities and whether all data points or just the longer oligomer data are included. We choose to fit a quadratic curve to each data set and then extrapolate to the infinite chain excitation energy. This is illustrated in Figure 2a for the CAM-B3LYP functional. For B3LYP, BHHLYP, and CAM-B3LYP, the estimated infinite chain excitation energies obtained from this procedure are 1.1, 2.0, and 2.1 eV. This B3LYP estimate is close to the value estimated above, as expected. The BHHLYP and CAM-B3LYP values are notably larger, slightly overestimating the experimental range of 1.5−1.8 eV. Figure 1c presents the oligomer excitation energies as a function of $1/N$, together with the estimated infinite chain values (at $1/N = 0$). The dependence on $1/N$ is very similar to that of the HO−LU gaps in Figure 1b. Consistent with ref 63, our results highlight that a simple linear extrapolation to the infinite limit can lead to underestimated infinite chain results.

TABLE 2: TDDFT Excitation Energies and HO−LU Gaps in Polyyne Oligomers, as a Function of the Number of Carbon Atoms, *N* (All Values in eV)

N	B3LYP	BHHLYP	CAM- B3LYP	expt[a]
		Excitation Energy		
4	8.51	8.98	8.79	7.54
6	6.87	7.42	7.25	6.77
8	5.83	6.43	6.29	5.98
10	5.10	5.74	5.62	5.33
12	4.56	5.24	5.13	4.99
14	4.13	4.86	4.76	4.67
16	3.79	4.56	4.48	4.41
18	3.52	4.33	4.25	4.19
20	3.29	4.14	4.07	4.02
22	3.09	3.99	3.92	3.87
24	2.93	3.86	3.80	3.74
		HO−LU Gap		
4	6.46	9.21	9.48	
6	5.14	7.71	8.00	
8	4.36	6.81	7.10	
10	3.83	6.22	6.52	
12	3.45	5.80	6.10	
14	3.17	5.50	5.80	
16	2.95	5.27	5.57	
18	2.78	5.09	5.39	
20	2.64	4.95	5.25	
22	2.52	4.83	5.13	
24	2.43	4.74	5.04	
∞	1.59	4.04	4.33	

[a] References 64−66.

The CAM-B3LYP functional has only 65% exact orbital exchange at large r_{12}. We have previously investigated the influence of increasing this fraction[10] and we have performed a similar investigation in the present study. Specifically, we considered the $\alpha = 0.2$, $\beta = 0.8$, and $\mu = 0.4\ a_0$ functional, highlighted in ref 10, together with the $\alpha = 0.0$, $\beta = 1.0$, and $\mu = 0.4\ a_0$ functional, which more closely resembles the form in ref 3. Both have 100% exchange at large r_{12}. The BLAs converge rapidly with N, to values of 10.9 and 10.7 pm, respectively, which are clearly too large. The use of these functionals therefore cannot be recommended for the present study and we do not consider them further.

4. Polyyne (PY)

Figure 3a presents the BLA values of PY oligomers containing N carbon atoms, for $4 \leqslant N \leqslant 24$, as a function of $1/N$. Results for longer chains are not presented due to convergence difficulties. Once again, BHHLYP and CAM-B3LYP yield similar BLA values (although the ordering is reversed compared to PA), which are notably larger than those of B3LYP. For BHHLYP and CAM-B3LYP, the convergence to the infinite chain BLA resembles that observed for PA. The B3LYP convergence is different from that of PA, but this may just reflect the shorter chain lengths. The infinite chain BHHLYP and CAM-B3LYP BLA values are 13.3 and 13.1 pm, respectively, which are close to the estimated reference value of 13 pm in ref 33. Once again, the B3LYP BLA value of 8.8 pm is much smaller.

Table 2 lists excitation energies and HO−LU gaps in PY, as functions of N, together with reference experimental values. For the larger chain lengths, where basis set effects are less pronounced, the BHHLYP and CAM-B3LYP excitation energies are a notable improvement over those of B3LYP. In contrast to the PA results, the HO−LU gap is a poor approximation to the excitation energy for all three functionals. Table 2 also presents the HO−LU gap from the infinite chain calculations. The convergence of this quantity from oligomer to infinite chain is shown in Figure 3b. For the infinite chain, the HO−LU gaps exhibit a similar trend to that of PA, with values of 1.6, 4.0, and 4.3 eV, for B3LYP, BHHLYP, and CAM-B3LYP, respectively.

We have applied the same quadratic extrapolation procedure as in the previous section to estimate excitation energies for the infinite chain, obtaining values of 1.6, 2.9, and 2.9 eV, for B3LYP, BHHLYP, and CAM-B3LYP, respectively—see Figures 2b and 3c. Interestingly, the B3LYP value is again close to the infinite chain HO−LU gap, suggesting that the approximation is reasonable in the limit, although it is not so for short oligomers (Table 2). As with PA, the B3LYP value is significantly below the experimental optical gap, estimated to be 2.3−2.4 eV in ref 33, using a linear extrapolation of experimental oligomer optical absorption results. The BHHLYP and CAM-B3LYP values are higher than this estimate, but note the comment above and in ref 63 regarding the validity of the linear extrapolation used to determine this estimate.

5. Conclusions

We have investigated the BLA, HO−LU gap, and TDDFT excitation energy in *trans*-polyacetylene (PA) and polyyne (PY) using the B3LYP, BHHLYP, and CAM-B3LYP exchange−correlation functionals. BLA values and HO−LU gaps have been determined using both finite oligomer and infinite chain calculations, subject to periodic boundary conditions. TDDFT excitation energies have been determined for the oligomers. The oligomer excitation energies and HO−LU gaps have then been used, in conjunction with the infinite chain HO−LU gap, to estimate the infinite chain excitation energy. Overall, BHHLYP and CAM-B3LYP give BLA values and excitation energies that are larger and more accurate than those obtained using B3LYP.

The study also highlights the extent to which TDDFT excitation energies can be approximated using HO−LU gaps. Parts b and c of Figures 1 and 3 demonstrate that the HO−LU gap varies significantly as the amount of exact exchange in the functional varies, whereas the excitation energy is relatively insensitive. The amount of exact exchange in B3LYP is such that these two quantities are similar for long chains of PA and for infinite chain PY. In moving to BHHLYP and CAM-B3LYP, however, the amount of exact exchange increases and the HO−LU gap becomes larger than the excitation energy. Conversely, we have confirmed that as the amount of exchange is reduced (e.g., by using a generalized gradient approximation with no exact exchange), the HO−LU gap becomes smaller than the excitation energy. The observations are consistent with the finding of Yang and Kertesz,[33] that the BHHLYP HO−LU gap, despite being evaluated at the good quality BHHLYP geometry, significantly overestimates the experimental optical gap, whereas the B3LYP HO−LU gap evaluated at the BHHLYP geometry is more accurate. The present study demonstrates that the need to combine two functionals can be avoided by estimating the TDDFT excitation energy using either BHHLYP or CAM-B3LYP, at their respective geometries.

Previous investigations have established that CAM-B3LYP is a good quality, all-round functional, exhibiting improved long-range behavior over conventional approximations. The BHHLYP functional works well for properties requiring large amounts of exact orbital exchange but is a less successful all-round functional. The present study supports these observations.

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References and Notes

(1) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.

(2) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

(3) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540−3544.

(4) Gerber, I. C.; Ángyán, J. G. *Chem. Phys. Lett.* **2005**, *415*, 100−105.

(5) Vydrov, O. A.; Heyd, J.; Krukau, A. V.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 074106.

(6) Baer, R.; Neuhauser, D. *Phys. Rev. Lett.* **2005**, *94*, 043002.

(7) Cohen, A. J.; Mori-Sanchez, P.; Yang, W. *J. Chem. Phys.* **2007**, *126*, 191109.

(8) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51−57.

(9) Peach, M. J. G.; Helgaker, T.; Sałek, P.; Keal, T. W.; Lutnaes, O. B.; Tozer, D. J.; Handy, N. C. *Phys. Chem. Chem. Phys.* **2006**, *8*, 558−562.

(10) Peach, M. J. G.; Cohen, A. J.; Tozer, D. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4543−4549.

(11) Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 234109.

(12) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 224106.

(13) Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2004**, *120*, 8425−8433.

(14) Chiba, M.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2006**, *124*, 144106.

(15) Day, P. N.; Nguyen, K. A.; Pachter, R. *J. Chem. Phys.* **2006**, *125*, 094103.

(16) Nguyen, K. A.; Day, P. N.; Pachter, R. *J. Chem. Phys.* **2007**, *126*, 094303.

(17) Cai, Z.-L.; Crossley, M.; Reimers, J.; Kobayashi, R.; Amos, R. *J. Phys. Chem. B* **2006**, *110*, 15624−15632.

(18) Yanai, T.; Harrison, R. J.; Handy, N. C. *Mol. Phys.* **2005**, *103*, 413−424.

(19) Kobayashi, R.; Amos, R. D. *Chem. Phys. Lett.* **2006**, *420*, 106.

(20) Ferrighi, L.; Frediani, L.; Cappelli, C.; Sałek, P.; Ågren, H.; Helgaker, T.; Ruud, K. *Chem. Phys. Lett.* **2006**, *425*, 267−272.

(21) Baev, A.; Norman, P.; Henriksson, J.; Ågren, H. *J. Phys. Chem. B* **2006**, *110*, 20912−20916.

(22) Pecul, M. *Chem. Phys. Lett.* **2006**, *418*, 1.

(23) Song, J.-W.; Hirosawa, T.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2007**, *126*, 154105.

(24) Katagiri, H.; Shimoi, Y.; Abe, S. *Chem. Phys.* **2004**, *306*, 191−200.

(25) Weimer, M.; Hieringer, W.; Sala, F. D.; Görling, A. *Chem. Phys.* **2005**, *309*, 77−87.

(26) Yang, S.; Olishevski, P.; Kertesz, M. *Synth. Met.* **2004**, *141*, 171−177.

(27) Jacquemin, D.; Andre, J.-M.; Perpete, E. A. *J. Chem. Phys.* **2004**, *121*, 4389−4396.

(28) Poulsen, T. D.; Mikkelsen, K. V.; Fripiat, J. G.; Jacquemin, D.; Champagne, B. *J. Chem. Phys.* **2001**, *114*, 5917−5922.

(29) Hutchison, G. R.; Zhao, Y.-J.; Delley, B.; Freeman, A. J.; Ratner, M. A.; Marks, T. J. *Phys. Rev. B* **2003**, *68*, 035204.

(30) Jacquemin, D.; Femenias, A.; Chermette, H.; Andre, J.-M.; Perpete, E. *J. Phys. Chem. A* **2005**, *109*, 5734−5741.

(31) Jacquemin, D.; Femenias, A.; Chermette, H.; Ciofini, I.; Adamo, C.; Andre, J.-M.; Perpete, E. *J. Phys. Chem. A* **2006**, *110*, 5952−5959.

(32) Jacquemin, D.; Perpete, E. A.; Scalmani, G.; Frisch, M. J.; Kobayashi, R.; Adamo, C. *J Chem. Phys.* **2007**, *126*, 144105.

(33) Yang, S.; Kertesz, M. *J. Phys. Chem. A* **2006**, *110*, 9771−9774.

(34) Jacquemin, D.; Perpete, E. A.; Ciofini, I.; Adamo, C. *Chem. Phys. Lett.* **2005**, *405*, 376−381.

(35) Hirata, S.; Iwata, S. *J. Chem. Phys.* **1997**, *107*, 10075−10084.

(36) Choi, C. H.; Kertesz, M.; Karpfen, A. *J. Chem. Phys.* **1997**, *107*, 6712−6721.

(37) Pino, R.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 8113−8119.

(38) Kudin, K. N.; Scuseria, G. E. *Phys. Rev. B* **2000**, *61*, 16440−16453.

(39) DALTON, a molecular electronic structure program, Release 2.0, 2005; see http://www.kjemi.uio.no/software/dalton/dalton.html.

(40) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(41) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(42) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(43) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(44) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

(45) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(46) Tellgren, E. I.; Helgaker, T.; Reine, S. To be published.

(47) *Quantum-Mechanical Ab-initio Calculation of the Properties of Crystalline Materials*; Pisani, C., Ed.; Lecture Notes in Chemistry 67; Springer: Berlin, 1996.

(48) Kudin, K. N.; Scuseria, G. E. *Chem. Phys. Lett.* **1998**, *289*, 611−616.

(49) Kudin, K. N.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 2886−2890.

(50) Suhai, S.; Bagus, P. S.; Ladik, J. *Chem. Phys.* **1982**, *68*, 467−471.

(51) Jacquemin, D.; Champagne, B. *Int. J. Quantum Chem.* **2000**, *80*, 863−870.

(52) Ahlenius, T.; Calais, J.-L.; Löwdin, P.-O. *J. Phys. C* **1973**, *6*, 1896−1908.

(53) Yannoni, C. S.; Clarke, T. C. *Phys. Rev. Lett.* **1983**, *51*, 1191−1193.

(54) Duijvestijn, M. J.; Manenschijn, A.; Smidt, J.; Wind, R. A. *J. Magn. Reson.* **1969**, *64*, 461−469.

(55) Kahlert, H.; Leitner, O.; Leising, G. *Synth. Met.* **1987**, *17*, 467−472.

(56) McDiarmid, R. *J. Chem. Phys.* **1976**, *64*, 514−521.

(57) Flicker, W. M.; Mosher, O. A.; Kuppermann, A. *Chem. Phys. Lett.* **1977**, *45*, 492−497.

(58) Leopold, D. G.; Pendley, R. D.; Roebber, J. L.; Hemley, R. J.; Vaida, V. *J. Chem. Phys.* **1984**, *81*, 4218−4229.

(59) D'Amico, K. L.; Manos, C.; Christensen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1777−1782.

(60) Ma, J.; Li, S.; Jiang, Y. *Macromolecules* **2002**, *35*, 1109−1115.

(61) Tani, T.; Grant, P. M.; Gill, W. D.; Street, G. B.; Clarke, T. C. *Solid State Commun.* **1980**, *33*, 499−503.

(62) Fincher, C. R.; Chen, C. E.; Heeger, A. J.; MacDiarmid, A. G.; Hastings, J. B. *Phys. Rev. Lett.* **1982**, *48*, 100−104.

(63) Gierschner, J.; Cornil, J.; Egelhaaf, H.-J. *Adv. Mater.* **2007**, *19*, 173−191.

(64) Pino, T.; Ding, H.; Guthe, F.; Maier, J. P. *J. Chem. Phys.* **2001**, *114*, 2208−2212.

(65) Kloster-Jensen, E.; Haink, H.-J.; Christen, H. *Helv. Chim. Acta* **1974**, *57*, 1731−1744.

(66) Grutter, M.; Wyss, M.; Fulara, J.; Maier, J. *J. Phys. Chem. A* **1998**, *102*, 9785−9790.