shifts and successfully applied to the $(FH)_2$ complex (Dkhissi, Alikhani, and Bouteiller, 1997). Also an empirical modification of the adjustable $\beta$-parameter in the B88 functional used in combination with exact exchange has been proposed and led to improved intermolecular distances and frequency shifts for the $(H_2O)_2$ and the $(FH)_2$ system. Non-uniform results, however, were obtained for other weakly interacting species (García et al., 1997).

In conclusion, it seems that the thermochemical, structural and vibrational properties of a broad variety of hydrogen bonded species in very different binding situations can be described reasonably well by gradient-corrected and hybrid density functional methods. The applicability of DFT methods to hydrogen bonded systems has been confirmed by benchmarking the results with experimental and higher level theoretical data. As of today, a wealth of papers has appeared,[57] which exploit the performance of DFT methods as a practical means to supplement and guide experimental work. Representative examples comprise studies on molecular clusters (Hagemeister, Gruenloh, and Zwier, 1998, and Pribble, Hagemeister, and Zwier, 1997), correlation between proton NMR chemical shift and hydrogen bond strength (Kumar and McAllister, 1998, Garcia-Viloca et al., 1998) molecular dynamics (Wei and Salahub, 1994 and 1997, Termath and Sauer, 1997, Haase, Sauer, and Hutter, 1997, Cheng 1998), molecular adsorption in zeolites (Krossner and Sauer, 1996, Sauer, 1998, Zygmunt et al., 1998), binding and vibrational properties of nucleic acid bases (Šponer and Hobza, 1998, Santamaria et al., 1999), cooperative hydrogen bonds in enzyme catalysis (Guo and Salahub, 1998) and many more. While the interactions in strongly bound species are generally overestimated, weaker hydrogen bonds are often found to be underestimated in stability. Many functionals reach an accuracy in the description of binding energies in the order of 1–2 kcal/mol provided that sufficiently flexible basis sets of at least polarized triple-zeta quality are used. Even though this is what is called chemical accuracy, it is not sufficient to achieve predictive power for very weakly bound species. Finally, we mention a study by Milet et al., 1999. These authors corroborate the above conclusions that DFT is able to deliver reasonably reliable results for minimum structures of such complexes. But they also point out that density functionals have more severe problems when it comes to probing other regions of the PES. For example, the angular dependence of the water dimer energy is described significantly worse by the GGA and hybrid functionals used than the properties of the minimum structure.

## 12.4  The Dispersion Energy Problem

In reviewing the performance of density functional theory applied to hydrogen bonded complexes of moderate strength, we repeatedly noted a systematic underestimation of the interaction energies for many types of functionals, usually below 2 kcal/mol. This has been related by some researchers to the inability of modern functionals to describe those contributions to intermolecular binding energies which stem from dispersion forces. Dispersion

---

[57] Searching the Chemical Abstracts database for the combined keywords 'DFT' and 'hydrogen bond' reveals 201 entries for the time between January 1997 and August 1999.

forces, also referred to as London forces, are long-range attractive forces which act between separated molecules even in the absence of charges or permanent electric moments. These forces, which are purely quantum mechanical in nature, arise from an interplay between electrons belonging to the densities of two otherwise non-interacting molecules or atoms. Owing to their like electric charges, the molecular electron densities of two different systems repel each other if they come too close together. But at intermediate distances the motion of electrons in one unit induces slight perturbations in the otherwise evenly distributed electron densities of the neighboring molecule. This correlation of electronic motion leads to a temporary dipole moment. The induced dipole moment, in turn, induces a charge polarization in the first molecule, creating an attractive force between the two systems. In the asymptotic limit, this induced dipole-induced dipole attraction decays with the inverse sixth power of the intermolecular distance. The actual presence of interactions from higher order electric moments leads also to other terms like induced quadrupole-dipole, quadrupole-quadrupole interactions, etc., which vary as $1/r^8$, $1/r^{10}$ and so on. It is solely this type of interaction which is responsible for the minute binding forces between rare gas atoms and is the only reason why, for example, He even liquefies at very low temperatures. This effect is entirely due to electron correlation and the Hartree-Fock model is therefore not applicable to such situations.

Clearly, the so far unknown exact density functional must account for such electron correlation effects. However, in present implementations only the exchange-correlation energy of a given, local molecular electron density is considered and remains unaffected by the density of another, distant system if no overlap is present. The exchange-correlation potential $V_{XC}(\vec{r})$ at a point $\vec{r}$ is determined by the density (and its gradients and perhaps other local information) exactly at this point. In other words, two unshared electron distributions do not contribute by any means to an energy lowering in functional forms which depend only on a local electron density. In order to describe London interactions, a fully nonlocal functional must be applied and a local density functional is in principle not capable of describing this long-range, nonlocal correlation effect. Accordingly, some standard functionals, while correctly describing the short-range repulsion, were found to completely fail in the description of the attractive branches in the potentials of van der Waals complexes like $He_2$, $Ne_2$ or $Ar_2$. Numerical applications show in fact minima on the potential energy surfaces of such systems, although too deep and at the wrong positions, but these usually vanish after correcting for basis set superposition errors. The presence of actual minima has been attributed to overlapping densities, which decay exponentially in r, and not to a physically correct description of true dispersion interactions dominated by the long range fluctuating dipole $(1/r^6)$ term (Kristyán and Pulay, 1994). Pérez-Jordá and Becke, 1995, investigated the performance of the SVWN and BP86 functionals as well as Becke's two hybrid approaches for the description of the $He_2$, $Ne_2$, $Ar_2$, HeNe, HeAr, and NeAr rare gas dimers. Also this group found a strong overbinding for the LDA with minima located at too short distances, and only repulsive interactions for the GGA and the related hybrid functional. Interestingly, the half-and-half approach not including any gradient corrections provided a quite reasonable description of the potential shapes, but this approach gave minima which were too shallow. From the latter finding it appears that some DFT models

might in fact give reasonable results for related systems. But as so many times before, this is not the right answer for the right reason, i. e., a proper description of the physics of dispersion forces, but merely a consequence of error cancellation. Others have outlined the strengths and weaknesses of density functional theory associated with the description of weakly interacting systems dominated by charge-transfer interactions and dispersion forces (for helpful entry points into the recent literature consult Hobza, Šponer, and Reschel, 1995, Kang, 1996, Jeong and Han, 1996, Ruiz, Salahub, and Vela, 1996, Meijer and Sprik, 1996, Wesolowski et al., 1997, and Lundell and Latajka, 1997).

While calculations at the GGA level with the B88 exchange functional plus some correlation functional have been shown to give purely repulsive interactions for van der Waals complexes, other functionals yield relatively strong binding interactions. Work along these lines, although rather sparse, has been put forward in the literature. For instance, Patton and Pederson, 1997, tested two standard gradient-corrected functionals in combination with mostly converged basis sets and demonstrated a reasonable performance for the description of a variety of rare gas dimers. While the LDA gave grossly overestimated atomization energies, the PWPW91 GGA functional led to reduced errors. For the gradient-corrected PBE protocol a reasonable agreement with experimental energies, bond distances, and even vibrational frequencies was obtained for the lighter $He_2$ and $Ne_2$ diatomics. Dimers consisting of heavier rare gas atoms, however, were found to be too weakly bound at this level, and better agreement was found with the PWPW91 functional. Zhang, Pan, and Yang, 1997, published a comparative study on the performance of seven different gradient-corrected exchange functionals in combination with the PW91 correlation functional on the same six rare gas diatomics which Peréz and Becke have explored. The former authors emphasized the particular influence that the choice of exchange functional has on the outcome of calculations on these van der Waals systems. Hence, it might well be that inclusion of data for weakly interacting systems into the data base used for the construction (empirical fitting) of new functionals might lead to progress in this field. Notwithstanding all criticism with respect to the lack of the underlying physics, such pragmatism has evidently helped a lot in the past. Thus, we conclude this chapter by noting that as of today density functional theory can be used successfully, albeit only with great care, for rather weakly bound systems (see also the discussion in Adamo, di Matteo, and Barone, 1999). However, for the most part contemporary density functional theory does not seem to offer sound and reliable predictive capabilities when it comes to describing systems dominated by very weak van der Waals forces. It will be interesting to see to what extent the many attempts to develop new functionals (see, Lundqvist et al., 1995, Andersson, Langreth, and Lundqvist, 1996, Dobson and Dinte, 1996, Osinga et al., 1997, Kohn, Meir, and Makarov, 1998, Dobson, 1998, Lein, Dobson, and Gross, 1999) or to improve existing ones (e. g., Adamo and Barone, 1998b) will lead finally to an adequate and satisfying description also of the energetically low energy end of chemical interactions.