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# Anisotropic intermolecular interactions in van der Waals and hydrogen-bonded complexes: What can we get from density functional calculations?

Anne Milet

*Laboratoire de Chimie Quantique, UMR 7551 CNRS/ULP, Institut Le Bel, Université Louis Pasteur, BP 296, F-67008 Strasbourg Cedex, France and Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

Tatiana Korona

*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

Robert Moszynski<sup>a)</sup> and Elise Kochanski

*Laboratoire de Chimie Théorique, UMR 7551 CNRS/ULP, Institut Le Bel, Université Louis Pasteur, BP 296, F-67008 Strasbourg Cedex, France and Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

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The applicability of various density functional theory (DFT) methods to describe the anisotropy of the intermolecular potential energy surfaces of hydrogen-bonded  $[\text{OH}^- - \text{H}_2\text{O}, (\text{H}_2\text{O})_2]$  and van der Waals  $[\text{CO} - \text{H}_2\text{O}, \text{He} - \text{CO}_2]$  complexes has been tested by comparison with supermolecule CCSD(T) (coupled-cluster method restricted to single, double, and noniterative triple excitations) and perturbational SAPT (symmetry-adapted perturbation theory) results computed for the same geometries and with the same basis sets. It is shown that for strongly bound ionic hydrogen-bonded complexes, like  $\text{OH}^- - \text{H}_2\text{O}$ , hybrid approaches provide accurate results. For other systems, including the water dimer, the DFT calculations fail to reproduce the correct angular dependence of the potential surfaces. It is also shown that a hybrid functional adjusted to reproduce the CCSD(T) value of the binding energy for the water dimer produces results worse than the standard hybrid functionals for  $\text{OH}^- - \text{H}_2\text{O}$ , and fails to describe the correct anisotropy of the  $\text{CO} - \text{H}_2\text{O}$  interaction.

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## I. INTRODUCTION

Recent advances in the experimental investigations of the intermolecular interaction phenomena have stimulated theoretical developments of the *ab initio* perturbational<sup>1</sup> and supermolecular<sup>2</sup> approaches, as well as of the dynamical methods to generate the (high-resolution) spectra and (state-to-state) scattering cross sections.<sup>3–5</sup> For some complexes the data from spectroscopic experiments can be interpreted by performing the geometry optimization followed by a frequency calculation in the harmonic approximation. In most cases, however, the knowledge of the full intermolecular potential energy surfaces is necessary to make the assignments of the experimentally observed positions of lines and intensities. This is true even for quite strongly bound hydrogen-bonded complexes like the ammonia dimer<sup>6–9</sup> or the water trimer.<sup>10,11</sup>

In recent years important advances have been made in the developments of density functional theory (DFT) methods, and their applications to various chemical problems (see Refs. 12–14 for recent collections of review papers in this field). The applicability of various DFT approaches to describe intermolecular interactions in van der Waals and

hydrogen-bonded complexes has been the subject of numerous papers, for instance, Refs. 15–35. Most of these studies were restricted to a few geometries and properties of various complexes. The numerical results reported suggested that DFT yields reliable predictions for the geometries corresponding to the global minima on the potential energy surfaces and the stabilization energies of some hydrogen-bonded and ionic complexes. To our knowledge, the accuracy of the DFT approaches to reproduce the anisotropy of the potential energy surfaces (to which the spectra are the most sensitive) has not been tested thus far.

In a recent paper Handy and collaborators<sup>33</sup> reported a DFT calculation of the full potential energy surface for the water dimer. The authors of Ref. 33 did not employ a standard functional available in the literature, but instead, they adjusted one parameter in a hybrid functional to reproduce the experimental geometries of the monomers and of the dimer. The global minimum and the transition states are correctly located on the resulting potential energy surface, while the binding energy and the barriers are slightly underestimated. Obviously, an application of the procedure employed in Ref. 33 requires some *a priori* knowledge of the properties of the complex under study. However, it is interesting to check if the adjusted functional works just for a given com-

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: rmoszyns@chem.uw.edu.pl

plex, or if it can be applied with trust to describe anisotropic interactions in similar systems.

In this paper we report a theoretical study of the applicability of the density functional approaches to describe anisotropic interactions in hydrogen-bonded and van der Waals complexes. The results of DFT calculations are compared with the data from highly correlated calculations using the coupled-cluster method (with single, double, and approximate triple excitations), CCSD(T), and the symmetry-adapted perturbation theory (SAPT). We also check whether a density functional adjusted to reproduce the anisotropy of the potential energy surface of one system can be used with trust for other systems. The plan of this paper is as follows. In Sec. II we briefly present the theoretical methods used in the calculations. In Sec. III we describe the details of calculations. In Sec. IV we report the numerical results for the hydrogen-bonded systems  $\text{OH}^-$ - $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$ , and the van der Waals complexes  $\text{CO}$ - $\text{H}_2\text{O}$  and  $\text{He}$ - $\text{CO}_2$ . Finally, concluding remarks are given in Sec. V.

## II. METHODS OF CALCULATION

We consider the interaction of two closed-shell molecules A and B. The supermolecule interaction energy for the complex AB is given by the standard formula

$$E_{\text{int}}^{\text{SM}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}, \quad (1)$$

where  $E_{\text{AB}}$ ,  $E_{\text{A}}$ , and  $E_{\text{B}}$  denote the total energies of the dimer AB, and monomers A and B, respectively. The superscript SM is the short-hand notation for the supermolecule method used in actual calculations. The superscript HF is used for the Hartree-Fock calculations, and CCSD(T) for the coupled-cluster single and double excitations calculations with an approximate inclusion of the connected triple excitations.<sup>36,37</sup> The usual symbols BP86, BLYP, and BPW91 will be used for the density functional approaches based on the exchange potential of Becke,<sup>38</sup> and the correlation potentials of Perdew,<sup>39,40</sup> Lee *et al.*,<sup>41</sup> and Perdew *et al.*,<sup>42,43</sup> respectively. The hybrid approaches<sup>44</sup> utilizing a suitable combination of the Hartree-Fock-type and Becke's<sup>38</sup> exchange potentials, as well as the correlation potentials quoted above will be denoted by B3P86, B3LYP, and B3PW91, respectively.

The results of supermolecule calculations were analyzed using symmetry-adapted perturbation theory (SAPT).<sup>1</sup> The interaction energy  $E_{\text{int}}^{\text{SAPT}}$  was represented by the sum of the first- and second-order contributions<sup>1</sup>

$$E_{\text{int}}^{\text{SAPT}} = E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-def}}^{(2)} + E_{\text{exch-disp}}^{(2)}, \quad (2)$$

where  $E_{\text{elst}}^{(1)}$  is the electrostatic energy,  $E_{\text{exch}}^{(1)}$  is the first-order exchange-repulsion energy,  $E_{\text{ind}}^{(2)}$  and  $E_{\text{disp}}^{(2)}$  denote the induction and dispersion energies, and  $E_{\text{exch-ind}}^{(2)}$ ,  $E_{\text{exch-def}}^{(2)}$ , and  $E_{\text{exch-disp}}^{(2)}$  are the exchange-induction, exchange-deformation, and exchange-dispersion energies. In practice

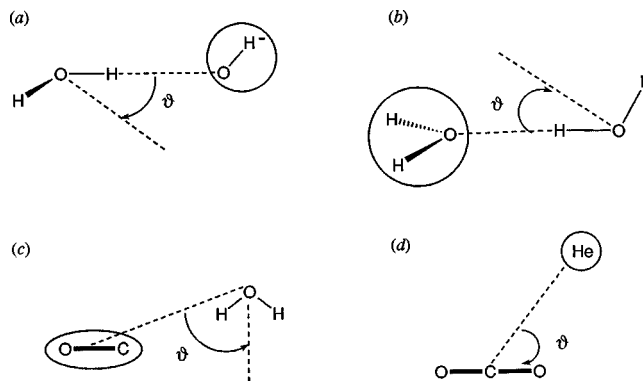


FIG. 1. Definitions of the geometrical parameters of the (a)  $\text{OH}^-$ - $\text{H}_2\text{O}$ , (b)  $(\text{H}_2\text{O})_2$ , (c)  $\text{CO}$ - $\text{H}_2\text{O}$ , and (d)  $\text{He}$ - $\text{CO}_2$  complexes. The monomer rotated is put in the circle.

Eq. (2) was evaluated using the techniques developed in Refs. 45–52. The SAPT computational procedure employed in the present paper is the same as in Ref. 53.

## III. COMPUTATIONAL DETAILS

In this paper we study four representative systems:  $\text{OH}^-$ - $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ ,  $\text{CO}$ - $\text{H}_2\text{O}$ , and  $\text{He}$ - $\text{CO}_2$ . These complexes can be considered as representatives of systems bound by strong electrostatic [ $\text{OH}^-$ - $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ ], induction and dispersion [ $\text{CO}$ - $\text{H}_2\text{O}$ ], and dispersion [ $\text{He}$ - $\text{CO}_2$ ] forces. The interaction energies at the minima range from about 22 kcal/mol for  $\text{OH}^-$ - $\text{H}_2\text{O}$  to 0.1 kcal/mol for  $\text{He}$ - $\text{CO}_2$ .

For the  $\text{OH}^-$ - $\text{H}_2\text{O}$  ion we used the aug-cc-pVDZ<sup>54</sup> basis set. The geometries of the hydroxide and water subsystems were fixed at their experimental values:  $d(\text{OH}) = 0.964 \text{ \AA}$  for  $\text{OH}^-$ , and  $d(\text{OH}) = 0.9572 \text{ \AA}$ ,  $\angle \text{HOH} = 104.52^\circ$  for the water molecule.

For the water dimer we used the medium-polarized basis set of Sadlej<sup>55</sup> augmented with a diffuse  $f$  function on the oxygen (0.363), and a diffuse  $d$  function on the hydrogen (0.328). The geometry of the water monomer was the same as in the  $\text{OH}^-$ - $\text{H}_2\text{O}$  case.

For the  $\text{CO}$ - $\text{H}_2\text{O}$  complex we also used the medium-polarized basis set of Sadlej,<sup>55</sup> but no diffuse functions were added. The geometry of the water monomer was the same as in  $\text{OH}^-$ - $\text{H}_2\text{O}$ , and the CO distance was fixed at its experimental value,  $d(\text{CO}) = 1.128 \text{ \AA}$ .

For the He atom we employed the  $[5s3p2d]$  basis used in our previous studies of the He-molecule complexes.<sup>56</sup> For  $\text{CO}_2$  we used the basis B2 of Maroulis and Thakkar.<sup>57</sup> The geometry of  $\text{CO}_2$  was also fixed at its experimental value,  $d(\text{CO}) = 2.1944 \text{ bohr}$ .

For each system we performed supermolecule DFT, HF, and CCSD(T) calculations, as well as SAPT calculations for several relative orientations of the monomers (one of the monomers is rotated by an angle  $\vartheta$  starting from the position of the minimum). The definition of the angular coordinate varied in the calculations is given in Fig. 1. The details of the geometric parameters and basis sets used in the calculations can be obtained from the authors on request. All supermolecule calculations were done with the GAUSSIAN 94 code.<sup>58</sup> The computed interaction energies were corrected for the

TABLE I. Electric properties (in a.u.) of the  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{OH}^-$ ,  $\text{CO}_2$ , and He monomers calculated by various methods.

	HF	CCSD(T)	BLYP	BP86	BPW91	B3LYP	B3P86	B3PW91	Experimental
$\text{H}_2\text{O}$									
$\mu$	0.781	0.724	0.709	0.708	0.708	0.731	0.731	0.730	0.727 <sup>a</sup>
$\alpha_{xx}$	7.766	9.347	10.374	10.242	10.079	9.490	9.293	9.318	9.549 <sup>b</sup>
$\alpha_{yy}$	9.199	10.108	10.870	10.726	10.606	10.326	10.149	10.147	10.311 <sup>b</sup>
$\alpha_{zz}$	8.533	9.738	10.651	10.538	10.396	9.972	9.803	9.806	9.907 <sup>b</sup>
$\text{CO}$									
$\mu$	-0.100	0.055	0.073	0.087	0.087	0.036	0.044	0.047	0.048 <sup>c</sup>
$\alpha_{\perp}$	11.088	11.720	12.306	12.224	12.080	11.877	11.742	11.739	12.169 <sup>d</sup>
$\alpha_{\parallel}$	14.431	15.870	16.110	15.998	15.849	15.555	15.382	15.389	15.746 <sup>d</sup>
$\text{OH}^-$									
$\mu$	0.604	0.545	0.541	0.538	0.537	0.557	0.554	0.554	e
$\alpha_{\perp}$	15.431	23.556	31.985	30.847	30.176	24.919	23.583	24.040	e
$\alpha_{\parallel}$	15.006	17.860	19.654	19.812	19.514	18.202	18.144	18.091	e
$\text{CO}_2$									
$Q_{zz}$	-3.833	-3.173	-3.246	-3.116	-3.121	-3.354	-3.250	-3.256	-3.180 <sup>f</sup>
$\alpha_{\perp}$	11.951	12.800	13.420	13.331	13.185	12.936	12.795	12.784	12.910 <sup>g</sup>
$\alpha_{\parallel}$	23.764	26.600	26.965	26.751	26.604	26.134	25.883	25.897	26.610 <sup>g</sup>
$\text{He}$									
$\alpha$	1.318	1.387	1.548	1.549	1.534	1.488	1.479	1.479	1.383 <sup>h</sup>

<sup>a</sup>Reference 61.<sup>b</sup>Reference 62.<sup>c</sup>Reference 63.<sup>d</sup>Reference 64.<sup>e</sup>No experimental data available.<sup>f</sup>Reference 65.<sup>g</sup>Reference 66.<sup>h</sup>Reference 67.

basis-set superposition error using the Boys–Bernardi prescription.<sup>59</sup> The SAPT calculations were performed with the SAPT system of codes.<sup>60</sup>

## IV. NUMERICAL RESULTS AND DISCUSSION

### A. Electric properties of the monomers

Before we discuss the applicability of various DFT methods to describe anisotropic interactions in hydrogen-bonded and van der Waals complexes, we first analyze the performance of DFT to reproduce the electric properties of the monomers. Comparison of the DFT, CCSD(T), and experimental results for the lowest electric moments and polarizabilities will give us an idea about the accuracy of the DFT electron densities and static linear response functions of the monomers. This point is quite important for our further analysis since the accuracy of the electrostatic and induction terms depends on the accuracy of the electron densities and static linear response functions of the monomers.<sup>45,48</sup>

The results of the CCSD(T) and DFT calculations are reported in Table I. For comparison, we also included the most recent experimental results.<sup>61–67</sup> The CCSD(T) results were obtained from finite-field calculations with a field strength of 0.001 a.u. The DFT calculations employed analytic techniques. An inspection of Table I shows that, except for the small dipole moment of CO, all DFT methods considered in the present paper reproduce accurately the CCSD(T) and experimental electric moments of the monomers, the errors being of the order of a few percent. For the difficult case of the CO molecule the functionals based on the pure Becke exchange<sup>38</sup> overestimate the CCSD(T) result by 30%–50%. The hybrid methods work better, and the corresponding error ranges are reduced to 15%–35%. One may note that the B3P86 and B3PW91 functionals reproduce the

dipole moment of the CO molecule better than the CCSD(T) approach. We believe that this very good agreement is somewhat fortuitous given the *spd* quality of the basis used in the calculations. The overall agreement is rather satisfactory, which gives us confidence that the electrostatic term will be correctly reproduced in the DFT calculations of the interaction energies.

Similar conclusions about the accuracy of DFT can be drawn for the static dipole polarizabilities. Except for the He atom polarizability, all DFT methods reproduce accurately the CCSD(T) and experimental polarizabilities of the monomers. Again, the errors are of the order of a few percent. For the helium atom better results are obtained from the hybrid functionals, the error being around 6% instead of  $\approx 11\%$  for the functionals based on the pure Becke's exchange. In general, the results of the CCSD(T) and DFT calculations compare very favorably. This suggests that within the DFT framework the static linear response functions of the monomers are rather accurate. Thus, the induction energies included in the supermolecule DFT interaction energies should be correct.

It is worth noting that the CCSD(T) values for the electric moments and static dipole polarizabilities agree very well with the available experimental data.<sup>61–67</sup> This shows that the quality of the basis sets used in the calculations is rather good, and in consequence, our results for the interaction energies of various complexes should be reliable.

### B. Hydrogen-bonded complexes: $\text{OH}^- - \text{H}_2\text{O}$ and $(\text{H}_2\text{O})_2$

The results of supermolecule HF, CCSD(T), and DFT calculations for the hydrogen-bonded complexes,  $\text{OH}^- - \text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$ , are reported in Tables II and III, respectively.

TABLE II. Angular dependence of the OH<sup>-</sup>-H<sub>2</sub>O interaction energies (in kcal/mol) calculated by various methods.

$\vartheta$	-128°	-98°	-68°	-38°	-8°	22°	52°
$E_{\text{elst}}^{(1)}$	11.77	8.82	-0.07	-14.96	-29.71	-30.38	-26.01
$\epsilon_{\text{elst}}^{(1)}$	-2.18	-2.00	-1.54	-0.70	0.21	0.12	-0.17
$E_{\text{exch}}^{(1)}$	11.76	11.70	12.68	18.15	27.45	26.45	21.79
$\epsilon_{\text{exch}}^{(1)}$	2.86	2.91	3.16	3.90	5.16	5.40	5.01
$E_{\text{ind}}^{(2)}$	-11.87	-12.00	-13.07	-16.70	-22.02	-21.07	-18.31
$\epsilon_{\text{ind}}^{(2)}$	-2.88	-2.91	-3.09	-3.42	-3.92	-4.14	-4.11
$E_{\text{exch-ind}}^{(2)}$	7.39	7.58	8.44	9.94	11.50	12.15	12.12
$\epsilon_{\text{exch-ind}}^{(2)}$	1.79	1.84	1.99	2.03	2.05	2.39	2.72
$E_{\text{disp}}^{(2)}$	-3.77	-3.79	-4.08	-5.26	-7.09	-7.04	-6.27
$E_{\text{exch-disp}}^{(2)}$	1.02	1.01	1.04	1.32	1.79	1.81	1.62
$E_{\text{exch-def}}^{(2)}$	-0.85	-0.88	-1.00	-2.09	-4.30	-3.14	-1.29
$E_{\text{SAPT}}^{\text{int}}$	15.44	12.44	3.94	-9.55	-22.25	-21.22	-16.33
$E_{\text{CCSD(T)}}^{\text{int}}$	15.06	12.15	3.84	-9.09	-20.87	-20.02	-15.62
$E_{\text{HF}}^{\text{int}}$	18.60	15.39	6.45	-7.42	-20.45	-19.75	-15.15
$E_{\text{BLYP}}^{\text{int}}$	11.65	9.27	2.23	-9.64	-20.89	-19.77	-15.23
$E_{\text{BP86}}^{\text{int}}$	12.47	10.03	2.69	-9.76	-21.53	-20.42	-15.73
$E_{\text{BPW91}}^{\text{int}}$	13.18	10.73	3.43	-8.98	-20.75	-19.60	-14.88
$E_{\text{B3LYP}}^{\text{int}}$	14.10	11.40	3.41	-9.69	-21.97	-20.96	-16.21
$E_{\text{B3P86}}^{\text{int}}$	14.60	11.81	3.55	-10.06	-22.81	-21.79	-16.87
$E_{\text{B3PW91}}^{\text{int}}$	15.09	12.35	4.24	-9.16	-21.76	-20.71	-15.83
$E_{\text{HFPW91}}^{\text{int}}$	17.62	14.37	5.11	-9.77	-23.98	-23.14	-18.06

See also Figs. 2 and 3 for graphical illustrations. Also reported are the SAPT contributions as defined by Eq. (2), and the intramolecular correlation contributions to the electrostatic, first-order exchange, induction, and exchange-induction energies, denoted by  $\epsilon_{\text{elst}}^{(1)}$ ,  $\epsilon_{\text{exch}}^{(1)}$ ,  $\epsilon_{\text{ind}}^{(2)}$ , and  $\epsilon_{\text{exch-ind}}^{(2)}$ , respectively. Note that the dispersion and exchange-dispersion energies are correlation effects themselves, so we do not report the corresponding intramonomer correlation contributions. Note also that the exchange-deformation energy is a Hartree-Fock quantity,<sup>52</sup> so there is no intramonomer correlation contribution to it. The last line of Tables II–IV will be discussed in Sec. IV D.

An inspection of Table II shows that the functionals based on the exchange of Becke<sup>38</sup> perform very well in the attractive region, but give rather large deviations from the benchmark CCSD(T) results in the repulsive region. Indeed, around the minimum ( $\vartheta = -8^\circ$ ) the deviation of the DFT interaction energy from the corresponding CCSD(T) value varies from 0.2% to 7%, while for the most repulsive geometry these errors are between 12% and 23%. The performance of the hybrid functionals is much better and more uniform. In the repulsive region the agreement between the DFT and CCSD(T) results is within 6.5% at worst. Around the minimum the errors of the hybrid DFT energies with respect to the CCSD(T) results are of the order of 4%–9%. Figure 2 shows that the best agreement occurs in the intermediate region (for  $\vartheta$  around  $40^\circ$ ).

A more detailed analysis of the results presented in Table II shows that the B3PW91 functional gives the best results. Indeed, both in the repulsive and in the attractive regions the differences between  $E_{\text{int}}^{\text{B3PW91}}$  and  $E_{\text{int}}^{\text{CCSD(T)}}$  do not

TABLE III. Angular dependence of the (H<sub>2</sub>O)<sub>2</sub> interaction energies (in kcal/mol) calculated by various methods.

$\vartheta$	-52°	-22°	8°	38°	68°	98°	128°
$E_{\text{elst}}^{(1)}$	-2.28	-5.93	-6.70	-4.37	-4.51	-6.22	-3.99
$\epsilon_{\text{elst}}^{(1)}$	-0.01	0.16	0.11	-0.03	0.01	0.02	-0.20
$E_{\text{exch}}^{(1)}$	2.16	4.49	6.40	4.75	4.64	6.38	4.70
$\epsilon_{\text{exch}}^{(1)}$	0.46	0.82	1.26	1.09	1.06	1.25	0.90
$E_{\text{ind}}^{(2)}$	-0.85	-1.85	-2.43	-1.79	-1.76	-2.62	-1.91
$\epsilon_{\text{ind}}^{(2)}$	-0.16	-0.29	-0.25	-0.39	-0.37	-0.44	-0.33
$E_{\text{exch-ind}}^{(2)}$	0.50	0.96	1.45	1.20	1.16	1.44	1.06
$\epsilon_{\text{exch-ind}}^{(2)}$	0.09	0.15	0.25	0.26	0.24	0.24	0.18
$E_{\text{disp}}^{(2)}$	-1.37	-2.01	-2.46	-2.13	-2.12	-2.46	-2.05
$E_{\text{exch-disp}}^{(2)}$	0.15	0.26	0.34	0.29	0.29	0.35	0.26
$E_{\text{exch-def}}^{(2)}$	-0.10	-0.40	-0.62	-0.24	-0.23	-0.61	-0.41
$E_{\text{SAPT}}^{\text{int}}$	-1.78	-4.15	-4.22	-2.36	-2.53	-3.76	-2.34
$E_{\text{CCSD(T)}}^{\text{int}}$	-1.74	-4.10	-4.23	-2.37	-2.48	-3.76	-2.45
$E_{\text{HF}}^{\text{int}}$	-0.94	-3.24	-3.26	-1.45	-1.64	-2.71	-1.10
$E_{\text{BLYP}}^{\text{int}}$	-0.93	-3.38	-3.61	-1.54	-1.61	-3.14	-1.86
$E_{\text{BP86}}^{\text{int}}$	-0.72	-3.28	-3.66	-1.56	-1.61	-3.19	-1.82
$E_{\text{BPW91}}^{\text{int}}$	-0.32	-2.73	-3.03	-0.99	-0.97	-2.57	-1.25
$E_{\text{B3LYP}}^{\text{int}}$	-1.23	-3.78	-4.03	-1.96	-2.05	-3.54	-2.09
$E_{\text{B3P86}}^{\text{int}}$	-1.09	-3.76	-4.13	-2.02	-2.11	-3.64	-2.10
$E_{\text{B3PW91}}^{\text{int}}$	-0.71	-3.21	-3.50	-1.45	-1.54	-3.01	-1.54
$E_{\text{HFPW91}}^{\text{int}}$	-1.42	-4.15	-4.44	-2.39	-2.57	-3.87	-2.00

exceed 5% (the large relative error at  $\vartheta = -68^\circ$  is not really significant given the small value of the interaction energy). The very good agreement between the B3PW91, CCSD(T), and SAPT results could suggest that the B3PW91 functional accounts for all physical contributions as defined by SAPT. This is not the case, however, and the results for other systems considered in this paper (and discussed below) do not support this conclusion. A detailed inspection of the SAPT results reported in Table II suggests that the hybrid functionals correctly account for the electrostatic, first-order exchange, induction, exchange-induction, and exchange-deformation energies. In fact the sum  $E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(10)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-def}}^{(2)}$ , where  $E_{\text{exch}}^{(10)} \equiv E_{\text{exch}}^{(1)} - \epsilon_{\text{exch}}^{(1)}$  is the first-order exchange energy neglecting the intramonomer correlation effects, agrees rather well with the results of hybrid DFT calculations. In particular, the agreement with the results of the B3PW91 calculations is remarkably good, the largest error being 5%. However, on the example of the OH<sup>-</sup>-H<sub>2</sub>O complex we can hardly discriminate between the various density functionals considered, and cannot check whether our conjecture concerning the decomposition of  $E_{\text{int}}^{\text{DFT}}$  in terms of some physically meaningful contributions is correct or not.

In Table III and Fig. 3 we report the results of the DFT, CCSD(T), and SAPT calculations for the water dimer. An inspection of this table shows that for this system the agreement between various DFT results and the data from the CCSD(T) calculations is less satisfactory. The functionals based on the Becke exchange potential<sup>38</sup> strongly underestimate the interaction energy of (H<sub>2</sub>O)<sub>2</sub> for all geometries considered. A closer analysis of the results shows that the



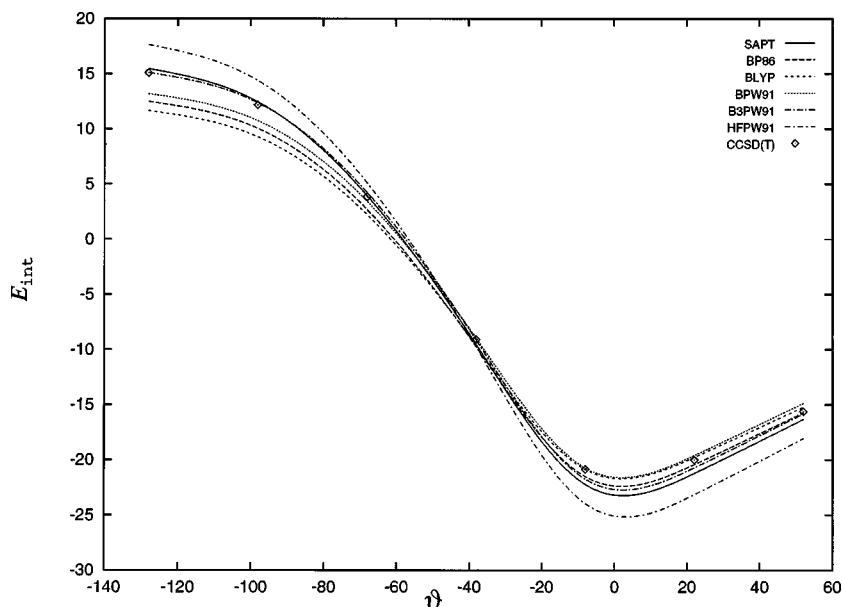


FIG. 2. Comparison of the angular dependence of the  $\text{OH}^-$ - $\text{H}_2\text{O}$  interaction energy (in kcal/mol) calculated by various methods. The B3LYP, B3P86, and B3PW91 curves are indistinguishable.

BLYP and BP86 functionals reproduce the supermolecule Hartree-Fock interaction energies. Larger deviations occur for the BPW91 functional.

The situation is quite different for the hybrid functionals. The B3LYP and B3P86 work reasonably well. The interaction energy around the minimum ( $\vartheta = 8^\circ$ ) is reproduced within 2.5% and 5% for B3P86 and B3LYP, respectively. For other geometries considered in Table III this good agreement deteriorates somewhat, and the deviations of the B3P86 and B3LYP results from the CCSD(T) values range from 3% to 40%, and from 6% to 30%, respectively. The B3PW91 functional, in turn, uniformly underestimates the interaction energy of the water dimer for the entire range of geometries considered in Table III.

It is quite difficult to explain the good performance of the B3LYP and B3P86 functionals around the minimum, and their rather bad performance for other angles. In fact, any

combination of the SAPT results (excluding the dispersion and exchange-dispersion terms) does not reproduce  $E_{\text{int}}^{\text{B3LYP}}$  or  $E_{\text{int}}^{\text{B3P86}}$  within some reasonable error bars. We can only observe that the agreement between these DFT results and the CCSD(T) data strongly deteriorates when the interaction energy is small. The situation is quite different for the B3PW91 functional. Similarly as in the case of the  $\text{OH}^-$ - $\text{H}_2\text{O}$  interaction the sum  $E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(10)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-def}}^{(2)}$  reproduces  $E_{\text{int}}^{\text{B3PW91}}$  reasonably well, the deviations ranging from 0.3% to 14%. (The only exception is  $\vartheta = -52^\circ$  where the interaction energy is close to zero.) Thus, the B3PW91 calculation, supplemented with the SAPT results for  $\epsilon_{\text{exch}}^{(1)}$ ,  $E_{\text{disp}}^{(2)}$ , and  $E_{\text{exch-disp}}^{(2)}$ , is able to produce accurate results for the water dimer. Unfortunately, this ansatz does not represent a viable alternative for SAPT or CCSD(T), since the calculations of the energy contributions mentioned above are the most time consuming.

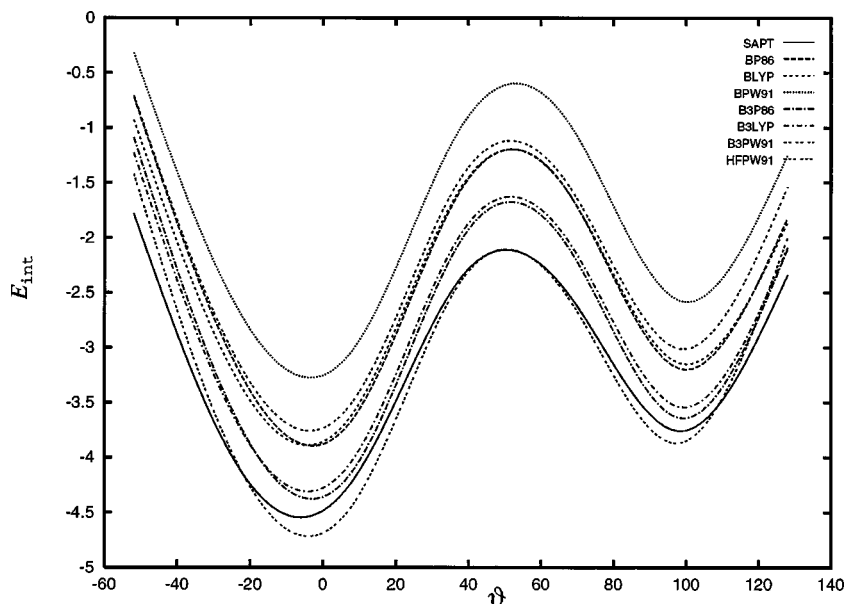


FIG. 3. Comparison of the angular dependence of the  $(\text{H}_2\text{O})_2$  interaction energy (in kcal/mol) calculated by various methods. The SAPT and CCSD(T) curves are indistinguishable.

TABLE IV. Angular dependence of the CO–H<sub>2</sub>O interaction energies (in cm<sup>−1</sup>) calculated by various methods.

$\vartheta$	−52°	−22°	7°	37°	67°	97°	127°
$E_{\text{elst}}^{(1)}$	−33.54	−446.76	−765.69	−548.24	−468.36	−742.50	−667.49
$\epsilon_{\text{elst}}^{(1)}$	−28.15	−59.07	−56.75	−72.08	−87.49	−64.39	−30.14
$E_{\text{exch}}^{(1)}$	310.09	651.64	972.46	752.03	721.27	968.33	713.45
$\epsilon_{\text{exch}}^{(1)}$	26.25	50.09	99.23	100.29	100.77	103.71	53.48
$E_{\text{ind}}^{(2)}$	−107.95	−241.09	−344.22	−228.96	−216.43	−336.73	−258.57
$\epsilon_{\text{ind}}^{(2)}$	−10.15	−17.42	−29.54	−27.68	−26.75	−30.20	−20.71
$E_{\text{exch-ind}}^{(2)}$	68.65	127.73	181.28	149.91	146.35	180.75	136.37
$\epsilon_{\text{exch-ind}}^{(2)}$	6.46	9.23	15.55	18.12	18.09	16.21	10.92
$E_{\text{exch-def}}^{(2)}$	−16.65	−56.30	−90.13	−37.81	−32.18	−85.44	−63.60
$E_{\text{disp}}^{(2)}$	−256.54	−372.41	−456.35	−384.07	−376.09	−453.58	−387.63
$E_{\text{exch-disp}}^{(2)}$	21.04	34.97	47.52	39.06	37.65	47.24	37.75
$E_{\text{int}}^{\text{SAPT}}$	−14.93	−302.22	−455.12	−258.09	−188.29	−421.93	−489.73
$E_{\text{int}}^{\text{CCSD(T)}}$	−15.93	−307.89	−454.87	−255.82	−191.66	−426.25	−484.87
$E_{\text{int}}^{\text{HF}}$	226.17	52.34	−74.79	68.27	146.03	−40.91	−153.40
$E_{\text{int}}^{\text{BLYP}}$	188.28	−174.06	−349.98	−91.29	−21.93	−316.14	−355.44
$E_{\text{int}}^{\text{BP86}}$	237.96	−114.45	−353.89	−94.90	−25.25	−320.72	−330.21
$E_{\text{int}}^{\text{BPW91}}$	319.26	−23.45	−213.31	36.01	103.95	−180.94	−205.34
$E_{\text{int}}^{\text{B3LYP}}$	133.48	−210.74	−394.34	−154.90	−83.50	−363.34	−401.27
$E_{\text{int}}^{\text{B3P86}}$	166.91	−196.81	−410.28	−167.37	−95.31	−379.51	−391.41
$E_{\text{int}}^{\text{B3PW91}}$	246.93	−79.15	−255.71	−38.77	31.44	−240.15	−269.13
$E_{\text{int}}^{\text{HFPW91}}$	133.69	−109.65	−292.47	−112.61	−31.98	−259.75	−321.09

### C. van der Waals complexes: CO–H<sub>2</sub>O and He–CO<sub>2</sub>

The results for the van der Waals complexes, CO–H<sub>2</sub>O and He–CO<sub>2</sub>, are reported in Tables IV and V, respectively. See also Figs. 4 and 5 for graphical illustrations. An inspection of Table IV shows that the results of the DFT calculations for CO–H<sub>2</sub>O behave in an erratic way, whichever functional was used. The values from the BLYP and BP86 calculations are close to each other, but very different from the CCSD(T) and SAPT results. For the most attractive configurations they are off by about 30%. For other geometries they differ from the CCSD(T) results by a factor of two or three. Unlike for the water dimer, they are far from the Hartree–Fock values, suggesting that some correlation contributions are included. Unfortunately, the SAPT results reported in Table IV cannot explain the origins of these contributions. The performance of the BPW91 functional is even worse: For some geometries the corresponding interaction energies have an incorrect sign.

The performance of the B3LYP and B3P86 functionals is quite similar as for the case of the water dimer. For the most attractive configurations these two approaches work reasonably well, and reproduce the CCSD(T) data within 10%–30%. For other geometries the agreement is much less satisfactory. It is worth noting that the performance of the B3LYP and B3P86 functionals is much better than that of BLYP and BP86. This conclusion is valid for all three complexes considered thus far, and suggests that the inclusion of the Hartree–Fock-type exchange greatly improves the results. This is not so surprising, since in view of the analysis presented in Ref. 68, the hybrid functionals should give a

better description of the exchange contributions to the interaction energy.

The results obtained from the B3PW91 calculations are again quite different from those obtained using other func-

TABLE V. Angular dependence of the He–CO<sub>2</sub> interaction energies (in cm<sup>−1</sup>) calculated by various methods.

$\vartheta$	0°	30°	60°	90°
$E_{\text{elst}}^{(1)}$	−62.68	−29.78	−4.88	−0.85
$\epsilon_{\text{elst}}^{(1)}$	−7.30	−3.51	−0.74	−0.19
$E_{\text{exch}}^{(1)}$	338.78	162.73	27.65	4.81
$\epsilon_{\text{exch}}^{(1)}$	55.80	26.29	5.10	1.21
$E_{\text{ind}}^{(2)}$	−26.13	−11.41	−1.95	−0.79
$\epsilon_{\text{ind}}^{(2)}$	−2.39	−0.82	0.06	0.35
$E_{\text{exch-ind}}^{(2)}$	21.69	9.10	1.15	0.11
$\epsilon_{\text{exch-ind}}^{(2)}$	1.98	0.65	−0.04	−0.05
$E_{\text{disp}}^{(2)}$	−177.74	−115.54	−47.69	−29.72
$E_{\text{exch-disp}}^{(2)}$	12.88	6.20	1.07	0.23
$E_{\text{exch-def}}^{(2)}$	−15.92	−8.93	−1.51	−0.18
$E_{\text{int}}^{\text{SAPT}}$	90.88	12.39	−26.14	−26.38
$E_{\text{int}}^{\text{CCSD(T)}}$	93.62	15.83	−24.72	−25.70
$E_{\text{int}}^{\text{HF}}$	207.65	99.10	16.09	1.78
$E_{\text{int}}^{\text{BLYP}}$	231.29	125.37	48.76	33.24
$E_{\text{int}}^{\text{BP86}}$	357.13	220.06	91.38	54.93
$E_{\text{int}}^{\text{BPW91}}$	409.24	244.66	87.84	47.01
$E_{\text{int}}^{\text{B3LYP}}$	164.79	79.05	25.69	17.83
$E_{\text{int}}^{\text{B3P86}}$	259.61	150.43	57.42	33.35
$E_{\text{int}}^{\text{B3PW91}}$	314.81	179.39	58.74	29.68

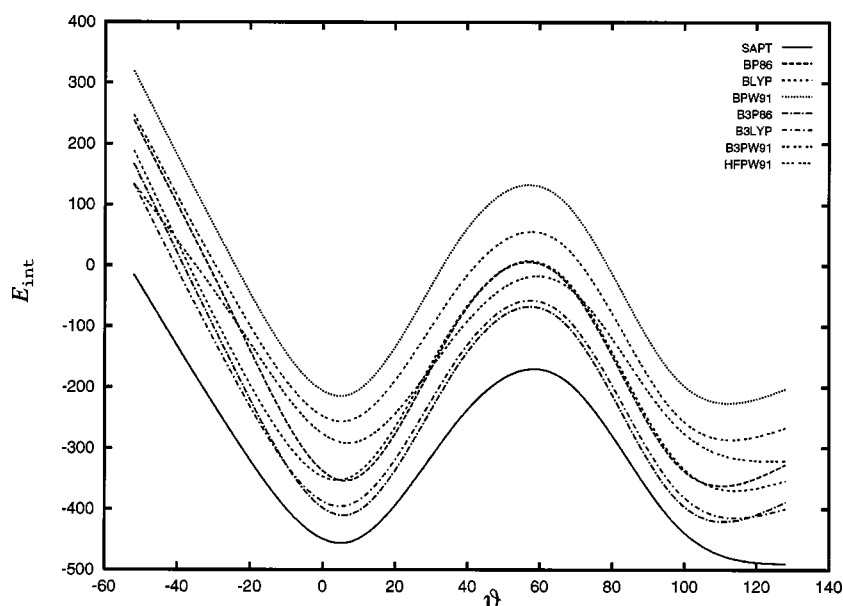


FIG. 4. Comparison of the angular dependence of the CO-H<sub>2</sub>O interaction energy (in cm<sup>-1</sup>) calculated by various methods. The SAPT and CCSD(T) curves are indistinguishable.

tionals. As for other systems  $E_{\text{int}}^{\text{B3PW91}}$  follows the sum  $E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(10)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-def}}^{(2)}$ , the agreement being only qualitative in this case.

Since the DFT approaches considered in this paper failed to reproduce the potential anisotropy for CO-H<sub>2</sub>O complex, the results for a typical van der Waals complex like He-CO should be even worse. An inspection of Table V shows that this is indeed the case. None of the functionals reproduces the weak binding around  $\vartheta = 90^\circ$ . This is not surprising since this energy is almost exclusively determined by the dispersion component. It is worth noting that the results of all DFT calculations are much more repulsive than the supermolecule Hartree-Fock interaction energy. For many angles they are even more repulsive than the sum of all exchange contributions. This suggests that some large unphysical contributions are included in  $E_{\text{int}}^{\text{DFT}}$  for this system.

#### D. Applicability of a hybrid functional adjusted to the CCSD(T) binding energy of (H<sub>2</sub>O)<sub>2</sub> to anisotropic interactions in OH<sup>-</sup>-H<sub>2</sub>O and CO-H<sub>2</sub>O

As discussed in the Introduction, Handy and collaborators<sup>33</sup> fitted a functional for the water dimer interaction to reproduce the experimental geometries of the water monomers and of the dimer. In this section we will check if such a functional can be used with trust for other hydrogen-bonded systems. We recall the reader that a general hybrid density functional  $\hat{v}_{\text{xc-hyb}}$  is given by:<sup>44</sup>

$$\hat{v}_{\text{xc-hyb}}[\rho] = \alpha \hat{k}[\rho] + \hat{v}_{\text{xc}}[\rho; \alpha, \beta, \gamma], \quad (3)$$

where  $\rho$  is the electron density,  $\hat{k}$  is the standard exchange operator of the Hartree-Fock theory, while  $\hat{v}_{\text{xc}}[\rho; \alpha, \beta, \gamma]$  is

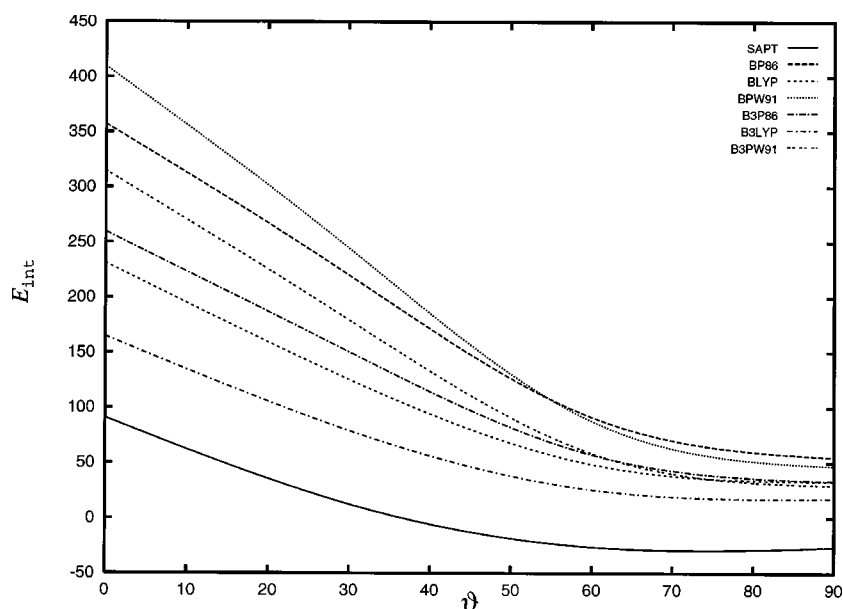


FIG. 5. Comparison of the angular dependence of the He-CO<sub>2</sub> interaction energy (in cm<sup>-1</sup>) calculated by various methods. The SAPT and CCSD(T) curves are indistinguishable.



an exchange-correlation functional depending on some adjustable parameters  $\alpha$ ,  $\beta$ , and  $\gamma$ . We did not use the original functional of Ref. 33, but instead we put  $\alpha=1$  and  $\beta=0$  in Eq. (3), and adjusted the value of  $\gamma$  to reproduce the CCSD(T) value of the binding energy in our basis set. This gave  $\gamma=0.8$ . Note that with our choice of the parameters  $\alpha$  and  $\beta$  the exchange potential is entirely given by the Hartree–Fock-type exchange. One can show<sup>68</sup> that with this choice of  $\alpha$  and  $\beta$  the first-order exchange and the exchange-induction contributions should be correctly reproduced. Since this functional includes only the Hartree–Fock-type exchange and the PW91 correlation potential, hereafter it will be called HFPW91.

An inspection of Table III shows that the fitted functional reproduces rather well the CCSD(T) interaction energies of  $(\text{H}_2\text{O})_2$  for most of the angles considered in the present paper. Unfortunately, the agreement for the  $\text{OH}^- - \text{H}_2\text{O}$  and  $\text{CO} - \text{H}_2\text{O}$  complexes is much less satisfactory. As the results reported in the last rows of Tables II and IV demonstrate, for  $\text{OH}^- - \text{H}_2\text{O}$  this functional produces results worse than the standard hybrid functionals, while for  $\text{CO} - \text{H}_2\text{O}$  it fails to reproduce the correct anisotropy of the potential energy surface. Thus, the procedure used by Handy and collaborators<sup>33</sup> for the water dimer potential energy surface is strongly system-dependent, and does not lead to functionals that are transferable from one system to another.

## V. CONCLUSIONS

In this paper we reported the first theoretical and numerical analysis of the performance of the density functional theories applied to anisotropic interactions in hydrogen-bonded and van der Waals complexes. The results of this paper can be summarized as follows.

- (1) For strongly bound ionic hydrogen-bonded complexes, like  $\text{OH}^- - \text{H}_2\text{O}$ , hybrid approaches provide accurate results. For other systems, including the water dimer, all functionals fail to reproduce the correct angular dependence of the potential surfaces, although the B3LYP and B3P86 functionals work reasonably well for the most attractive geometries of the  $(\text{H}_2\text{O})_2$  and  $\text{CO} - \text{H}_2\text{O}$  complexes.
- (2) An analysis of the results obtained using the B3PW91 functional in terms of physical contributions as defined by SAPT suggests that, except for the  $\text{He} - \text{CO}_2$  complex, this functional approximately reproduces the electrostatic, induction, and exchange–induction energies, as well as that part of the first-order exchange term that neglects the intramonomer correlation effects.
- (3) A hybrid functional adjusted to reproduce the CCSD(T) value of the binding energy for the water dimer produces results worse than the standard hybrid functionals for  $\text{OH}^- - \text{H}_2\text{O}$ , and fails to describe the correct anisotropy of the  $\text{CO} - \text{H}_2\text{O}$  interaction. Thus, the procedure used by Handy and collaborators<sup>33</sup> for the water dimer potential energy surface does not lead to functionals that are transferable from one system to another.
- (4) It seems that a new class of functionals especially devised to describe the long-range London-type interac-

tions is needed to correctly describe weakly bound hydrogen-bonded and van der Waals complexes. Work in this direction is in progress. Another promising possibility is to combine the density functionals with the correlated configuration interaction or Møller–Plesset approaches.<sup>69</sup>

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