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Symmetry-Adapted Perturbation Theory Applied to Endohedral Fullerene Complexes: A Stability Study of $H_2@C_{60}$ and $2H_2@C_{60}$

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Abstract: Because of difficulties in a description of host–guest interactions, various theoretical methods predict different numbers of hydrogen molecules which can be inserted into the C_{60} cavity, ranging from one to more than 20. On the other hand, only one H_2 molecule inside the C_{60} fullerene has been detected experimentally. Moreover, a recently synthesized $H_2@C_{70}$ complex prevails in the mixture formed with $2H_2@C_{70}$. To get a deeper insight into the stability of the complexes created from C_{60} and hydrogen molecules, we carried out highly accurate calculations for complexes of one or two hydrogen molecules with fullerene applying symmetry-adapted perturbation theory (SAPT) and a large TZVPP basis set for selected points on the potential energy surfaces of $H_2@C_{60}$ and $2H_2@C_{60}$. The electron correlation in the host and guests has been treated by density functional theory. Our calculations yield the stability of the recently synthesized $H_2@C_{60}$ complex. In addition, for all tried positions of the H_2 dimer inside the C_{60} cage, the $2H_2@C_{60}$ complex has been characterized by a positive interaction energy corresponding to the instability of this species. Contrary to the conclusions of several theoretical studies, this finding, as well as model considerations and literature experimental data, indicates that only one hydrogen molecule can reside inside the C_{60} cage. The calculated energy components have been analyzed to identify the most important contributions to the interaction energy. Supermolecular interaction energies obtained with MP2, SCS-MP2, and DFT+Disp methods are also reported and compared to those of DFT-SAPT. The DFT-SAPT interaction energy has also been calculated for several points on the potential energy surface for a larger $2H_2@C_{70}$ complex, confirming, in agreement with recent experimental findings, that this species is stable. The DFT-SAPT approach has been used for the first time to obtain interaction energies for van der Waals endohedral complexes, demonstrating that the method is capable of handling such difficult cases.

Introduction

The possibility of filling a fullerene cage with atomic, ionic, or molecular guests was postulated soon after the serendipitous discovery of C_{60}[1] and development of the procedure for its purification.[2] Since then numerous proposals of possible applications of endohedral fullerene complexes[3]

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have appeared in different areas of science and technology, ranging from medicine[4] and environmental protection[5] to molecular optoelectronics[6] and renewable energetics.[7] Interestingly, almost none of them have been marketed yet, indicating the immense complexity of the task of filling and subsequent releasing guest molecules from the fullerene cavity. The utilization of fullerenes and carbon nanotubes as hydrogen storage devices has been recently one of the hot topics of research in view of their prospective practical applications.[8,9] However, the newest experimental evidence damped the expectations for storing a considerable amount of hydrogen inside these carbon forms.[10]

Similarly to the case of nanotubes, a hydrogen molecule can be either chemi- or physisorbed on the fullerene surface. The chemisorption consists in a hydrogenation of the fullerene (i.e., the covalent CH bonds are formed). During the physisorption, a hydrogen molecule is attached to the C_{60} ball without the covalent bond formation. In the latter case, an endohedral van der Waals complex (denoted as $H_2@C_{60}$) is formed if H_2 is placed inside the fullerene, otherwise a more usual, but weaker exohedral complex is obtained. A synthesis of $H_2@C_{60}$ by Komatsu et al.[11] consisted in a chemical creation of a hole in the fullerene cage, insertion of a hydrogen molecule,[12] followed by a chemical closure of the cage.[11] This process has been called a "molecular surgery" of fullerenes.[12−14] Note that a parting with an idea of a "brute force" insertion of hydrogen inside the fullerene under extreme conditions (high temperature and pressure) in favor of a milder chemical opening of the cage was suggested some time ago by Patchkovskii and Thiel for $He@C_{60}$[15] and by Dodziuk et al.[16] Very recently, Murata et al.[17,18] used a similar approach to obtain the $2H_2@C_{70}$ complex. It is noteworthy that the experimentally observed relative population of $H_2@C_{70}$ and $2H_2@C_{70}$ (97:3)[18] is very close to the values which can be deduced from a difference of 1.8 kcal/mol in the steric energy values determined by molecular mechanics.[19]

Two main issues have been addressed by theoreticians when studying endohedral complexes of fullerenes with hydrogen molecules: a height of the barrier hindering the guest from entering the fullerene cavity and an estimation of the number of hydrogen molecules which can be hosted by the fullerene cage. Both problems can be first analyzed on the basis of simple mechanistic considerations. By taking the length of the H−H bond of about 0.7 Å, the van der Waals radii of the H and C atoms of ca. 1.2 and 1.7 Å, respectively, and assuming the diameter of fullerene (treated approximately as a sphere) as 7.1 Å,[20] it is easy to estimate that there is no room left for another H_2 molecule inside the cage. Such a simple reasoning shows that only one hydrogen molecule can be hosted by C_{60}. Analogously, a comparison of the radii of the H and C atoms allows one to draw a conclusion that a hydrogen atom or molecule passing through the five- or six-membered ring should exhibit a strong repulsion because of an overlap of the electron clouds of the ring and the H atoms.

The problem of a barrier estimation for a guest entering the C_{60} cage has been studied in several articles,[21−23] yielding barriers of 3 eV[21] or 2 eV[23] for a hydrogen atom and 20 eV for H_2,[22] when passing through the six-membered ring. Subsequent molecular dynamics simulations have shown a very low probability for the process of catching a hydrogen atom inside the cage, while the same process in the case of the hydrogen molecule has been not observed in silico at all.[21] These calculations are in line with a lack of success in obtaining $H_2@C_{60}$ by a direct hydrogen insertion into an intact C_{60} fullerene (i.e., without opening the cage).[11,18]

The stability of complexes of hydrogen molecule(s) buried inside the C_{60} cage has been studied by various approaches, from molecular mechanics (MM),[24] through semiempirical and density-functional theory (DFT), to ab initio quantum

chemical (QM) methods. At the beginning, it should be stressed that a usage of the semiempirical approach for nonbonding interactions is rather counterproductive, since this method has been developed to provide approximate energies of chemically *bonded* systems, and for this very reason the calculations of *nonbonded* complexes performed with this class of methods cannot be reliable. One can also add that semiempirical methods are known to have difficulties even with a satisfactory description of hydrogen bonds,[25] which are by orders of magnitude stronger than interactions between a hydrogen molecule and a π-electron system. Therefore, the reports of Turker and Erkoc,[26] who found a stabilization of 24 hydrogen molecules inside C_{60} on the basis of semiempirical AM1 calculations, or those of Ren et al.,[27] who used the PM3 method combined with DFT and inserted 25 H_2 into the cage, are not reliable. A detailed criticism of the results of Turker and Erkoc can be found in refs 28 and 29. It should be noted that a recently developed OM*x* class of semiempirical methods compares somewhat better with QM calculations, but still without an empirical dispersion correction they predict no interaction for complexes containing π-electron systems.[30]

The accuracy of quantum chemical calculations for endohedral fullerene complexes is usually quite limited. The obvious reason for this state of affairs is the size of the system,[31] which precludes the use of the high-level ab initio electron-correlated theories, such as, for example, coupled cluster[32] (see, however, ref 33) and large orbital basis sets. The limitations in the choice of ab initio electron-correlated theories are especially serious in the case of nonpolar or slightly polar guest molecules, since in these cases the host−guest interactions are mainly dispersive and exchange ones while it is known that the dispersion energy (and the corresponding exchange-dispersion energy) is not accounted for by the Hartree−Fock method.[34] For instance, early self-consistent field (SCF) calculations of Cioslowski for $H_2@C_{60}$ yielded incorrectly the instability of this complex.[35]

Another popular method of accounting for the electron correlation is the DFT approach. The commonly employed DFT in its local density approximation or generalized gradient approximation variant is not an ab initio method, and the accuracy of reproducing the electron energy is strongly dependent on the quality of the functionals used. It is well-known that the DFT approach with commonly used functionals often strongly underestimates[36] the stabilizing dispersion interaction (and a smaller destabilizing exchange-dispersion contribution) and that a neglect of this part of the interaction energy can lead to qualitatively incorrect results (e.g., destabilization instead of the stabilization effect). It should be also stressed that the existence of a multitude of DFT functionals makes it very difficult for a nonspecialist to select the best one for his or her particular purpose, although recent comprehensive studies on the quality of various functionals for several classes of nonbonding interactions provide some general guidelines.[37] This situation results, unfortunately, in a broad misuse of functionals, leading to many erroneous conclusions. However, at present the reason why most functionals are incapable to describe dispersion interactions is well-known[38] and several solutions

to this problem exist, the most sophisticated of which are possibly the ones which derive nonlocal orbital functionals from many-body perturbation theory,[39] coupled cluster theory,[40] or the fluctuation−dissipation theorem DFT.[41] Another practical solution to the dispersion energy problem with DFT is to use empirical damped multipole expansions of the dispersion energy as a correction term to the DFT energy (see, for example, refs 42−44). In these methods, the dispersion coefficients are often calculated as combinations of atomic dispersion coefficients and thus the dispersion energy can be estimated very efficiently. It has to be added, though, that the dispersion energy obtained in this way should not be confused with the dispersion energy from an intermolecular perturbation theory and has in fact no physical meaning. To our best knowledge, the most popular method from this class (i.e., the DFT+Disp method of Grimme[42,43]) has not been used to study the stability of endohedral complexes of fullerenes yet. Another modification of the standard DFT method, known as DFT with tight binding (DFTB+),[44] correctly yields only one hydrogen molecule stabilized inside the C_{60} fullerene;[45] however, the latter authors claimed the stability of the highly strained endohedral complexes with up to 20 H_2, which, according to model considerations and available experimental results, cannot be obtained.

The existence of some new promising DFT functionals, which are especially designed to imitate the nonbonding interactions, should be also mentioned here. One of these functionals (MPWB1K,[46] thoroughly tested by Zhao and Truhlar[37]) has been recently used by Slanina et al.[47] to estimate the stabilization energies of H_2, Ne, and N_2 inside the C_{60} cavity. In agreement with the experimental evidence,[11,48] MPWB1K predicts that these complexes are stable. The values of the MPWB1K stabilization energies are similar to values obtained from the second-order Møller−Plesset (MP2) and spin-component-scaled MP2 (SCS-MP2)[49] calculations. However, as the authors of ref 47 notice, the MPWB1K functional does not provide a correct description of stacking interactions (like those between two benzene molecules), and therefore it cannot be excluded that sensible values of the interaction energies for three endohedral complexes studied there are just a result of an accidental error cancellation. Additionally, it is known that for complexes involving aromatic molecules the MP2 method often gives too large values of the attractive interaction energies,[50] and therefore a good agreement with MP2 cannot be viewed as an ultimate proof of the usefulness of the MPWB1K functional for such cases.

Unfortunately, DFT with standard functionals is still utilized to calculate energies of endohedral fullerene complexes without taking into account a missing dispersion component of the interaction energy. Among several such works dealing with the stabilization effect for hydrogen molecules in the C_{60} fullerene, one can list, for example, articles of Yang,[51] Pupysheva et al.,[9] and Lee and McKee.[52] These authors claim to find stable[51,52] or metastable[9] structures involving numerous H_2 molecules (plus eventually partly chemisorbed species) inside C_{60} using standard DFT functionals, although in the Yang and Lee and McKee articles

starting from the second added hydrogen molecule the energy of the complex is higher than the sum of the energies of isolated molecules. In the work of Pupysheva et al., two H_2 molecules are stabilized inside C_{60}, and for the number of hydrogen molecules in the fullerene cage greater or equal to 15 a partial chemisorption has been obtained yielding unphysically long CH bond of even 1.20 Å. Yang inserted up to 29 hydrogen molecules into the C_{60} cage and claimed that only for 29 guests the cage will be broken. He also modeled the hydrogen entrance into the cage, stating that 19 H_2 molecules can pass through a small opening involving nine bonds. This result contradicts the experimental studies[53] on the orifice size enabling the entrance of one hydrogen molecule inside C_{60}. The paper by Yang[51] has been criticized by Dolgonos,[54] who pointed to the unreliability of the DFT calculations in this case and to very short distances between the seemingly "nonbonded" hydrogen atoms. The Yang reply to the comment of Dolgonos has been unsubstantial.[55] Lee and McKee studied the reactivity of up to six H_2 molecules inside C_{60} using DFT and MP2 methods with unreliably small basis sets. Also, HH distances of 1.6 Å reported by Lee and McKee[52] are certainly too small and should lead to a considerable repulsive destabilization of the systems under consideration. The analyses by the latter authors and Pupysheva et al. of the pressure inside the fullerene cage filled with numerous hydrogen molecules seem immaterial since, as discussed earlier, these complexes cannot be realized. It should be stressed that if an endohedral complex with two or even more endohedral H_2 molecules had been formed, then, despite a high strain, it would not decompose unless the strain of the complex distributed over the whole cage would be sufficiently large to break it. However, no process that could provide complexes with more than one guest inside C_{60} seems feasible. On the other hand, recent claims[9,52] that endohedral fullerene complexes with hydrogen molecules can be of use for hydrogen storage seem unfounded, since the release of guest hydrogen molecules should lead to an irreversible cage destruction. A recent idea to store hydrogen in chemically opened fullerene cages[56] could be a route to overcome this obstacle.

In this work, the endohedral C_{60} complexes involving one or two hydrogen molecules will be investigated using a computationally efficient variant of intermolecular symmetry-adapted perturbation theory (SAPT),[57] which allows one to reliably estimate the interaction energies in the $H_2@C_{60}$ and $2H_2@C_{60}$ species. A simultaneous study of these two complexes allows us to investigate a delicate balance between the dispersion and repulsion energies, which dominate in the intermolecular interactions for these two species, thus demonstrating the applicability of the latter method for such complicated cases.

Methods

Let us consider the interaction of two or three closed-shell molecules (denoted A, B, C). In general, the interaction energy of m molecules A, B, C,... is defined as a difference,

$$E_{int}(ABC...) = E_{ABC...} - (E_A + E_B + E_C + ...) \quad (1)$$

where $E_{A,B,C...}$ is the energy of the complex ABC... and E_X is the energy of the molecule X (X = A, B, C, ...). The

interaction energy of the three molecules A, B, and C can be separated into the additive and nonadditive parts:

$$E_{int}(ABC) = E_{int}[2,3] + E_{int}[3,3] \qquad (2)$$

where $[n,m]$ denotes the n-body contribution for the complex of m molecules. The additive part $E_{int}[2,3]$ is thus defined as a sum of interaction energies of all pairs:

$$E_{int}[2,3] = E_{int}(AB) + E_{int}(BC) + E_{int}(CA) \qquad (3)$$

and the nonadditive part $E_{int}[3,3]$ accounts for a modification of the interaction caused by the third partner. Note that in eqs 1–3 the intramolecular geometry parameters of A, B, and C have not been changed when calculating energies of complexes (i.e., no geometry relaxation is taken into account).

Equations 1–3 directly define the so-called supermolecular approach (sometimes called supramolecular one) for the calculation of interaction energies. In the supermolecular method, one calculates energies of all molecules and complexes (A, B, AB, etc.) by a given method and just makes the appropriate subtractions, according to eqs 1–3. Although appealing at first look, this approach has several disadvantages (see, for example, ref 58 for a detailed discussion). However, if a suitable theory is selected for the calculation of the electron energies and if the counterpoise correction of Boys and Bernardi[59] is used, the supermolecular approach can produce reliable potential energy surfaces (PES) for the van der Waals complexes.

It should be noted parenthetically that endohedral species such as $H_2@C_{60}$ are untypical examples of the van der Waals complexes since they cannot be separated into their constituent parts without the cage breaking. However, from the theoretical point of view there is no difference in a treatment of the endo- and exohedral van der Waals species.

SAPT Treatment of the Interaction Energy of Two Molecules. Another well-established approach for the calculation of the interaction energy for two closed-shell molecules is symmetry-adapted perturbation theory.[57,60] In SAPT, the interaction energy is obtained directly as a sum of well-defined physical contributions and *not* as a difference between two similar numbers (see eq 1). Up to the second order in terms of the intermolecular interaction operator $V = H_{AB} - H_A - H_B$ (where H_X is the electron Hamiltonian of a molecule or a complex $X, X = AB, A, B$), these contributions comprise: the first-order electrostatics ($E_{elst}^{(1)}$), second-order induction ($E_{ind}^{(2)}$) and dispersion ($E_{disp}^{(2)}$) energies, and their exchange counterparts: first-order exchange ($E_{exch}^{(1)}$), second-order exchange-induction ($E_{exch-ind}^{(2)}$) and exchange-dispersion ($E_{exch-disp}^{(2)}$), accounting for the electron tunneling between the interacting constituent molecules. The SAPT method up to the second order in V gives the main part of the interaction energy. As an estimation of the higher-order induction and exchange-induction energies, the Hartree–Fock "delta" correction term δE_{HF} is usually utilized.[34,61] Summarizing, the interaction energy in SAPT is calculated as:

$$E_{int}^{SAPT} = E_{elst}^{(1)} + E_{ind}^{(2)} + E_{disp}^{(2)} + E_{exch}^{(1)} + E_{exch-ind}^{(2)} + E_{exch-disp}^{(2)} + \delta E_{HF} \qquad (4)$$

To calculate the energy contributions listed above, the exact wave functions of molecules A and B should be known in principle. Since usually these solutions are not available, one has to resort to some approximate methods. The simplest solution is the utilization of the Hartree–Fock (HF) determinants, in which case the so-called SAPT(HF) method is obtained. In this method, the effect of the electron correlation inside the A and B molecules is completely neglected. Thus far, three methods have been developed which enable to include the effect of the electron correlation inside the interacting molecules: (i) historically the first and the most popular SAPT(MP) approach,[62,63] where the molecules A and B are treated by Møller–Plesset (MP) theory, (ii) SAPT(CC) approach,[64] developed by Korona and Jeziorski, where these molecules are described at the coupled cluster level (see also early works[63,65]), and (iii) the SAPT method with intramolecular electron correlation described by DFT. Only the latter method can treat molecules of the fullerene size, and therefore it will be described below in more detail.

A possibility of using DFT to account for the intramolecular correlation in SAPT was first pointed out in ref 66. The formalism of the DFT-SAPT method has been developed independently in two groups: Hesselmann and Jansen[67,68] and Misquitta et al.[69] The implementation of DFT-SAPT, followed by a recent inclusion of the density-fitting (DF) formalism[70] for the calculation of two-electron repulsion integrals, allows one to extend treatable sizes of molecules by an order of magnitude. In particular, a DFT-SAPT calculation for a molecule of the C_{60} size has become feasible. The idea of DFT-SAPT consists in using the Kohn–Sham (KS) and the coupled-perturbed KS (CKS) orbitals instead of the HF and coupled-perturbed HF orbitals in SAPT(HF). In this way, the electron correlation of molecules A and B, present in DFT orbitals, is taken into account in SAPT at cost of the SAPT(HF) method. It should be stressed that DFT-SAPT is a different method from the supermolecular DFT and that the individual interaction energy terms in DFT-SAPT cannot be obtained from an energy decomposition of the supermolecular DFT energy. In particular, DFT-SAPT accounts correctly for the dispersion effect, since the dispersion and exchange-dispersion energies are calculated as the corresponding SAPT corrections. The accuracy of the DFT-SAPT method has been recently confirmed by a comparison with benchmark SAPT(CC) calculations[64] and with the supermolecular CCSD(T) approach (see, for example, ref 71).

Interaction Energies of Three Molecules. The SAPT method has been extended for the interaction of three molecules in ref 72. In this approach, apart from the calculation of the usual SAPT interaction energies for three pairs of the complexes (AB, BC, and CA), one has to obtain the nonadditive contributions to the interaction energy. However, the program which calculates these corrections is strongly limited to small molecules. Fortunately enough, it can be demonstrated that an approximate sum of some of these corrections is incorporated, along with some higher-order corrections, in the nonadditive part of the supermolecular interaction energies, calculated at various levels of the supermolecular approach. Recently, using this feature,

SAPT Applied to Endohedral Fullerene Complexes

J. Chem. Theory Comput., Vol. 5, No. 6, 2009 **1589**

Podeszwa and Szalewicz[73] developed two hybrid schemes for calculating these contributions. Both schemes divide the nonadditive interaction energy into two parts: one calculated by the supermolecular approach and another part calculated by perturbation theory. For this study, we selected the scheme denoted in ref 73 as MP2+SDFT. In the MP2+SDFT approach, the nonadditive part of the interaction energy is calculated as a sum of the MP2 supermolecular nonadditive interaction energy $E_{int}^{MP2}[3,3]$ and the perturbational three-body dispersion energy $E_{disp}^{(3)}(CKS)[3,3]$, calculated from the CKS propagators of constituent molecules

$$E_{int}[3,3] = E_{int}^{MP2}[3,3] + E_{disp}^{(3)}(CKS)[3,3] \quad (5)$$

It was stated in ref 73 that the $E_{int}^{MP2}[3,3]$ term provides an estimation for the following nonadditive contributions: first-order exchange, second- and higher-order induction and exchange-induction, and a third-order mixed induction-dispersion terms. The third-order dispersion correction $E_{disp}^{(3)}$ is absent in the supermolecular MP2 method, and it should be therefore calculated separately. It should be stressed that at least third-order Møller–Plesset theory (MP3) is required to account for $E_{disp}^{(3)}$, which for the nonpolar species is a dominant nonadditive long-range effect. Summarizing, the total interaction energy in the hybrid scheme is obtained as a sum of the following contributions:

$$E_{int}^{hybrid} = E_{int}^{SAPT}(AB) + E_{int}^{SAPT}(BC) + E_{int}^{SAPT}(CA) + \\ E_{int}^{MP2}[3,3] + E_{disp}^{(3)}(CKS)[3,3] \quad (6)$$

Computational Details

All calculations were performed with the development version of the MOLPRO suite of programs.[74] In addition to the DFT-SAPT calculations, supermolecular calculations were performed with the MP2, SCS-MP2,[49] and dispersion-corrected DFT functional using the damped multipole expansion scheme developed by Grimme[43] to assess the quality of these methods in comparison to DFT-SAPT. The Boys–Bernardi counterpoise correction was used for all supermolecular calculations.[59]

DFT Calculations for a Fullerene and a Hydrogen Molecule. The C_{60} and H_2 molecules in DFT-SAPT were treated with the PBE functional[75] using an additional asymptotic correction of the exchange-correlation (xc) potential, as proposed by Grüning et al.[76] The utilization of this correction is crucial in this method, since otherwise the asymptotic density is in general too diffuse, leading to a poor description of magnitudes of intermolecular interactions.[67,69] This asymptotic correction is currently performed using a scheme which connects the respective xc potential in the bulk region with an asymptotic xc potential (having a Coulombic $-1/r$ behavior) by shifting the bulk potential by the so-called derivative discontinuity (i.e., the difference between (negative) ionization potential and HOMO energy of the underlying xc functional). For the case of the C_{60} molecule, the value of this correction was set to 0.0641 hartree and for the hydrogen molecule to 0.185 hartree. These values were obtained from the experimental vertical ionization potentials of C_{60} (0.279 hartree)[77] and H_2 (0.566 hartree)[78]

and the corresponding HOMO energies of both systems using the PBE xc functional in the TZVPP basis set (-0.215 and -0.381 hartree, respectively). The latter functional was also used in the DFT+Disp method.[43]

A total nonadditive contribution to the interaction energy was calculated by the MP2+SDFT method. Additive (i.e., two-body) contributions were calculated by DFT-SAPT. Because of the absence of the basis-set superposition error[59] in the perturbational approach, the $H_2 \cdots H_2$ and $H_2@C_{60}$ interaction energies in the $2H_2@C_{60}$ complex can be calculated without using the basis on the ghost molecule. In this way, we can utilize the results from the $H_2@C_{60}$ calculations. The additive contributions of the third order were neglected in the present study, unless they are present in the δE_{HF} term.

The core electrons (1s) for carbon atoms were frozen in all correlated calculations.

Choice of the Basis Set and Complex Geometries. The selection of a proper orbital basis set is crucial to obtain reasonable results. Because of the size of the system, we had to find a balance between the accuracy and the computational cost of the method. After some testing, we found that the TZVPP basis set[79,80] is the smallest reliable basis for our purposes. The corresponding cc-pVTZ/JKFIT[81] DF auxiliary basis set was used for the calculation of Coulombic and exchange integrals in SCF and the first-order interaction energy contributions while all doubly external integrals and all xc-type integrals occurring in the second-order DFT-SAPT were computed using the TZVPP/MP2FIT[82] fitting basis set. With these basis sets, the calculations for a single DFT-SAPT point (without the δE_{HF} correction) take about 5.5 days on Opteron/2 GHz and 2.5 days on Woodcrest/2.4 GHz computers.

The CC bond lengths of 1.458 and 1.401 Å were assumed[83] for the bonds in a pentagon ring and those between pentagon rings which, due to the I_h symmetry, fully determine the C_{60} geometry. As recommended in ref 84, we use the value of the vibrationally averaged R_{H-H} of 0.7668 Å. In view of the large size of the complexes under study, their full PES values could not be calculated. Instead, only few potentially interesting geometries of these two species were analyzed. For the $H_2@C_{60}$ complex, these geometries comprise three orientations relative to a selected pentagon ring of the fullerene (with the geometrical center of the hydrogen molecule lying on the fivefold symmetry axis of this pentagon), and two orientations related to a selected hexagon ring of the fullerene (with the geometrical center of the hydrogen molecule lying on the threefold symmetry axis of this hexagon). These orientations will be denoted as:

TP, a hydrogen molecule perpendicular to a selected pentagon ring;

PP, a hydrogen molecule parallel to a selected pentagon ring, H_2 lies in one of five symmetry planes of this pentagon;

SP, a hydrogen molecule forming the angle 45° to a selected pentagon ring; as in the case of the PP mutual orientation, H_2 lies in one of five symmetry planes of this pentagon;

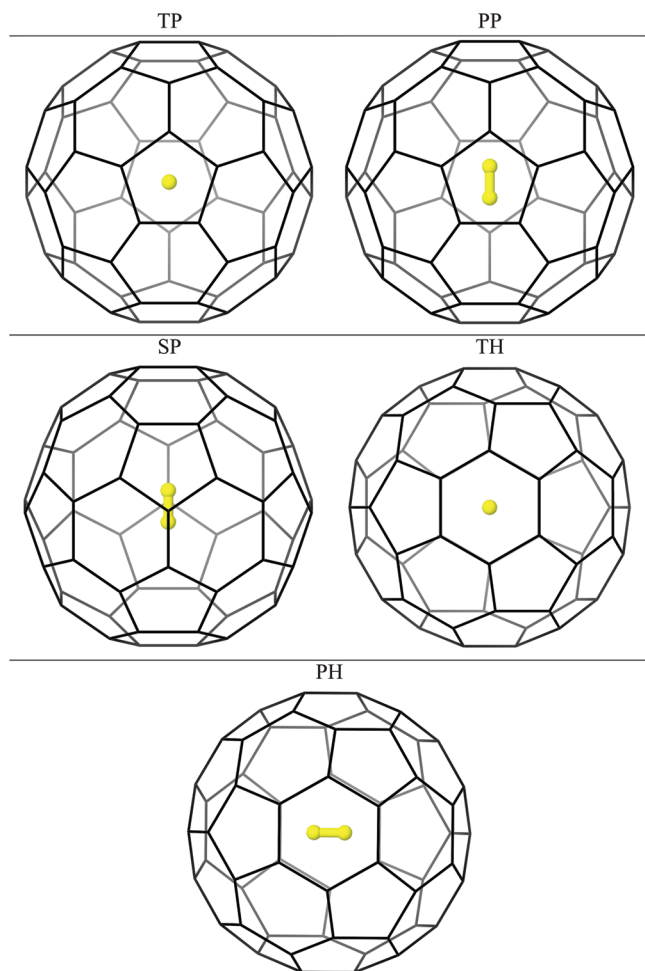**TH**, a hydrogen molecule perpendicular to a selected hexagon ring;

Figure 1. Studied orientations of one hydrogen molecule inside the fullerene molecule.

PH, a hydrogen molecule parallel to a selected hexagon ring, H_2 lies in one of three symmetry planes of this hexagon.

These orientations are also depicted in Figure 1. For each of these orientations, several distances r from the center of mass of the hydrogen molecule to the center of the fullerene were used. In two cases also distances $r > 3.5$ Å were taken into account, which correspond to the C_{60} complex with a hydrogen molecule outside the cage.

To select potentially interesting structures of $2H_2@C_{60}$, we first analyzed the CCSD(T) potential energy surface of the H_2 dimer, published recently by Hinde.[85] The global minimum for this system (-0.467 kJ/mol) occurs for a perpendicular (T) structure ($\theta_1 = 90°$, $\theta_2 = 0°$, coordinates defined in ref 85) at a distance of 3.36 Å between the geometrical centers of hydrogen molecules. To select revealing guest positions in the $2H_2@C_{60}$ complex, it is also important to know at which point the interaction energy of the $H_2 \cdots H_2$ dimer is equal to zero. For the case of the T-structure, this happens at 2.92 Å. The minimum is only slightly shallower (-0.436 kJ/mol) for the skew (S) structure ($\theta_1 = 45°$, $\theta_2 = 45°$, $\phi = 0°$) with the zero point at 2.95 Å. We also found that it will be of interest to check two "crossed" orientations: X1 ($\theta_1 = 90°$, $\theta_2 = 90°$, $\phi = 72°$) and X2 ($\theta_1 = 90°$, $\theta_2 = 90°$, $\phi = 60°$). The selected structures of the H_2 dimer were inserted into the fullerene molecule, so that (i) both hydrogen molecules are equidistant
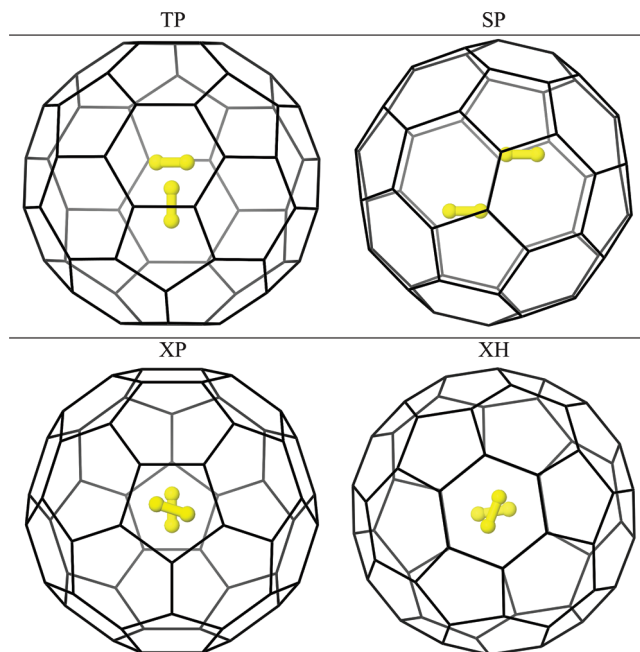

Figure 2. Studied orientations of two hydrogen molecules inside the fullerene molecule.

from the center of C_{60}, (ii) they are placed at the orientations previously used for $H_2@C_{60}$, and (iii) their geometrical centers lie on the same symmetry axis of fullerene. In this way, the following structures with two guest molecules were selected (the unspecified details of geometries are the same as for the $H_2@C_{60}$ case):

TP, a first hydrogen molecule parallel to a selected pentagon ring, the second one perpendicular to it (both H_2 forming the T-structure);

SP, both hydrogen molecules forming the 45° angle with a selected pentagon ring (both H_2 forming the S-structure);

XP, both hydrogen molecules parallel to a pentagon ring form the X1 structure;

XH, both hydrogen molecules parallel to a hexagon ring form the X2 structure.

These orientations are depicted in Figure 2.

Results and Discussion

C_{60} with One Hydrogen Molecule. The DFT-SAPT interaction energies for the complex of C_{60} with one H_2 molecule as a function of a distance from the cage center are presented in Table 1. The examination of this table reveals that there is a small stabilization effect for the endohedral complex of one hydrogen molecule with C_{60}. This effect is not large, since the minimum depth is equal to -19.35 kJ/mol, and already at $r = 1.0$ or 1.1 Å (depending on orientation), the interaction energy becomes positive. From the five orientations studied in this work, TH gives the lowest interaction energy, corresponding to the largest stabilization, although the differences between various orientations are very small, especially in the center of the fullerene cage. It is interesting to note that there is a shallow secondary minimum (or a saddle point) for the PH orientation, shifted by about 0.1 Å from the center. Another minimum region for this species occurs for the exohedral

SAPT Applied to Endohedral Fullerene Complexes

J. Chem. Theory Comput., Vol. 5, No. 6, 2009 **1591**

Table 1. DFT-SAPT Interaction Energy for Selected Orientations of the $H_2@C_{60}$ Complex[a]

r/orientation	PP	TP	SP	TH	PH
0.00	−19.26	−19.26	−19.30	−19.35	−18.59
0.10	−19.25			−19.12	−19.14
0.20	−18.89				−18.68
0.25	−18.68	−18.79	−18.62	−18.87	−18.76
0.30	−18.52				−18.38
0.50	−17.25	−16.67	−16.78	−16.56	−17.08
0.75	−12.29	−10.78	−11.46	−11.23	−12.21
0.80	−9.88	−9.07			
0.90	−7.09	−4.41			−6.91
1.00	−1.74	1.71	−0.25	0.64	−1.99
1.10	5.44	9.90		8.30	4.97
1.25	19.67	27.19	23.12	24.22	19.42
1.50	62.61	76.00	68.37	68.18	59.88
1.75	142.55	163.39			
2.00	283.67	310.91			
5.00		173.49			
6.00	1.25	4.38			
6.50	−3.07	−2.24			
7.00	−1.64	−2.17			
8.00	−0.60	−0.82			

[a] Energy values in kilojoules per mole (1 millihartree = 2.6255 kJ/mol); distances in angstroms. Note that for distances $r > 3.5$ Å the complex is *exohedral*.

complex at $r \approx 6.5$ Å, but in this case the stabilization energy is too small to enable the complex stability at room temperature.

A detailed division of the SAPT interaction energy into components and interaction energies obtained by the supermolecular MP2, SCS-MP2, and DFT+Disp[43] approaches are presented in Table 2 for the PP orientation (a parallel orientation was selected for a more detailed analysis since it turns out that this orientation is preferred for the $2H_2@C_{60}$ case). The energy components for TH, TP, SP, and PH orientations are very similar to the presented ones and are given in the Supporting Information. A distance dependence of the SAPT corrections for the PP orientation is depicted in Figure 3.

Let us first focus on the supermolecular interaction energies presented in Table 2. An inspection of these data indicates that the MP2 method overestimates the complex binding, which is the common behavior of MP2 for the interaction involving aromatic rings,[50] while SCS-MP2 is in a much better agreement with DFT-SAPT. Next, let us look at the results of the DFT+Disp method of Grimme. It can be observed that DFT+Disp performs well at the center, but for larger distances $E_{int}^{DFT+Disp}$ increases less steeply than E_{int}^{SAPT}. The reason for such a behavior of the DFT+Disp method can be ascribed to the "dispersion" contribution of the latter method which rapidly decreases as the H_2 molecule approaches the cage wall. As a result, too much space is available for the hydrogen molecule according to the Grimme method. In the strong repulsive region of $r > 1.5$ Å, the correspondence of DFT+Disp with DFT-SAPT improves because of the switching on the damping function in the DFT+Disp method and a decrease of the dispersion contribution as compared to the other contributions in the supermolecular PBE interaction energy. This behavior is also found for other orientations studied and leads to the conclusion that the DFT+Disp method may not be accurate enough

to study PES of endohedral hydrogen molecules in the C_{60} cage. However, we observed that the agreement of DFT+Disp with our DFT-SAPT reference data can be considerably improved by a modification of the damping parameter α from 20.0 to 9.2 and the prefactor $s6$ from −0.75 to −0.63 of the underlying original Grimme model.[43] While an application of this path may certainly not be advisable in general, it could provide a possible option to investigate the potential energy surface using a quantum chemistry method less expensive than MP2 or DFT-SAPT.

Let us analyze the behavior of the components of the SAPT interaction energy. The stabilization effect in the center of C_{60} comes mainly from the dispersion energy, while the first-order exchange energy gives the most important repulsive contribution. This trend continues as we approach the cage wall: both corrections grow in absolute values, but the dispersion effect increases slower, and finally the first-order exchange energy prevails leading to the repulsive character of the interaction. The induction energy is almost as important as the dispersion energy, but it is strongly damped by its exchange counterpart (this is a common effect for the short-range induction contribution; see, for example, ref 86). Nonetheless, for $r > 1.5$ Å the effective $E_{ind}^{(2)} + E_{exch-ind}^{(2)}$ contribution becomes more important than the dispersion energy.

The above analysis shows that great care should be exercised when modeling PES for endohedral fullerene complexes with a simple repulsion+dispersion model (see, for example, ref 87), since neglected short-range terms may become as large as the included ones, when approaching the cage wall.

An examination of Figure 3 reveals that for the PP orientation there is a shallow well in the attractive region and a steep repulsive potential wall for larger r, where the guest approaches the host cage. A similar pattern is found for other orientations. Table 1 shows that the center of the well is practically isotropic and large enough to allow for an almost free rotation of the H_2 guest. Anisotropy becomes more pronounced for larger distances (i.e., closer to the cage wall). A comparison of the data from the Supporting Information allows us to conclude that, as expected, the dispersion and exchange-dispersion energies are the most isotropic SAPT terms, while the first-order exchange, induction, and exchange-induction energies exhibit the largest anisotropy. However, even at $r = 1.5$ Å (highly repulsive region) this anisotropy does not exceed a few percent (e.g., first-order exchange corrections for the PH and TP orientations differ by 18% for this distance).

Let us analyze how the just presented results can be used to select the most interesting geometries describing the $2H_2@C_{60}$ complex. In view of the data from Table 1, shifting of a hydrogen molecule from the center by more than 1.0 Å will cause a strong repulsion from carbon atoms. This means that two hydrogen molecules in the fullerene cage can be separated by at most 2 Å, otherwise a strong repulsion from the cage wall will result. However, the PES for two hydrogen molecules is highly repulsive for such a small distance.[85] On the other hand, the PES for the H_2 dimer passes through zero at about 3 Å. If two hydrogen molecules are placed on

Table 2. Components of the DFT-SAPT Interaction Energy for the PP Orientation of the $H_2@C_{60}$ Complex[a]

r	$E_{elst}^{(1)}$	$E_{exch}^{(1)}$	$E_{ind}^{(2)}$	$E_{exch-ind}^{(2)}$	$E_{disp}^{(2)}$	$E_{exch-disp}^{(2)}$	δE_{HF}	E_{int}^{SAPT}	E_{int}^{MP2}	$E_{int}^{SCS-MP2}$	$E_{int}^{DFT+Disp}$
0.00	−7.20	21.16	−5.02	4.50	−36.09	4.13	−0.74	−19.26	−30.69	−21.58	−21.27
0.10	−7.34	21.54	−5.16	4.63	−36.38	4.21	−0.76	−19.25	−30.65	−21.52	
0.20	−7.77	22.70	−5.54	4.99	−36.81	4.35	−0.80	−18.89	−30.54	−21.31	
0.25	−8.10	23.58	−5.82	5.24	−37.20	4.46	−0.85	−18.68	−30.44	−21.14	−21.11
0.30	−8.49	24.65	−6.16	5.55	−37.81	4.62	−0.89	−18.52	−30.31	−20.93	
0.50	−11.12	31.71	−8.66	7.79	−41.34	5.54	−1.17	−17.25	−29.29	−19.39	−20.60
0.75	−17.58	48.81	−14.66	13.15	−47.59	7.39	−1.81	−12.29	−25.76	−14.84	−18.65
0.80	−19.53	53.91	−16.65	14.89	−47.83	7.30	−1.98	−9.88	−24.54	−13.35	
0.90	−24.29	66.30	−21.83	19.39	−53.31	9.00	−2.35	−7.09	−21.29	−9.52	
1.00	−30.28	82.02	−27.82	24.47	−57.90	10.50	−2.74	−1.74	−16.68	−4.23	−11.28
1.10	−38.15	102.45	−36.57	31.74	−63.12	12.14	−3.05	5.44	−10.23	3.00	
1.25	−54.38	144.78	−55.84	47.02	−73.99	15.10	−3.02	19.67	4.29	18.90	10.52
1.50	−99.70	262.47	−114.98	89.25	−97.96	21.35	2.18	62.61	48.95	66.59	58.43
1.75	−181.44	476.85	−234.40	156.91	−133.36	28.20	29.79	142.55	137.56	159.39	
2.00	−316.84	846.93	−447.64	230.62	−182.68	31.32	121.97	283.67	298.85	326.50	
6.00	−7.66	24.68	−5.78	5.24	−15.93	2.47	−1.78	1.25	−0.38	2.45	
6.50	−2.00	5.64	−0.76	0.69	−6.99	0.69	−0.34	−3.07	−3.62	−2.23	
7.00	−0.02	1.23	−0.14	0.12	−2.99	0.18	−0.02	−1.64	−2.51	−1.83	
8.00	0.06	0.05	0.00	0.00	−0.63	0.01	−0.09	−0.60	−0.77	−0.60	

[a] The total DFT-SAPT energy, as well as MP2, SCS-MP2, and DFT+Disp interaction energies are also given. Energy values in kilojoules per mole; distances in angstroms. Note that for distances $r > 3.5$ Å the complex is *exohedral*.
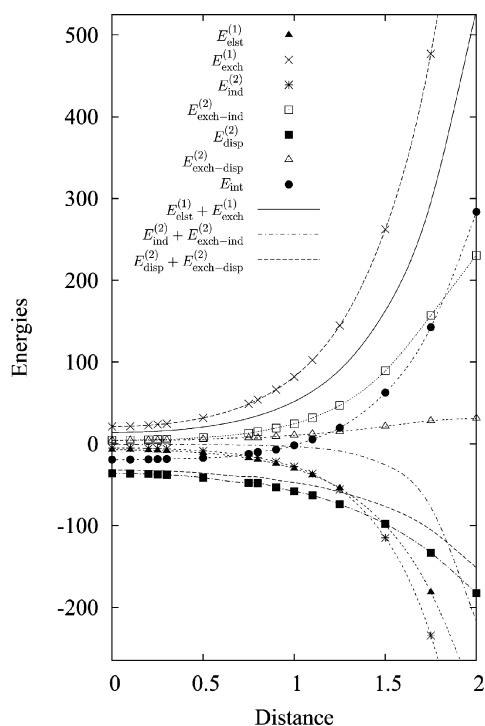
Figure 3. Components of the interaction energy for the PP orientation of $H_2@C_{60}$. Energy values are in kilojoules per mole, distances are in angstroms.

the opposite sides from the center of C_{60}, at a distance $r =$ 1.5 Å each, they will exhibit a strong repulsion from the cage wall, but the hydrogen molecules will not repel each other. Therefore, the most interesting geometries for the $2H_2@C_{60}$ complex are those with hydrogen molecules at distances from 1.0 to 1.5 Å from the C_{60} center. In this region, a minimum of the $2H_2@C_{60}$ interaction energy should be expected.

Accuracy of the Present Calculations. The DFT-SAPT approach is far too expensive to perform a geometry optimization of the $H_2@C_{60}$ and $2H_2@C_{60}$ complexes, raising questions about the accuracy of our results. The problem is

especially important in the latter case, in which strain should lead to the bond-length distortion. To address this issue, we performed several additional test calculations.

The most important question to be answered is: Does an appropriate deformation of the host and/or guest allow the insertion of a second H_2 molecule into C_{60}? As already noted, the optimization of the geometry is out of the question in our case, and therefore we tackled this problem in another way. We unphysically enlarged the fullerene cage by increasing all carbon−carbon distances by 5% and calculated the interaction energy for the TP orientation and distances $r = 1.1$ and 1.25 Å. The resulting DFT-SAPT interaction energies are equal to −1.52 and +4.85 kJ/mol, respectively. This simple test shows that the unphysically large blowup of the cage shifts the zero point of PES from about 1.0 to ca. 1.2 Å, the value still too small to avoid a repulsion between two hydrogen molecules. Therefore, it seems highly improbable that much smaller changes in the geometry of C_{60} during the geometry optimization would allow a deformed $H_2@C_{60}$ to accept one more hydrogen molecule. Additionally, we found that a change in the distance between the hydrogen atoms ($R_{H-H} = 0.7408$ Å) has a negligible effect of 0.1 kJ/mol on the DFT-SAPT energy for the PP orientation at $r = 1.0$ Å. Summarizing, these data strongly indicate that neither a deformation of the host nor that of the guest would result in stabilizing of the complex of C_{60} with two hydrogen molecules.

Finally, the basis set effects were analyzed by performing the DFT-SAPT calculations in a sequence of DZP, TZVP, and TZVPP basis sets for the TP orientation at $r = 0$. The results presented in Figure 4 indicate that the quality of the dispersion energy depends crucially on the basis set used, while all other SAPT corrections are almost saturated even for the smallest DZP basis set. However, because of the importance of the dispersion energy the DZP basis set cannot be used for the $H_2@C_{60}$ complex, as it recovers only 61% of the TZVPP dispersion term. On the other hand, the TZVP $E_{disp}^{(2)}$ energy is much closer to the TZVPP value (its absolute
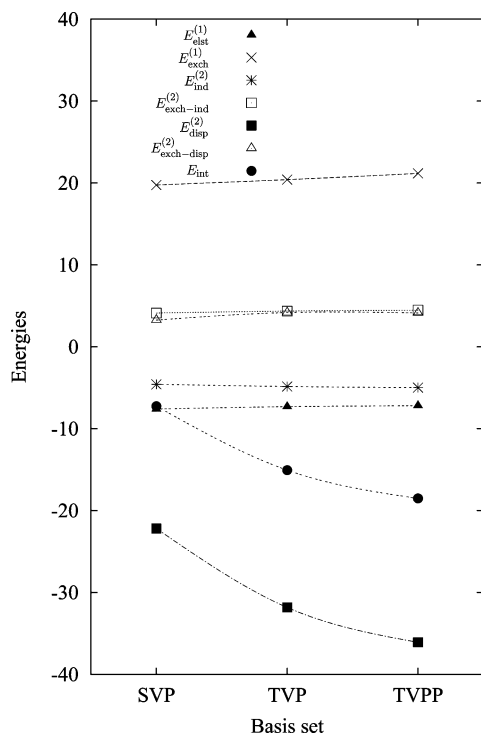
SAPT Applied to Endohedral Fullerene Complexes

J. Chem. Theory Comput., Vol. 5, No. 6, 2009 **1593**

Figure 4. Basis set dependence of the SAPT components for the TP orientation of $H_2@C_{60}$ at distance $r = 0$. Energies are in kilojoules per mole.

value is smaller by 12%), allowing us to draw a conclusion that the presented results should be reliable. The remaining error resulting from the unsaturation of the basis can be conservatively estimated as about 15%.

C_{60} with Two H_2 Molecules. The results of the calculations of the interaction energy of fullerene and two hydrogen molecules are presented in Table 3. In this table, in addition to the total interaction energy E_{int}^{hybrid}, also the following quantities are presented: a sum of the DFT-SAPT interaction energies of the first and second hydrogen molecule with the fullerene, the DFT-SAPT interaction energy for the dimer of the hydrogen molecule, the MP2 nonadditive contribution, and the nonadditive CKS third-order dispersion term. The total supermolecular MP2 interaction energy is also listed for comparison.

An examination of Table 3 shows that three-body effects for this case are rather small (less than 10% of the total interaction energy). Usually MP2 and third-order dispersion nonadditive effects are of the opposite signs, which makes the total nonadditive contribution even smaller. The third-order dispersion energy is found to be insignificant for almost all tested geometries. However, the MP2 supermolecular method cannot be used for the $2H_2@C_{60}$ case, anyway, since the two-body energies predicted by MP2 are too attractive for $H_2@C_{60}$ in comparison to the DFT-SAPT reference values.

The shape of the $2H_2@C_{60}$ potential is determined by the two-body effects. The anisotropy of the three-body interaction energy is quite pronounced. In all tested cases, the interaction energy is positive, denoting that the endohedral complex of fullerene with two H_2 molecules is not stabilized. The minimum repulsion (ca. 24.7 /kJ/mol) occurs for both

Table 3. Components of the Interaction Energy for Various Orientations of Hydrogen Molecules in the $2H_2@C_{60}$ Complex[a]

r	$\sum E_{int}^{SAPT}$ $(H_2@C_{60})$[b]	E_{int}^{SAPT} $(H_2\cdots H_2)$	$E_{int}^{MP2}[3,3]$	$E_{disp}^{(3)}(CKS)[3,3]$	E_{int}^{hybrid}	E_{int}^{MP2}
			TP			
0.50	−33.92	537.66	−1.04	−6.34	496.35	583.51
0.75	−23.07	133.97	4.46	−2.08	113.27	104.53
0.80	−18.95	100.56	4.69	−1.66	84.64	68.14
0.90	−11.50	55.22	4.63	−1.07	47.28	23.51
1.00	−0.04	29.18	4.19	−0.58	32.75	0.45
1.10	15.33	14.64	3.63	−0.25	33.35	2.97
1.25	46.86	4.77	2.85	−0.17	54.31	23.92
1.50	138.60	0.36	2.10	−0.03	141.03	116.52
1.75	305.94	−0.19	1.94	−0.05	307.65	305.65
			XP			
0.50	−34.51	469.32	0.59	−25.23	392.71	490.25
0.75	−24.58	120.33	4.47	−3.42	96.81	85.43
0.90	−14.18	48.97	4.08	−0.55	38.31	13.19
1.00	−3.49	25.98	3.59	−1.18	24.91	−3.16
1.10	10.87	13.44	3.12	−0.91	26.53	−4.11
1.25	39.33	4.81	2.56	−0.22	46.49	15.32
1.50	125.22	0.71	2.10	−0.18	127.85	100.21
			SP			
0.50	−33.56	460.05	0.77	−7.99	419.27	496.42
0.75	−22.92	132.00	4.32	−2.45	110.95	100.79
1.00	−0.50	29.37	3.86	−0.88	31.85	4.10
1.25	46.23	4.97	2.61	−2.63	51.18	23.19
1.50	136.73	0.44	1.97	−0.15	138.98	115.25
			XH			
0.50	−34.16	476.35	0.48	−7.08	435.59	497.80
0.75	−24.42	121.31	4.39	−2.80	98.48	86.46
0.90	−13.82	49.34	3.99	−1.70	37.82	13.56
1.00	−3.98	26.19	3.49	−0.91	24.79	−3.07
1.10	9.95	13.55	3.00	−0.59	25.91	−4.40
1.25	38.85	4.85	2.41	−0.46	45.66	13.86
1.50	119.77	0.73	1.89	−0.24	122.14	92.90

[a] The total interaction energy E_{int}^{hybrid} is a sum of additive DFT-SAPT energies and nonadditive ($E_{int}^{MP2}[3,3]$ and $E_{disp}^{(3)}(CKS)[3,3]$) energies; see eq 6. The total supermolecular MP2 interaction energy is listed in the last column. Energy values in kilojoules per mole; distances in angstroms. [b] A sum of interaction energies of both fullerene−hydrogen molecule pairs; see eq 4.

"crossed" structures for hydrogen molecules at distance of 2.0 Å from each other and of 1.0 Å from the center of C_{60}. It is noteworthy that these two orientations are different from the global-minimum orientation of the H_2 dimer (corresponding to the TP structure).[85] Evidently, the TP orientation is more repulsive (ca. 32.8 kJ/mol) since in such an orientation one hydrogen atom (of the H_2 molecule perpendicular to a pentagon ring) "touches" the cage wall sooner than in the case of the parallel orientation. Thus, for the "crossed" structures, the minimum is a result of an interplay of the two-body interaction energies of the $H_2\cdots H_2$ and $H_2@C_{60}$ species. It seems unlikely that interaction energies of other orientations would be significantly lower than the tried ones. Therefore, one can conclude that the present method does not yield the stabilization of the $2H_2@C_{60}$ complex. It can also be observed that E_{int}^{MP2} predicts falsely a small stabilization effect for "crossed" structures, which can be explained by too attractive interaction energies predicted for $H_2@C_{60}$ (Table 2 and the Supporting Information).

In view of the recent synthesis of two hydrogen molecules in a closed C_{70} cage,[18] we performed the DFT-SAPT calculations for several points of PES for the $2H_2@C_{70}$ complex. Because of the limitations of our third-order

1594 *J. Chem. Theory Comput., Vol. 5, No. 6, 2009*

Korona et al.

dispersion code, only the additive part of the interaction energy was obtained. The geometry of the C_{70} fullerene was taken from ref 88. The X1 structure of the H_2 dimer was used with the geometrical centers of H_2 lying on the fivefold symmetry axis of C_{70}, on the opposite sides from the cage center at distances $r = 1.2, 1.3, 1.4,$ and 1.5 Å from this center. The asymptotic shift of the bulk xc potential of the C_{70} fullerene was taken as 0.0596 hartree. A smaller TZVP basis was used. The additive part of the DFT-SAPT energy for these distances is equal to $-16.3, -19.8, -13.6,$ and -9.1 kJ/mol, respectively. It can be noted that the largest (in absolute value) interaction energy still occurs for the repulsive geometry of the $H_2 \cdots H_2$ dimer. Since the result is obtained in the TZVP basis and the attractive dispersion energy benefits the most from using the larger TZVPP basis, it can be estimated that the value of the interaction energy can be about 10−20% lower in the full basis set limit. The experience gained from the $2H_2@C_{60}$ case allows one to estimate the possible nonadditive effects as at most 10% of the total interaction energy. Thus, in agreement with the experimental findings,[11,18] the DFT-SAPT approach yields the stabilization of two hydrogen molecules inserted into the C_{70} fullerene and the destabilization of the smaller $2H_2@C_{60}$ complex.

Summary and Conclusions

The highly accurate DFT-SAPT method with density fitting used for two-electron repulsion integrals was shown to be applicable for an analysis of selected points of the potential energy surface for the nonbonding interactions of the C_{60} fullerene with hydrogen molecules.

The calculations were performed with DFT-SAPT in a reasonably large TZVPP orbital basis for selected orientations of one and two H_2 molecules inside the C_{60} fullerene. The nonadditive effects were modeled by a recently proposed hybrid method.[73] For the endohedral complex $H_2@C_{60}$, a small stabilization effect of about 19.4 kJ/mol (4.6 kcal/mol) was found, with the minimum of PES in the center of the fullerene. It can be noted that this value agrees nicely with a recent estimate of Slanina et al.,[47] who predicted the stabilization of at least 4 kcal/mol for this species. The PES of $H_2@C_{60}$ is almost flat in the vicinity of the cage center and nearly isotropic, especially in the attractive region. This result is consistent with a recent theoretical study of the translation-rotation spectrum of H_2 confined in C_{60},[89] where the first rotational level of $H_2@C_{60}$ is virtually identical to the level for the free hydrogen molecule. The hydrogen molecule inside the fullerene is bound mainly by the dispersion interaction, while the first-order exchange term represents the main repulsive component of the interaction energy. However, other SAPT corrections are far from being negligible. For instance, the induction energy is of the same order of magnitude as the dispersion energy, but is strongly quenched by its exchange counterpart in the vicinity of the cage center. A small exohedral minimum, expected on the basis of model considerations, was also observed.

For the $2H_2@C_{60}$ complex, no stabilization effect was found. This finding is in agreement with the lack of the

experimental reports of two H_2 molecules inside the opened and closed C_{60} cage and with only a small amount of the $2H_2@C_{70}$ obtained in the mixture with $H_2@C_{70}$. The lowest repulsion for the $2H_2@C_{60}$ complex occurs for the "crossed" orientation of the hydrogen molecules, which are separated by ca. 2.0 Å from each other. Interestingly enough, the stabilization of $H_2@C_{60}$ and destabilization of $2H_2@C_{60}$ was also predicted by a simple MM model.[16,19] For the same orientation of the hydrogen molecules in a larger C_{70} fullerene, separated by 2.6 Å, the DFT-SAPT method yields the negative interaction energy, confirming, in agreement with recent experimental findings, the stability of $2H_2@C_{70}$. Interestingly, also in this case the MM method yielded the stabilization of both $H_2@C_{70}$ and $2H_2@C_{70}$ species, correctly predicting their energy difference.[19]

Supporting Information Available: Results of calculations of DFT-SAPT, MP2, SCS-MP2, and DFT-Disp interaction energies, as well as DFT-SAPT energy components for the TP, TH, SP, and HP orientations of the $H_2@C_{60}$ complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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J. Chem. Theory Comput., Vol. 5, No. 6, 2009 **1595**

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