Binding Energies in Benzene Dimers: Nonlocal Density Functional Calculations

Aaron Puzder, Maxime Dion, and David C. Langreth

Center for Materials Theory, Department of Physics and Astronomy
Rutgers University, Piscataway, New Jersey 08854-8019

(Dated: December 23, 2021)

Abstract

The interaction energy and minimum energy structure for different geometries of the benzene dimer has been calculated using the recently developed nonlocal correlation energy functional for calculating dispersion interactions. The comparison of this straightforward and relatively quick density functional based method with recent calculations can elucidate how the former, quicker method might be exploited in larger more complicated biological, organic, aromatic, and even infinite systems such as molecules physisorbed on surfaces, and van der Waals crystals.

PACS numbers: 71.15.Mb, 31.15.Ew, 31.25.Nj

*Present address: Lawrence Livermore National Laboratory, Livermore, California 94550
I. INTRODUCTION

Nonempirical density functionals of semilocal or generalized gradient approximation (GGA) type have met with a good degree of success when applied to either isolated molecules or dense solid-state systems. Generally such approximations do not include the long range dispersion or van der Waals (vdW) interaction, and hence fail or at best give sporadic results for sparse matter or for the wide range of molecular complexes where the dispersion interaction is an important component of the binding. Even semiempirical gradient functionals typically fail for such systems, in the sense that their parameters must be varied from system to system, and thus lose most of their predictive power.

Over the course of the last several years the Chalmers-Rutgers collaboration has developed a nonempirical density functional for the correlation energy which showed considerable promise in alleviating the above undesirable situation. This correlation energy functional is not of the GGA type, but involves a fully non-local integration over pairs of densities at distant points. Nevertheless it is very quick to evaluate and does not significantly lengthen a simple GGA density functional calculation for a sufficiently large system. As proposed, this nonempirical correlation functional has no corresponding nonempirical exchange functional. Because the Zhang-Yang GGA “revPBE” exchange functional had been fitted to exact exchange calculations and because we indeed found that it gave the best representation of exchange for this type of problem of all the GGA exchange functionals tried, we adopted it as part of our recommended procedure. This total van der Waals density functional (vdW-DF) has been applied to layered structures where it produced reasonable agreement with experimental results. Such layered systems, namely bulk graphite, molybdenum sulfide, boron nitride as well as the corresponding layered dimers are all ones in which GGA fails completely. Going to a more general geometry tests were made on rare-gas dimers as well as the benzene dimer in the particularly simple “sandwich” or “atop-parallel” geometry.

The benzene dimer represents an ideal testing ground for new correlation density functionals because of the wealth of wave-function calculations on this system in different geometries. These represent both Møller-Plesset theory (MP2) and coupled-cluster theory (CCSD(T)); the more recent of the latter represent the current state-of-the-art and are extremely demanding computationally. Their expected accuracy has been well discussed by their practitioners. These theories based on wavefunction calculations may be adopted
as giving reference values, in lieu of conclusions from experimental work on such weakly binding systems, which require a number of assumptions to deduce binding structures and energies. More recently there have been a rather full set of MP2 and CCSD(T) calculations on the benzene-phenol, -toluene, -fluorobenzene, and -benzonitrile complexes. This has provided an opportunity for further testing of the functional on a wider variety of well referenced systems. Such a study has recently been made which shows promise for the functional for different geometries of those four systems as well.

In this paper, we make a thorough study of the behavior of this van der Waals density functional (vdW-DF) for a number of different benzene geometries. We calculate the interaction energy and lowest energy structure for different geometries of the benzene dimer with a converged calculation using the nonlocal correlation energy functional within the framework of a norm-conserving pseudopotential plane wave code. The comparison of this straightforward and relatively quick density functional based method with other methods can determine potential errors in this method and how such a method might be utilized in larger, more complicated biological, organic, and/or aromatic systems. We address the exchange functional by studying the effect of replacing the GGA exchange functional with a full Hartree-Fock (HF) calculation. Indeed, we find that slightly weaker repulsion of the full HF calculation gives improved bonding distances along with stronger binding. The various tradeoffs between the two methods are studied and discussed. We benchmark this functional on the benzene dimer system where a good amount of data is available from other calculations and where generated conclusions still conflict with one another. By comparing with these systems in which state-of-the-art results exist, we demonstrate that we can utilize this functional for much larger biological and organic systems which go beyond wavefunction calculations.

II. COMPUTATIONAL METHODS

Our calculations were performed using density functional theory (DFT) with nonlocal correlation energy. Our DFT calculations follow the previous prescription (which we continue to abbreviate as vdW-DF) for calculating binding energies in van der Waals bonded systems with this particular nonlocal correlation functional:

\[ E[\rho] = T_s[\rho] + V_{pp}[\rho] + J[\rho] + E_x[\rho] + E^L_C[\rho] + E^NL_C[\rho] \] (1)
where E is the total energy functional of the dimer or monomer, $T_s$ is the single-particle kinetic-energy functional, $V_{pp}$ is the ionic pseudopotential functional, $J$ is the Coulombic interaction functional, $E_x$ is the revPBE flavor of the generalized gradient approximation (GGA) exchange functional, $E^L_c$ is the local contribution to the total correlation energy, and $E^{NL}_c$ is the nonlocal contribution to the total correlation energy,

$$E^{NL}_c = \frac{1}{2} \int d^3 r_1 d^3 r_2 \rho(\vec{r}_1) \phi(\vec{r}_1, \vec{r}_2) \rho(\vec{r}_2).$$

(2)

The kernel can be written in a form allowing rapid evaluation

$$\phi(\vec{r}_1, \vec{r}_2) = \tilde{\phi}(Rf(\vec{r}_1), Rf(\vec{r}_2)),$$

(3)

where $f(\vec{r}_i)$ is a function only of $\rho(\vec{r}_i)$ and $|\nabla \rho(\vec{r}_i)|$ for $i = 1, 2$, and $R = |\vec{r}_1 - \vec{r}_2|$. The details are given in Ref. 5, which introduces a sum and difference variable decomposition that provides still further simplification.

Although similar in spirit to the calculations describing the nonlocal correlation functional in a previous work, we utilize some notable exceptions. First, we use norm-conserving pseudopotentials of the Troullier-Martins type for $V_{pp}$ within the framework of the abinit code. Second, we use the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential as well as charge densities derived from that calculation, i.e. $\rho$ is $\rho_{PBE}$ for the calculation of each functional. We calculated a number of representative binding energies using other DFT charge densities, but found negligible changes in all results. We calculate $E[\rho]$ using revPBE, then subtract the GGA correlation energy before adding $E^L_c$ with a local density approximation (LDA) correlation functional. Whereas each term is calculated using abinit, we calculate the nonlocal correlation energy $E^{NL}_c$ as a post process calculation to obtain our vdW-DF solution.

Except for the evaluation of $E^{NL}_c$, we employ a planewave approach with periodic boundary conditions applied to a supercell with large enough spacings such that no spurious interactions exist between periodic replica. All dimers are placed in a box with 15 to 20 Å of vacuum between the clusters. This amount of vacuum proved sufficient for the total charge density to approach zero ($10^{-9}$) well before the the supercell edge. The kinetic energy cutoff used is at least 50 Ry corresponding to about $2 \times 10^5$ plane waves in a cell of 21 Å per side. We found that larger supercells and higher energy cutoffs had negligible effect (less than 0.05%) on the total binding energy of any structure. The post process calculation of $E^{NL}_c$
FIG. 1: The benzene dimer in various geometries including a) the on top parallel (sandwich) structure b) the T-shape, orthogonal structure c) the slip parallel structure in which one benzene molecule is slipped along the carbon-hydrogen bond and d) the slip parallel structure in which one benzene molecule is slipped perpendicular to a carbon-carbon bond. Carbon is black and hydrogen is white in the ball and stick representation.

was evaluated on a real space grid at a size equal to the supercell and with grid spacings equal to the Fourier transform spacings in the planewave calculations. $E_{c}^{NL}$ was evaluated at each grid point and numerically integrated in a manner described in greater detail in a previous work. Although $E_{c}^{NL}$ is not calculated self-consistently at this time, other DFT charge densities yield no change in the results, suggesting self-consistency would not change any result appreciably or overall conclusions.

We calculated the binding energies of two distinct forms of the benzene dimer, the parallel and T-shape dimers (see Fig. 1). For parallel geometries, we considered the on-top parallel sandwich structure (Fig. 1(a)), and two different slip parallel structures (Fig. 1(c) and (d)). We calculated the total binding energies for the slip parallel structures by starting from the graphite-like AB stacked (minimum energy) geometry and moving one monomer vertically until a local minimum was reached. We subsequently moved that monomer horizontally along a C-H bond once that vertical minimum point had been ascertained. We then moved that same monomer in each direction to verify that this was a local minimum. Once we found this minimum (Fig. 1(c)), we started from a new slip parallel structure defined by slipping towards the C-C bond. We moved vertically and horizontally until a new slip parallel minimum was found (Fig. 1(d)). By slipping in two orthogonal directions, we hope to find
FIG. 2: Interaction energies ($E_{\text{int}}$) of the indicated benzene dimers using vdW-DF (Eq. 11), compared with previous Møller-Plesset perturbation (MP2) and coupled-cluster (CCSD(T)) calculations. These DFT calculations used nonlocal correlation energies and revPBE exchange energies. The abscissas ($R_{\text{centers}}$) give the center-to-center distance between the benzene monomers.

the lowest possible slip parallel structure. Every benzene molecule was locked at a fixed structure of 1.397 Å C-C length and 1.079 Å C-H length. Changing these structures, for example, to the minimum LDA or GGA geometries made no difference (< 0.0005 kcal/mol) to any final binding energy results.

III. RESULTS

Fig. 2 and Fig. 3 show the DFT, nonlocal correlation (vdW-DF) results of three structures including the parallel on top (sandwich) structure and two other potential lowest energy structures, the T-shape and the slip parallel structures. Each of these results is compared with recent CCSD(T) and MP2 calculations. The sandwich structure dimer is similar with a recent calculation using this same nonlocal correlation functional in that the minimum energy point and the value of the binding energy at that point agree, but disagrees slightly at larger separations of the dimer. The results here used very large box sizes and very refined integration cutoff parameters. The results for benzene dimers in this work should be taken as the results generated from this methodology.

In each case, we find that our calculations predict a significantly larger dimer separation,
FIG. 3: vdW-DF interaction energies of benzene dimers in the indicated configurations. The larger graph in each of these two panels shows the effect of vertically (see Fig. 1) separating of the monomer planes at a fixed horizontal slip distance of 1.398 Å between the monomer axes. The insets show the effect of varying this slip distance away from the energy minimum found from the previous movement: the total horizontal slip distance is 1.398 Å plus the abscissa of the respective inset. The abscissas of first two larger graphs are the values of the monomer intercenter distance $R_{\text{centers}}$ before the horizontal displacement indicated in the insets. The third panel shows for comparison MP2 and CCSD(T) calculations, where the vertical and horizontal distances were increased simultaneously in a fixed ratio (see text).

up to 18% larger when compared with CCSD(T) and MP2. We find that our binding energies agree extremely well with the CCSD(T) calculation for the magnitude of these binding energies, both of which are significantly less than those generated from the MP2
calculation. Additionally, we agree with these previous calculations as well as more recent MP2 and CCSD(T) calculations\textsuperscript{12,13} that, despite being nearly isoenergetic, the slip parallel is the lowest energy structure.\textsuperscript{11}

Although the dimer separation ($R_{\text{centers}}$) is always given here as the distance from the center of the benzene rings regardless of the structure, in the slip parallel case the previous CCSD(T) and MP2 results, with which we compare, were generated by fixing the angle between the center of mass line and the horizontal at 63°.\textsuperscript{11} In our calculation, we moved one benzene ring vertically and then horizontally as in Fig. 1(c) until we obtained a minimum. Additionally, we moved one benzene ring at an angle of 30° to this movement, but in the same plane (Fig. 1(d)). Surprisingly, we found a significantly stronger binding energy when moving in this alternate direction, suggesting that the structure represented by Fig. 1(d) is the lowest energy structure for the slip parallel geometry. This result is especially noteworthy as it represents a difference in stacking between the lowest energy structure of graphite and of the benzene dimer. Although disagreeing with some previous assumed slip parallel structures\textsuperscript{9,10} this geometry is actually similar to other previous studies\textsuperscript{10} including the structure found by recent and more complete CCSD(T) calculations\textsuperscript{12,13} although no discussion or comparison was made with the alternate structure in these works.

One of the major benefits of using the nonlocal correlation functional for organic, aromatic, and $\pi$-bonded systems is its compatibility with standard DFT planewave codes and the relative speed and lack of computer power needed. Indeed, these benzene dimers pushed CCSD(T) nearly to its peak. Even the less computationally demanding MP2-R12/A calculations were reported to have required two weeks on four processors.\textsuperscript{12} Calculations of the later type are important, not only in their own right, but are also also often used as input for a clever procedure to extract a best estimate of the basis set limit for the even more demanding CCSD(T) calculations. In contrast the the evaluation of $E_c^{\text{NL}}$ done here took a time of the same order as corresponding GGA calculation that proceeded it (about an hour per point on a Dual Athalon MP 2000+ processor), and the former will take comparably less time as the system size increases. Therefore, the benzene dimer represents a starting point for such systems within the present implementation, rather than nearly a limiting case as in CCSD(T). Although another DFT based methodology using symmetry-adapted perturbation theory\textsuperscript{25,26} is reported\textsuperscript{27} to have been recently optimized such as to offer comparable speeds for the benzene dimer, it nevertheless scales as the fifth power\textsuperscript{27} of the basis size, and
hence in contradistinction to the present DFT scheme, will rapidly become unmanageable as the system size increases. Other coupled-cluster schemes such as those placing effort into linear scaling might also offer comparable speeds, but that such a scheme would generate consistent results in van der Waals systems has not yet been indicated. Therefore, this current methodology offers the only method we know that gives a calculation speed comparable to that of an ordinary GGA calculation as the system size increases, and in order to utilize it fully, understanding the small disagreement of the predicted dimer separation in this work with the previous CCSD(T) calculations is vital to increase the applicability of this method.

IV. DISCUSSION

The results of the vdW-DF calculation when compared with the CCSD(T) and MP2 results are quite illuminating. First we note that the binding energy values are extremely consistent with the CCSD(T) results, much closer in the two minimum energy structures than the MP2 calculations. Furthermore, both these results are consistent with the CCSD(T) results in that both show that the T-shape and the slip parallel structures to be nearly isoenergetic with the slip parallel slightly lower. This result is a strong indicator that this method might be the most efficient for calculating binding energies in van der Waals systems.

CCSD(T) is considered the best and most complete answer to date but suffers from some serious scaling constraints as the system size increases. One can obtain useful results by using the best basis set possible, and then applying a clever method for estimating the basis set limit by making use of an MP2 calculation which can be made with a much larger basis set. The results used in our plots here used this method. A more recent calculation using this method with even a better basis set (aug-cc-pVQZ*) and using an MP2 calculation essentially at the basis set limit yields qualitatively similar results varying by a few tenths of a kcal/mol. Thus when searching for alternatives, it is clear that our method gives closer energies to CCSD(T) compared with MP2 at the basis set limit, while yielding inconsistent separations. Unfortunately, in addition to these slightly larger separations, this method also gives an inconsistent result in that the sandwich structure is lower in energy than the T-shape structure. To understand why requires greater analysis.

In addition to the interplay of all the typical interactions, the binding energy of benzene dimers is influenced by two competing interactions not necessarily as prominent as in
other physical systems: the attractive dispersion interaction and the repulsive electrostatic quadrupole-quadrupole interaction. How any method deals with these two interactions, tiny when compared with their total energies, is thus vital in determining which structure it might favor. Parallel structures, both the sandwich and the slip parallel, feature a more dominant quadrupole-quadrupole repulsion interaction than the T-shape structure, an interaction that tends to decrease the total binding energy when dispersion is not fully taken into account. If the counterbalancing dispersion interactions are neglected or only partially included, T-shape structures may then be found as the more stable structure. Conversely, any method that underestimates quadrupole-quadrupole interactions such as DFT based methods, or any method that overestimates nonlocal correlation effects, would bias the result towards favoring parallel structures.

The MP2 perturbation method is a sensible method for dealing with these two effects in a controllable manner. The correlation energy calculated through the MP2 method counterbalances the quadrupole-quadrupole interaction. The completeness of the Gaussian basis set used and the inclusion of disperse polarizability functions tends to increase the magnitude of the total electron correlation energy in MP2 calculations and thus the attractive dispersion interactions. As the basis sets are less complete, the dispersion energy will not compensate the electrostatic effect fully and T-shape structures will be found to be more favorable. Methods based on multipole expansion\textsuperscript{28,29} and underconverged MP2 methods\textsuperscript{7,10} led to this exact trend in the 1980s and the early to mid 1990s. As the capability of performing calculations with a more converged basis set occurred, the planar geometries felt the effect to a greater degree, while the T-shape geometries changed in energy negligibly. Eventually, the capability to do a converged basis set HF and MP2 calculation led to such an increase in binding energy (more negative interaction energy) for the planar structure, that planar geometries were recognized as the more favorable energy structure\textsuperscript{9,11,12,13}.

This historical analysis demonstrates how different methods will bias which nearly isoenergetic system will be found to be the lowest energy structure. In our case, we note that because the slip parallel dimer was found as the lowest energy structure, our method for including nonlocal correlation energy is consistent with the converged MP2 and the CCSD(T) calculations, \textit{i.e.} our nonlocal correlation functional captures an amount of correlation consistent with converged MP2 calculations. However, because we perform a DFT calculation and use DFT densities, the quadrupole moment is underestimated by \(\approx 18\) to \(23\%\), giving
a quadrupole repulsion in the sandwich configuration that is substantially too small. Thus
our sandwich binding energies will be too large because not enough repulsion is considered,
while the T-Shape is largely unaffected because of the larger distances. Because our T-shape
binding energy predictions were less than 0.09 kcal/mol weaker than the sandwich binding
energy predictions, this may be one source of the physical discrepancy of the sandwich bind-
ing energy being found stronger than the T-shape binding energy. Furthermore, this result
also demonstrates a caveat for using this method when the principal interaction is electro-
static and not van der Waals. Possibly this defect could be corrected ad hoc by applying a
density correction method as done in Refs. 25 and 26, but we have not yet explored this
possibility. Any method that features a complete quadrupole-quadrupole interaction energy
and dispersion energy may reveal that the T-shape is the more energetically favorable than
the slip parallel, but clearly both distinct structures are local minimums and should thus
both occur in nature.

One trend that we observe is the consistent overestimation of dimer separation in benzene
compared with CCSD(T). The possibility of this particular result being a specific trait
of benzene and the use of the revPBE exchange energy are investigated as two potential
explanations for this discrepancy.

With the lack of conclusive experimental equilibrium distances in gas phase benzene,
we performed a similar comparison with a system that has a known experimental dimer
separation. This comparison may also reveal if our overestimation of dimer separation
is specific to benzene or a general trait of this methodology. To this end, we calculated
the geometry and binding energy of the argon dimer. Similar to the previous published
result, we obtain a binding energy of 0.45 kcal/mol at 3.97 Å for the argon dimer. This
equilibrium distance overestimates the accepted experimental dimer separation by ≈ 0.2 Å or
6%. Unfortunately, this result is inconclusive in explaining our discrepancy in benzene as
it still overestimates the accepted argon experimental value, but not nearly as much as the
assumed overestimation in benzene.

Thus, we analyzed the effect of using revPBE exchange energies in our binding energy
calculation. Fig. 4 shows revPBE exchange binding energies compared with a Hartree-Fock
calculation for the sandwich structure. For the sandwich structure, we see that revPBE
is steeper than HF, and approaches zero more rapidly. These differences suggest that the
revPBE energy, not the nonlocal correlation energy correction is responsible for the dis-
crepancy in dimer separation with MP2 and CCSD(T). Furthermore, the revPBE exchange results also appear to be responsible for the slow approach towards zero from below in the total binding energy. Fig. 5 and Fig. 6 show the effect of using Hartree Fock as opposed to revPBE exchange on the total binding energy. In these results, the correlation energy is not changed at all, simply the revPBE exchange-only energy is subtracted from the total energy and HF energy is added. Both the dimer separation and the slow approach towards zero problems simultaneously disappear for the sandwich structure: the minimum displacement shifts inward by nearly 0.43 Å while the binding energy approaches zero from below more quickly and more consistently with the MP2 and CCSD(T) result. Also disappearing is the rather large energy difference between the two slip parallel equilibria, with the slip-parallel-2 geometry only 0.005 kcal/mol lower (i.e., more stable). Unfortunately, the change in exchange energy tends to increase the magnitude of the binding energy, placing it further away from the CCSD(T) calculations, although still comparable to the MP2 calculations. Based on this result, the very slight differences in revPBE with Hartree-Fock (HF) seem to be the root of most discrepancies, especially dimer separation, although revPBE is the most consistent exchange density functional of those tested for representing exchange-only effects. This difference can slightly alter equilibrium geometries in benzene dimers, and thus perhaps HF is a better starting point. We have redone our exchange only calculations for each benzene dimer with HF calculations instead of revPBE. In every case, we obtain a minimum point consistent with CCSD(T), and energies consistent with MP2. Additionally,
TABLE I: Equilibrium center-to-center distance ($R_{centers}$) in Å (and angle to basal planes for slip-parallel configuration) obtained by various methods: $^a$Ref. 12; $^b$Ref. 10; $^c$Ref. 17.

| Method          | Sandwich | T-Shaped | Slip Parallel-2 | Angle |
|-----------------|----------|----------|------------------|-------|
| vDW-DF          | 4.1      | 5.3      | 4.4              | 64°   |
| vDW-DF(HF)      | 3.8      | 4.9      | 3.7              | 64°   |
| MP2$^a$         | 3.7      | 4.9      | 3.8              | 65°   |
| CCSD(T)$^b$     | 4.1      | 5.0      | 4.0              | 63°   |
| Experiment$^c$  |          |          |                  | 4.96  |

TABLE II: Binding energies in kcal/mol of benzene dimers in different configurations. Except where indicated the slip parallel configurations are slip-parallel-2. The MP2 and CCSD(T) numbers are estimates given in Ref. 12 of the values that would be obtained in the basis set limit: these differ somewhat from the depths of the MP2 and CCSD(T) curves in our figures [Model II of Ref. 11]. $^a$The number for the slip-parallel-1 configuration is 2.74. $^b$The value for the slip-parallel-1 configuration is 0.005 kcal/mole smaller.

| Method          | Sandwich | Slip parallel | T-shape |
|-----------------|----------|----------------|---------|
| CCSD(T)         | 1.81     | 2.78           | 2.74    |
| vDW-DF          | 2.37     | 2.80$^a$       | 2.28    |
| vDW-DF(HF)      | 2.77     | 4.48$^b$       | 4.38    |
| MP2             | 3.64     | 4.95           | 3.63    |

as HF and revPBE differ in slightly different manners in each system, we find that the T-shape dimer now binds much more strongly than the sandwich dimer. In Table II the geometric predictions of both versions of exchange and the nonlocal correlation functional are compared with a most recent large basis set MP2 calculation$^{12}$ and with experiment.$^{17}$ The agreement shown by the HF version, vDW-DF(HF), is clearly outstanding. For reference, the predictions of an earlier CCSD(T) calculation are also shown.$^{10}$ A comparison of the binding energies is given in Table III.
FIG. 5: Calculated interaction energies using the vdW-DF(HF) functional [Eq. (1), with Hartree-Fock exchange substituted for revPBE exchange]. The description of the plots is analogous to that for Fig. 2.

Thus, the DFT nonlocal correlation is a very efficient way to obtain MP2 level accuracy at a fraction of the computational cost with slightly varying results depending on the method for calculating all non-correlation energy.

V. CONCLUSIONS

In conclusion, we have applied a nonlocal correlation functional capable of describing dispersion interactions to the benzene dimer. We find that slip parallel is the lowest energy structure although all three geometries are nearly isoenergetic. Our binding energies and qualitative predictions are consistent with CCSD(T) and MP2 calculations, although, our equilibrium geometries are slightly larger; however, the discrepancies in geometry are due to differences between revPBE and HF, not the nonlocal correlation energy functional. Our method thus gives useful values for spacings and energies, at a tiny fraction of the cost of the wave function methods. Specifically this cost is comparable to that for calculations of the GGA type, which typically give sporadic and often unphysical results for systems whose properties depend on the long range van der Waals interaction.

This benchmarking study has provided the evidence that this functional may be used in and even larger systems. The consistency of our results with state-of-the-art wavefunction calculations allows us to pursue much larger and sometimes infinite systems. Indeed, the
FIG. 6: Calculated interaction energies using the vdW-DF(HF) functional. The description of the plots is analogous to that for Fig. 3.

The functional has already been applied by the Chalmers part of our collaboration/cooperation to a physisorbed molecule on an infinite surface, to an infinite polyethylene crystal, and to naphthalene, anthracene, and pyrene dimers. The two infinite system examples are cases in which other functionals that have been applied fail completely and in which the experimental data is sparse (one or two data points) with error bars that are larger than optimal. The dimer examples were compared with CCSD(T) calculations for naphthalene with favorable results. As a result, we plan to continue with comparisons to other wavefunction calculations when possible, even when such calculations are not completely converged, and to move to even much larger systems such as base pairs of DNA.
Acknowledgments

The authors thank Svetla Chakarova-Käck, Jesper Kleis, Elsebeth Schröder, Per Hylle-gaard, and Bengt Lundqvist for helpful communications on benzene and calculations with the nonlocal functional and Timo Thonhauser for helpful computational programs to speed up the work. This work was supported in part by NSF Grants DMR-0093079 and DMR-0456937.

1 V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, J. Chem. Phys. 119, 12129 (2003).
2 V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Phys. Rev. B 69, 075102 (2004).
3 H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyllegaard, S. I. Simak, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. Lett. 91, 126402 (2003).
4 D. C. Langreth, M. Dion, H. Rydberg, E. Schröder, and B. I. Lundqvist, Int. J. Quantum Chem. 101, 599 (2005).
5 M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92, 246401 (2004).
6 Y. Zhang and W. Yang, Phys. Rev. Lett. 80, 890 (1998).
7 P. Hobza and H. S. E. W. Schlag, J. Chem. Phys. 93, 5893 (1990).
8 P. Hobza, H. L. Selzle, and E. W. Schlag, J. Am. Chem. Soc. 116, 3500 (1994).
9 R. L. Jaffe and G. D. Smith, J. Chem. Phys. 105, 2780 (1996).
10 P. Hobza, H. L. Selzle, and E. W. Schlag, J. Phys. Chem. 100, 18790 (1996).
11 S. Tsuzuki, K. Honda, M. Mikami, and K. Tanabe, J. Am. Chem. Soc. 124, 104 (2002).
12 M. O. Sinnokrot, E. F. Valeev, and C. D. Sherrill, J. Am. Chem. Soc. 124, 10887 (2002).
13 M. O. Sinnokrot and C. D. Sherrill, J. Phys. Chem. A 108, 10200 (2004).
14 K. O. Bornsen, H. L. Selzle, and E. W. Schlag, J. Chem. Phys. 85, 1726 (1986).
15 J. R. Grover, E. A. Walters, and E. T. Hui, J. Phys. Chem. 91, 3233 (1987).
16 H. Krause and H. J. Neusser, Chem. Rev. 94, 1829 (1994).
17 E. Arunan and H. S. Gutowsky, J. Chem. Phys. 98, 4294 (1993).
18 P. M. Felker, P. M. Maxton, and M. W. Schaeffer, Chem. Rev. 94, 1787 (1994).
19 M. O. Sinnokrot and C. D. Sherrill, J. Am. Chem. Soc. 126, 7690 (2004).
20 T. Thonhauser, A. Puzder, and D. C. Langreth, submitted to J. Chem. Phys.

21 N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).

22 X. Gonze, J.-M. Beukn, R. Caracus, F. Detraux, M. Fuchs, G.-M. Rignansce, L. Sindic, M. Ver-stracte, G. Zerah, F. Jollet, et al., Comp. Mat. Sci. 25, 478 (2002).

23 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

24 The currently used code for evaluating $E_{NL}^c$ is not optimized and uses a uniform grid, which is wasteful in the large low density regions. We believe that a substantial speedup is possible.

25 A. J. Misquitta, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. 91, 033201 (2003).

26 R. Podeszwa and K. Szalewicz, preprint.

27 K. Szalewicz, private communication.

28 J. Pawliszyn, M. M. Szczesniak, and S. Scheiner, J. Phys. Chem. 88, 1726 (1984).

29 S. L. Price and A. J. Stone, J. Chem. Phys. 86, 2859 (1987).

30 E. J. Meijer and M. Sprik, J. Chem. Phys. 105, 8684 (1996).

31 R. van Leeuwen and E. J. Baerends, Phys. Rev. A 49, 2421 (1994).

32 D. J. Tozer and N. C. Handy, J. Chem. Phys. 109, 10180 (1998).

33 S. D. Chakarova-Käck et al., to be published.

34 J. Kleis et al., to be published.

35 S. D. Chakarova-Käck and E. Schröder, to be published.

36 S. Tsuzuki, K. Honda, T. Uchimaru, and M. Mikami, J. Chem. Phys. 120, 647 (2004).