J. Phys. Chem. A **2007,** *111,* 2028−2032

Polarizability of Small Carbon Cluster Anions from First Principles

Olga Guliamov and Leeor Kronik*

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

Jan M. L. Martin[†]

Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth 76100, Israel

Received: December 8, 2006; In Final Form: January 11, 2007

We examine the applicability of density functional theory (DFT) to the polarizability of C_n^- ($n = 3-9$) cluster anions. This was achieved by comparing DFT calculations using two different exchange-correlation functionals (the non-empirical local density approximation, LDA, and the semiempirical hybrid functional B97-1) to quantum chemical calculations using the coupled cluster method in the CCSD(T) "gold standard" approximation. We find that, unless the extra electron is not bound at all by DFT, both LDA and B97-1 agree with the CCSD(T) calculation to within 5−10%, allowing for a meaningful qualitative and semiquantitative analysis. Furthermore, the polarizability is found to increase monotonically with chain size, consistent with the trend inferred from electron detachment experiments.

I. Introduction

The electric-dipole polarizability, i.e., the response of the electrical dipole to an external electric field, is a very important property of atoms, molecules, and clusters.[1,2] For example, the polarizability plays an important role in understanding electromagnetic field-matter interactions and in understanding interparticle collision phenomena. Importantly, the polarizability of a given object is a strong function of its size, shape, electronic structure, etc. Specifically, experimental and theoretical studies of cluster polarizability as a function of size have been used extensively for understanding trends in geometrical and electronic structure evolution in clusters (see, e.g., refs 3−9).

The above studies were all performed on neutral clusters. Very little work has been devoted to anion polarizability. Experimentally, the reason is that anion polarizabilities are very difficult to measure, as the response to an external electric field is dominated by the monopole contribution. Perhaps as a consequence, we are aware of only a few theoretical calculations of anion polarizability for atoms and molecules[10−12] (all without comparison to experiment) and none for clusters.

Even if not directly accessible experimentally, anion polarizability may still be significant in other cluster measurements. An important recent example is given by electron detachment experiments, where polarization by the incident electron is believed to play an important role in the detachment process.[13−15] This can be understood phenomenologically by considering that electron detachment occurs mainly at the point of closest approach, where the incoming electron has minimal kinetic energy.[16] The attractive nature of the polarization potential will reduce the distance of closest approach, thus resulting in a larger distortion of the initial wave function and an enhanced electron detachment. Several theoretical studies have included a phenomenological polarization potential, [17,18] but the contribution of the polarizability to the electron detachment process has never been studied systematically, mostly due to lack of relevant experimental or theoretical data.

In light of the above, an accurate theoretical approach for computing anion polarizability from first principles is of interest. Density functional theory (DFT),[19] the "work-horse" of electronic structure calculations for "real-world" materials, is a natural candidate for such calculations. However, there are serious concerns as to the accuracy with which present-day approximate density functionals can correctly describe small anions. All functionals in common use today (including hybrid functionals) suffer from a spurious self-interaction error.[20] This means that the exchange-correlation energy does not exactly cancel the spurious Coulomb repulsion of an electron with itself, present in the classical electrostatic (Hartree) energy. As a consequence, the asymptotic behavior of the exchange-correlation potential is described incorrectly, decaying as $-(Z - N)/r$ instead of the correct $-(Z - N + 1)/r$, where Z is the number of protons in the nuclei, N represents the number of electrons in the system, and r stands for the distance from the system's center. Therefore, density functional calculations often fail to bind the extra electron in anions,[21] and other physical properties, including polarizability, can be in serious error. Obviously wave function based quantum chemistry approaches, and in particular the coupled cluster (CC) method,[22] which is often considered to be the "gold standard of quantum chemistry", do not suffer from this problem. However, their computational cost increases very rapidly with increasing cluster/molecule size.

In this article, we examine the applicability of DFT to the study of cluster anion polarizability. This is accomplished by studying theoretically the polarizability of small C_n^- cluster anions ($3 \le n \le 9$).[23] Those are chosen as a model system for two main reasons: First, both carbon cluster neutrals[24−29] and anions[26,30−33] have been well-investigated in general and in particular are known to possess a linear chain ground state structure, eliminating complications arising from structure (mis)identification. Second, carbon cluster anions have been recently studied by electron detachment experiments,[13] thus

---

* Corresponding author. E-mail: leeor.kronik@weizmann.ac.il.

[†] E-mail: Gershom.Martin@weizmann.ac.il.

10.1021/jp068443y CCC: $37.00

TABLE 1: Calculated and Experimental Geometries of Linear Neutral Carbon Clusters[a]

cluster	method	bond length
C_3	experiment[58]	1.297
	B97-1/aug-pc1	1.299
	B97-1/aug-pc2	1.292
	B3LYP/cc-pVDZ[28]	1.301
	UHF/6-31G*[25]	1.278
	ROHF/DZP[26]	1.286
	MBPT(2)/6-31G*[24]	1.303
	CCSD(T)/cc-pVDZ[29]	1.321
C_4	B97-1/aug-pc1	1.317;1.297
	B97-1/aug-pc2	1.309;1.287
	B3LYP/cc-pVDZ[28]	1.319;1.298
	DFT/BP86[27]	1.322;1.299
	ROHF/DZP[26]	1.300;1.288
	CCSD(T)/cc-pVDZ[29]	1.336;1.312
	MBPT(2)/6-31G*[24]	1.313;1.296
C_5	B97-1/aug-pc1	1.295;1.289
	B97-1/aug-pc2	1.287;1.282
	B3LYP/cc-pVDZ[28]	1.296;1.291
	DFT/BP86[27]	1.299;1.290
	UHF/6-31G*[25]	1.271;1.275
	ROHF/DZP[26]	1.278;1.281
	MBPT(2)/6-31G*[24]	1.300;1.291
	CCSD(T)/cc-pVDZ[29]	1.316;1.306
C_6	B97-1/aug-pc1	1.308; 1.294; 1.281
	B3LYP/cc-pVDZ[28]	1.309; 1.296; 1.283
	DFT/BP86[27]	1.312; 1.296; 1.282
	ROHF/DZP[26]	1.287; 1.285; 1.274
	MBPT(2)/6-31G*[24]	1.301; 1.294; 1.281
	CCSD(T)/cc-pVDZ[29]	1.326; 1.309; 1.297
C_7	B97-1/aug-pc1	1.294; 1.294; 1.279
	B3LYP/cc-pVDZ[28]	1.296; 1.295; 1.281
	DFT/BP86[27]	1.299; 1.294; 1.280
	UHF/6-31G*[25]	1.270; 1.280; 1.264
	ROHF/DZP[26]	1.276; 1.285; 1.269
	MBPT(2)/6-31G*[24]	1.301; 1.295; 1.282
	CCSD(T)/cc-pVDZ[29]	1.316; 1.310; 1.296
C_8	B97-1/aug-pc1	1.303; 1.296; 1.280; 1.287
	B3LYP/cc-pVDZ[28]	1.305; 1.297; 1.282; 1.289
	DFT/BP86[27]	1.307; 1.297; 1.281; 1.288
	ROHF/DZP[26]	1.281; 1.288; 1.270; 1.277
	MBPT(2)/6-31G*[24]	1.294; 1.297; 1.279; 1.287
	CCSD(T)/cc-pVDZ[29]	1.321; 1.311; 1.296; 1.302
C_9	B97-1/aug-pc1	1.294; 1.296; 1.277; 1.283
	B3LYP/cc-pVDZ[28]	1.295; 1.298; 1.279; 1.285
	DFT/BP86[27]	1.298; 1.297; 1.278; 1.283
	UHF/6-31G*[25]	1.269; 1.283; 1.261; 1.269
	ROHF/DZP[26]	1.275; 1.289; 1.265; 1.273
	MBPT(2)/6-31G*[24]	1.302; 1.298; 1.281; 1.286
	CCSD(T)/cc-pVDZ[29]	1.316; 1.312; 1.295; 1.299

[a] For each cluster size, bond lengths are given in the order of appearance from chain edge to chain center.

facilitating at least an indirect comparison between theory and experiment. The applicability of DFT is assessed by performing DFT calculations with two different approximations for the exchange-correlation functional: the non-empirical local density approximation (LDA)[34] and the semiempirical hybrid functional B97-1.[35,36] The resulting trends are then compared to both highly accurate CC calculations (using single, double, and triple excitations, with triple excitations treated perturbatively [CCSD(T)]) and to trends expected from the electron detachment experiments.

II. Computational Details

Non-empirical DFT calculations were performed using LDA.[34] This is the simplest, and historically the first,[19] modern approximate exchange-correlation functional. In LDA, the exchange-correlation energy contribution of each point in space is taken as that of a homogeneous electron gas possessing the local density. All DFT-LDA calculations were performed by employing norm-conserving pseudopotentials[37] in conjunction with a uniform real-space grid,[38] using the PARSEC[39] software suite. The grid was set up within a spherical domain as large as 26 a.u., with a grid spacing of 0.3 au. Polarizabilities were computed numerically using the finite field approach[4,5] with an external electric field value chosen to be 10^{-3} a.u.

Semiempirical DFT calculations were performed using the B97-1 hybrid functional.[35,36] Hybrid functionals are typically comprised of a weighted sum of LDA exchange-correlation, density gradient corrections to the LDA, and Fock exchange.[40] The corresponding weights are optimized empirically so as to provide for best agreement across a large set of experimental data, typically collected for various organic molecules. We choose the B97-1 re-parametrization of the Becke functional because it is well-tested, producing structures that are similar to (or even slightly better than) those obtained by the better-known B3LYP,[41] while outperforming B3LYP in the prediction of energetic properties.[42] All B97-1 calculations were performed using the polarization-consistent aug-pc-1 basis set developed by Jensen et al.[43] specifically for DFT, using the GAUSSIAN03 software suite.[44] This basis set was found to be adequate for our purposes through comparison with calculations using a larger basis set from the same "family"—aug-pc-2.[43] Polarizability calculations were performed analytically.

All wavefunction-based calculations were performed using the coupled cluster (CC) approximation. In principle, this method can be arbitrarily accurate. In practice, its application involves two approximations: One due to the use of a finite (and low) order of expansion and another due to a truncation error associated with the use of a finite basis set. Here, we have employed the popular CCSD(T)[45] method and additionally compared its results with those obtained from the simpler CCSD[46] method (where no triple excitations are considered). We performed the CC calculations based on both a restricted open and an unrestricted Hartree−Fock configuration, using the MOLPRO[47] and GAUSSIAN03 software suites, respectively. The aug-cc-pvdz and aug-cc-pvtz basis sets[48] were used in both calculations, with some additional aug-cc-pvqz calculations for testing convergence. Polarizability was computed analytically within GAUSSIAN and numerically, using a finite field of 0.0025 a.u., within MOLPRO.

In the DFT calculations, linear carbon cluster neutrals and anions were optimized such that all forces were smaller than $7 \cdot 10^{-4}$ Ry/au. For the CC calculations, the B97-1/aug-pc-1 geometries were used.

III. Results and Discussion

To provide a reference point for the expected differences between the DFT and CC results, we started by computing polarizabilites of neutral C_n ($3 \leq n \leq 9$) clusters, in their linear geometry. The results, compared with those of previous theoretical studies (and with experiment for C_3), are given in Table 1. Clearly, agreement with both past theoretical results and experiment is quite satisfactory.

The results of both DFT and (restricted open-shell) CC neutral polarizability calculations are shown in Figure 1 (numerical

TABLE 2: Calculated and Experimental Geometries of Linear Carbon Cluster Anions[a]

cluster	method	bond length
C_3^-	B97-1/aug-pc1	1.313
	B97-1/aug-pc2	1.305
	DFT/LDA	1.321
	ROHF/DZP[26]	1.301
	HF/6-31G*[30]	1.301
	MBPT(2)/6s4p1d[31]	1.317
C_4^-	B97-1/aug-pc1	1.283;1.343
	B97-1/aug-pc2	1.275;1.337
	DFT/LDA	1.287;1.366
	ROHF/DZP[26]	1.265;1.349
	SQD-MBPT(4)/5s4p1d[32]	1.283;1.343
C_5^-	B97-1/aug-pc1	1.292;1.307
	B97-1/aug-pc2	1.284;1.300
	DFT/LDA	1.290;1.322
	ROHF/DZP[26]	1.269;1.309
	MBPT(2)/6s4p1d[31]	1.296;1.323
C_6^-	B97-1/aug-pc1	1.280; 1.332; 1.259
	DFT/LDA	1.276; 1.330; 1.267
	ROHF/DZP[26]	1.258; 1.340; 1.237
	MBPT(2)/6s4p1d[33]	1.293; 1.341; 1.290
C_7^-	B97-1/aug-pc1	1.286; 1.314; 1.284
	DFT/LDA	1.279; 1.312; 1.296
	ROHF/DZP[26]	1.261; 1.321; 1.270
C_8^-	B97-1/aug-pc1	1.280; 1.328; 1.259; 1.320
	DFT/LDA	1.275; 1.322; 1.271; 1.336
	ROHF/DZP[26]	1.257; 1.337; 1.234; 1.332
C_9^-	B97-1/aug-pc1	1.284; 1.317; 1.275; 1.293
	DFT/LDA	1.272; 1.298; 1.278; 1.310
	ROHF/DZP[26]	1.257; 1.327; 1.251; 1.292

[a] For each cluster size, bond lengths are given in the order of appearance from chain edge to chain center.

values are tabulated in the Supporting Information). In this figure, LDA results are taken from ref 49, but in order to ascertain the accuracy of our own LDA calculations we have successfully reproduced a selection of these LDA values. Clearly, for most cluster sizes, the deviation between values obtained using different methods is several percent at most. Within DFT, the LDA and B97-1 polarizability values deviated by less than 1.5%, except for C_9, where the deviation was a larger 5.5%. Within CC, differences between CCSD and CCSD(T) calculations tended to increase with cluster size, with a maximal deviation of ~5% for C_9. The deviation between the CCSD(T) and DFT/ B97-1 results also tended to grow with cluster size. It reached a sizable ~15% for C_9, but was only, e.g., ~5% for C_8. These trends agree with the recent work of Sałek et al., who found differences of the same magnitude between the DFT and CC polarizabilities of, e.g., HF, CO, and H_2O.[50]

Next, we turned to calculations of the cluster anion polarizabilities, again starting with geometry optimization. Computed geometries, The results, compared with those of previous theoretical studies,[26,30−33] are given in Table 2. Clearly, agreement here is essentially as good as for the neutrals.

The results of both DFT and (spin-unrestricted) CC anion polarizability calculations are shown in Figure 2 (numerical values are tabulated in the Supporting Information). Three values are missing from the figure: For C_3^-, LDA failed to bind the extra electron (i.e., yielded a highest occupied molecular orbital energy greater than zero), yielding essentially infinite (and obviously physically meaningless) polarizability values which were omitted.[51] For C_8^-, the CC polarizability calculations exhibited serious convergence problems and both the CCSD and the CCSD(T) values are omitted.

Unlike for the neutrals, CC calculations of anions were based on an unrestricted Hartree−Fock (UHF)[52] configuration. CC calculations based on restricted-open Hartree−Fock (ROHF)[53] were also performed. However, in some cases, they gave highly erroneous results—an underestimate of 11.4% and 26.5% for C_4^- and C_6^- clusters, respectively. We believe that this is due to a symmetry breaking problem[54] during the solution of ROHF under an electric field perturbation, which renders the restricted calculation irrelevant.

Importantly, we find that, just as for the neutrals, the polarizability trends calculated by all methods are qualitatively the same. Within DFT, a maximal deviation of ~7% between the LDA and B97-1 results was found (for C_5^-), but the average deviation was only ~3.5%. Within CC, the maximal deviation between CCSD and CCSD(T) results was ~10%. Interestingly, this deviation is somewhat larger than for the neutrals, despite a similar role for high-order correlations in the total atomization energy of neutrals and anions. This indicates a slightly larger role of high-order correlations for the anions under an electric field. Overall, the average deviation of polarizability values between the DFT and CC calculations was ~5%. Interestingly, the maximum deviation between the LDA and the CCSD(T) results is only ~7%. This is actually no worse, and in fact slightly better, than for the neutrals, despite the apparent crudeness of the LDA in this case.

That DFT provides polarizability values that are within a few percent of those obtained from highly accurate CC calculations—despite the fact that (at least) the orbital of the highest electron is sufficiently delocalized to "feel" the incorrect asymptotic regime—merits a physical explanation. It was previously pointed out, in the context of vibrational spectra of linear carbon cluster neutrals, that complete neglect of electron correlation in such borderline-multireference systems appears to be more likely to yield qualitatively correct results than low-order inclusion of electron correlation.[55] Here, for both the carbon neutrals and anions, the contribution of correlation to the polarizability (per a given DFT-based geometry) was not large. This is evident from the relatively modest differences between CCSD(T) and CCSD, but even the Hartree−Fock polarizability was reasonably similar to the CCSD(T) one. However, this does not explain the success of the DFT calculations because a major problem with DFT (with either LDA or hybrid functionals) is that the exchange term is also approximated, and this results, e.g., in the incorrect asymptotic behavior of the potential. This problem is well-illustrated by considering the case of a model hydrogen chain.[56] Grossly overestimated values were obtained with LDA. However, using exact exchange (and no correlation) within DFT yielded polarizability values that were essentially the same as those obtained from Hartree−Fock and close to those obtained from correlated wave function calculations. Why is it, then, that the approximate treatment of exchange does not cause such a catastrophic failure here? It has been previously observed that there are cases where DFT (and, in particular, LDA) produces an eigenvalue spectrum that is grossly underbound, but the shape of the orbitals is still very close to the correct one.[57] In such cases, the dipole—as well as its response to the electric field, i.e., the polarizability—will still be reasonable. Of course, if the electron is not at all bound, as in the LDA of C_3^-, this does not

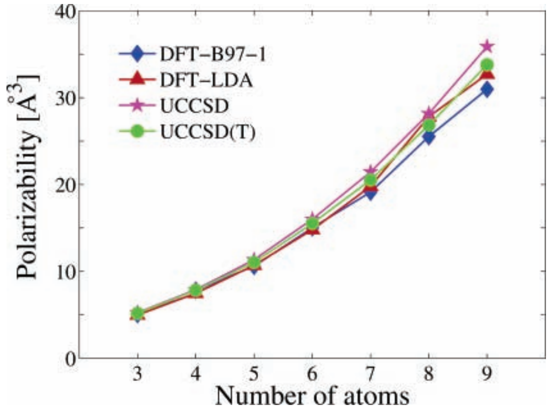

Figure 1. Average total polarizability of neutral carbon chains.

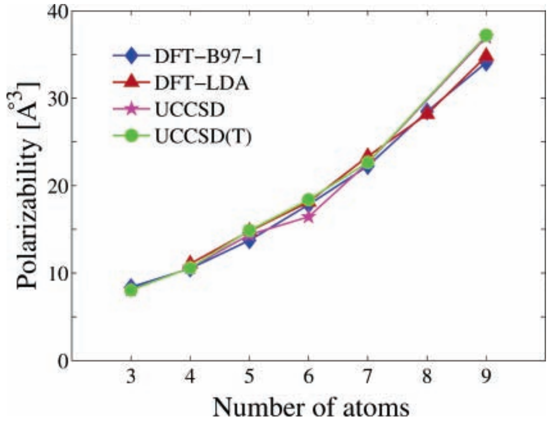

Figure 2. Average total polarizability of anion carbon chains.

help. But in all other cases it suffices for obtaining a result that is at least in semiquantitative agreement with more accurate calculations.

Comparing Figures 1 and 2, we find that the polarizability increases monotonically with cluster size, with a similar overall trend. However, polarizabilities for the anion clusters are always larger than those for the corresponding neutral cluster (computed using the same method). This is simply due to the presence of an additional, relatively weakly bound, electron to polarize. However, this effect decreases rapidly with cluster size, such that for C_9^- the anion/neutral polarizability ratio is only ∼1.06. This is because the larger the cluster is, the smaller the relative contribution of the excess electron. This provides clear-cut computational support to an interpretation of detachment cross-section trends in terms of polarizability.[13] It rationalizes the fact that, for carbon anions, both the detachment cross-section and the binding energy increase on average with increasing cluster size, whereas in the absence of polarization effects they should exhibit opposite trends.

IV. Conclusions

In conclusion, we have computed the polarizability of carbon cluster anions by means of both CC and DFT, in order to assess the applicability of the latter method to the calculation of anion polarizability. We found that DFT calculations with either LDA or a hybrid functional agree with highly accurate CCSD(T) calculations to within ∼5−10%, unless the extra electron is not bound at all within DFT. This allows for a meaningful qualitative and semiquantitative analysis. In particular, we found that the carbon cluster anion polarizability increases monotonically with chain size, an observation consistent with the trend inferred from electron detachment experiments.

Acknowledgment. We wish to thank D. Zajfman (Weizmann Institute) and L. Cederbaum (Max-Planck-Institut, Heidelberg) for motivating this work and for illuminating discussions. We also thank S. Kümmel (Bayreuth University) for illuminating discussions. L.K. acknowledges the support of the Delta Career Development Chair and the ‘‘Phoremost” European Network of Excellence. J.M.L.M. is the Baroness Thatcher Professor of Chemistry and acknowledges support by the Minerva Foundation, the Lise Meitner−Minerva Center for Computational Quantum Chemistry, the Israel Science Foundation, and the Ilse Katz Institute for Materials and Magnetic Resonance Research (Weizmann Institute).

Supporting Information Available: Tables of total polarizabilities. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bonin, K. D.; Kresin, V. V. *Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters*; World Scientific: Singapore, 1997. and references therein.

(2) Maroulis, G. Editor, *Atoms, Molecules and Clusters in Electric Fields: Theoretical Approaches to the Calculation of Electric Polarizability*; Imperial College Press: London, 2006. And references therein.

(3) Knight, W. D.; Clemenger, K.; de Heer, W. A.; Saunders, W. A. *Phys. Rev. B* **1985**, *31*, 2539.

(4) Kümmel, S.; Akola, J.; Manninen, M. L. *Phys. Rev. Lett.* **2000**, 84, 3827; Kronik, L.; Vasiliev, I.; Jain, M.; Chelikowsky, J. R. *J. Chem. Phys.* **2001**, *115*, 4322.

(5) Vasiliev, I.; Öğüt, S.; Chelikowsky, J. R. *Phys. Rev. Lett.* **1997**, *78*, 4805.

(6) de Heer, W. A.; Milani, P.; Chatelain, A. *Phys. Rev. Lett.* **1989**, *63*, 2834.

(7) Benichou, E., Antoine, R.; Rayane, D.; Vezin, B.; Dalby, F. W.; Dugourd, P.; Broyer, M.; Ristori, C.; Chandezon, F.; Huber, B. A.; Rocco, J. C.; Blundell, S. A.; Guet, C. *Phys. Rev. A* **1999**, *59*, R1.

(8) Troparevsky, M. C.; Chelikowsky, J. R. *J. Chem. Phys.* **2000**, *114*, 943; Karamanis, P.; Maroulis, G.; Pouchan, C. *J. Chem. Phys.* **2006**, *124*, 071101.

(9) Pouchan, C.; Bégué, D.; Zhang, D. Y. *J. Chem. Phys.* **2004**, *121*, 4628.

(10) Ventura, O. N.; Kieninger, M.; Cernusak, I. *J. Mol. Struct.* **1997**, *436−437*, 489.

(11) Xue, Z.; Chen, C. *Electrochim. Acta* **2004**, *49*, 5167.

(12) Domene, C.; Fowler, P. W.; Jemmer, P.; Madden, P. *Chem. Phys. Lett.* **1999**, *299*, 51.

(13) Diner, A.; Toker, Y.; Strasser, D.; Heber, O.; Ben-Itzhak, I.; Witte, P. D.; Wolf, A.; Schwalm, D.; Rappaport, M. L.; Bhushan, K. G.; Zajfman, D. *Phys. Rev. Lett.* **2004**, *93*, 063402.

(14) Zajfman, D.; Heber, O.; Diner, A.; Witte, P.; Strasser, D.; Toker, Y.; Rappaport, M.; Ben-Itzhak, I.; Guliamov, O.; Kronik, L.; Schwalm, D.; Wolf, A. *Inst. Phys. Conf. Ser.* **2005**, *183*, 173.

(15) El Ghazaly, M. O. A.; Svendsen, A.; Bluhme, H.; Nielsen, S. B.; Andersen, L. H. *Chem. Phys. Lett.* **2005**, *405*, 278.

(16) Robicheaux, F. *Phys. Rev. Lett.* **1999**, *82*, 707; Robicheaux, F. *Phys. Rev. A* **1999**, *60*, 1206.

(17) Pindzola, M. *Phys. Rev. A* **1996**, *54*, 3671.

(18) Ostrovsky, M.; Taulbjerg, K. *J. Phys. B* **1996**, *29*, 2573.

(19) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, B136; Kohn, W.; Sham, L. *Phys. Rev.* **1965**, A1403.

(20) Perdew, J. P.; Zunger, A. *Phys. Rev.* **1981**, *B23*, 5048.

(21) See, e.g., Rösch, N.; Trickey, S. B. *J. Chem. Phys.* **1997**, *106*, 8940. and references therein. Because of error cancellation between neutral and anionic forms, and because the use of finite Gaussian basis sets effectively confines the unbound electron to a spherical “box”, electron affinities for such systems are often quite reasonable: see, e.g., de Oliveira, G.; Martin, J. M. L.; de Proft, F.; Geerlings, P. *Phys. Rev. A* **1999**, *60*, 1034; and references therein.

(22) Čížek, J. *J. Chem. Phys* **1966**, *45*, 4256.

(23) We do not discuss the carbon dimer here because it is well-known to have a “pathological” multi-reference character and lessons learned from it are not directly applicable to the larger systems. See, e.g., Sherrill, C. D.; Piecuch, P. *J. Chem. Phys.* **2005**, *122*, 124104, and references therein.

(24) Kurtz, J.; Adamowicz, L. *Astrophys. J.* **1991**, *370*, 784.

(25) Raghavachari, K.; Binkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191.

(26) Watts, J.; Bartlett, R. *J. Chem. Phys.* **1992**, *97*, 3445.

(27) Hutter, J.; Lüthi, H. P.; Diederich, F. *J. Am. Chem. Soc.* **1994**, *116*, 750.

(28) Martin, J. M. L.; El-Yazal, J.; François, J. P. *Chem. Phys. Lett.* **1995**, *242*, 570.

(29) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem.* **1996**, *100*, 6047.

(30) Raghavachari, K. *Chem. Phys. Lett.* **1990**, *171*, 249.

(31) Adamowicz, L. *Chem. Phys. Lett.* **1991**, *180*, 466.

(32) Watts, J.; Cernusak I.; Bartlett, R. J. *Chem. Phys. Lett.* **1991**, *178*, 259.

(33) Adamowicz, L. *Chem. Phys. Lett.* **1991**, *182*, 45.

(34) Ceperley, D. M.; Alder, B. J. *Phys. Rev. Lett.* **1980**, *45*, 566; Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(35) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554.

(36) Hamprecht, F.; Cohen, A.; Tozer, D.; Handy, N. *J. Chem. Phys.* **1998**, *109*, 6264.

(37) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993. A carbon pseudopotential based on an electronic configurations of $2s^2 2p^2$ with a core cutoff radius of 1.3 au for both s and p electrons was used.

(38) Chelikowsky, J. R.; Troullier, N.; Saad, Y. *Phys. Rev. Lett.* **1994**, *72*, 1240.

(39) Kronik, L.; Makmal, A.; Tiago, M. L.; Alemany, M. M. G.; Jain, M.; Huang, X. Y.; Saad, Y.; Chelikowsky, J. R. *Phys. Stat. Sol. (b)* **2006**, *243*, 1063.

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

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

(42) Boese, A. D.; Martin, J. M. L.; Handy, N. C. *J. Chem. Phys.* **2003**, *119*, 3005.

(43) Jensen, F. *J. Chem. Phys.* **2002**, *116*, 7273.

(44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.01wis2 (WIS customized version 2); Gaussian, Inc., Wallingford, CT, 2004.

(45) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(46) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041.

(47) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklaβ, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO*, version 2002.6 (www.molpro.net).

(48) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(49) Abdurahman, A.; Shukla, A.; Seifert, G. *Phys. Rev. B* **2002**, *66*, 155423.

(50) Sałek, P.; Helgaker, T.; Vahtras, O.; Ågren, H.; Jonsson, D.; Gauss, J. *Mol. Phys.* **2005**, *103*, 439.

(51) Note that in the preliminary work of ref. 14, finite LDA polarizability values for C_2^- and C_3^- were shown. These values are not physically meaningful. Finite values will always be obtained for any choice of a finite real-space domain, as the "walls" of the domain limit the variational freedom of the Kohn−Sham orbitals. In a similar vein, finite values for polarizability of anions that are unbound within LDA can also be obtained with a finite localized basis set [see, e.g., Galbraith, J. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1996**, *105*, 862]. As pointed out in ref. 21, these values are not physical either. Also note that the B97-1 calculation yielded a marginally bound electron and, to an extent, may be susceptible to the same problem despite its good agreement with the CC calculations.

(52) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(53) McWeeny, R.; Dierksen, G. *J. Chem. Phys.* **1968**, *49*, 4852.

(54) Martin, J. M. L.; El-Yazal, J.; François, J. P.; Gijbels, R. *Mol. Phys.* **1995**, *85*, 527.

(55) Martin, J. M. L.; François, J. P.; Gijbels, R. *J. Chem. Phys.* **1990**, *93*, 8850.

(56) Kümmel, S.; Kronik, L.; Perdew, J. P. *Phys. Rev Lett.* **2004**, *93*, 213002; and references therein.

(57) Wasserman, A.; Burke, K. *Phys. Rev. Lett.* **2005**, *95*, 163006.

(58) Hinkle, K. W.; Keady, J. J.; Bernath, P. F. *Science* **1988**, *241*, 1319.