



Performance of the Vienna ab initio simulation package (VASP) in chemical applications[☆]

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Abstract

Five different density functionals in combination with ultra-soft pseudopotentials and plane wave basis sets were used to optimize the geometries of common chemical systems using solid state program Vienna ab initio simulation package (VASP). These systems included diatomics, N₂, O₂, F₂ and CO, and carbon based organic systems, ethane, ethylene, acetylene, 1,3-butadiene, 1,3,5-hexatriene, benzene, biphenyl, naphthalene, graphene, polyethylene and all-*trans*-polyacetylene. The four functionals based on the generalized gradient approximation gave very good agreement on bond lengths and angles as compared with each other, with localized Gaussian basis set calculations and with experimental values. Reasonable results were also obtained for vibrational frequencies of selected normal modes of benzene and for torsional potentials of 1,3-butadiene and biphenyl. On the other hand, local density approximation tends to underestimate bond lengths. The performance of VASP for these properties is very similar to Gaussian type implementations of density functional theory explaining its successes in molecular, solid state, surface and polymer applications.

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1. Introduction

Density functional theories (DFTs) are very successful techniques for understanding

the electronic, structural and vibrational properties of large molecular systems. Well-known quantum chemical computational packages like GAUSSIAN 98 contain DFT as an option. The Vienna ab initio simulation package (VASP) is an efficient DFT code developed recently [1–3] for studying 3D bulk systems with periodic boundary condition. Most applications so far have been based on plane-wave basis set and ultrasoft pseudopotential approximation, although the newer version contains an all-electron option. Plane wave basis sets are

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somewhat unusual for molecular applications, because of the association of plane wave basis sets with free electron like systems. Of course when a basis set is large enough, such associations are groundless. For instance, VASP proved to be very useful in investigating diamond, graphite and carbon nanotubes [4–6], and numerous other chemical applications that involve electronic systems that are not free electron-like [7–12]. However, it is an open question that to what extent VASP is comparable with traditional, quantum chemical ab initio programs based on local (atom centered Gaussian) basis sets. Our aim was to test the performance of VASP for geometries and vibrational frequencies of simple systems.

We have selected a few common chemical problems. We focused on optimizing geometries for which DFT is usually quite reliable. Four diatomics, including N₂, O₂, F₂ and CO, and a number of carbon-based systems that are prototypical, ethane, ethylene, acetylene, 1,3-butadiene, 1,3,5-hexatriene, benzene, biphenyl, naphthalene, graphene, polyethylene and trans-polyacetylene were calculated. We have also looked at a number of selected vibrational frequencies of benzene. An important area of application of total energy calculations is determining the energy differences of various isomers, conformers and tautomers. For testing purposes we have studied two well-understood rotational barriers where DFT is known to perform rather well: butadiene and biphenyl [13]. The optimized geometries of polyethylene and all-*trans*-polyethylene were calculated. Furthermore, the bond length alternation problem in all-*trans*-polyacetylene, which poses a serious challenge [14] to any total energy method, is addressed.

Fig. 1 depicts some of the molecules studied.

2. Computation details

In the VASP (version 4.4.2) calculations the geometries of N₂, O₂, F₂, CO, ethane, ethylene, acetylene, butadiene, 1,3,5-hexatriene, benzene, biphenyl, naphthalene, polyethylene, all-*trans*-polyacetylene and graphene were optimized with local density approximation (LDA) as well as with

Generalized Gradient Approximations (GGA). Several GGA functionals, including Perdew–Becke (PB) [15], Langreth–Mehl–Hu (LM) [16,17], Perdew–Wang 86 (PW86) [18] and Perdew–Wang 91 (PW91) [19], were used to test their performance. The ultra-soft LDA pseudopotentials were used for LDA calculations, while the ultra-soft pseudopotentials generated for PW91 exchange functional were used for all GGA calculations. For the pseudopotentials default cut-off energies were used (290 eV for C, 350 eV for N, 400 eV for O and 425 eV for F).

Tetragonal lattices were utilized for all systems except for benzene and graphene where hexagonal lattices were used. A $1 \times 1 \times 1$ k-point mesh was used for all molecular systems. For polymeric systems, 30 k-points including the end points, and for graphene $30 \times 30 \times 1$ k-point mesh, were used. Since VASP always employs three-dimensional periodic boundary condition, a minimum of 6 Å inter-molecular distance was kept for all systems to ensure that the inter-molecular interaction is sufficiently small. The geometry convergence criterion was set on forces where $|F_{\max}| = 0.001$ eV/Å. The convergence in total energy proved to be always better than 0.001 eV.

The vibrational frequencies of the four diatomics and four selected normal modes of benzene ($2A_{1g} \oplus 2B_{2u}$) were obtained by the ‘frozen phonon’ calculations. This involved point by point total energy calculations and were done manually, because it is not automatic in VASP. For the diatomics, a parabolic fit was done to the total energies calculated in seven points around the equilibrium, using 0.05 Å steps. In the case of benzene, a two dimensional quadratic fit was done to nine points on the potential energy surface, using 0.01 Å steps in both directions, for each of the symmetry species. Calculations for the vibrational frequencies were carried out by both LDA and PW91 exchange functionals.

For comparative purposes, calculations involving molecular systems were also done using PW91 functional with the GAUSSIAN 98 package [20].

The torsional potential energy curves of butadiene and biphenyl were obtained by the rigid rotor model, where during the potential scan the bond lengths and angles were kept fixed at the optimized values of the most stable conformer.

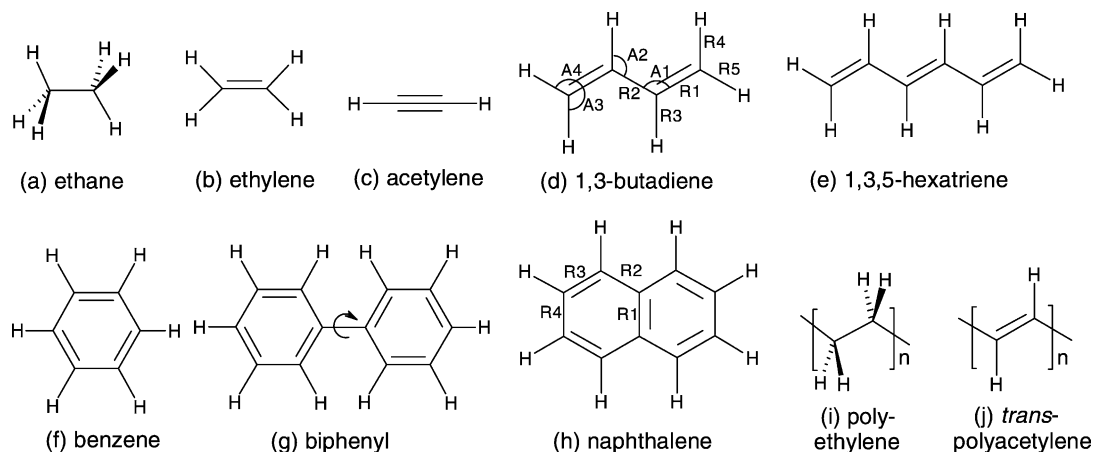


Fig. 1. Some molecular and polymeric systems studied in this work.

3. Results and discussion

Extensive experimental and theoretical efforts have been devoted to understand the structures and various physical properties of the species studied here. Our purpose of this study, however, is to test the performance of VASP program on molecular systems, thus only the most recent experimental and theoretical data will be listed and compared to our results.

The theoretical bond lengths and vibrational frequencies of N_2 , O_2 , F_2 and CO calculated with LDA and PW91 functionals are listed in Table 1 together with the experimental values [21–24] and theoretical values calculated with localized Gaussian basis set using GAUSSIAN 98. In general, the VASP calculated bond lengths of diatomics agree with experimental results, with the largest difference being 0.015 Å for LDA and 0.030 Å for PW91. The somewhat large deviation of 0.030 Å for O_2 given by PW91 shows the performance of VASP on an open shell system. In general, LDA gives shorter bond lengths than PW91 for all four diatomics studied here.

When different implementations of PW91 are compared, both GAUSSIAN 98 and VASP give reasonable results. VASP calculations [25] have been applied earlier to O_2 and CO using the Perdew–Zunger (PZ) functional resulting in bond lengths for O_2 and CO and vibrational frequency for CO agree well with our PW91 results, while the frequency for O_2 is predicted at 1552 cm^{-1} .

The agreement between the Gaussian 6-31G* calculation and the plane-wave calculation is remarkably close. The quality of calculated vibrational frequencies is comparable with that of the calculated bond lengths, and would require some scaling [26] to achieve acceptable agreement with experiment.

The calculated and experimental [27] structural parameters of ethane, ethylene and acetylene are listed in Table 2. Both LDA and GGA give reasonable agreement on bond lengths and bond angles in these systems. Earlier local-density functional calculations [28] on ethylene and acetylene using VASP agree well with current results. A closer inspection shows that LDA gives bond lengths for all C–C bonds shorter than experimental ones with the largest absolute deviation of 0.023 Å. All GGA approaches studied here give improved agreements over LDA for C–C bonds. Bond angles are well predicted by both LDA and GGA. Overall, VASP results are very similar to the 6-31G* Gaussian results on ethane, ethylene and acetylene using the same functional.

Table 3 lists the calculated geometrical parameters of *trans*-1,3-butadiene. As in the above cases, VASP results agree well with those of experimental [29] and earlier theoretical studies [30,31]. All GGA functionals give correct predictions on the bond lengths, while LDA predictions of the single and double CC bonds are too short by 0.034 and 0.018 Å, respectively. Both GGA and LDA give very good agreement on bond angles. Again, the Gaussian basis set 6-31G*

Table 1

The theoretical and experimental bond lengths and vibrational frequencies of selected diatomic molecules

	Bond length				Vibrational frequency			
	LDA	PW91	PW91PW91/6-31G* ^a	Exp.	LDA	PW91	PW91PW91/6-31G* ^a	Exp. ^b
N ₂	1.109	1.113	1.116	1.098 ^c	2313	2294	2364	2331(2360) ^d
O ₂ ^c	1.223	1.237	1.228	1.208 ^d	1616	1517	1576	1556(1580) ^d
F ₂	1.398	1.424	1.418	1.412 ^c	1063	1015	1017	1110 (–) ^f
CO	1.138	1.145	1.148	1.128 ^g	2145	2116	2127	2143(2170) ^g

Bond lengths in Å, frequencies in cm^{–1}. Calculations refer to VASP results except otherwise noted.^a This work. GAUSSIAN 98 calculations.^b Experimentally measured frequencies and, in parenthesis, harmonic values.^c Taken from Ref. [21].^d Taken from Ref. [22].^e Open shell calculations.^f Taken from Ref. [24].^g Taken from Ref. [23].

results are very close to the plane wave basis set (VASP) results.

Using the optimized geometrical parameters of *trans*-1,3-butadiene, the torsional potential of butadiene was calculated by LDA and PW91. Fig. 2 shows the VASP results and two other curves calculated with GAUSSIAN 98 by PW91PW91/6-31G*, one by the rigid rotor model and one by the relaxed scan. It should be noted that only rigid rotor calculations are possible within VASP. Also shown are earlier relaxed scans by SCF and MP2 [13]. The overall shapes of our three rigid rotor curves are very similar. These curves

also agree with the relaxed scan curve except around the *cis*-conformation, where the largest changes in structural parameters occur.

As compared with the SCF and MP2 results, the DFT curves give a higher *trans*–*gauche* barrier and a bigger *trans*–*gauche* energy difference. The relaxed PW91 curve has a *cis*–*gauche* energy difference of 0.1 kcal/mol, while the rigid rotor PW91 curves have *cis*–*gauche* energy differences more like that by SCF and MP2.

To further test the performance of VASP on conjugated systems, the torsional potential of

Table 2

The theoretical and experimental bond lengths of ethane, ethylene and acetylene

		LDA	PB	LM	PW86	PW91	PW91PW91/6-31G* ^a	Exp. ^b
CH ₃ CH ₃	R _{C–C}	1.508	1.528	1.521	1.531	1.529	1.531	1.531
	R _{C–H}	1.102	1.099	1.108	1.099	1.098	1.102	1.096
	A _{C–C–H}	111.7	111.5	111.6	111.4	111.4	111.4	
	A _{H–C–H}	107.2	107.4	107.3	107.4	107.4	107.5	107.8
CH ₂ CH ₂	R _{C=C}	1.320	1.327	1.332	1.330	1.329	1.338	1.339
	R _{C–H}	1.094	1.091	1.101	1.090	1.090	1.093	1.085
	A _{C=C–H}	121.7	121.8	121.7	121.8	121.8	121.8	
	A _{H–C–H}	116.6	116.3	116.7	116.4	116.4	116.4	117.8
CHCH	R _{C≡C}	1.195	1.200	1.207	1.201	1.199	1.214	1.203
	R _{C–H}	1.072	1.066	1.078	1.065	1.066	1.073	1.061

Bond lengths in Å, bond angles in degree. Calculations refer to VASP results except otherwise noted.

^a This work. GAUSSIAN 98 calculations.^b Experimental values are taken from ref. Ref. [27].

Table 3

The theoretical and experimental geometrical parameters of *trans*-1,3-butadiene

	LDA	PB	LM	PW86	PW91	B3LYP/6-31G* ^a	PW91PW 91/6-31G* ^b	Exp. ^c
R1	1.331	1.341	1.343	1.343	1.339	1.341	1.349	1.349
R2	1.433	1.448	1.445	1.451	1.448	1.458	1.454	1.467
R3	1.099	1.095	1.106	1.095	1.094	1.091	1.097	1.108
R4	1.096	1.092	1.102	1.092	1.091	1.088	1.094	1.108
R5	1.092	1.089	1.099	1.089	1.089	1.086	1.092	1.108
A1	124.0	124.5	123.9	124.5	124.1	124.3	124.3	124.4
A2	116.2	116.3	116.3	116.2	116.4	116.2	116.3	114.7
A3	120.7	121.4	120.7	121.3	121.3	121.6	121.4	120.9
A4	122.0	121.8	122.0	121.8	121.8	121.8	121.8	120.9

Bond lengths in Å, angles in deg. See Fig. 1 for parameter definitions. Calculations refer to VASP results except otherwise noted.

^a Taken from Refs. [30,31].^b This work. GAUSSIAN 98 calculation.^c Taken from Ref. [29].

biphenyl was calculated, again by LDA and PW91. The results are shown in Fig. 3 along with earlier predictions from literature. As noted by Karpfen et al. [13], the HF and MP2 methods predict that the staggered conformation has lower energy than the eclipsed one, while the DFT methods show the reversed trend. The most stable conformations predicted by HF and MP2 have torsion angles between 40 and 50°, and between 30 and 40° by DFT methods. Our VASP results follow this general trend in that both curves of LDA and PW91 show that the staggered conformation is less stable than the eclipsed one and the most stable conformer lies between 30 and 40°. It is noteworthy that the LDA predicted relative energy of the staggered conformation is about 1 kcal/mol higher than obtained by the more refined GGA functionals.

Again we observe that the 6-31G* Gaussian basis set calculations are very similar to the VASP calculations if the same functional is used in the rigid rotor context.

Table 4 lists the VASP calculated and experimental [32–36] geometrical parameters of graphene and benzene as well as the frequencies of four selected normal modes of benzene. All four GGA functionals give good agreement with experimental results on benzene structural parameters, while the LDA gives C–C bond length short by 0.010 Å. The same trend can be seen in the calculated bond length of graphene.

VASP and GAUSSIAN 98 perform very similarly with the same density functional.

Using frozen phonon approximation, we were able to obtain vibrational frequencies of four selected normal modes of benzene, namely, two A_{1g} and two B_{2u}. The low frequency A_{1g} is excellent, and gives a good a posteriori justification for the use of this method for the Radial Breathing Mode (RBM) studies

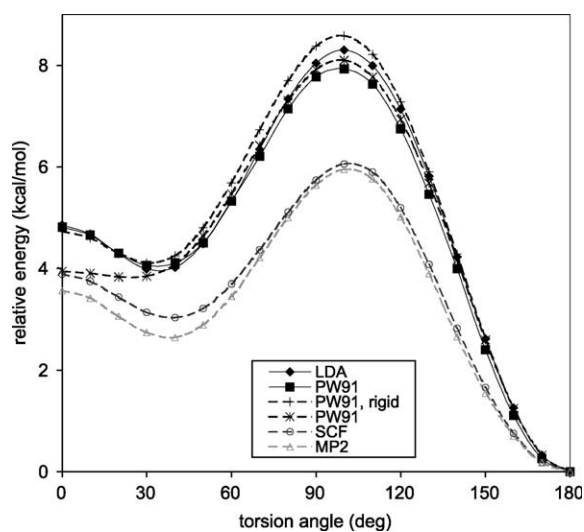


Fig. 2. Torsional potentials of 1,3-butadiene around the central CC single bond. Solid lines by VASP (rigid rotor), dashed lines by GAUSSIAN 98 using 6-31G* basis set. SCF and MP2 curves are based on data from Ref. [13].

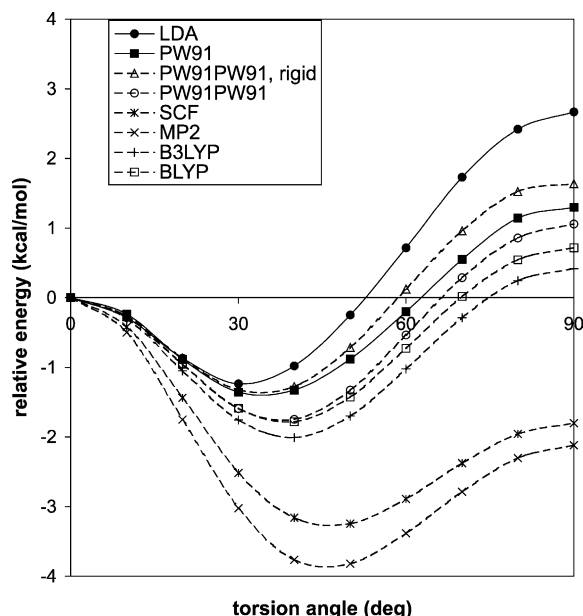


Fig. 3. Torsional potentials of biphenyl around the central CC single bond. Solid lines by VASP (rigid rotor), dashed lines by GAUSSIAN 98 using 6-31G* basis set. SCF, MP2, and B3LYP curves are based on data from Ref. [13].

of Single-walled Carbon Nanotubes (SWCN's) [5]. The C–H A_{1g} mode is, as expected, far from experiment. The B_{2u} mode at 1309 cm^{-1} is bad and this error is related to the correlation problem as discussed by Pulay et al. [26]. Still, the plane-wave and Gaussian type implementations perform similarly.

Naphthalene is included as an example of a polycyclic aromatic hydrocarbon. Bond distances for naphthalene are compared in Table 5. The pattern observed before is repeated here: LDA underestimates all CC bond lengths. The four GGA functionals produce similar results. In all cases bond R3 is the shortest, in agreement with both X-ray and gas-phase electron diffraction experiments [37,38]. Again, the Gaussian based PW91 results and the plane wave PW91 functionals produce similar geometries.

For polymeric systems, we calculated the optimized geometry of polyethylene and *trans*-polyacetylene as examples. The optimized geometrical parameters are listed in Table 6 along with experimental data [39–41]. As in molecular systems, LDA approximation in VASP generally gives short C–C bond length as compared to GGA approximations and GGA results agree with experimental results quite well. Using (7111/411/1*) basis set, Miao et al. [42] obtained bond lengths close to experimental values for polyethylene by LDA. The differences between the results corresponding to different functionals and local vs. plane wave basis sets are not negligible, and amount to as much as $0.02\text{--}0.03\text{ \AA}$.

Bond length alternation of *trans*-polyacetylene has attracted considerable attention. As a solid state program, it is of interest to know how VASP behaves on this problem. In addition to 1,3-butadiene and *trans*-polyacetylene, we performed geometry

Table 4

The theoretical and experimental geometrical parameters of graphene and benzene and the frequencies of the A_{1g} and B_{2u} modes of benzene

	LDA	PB	LM	PW86	PW91	PW91PW91/6-31G** ^a	Exp.
R_{CC} (graph)	1.409	1.422	1.422	1.426	1.422	–	1.42 ^b
R_{C-C}	1.382	1.392	1.394	1.396	1.393	1.402	1.3902 ^c
R_{C-H}	1.093	1.092	1.102	1.092	1.089	1.094	1.0862 ^c
A_{1g}	1017				992	1001	993 (994) ^d
A_{1g}	3104				3129	3149	3074 (3191) ^d
B_{2u}	1161				1136	1156	1150 (1150) ^d
B_{2u}	1393				1352	1366	1309 (1309) ^d

Bond lengths in \AA , angles in degrees, frequencies in cm^{-1} . Calculations refer to VASP results except otherwise noted.

^a This work. GAUSSIAN 98 calculation.

^b Taken from Refs. [32–34].

^c Taken from Ref. [35].

^d Taken from Ref. [36]. Harmonic values in parentheses.

Table 5

The theoretical and experimental geometrical parameters of naphthalene

	LDA	PB	LM	PW86	PW91	B3LYP/6-31G*	PW91PW91/6-31G*	X-ray ^a	GED ^b
R1	1.421	1.436	1.433	1.440	1.432	1.434	1.441	1.426(1)	1.412(8)
R2	1.404	1.417	1.417	1.420	1.417	1.421	1.424	1.425(1)	1.422(2)
R3	1.365	1.376	1.378	1.379	1.376	1.377	1.384	1.378(1)	1.381(2)
R4	1.401	1.413	1.414	1.417	1.412	1.417	1.419	1.421(1)	1.417(4)

Bond lengths in Å, angles in deg. See Fig. 1 for parameter definitions. Calculations refer to VASP results except otherwise noted.

^a X-ray data from Ref. [37].^b Gas electron diffraction data from Ref. [38].

optimizations on 1,3,5-hexatriene using PW91 functional. For comparison, geometries of 1,3,5-hexatriene were also optimized using PW91PW91/6-31G* by GAUSSIAN 98.

The bond length alternation results for 1,3-butadiene, 1,3,5-hexatriene and *trans*-polyacetylene are summarized in Fig. 4. Also shown in Fig. 4 are typical results from earlier work [14], where a more broad selection of theoretical approaches, including HF, MP2, UNOCAS, BLYP and B3LYP with various basis sets, are used. The plane wave basis set based PW91 bond length alternation values for 1,3-butadiene and 1,3,5-hexatriene are essentially the same as the PW91/6-31G* values.

The bond length alternation of *trans*-polyacetylene is predicted as 0.029 Å by the plane wave PW91 VASP calculation. This prediction falls into the general range of 0.01–0.05 Å given by post-HF methods [14], MP2, and DFT, but is significantly smaller than the experimentally established range of 0.08–0.09 Å [40,41].

VASP calculation using LDA functional gives 0.025 Å bond length alternation in *trans*-polyacetylene, which is essentially the same to earlier result using 9s5p/4s1p basis by Mintmire and White [43], although their bond lengths are about 0.02–0.03 Å longer than ours due to their fixed lattice spacing. The series of PW91 calculations for $N = 4, 6$, and

Table 6

The theoretical and experimental geometrical parameters of polyethylene and polyacetylene

		LDA	PB	LM	PW86	PW91	LDA ^{a,b}	LDA ^c	Exp. ^{d,e}	Exp. ^f
Polyethylene	R_{C-C}	1.504	1.529	1.518	1.532	1.528	1.534 ^a	1.515 ^c	1.541 ^d	
	R_{C-H}	1.107	1.103	1.114	1.103	1.102				
	A_{C-C-C}	113.6	113.7	113.5	113.7	113.6	113.0 ^a	113.0 ^c	112.0 ^d	
	A_{C-C-H}	109.4	109.3	109.3	109.2	109.3	110.0 ^a	109.7 ^c		
	A_{H-C-H}	105.5	105.8	105.7	105.9	105.9				
Polyacetylene	$R_{C=C}$	1.365	1.377	1.379	1.379	1.378	1.399 ^b		1.36 ^e	1.36 ^f
	R_{C-C}	1.390	1.408	1.405	1.411	1.407	1.430 ^b		1.45 ^e	1.44 ^f
	R_{C-H}	1.101	1.095	1.106	1.095	1.094				
	$A_{C=C-C}$	124.1	124.7	124.4	124.7	124.6			122 ^e	
	$A_{C=C-H}$	118.2	118.0	118.1	118.0	118.0				
	A_{C-C-H}	117.7	117.3	117.5	117.3	117.4				

Bond lengths in Å, angles in degrees. VASP calculations except otherwise noted.

^a Taken from Ref. [39] using GKS exchange and 7111/411/1* basis set.^b Taken from Ref. [40] using 9s5p/4s1p basis set.^c Taken from Ref. [39] using PZ method and 7111/411/1* basis set.^d Taken from Ref. [36].^e Taken from Ref. [37].^f Taken from Ref. [38].

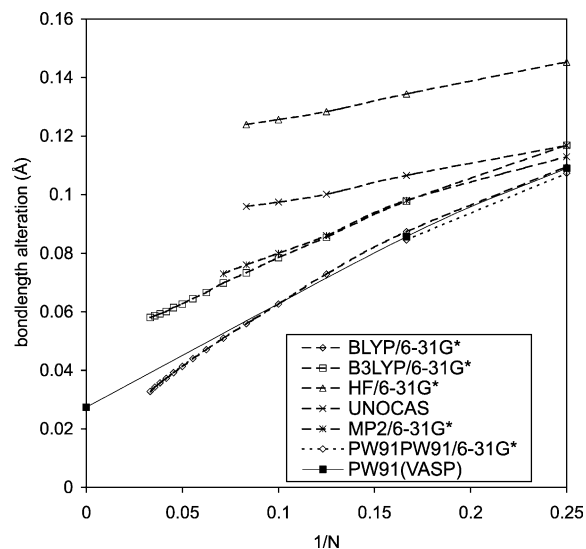


Fig. 4. Calculated bond length alteration of oligoenes and polyacetylene as a function of $1/N$, the number of carbon atoms. All curves except the ones with the PW91 density functional are based on data from Ref. [14].

∞ (1D infinite polymer), reflect a similar trend, predicting an alternation that is not much of an improvement over the LDA results. The solution of this problem awaits better density functionals. It is important to note in the context of the present comparative study, however, that the performance of VASP on this problem is fully consistent with Gaussian basis set calculations. We have used the VASP program to investigate periodic systems ranging from neutral and doped *trans*-polyacetylene [44], intercalated graphite [45] and single-walled carbon nanotubes [45,46], where good agreement with available experimental data were obtained.

In conclusion, the plane wave VASP code performs very similarly to the Gaussian implementation of PW91 density functional theories at a medium basis set level (6-31G*) for a variety of chemical systems and problems involving total energy differences, optimized geometries and normal mode frequencies. It is expected, that plane wave codes including VASP will continue to be applied successfully to chemical problems traditionally thought of as involving electronic systems that are not free-electron like.

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