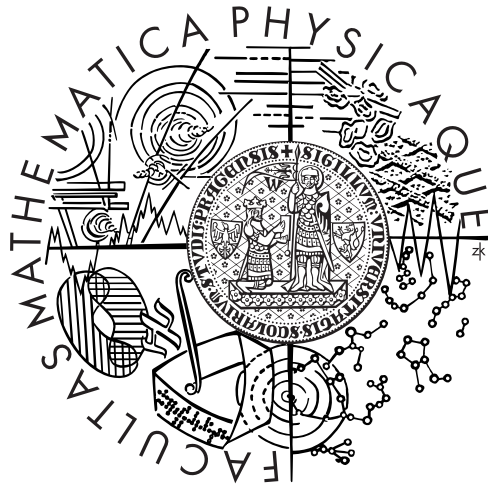Charles University in Prague

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BACHELOR'S THESIS

Jan Hermann

Assessment of Dispersion Corrected Density Functional Methods

Department of Chemical Physics and Optics

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Title Assessment of Dispersion Corrected Density Functional Methods

Author Bc. Jan Hermann

Department Department of Chemical Physics and Optics

Supervisor RNDr. Ota Bludský, CSc.

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Abstract The problem of dispersion interaction in the DFT is reviewed, followed by a systematic study of the behaviour, in particular the transferability, of the LAP method. Dispersion is a kind of van der Waals forces, dominant in important molecular systems such as biomolecules or adsorption systems. The DFT is an ever increasingly used method for modelling chemical systems. However, dispersion is rendered rather poorly in the DFT. We give an illustration of the problem and present some known correction methods. One of them is the local atomic potential (LAP) approach which we develop further from its original formulation, and this enables us to exactly match the benchmark interaction curves. We apply this development on systems consisting of benzene and a noble gas. We construct the LAPs for noble gas atoms and for carbon. It is shown that the LAP approach is poorly transferable based on our calculations. The investigation reported in this bachelor's thesis represents the first attempt for an detailed study of the behaviour of the LAP method.

Název práce Studie metod funkcionálu hustoty opravených na disperzi

Autor Bc. Jan Hermann

Katedra Katedra chemické fyziky a optiky

Vedoucí bakalářské práce RNDr. Ota Bludský, CSc.

Klíčová slova DFT, disperze, LAP

Abstrakt Práce se zabývá problémem disperzní interakce v DFT, o kterém je nejprve podán stručný přehled, následován systematickou studií chování metody LAP, zejména její transferability. Disperze je druh van der Waalsovských sil, dominantní v důležitých molekulárních systémech jako jsou biomolekuly nebo adsorpční systémy. DFT je stále častěji používaná metoda pro modelování chemických systémů. Přesto je disperze v DFT reprodukována špatně. Podáváme jednoduchou ilustraci problému a představíme několik známých opravných metod. Jedna z nich je metoda lokálních atomických potenciálů, kterou rozvíjíme z její originální formulace, což nám umožní přesnou shodu s referenčními interakčními křivkami. Naši úpravu použijeme na systémy sestávající z molekuly benzenu a atomu vzácného plynu. Vytvoříme potenciály pro atomy vzácných plynů a uhlík. Z našich výpočtů vyplývá, že metoda LAP není příliš transferabilní. Výpočty popsané v této bakalářské práci představují první pokus o detailní studii chování metody LAP.

Contents

Introduction

In quantum mechanics, the state of a system is usually described by a vector from an appropriate Hilbert space. When discussing the electronic structure of a molecular system with N electrons, the Hilbert space of choice is an antisymmetric subspace of the tensor product of N one-electron Hilbert spaces. As the Hamiltonian of a molecule does not refer to the spin of an electron, the electronic eigenstates take the form of a product of the space part $|\psi\rangle$ and a spin part, one of which must be symmetric and the other antisymmetric with respect to the exchange of electrons [1].

The problems of quantum chemistry are often solved in x-representation, *i.e.* in the basis of the position vectors $|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle$, where $\mathbf{x}_i$ denotes the position of the ith electron. The key role is played by the electronic wave function $\psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \langle \mathbf{x}_1 \ldots \mathbf{x}_N | \psi \rangle$. The Hartree–Fock (HF) method of solving the Schrödinger wave equation for ψ and its numerous extensions called post-HF methods have been main tools of quantum chemistry for decades [2].

The main disadvantage of this approach is the complexity of the wave function coming from its dependence on $3N$ electronic coordinates. Despite the enormous advances in computer technology, the resulting unfavourable scaling of the computational cost of accurate post-HF methods with the number of electrons prevents these methods from being used for large systems [3].

Known from the beginnings of quantum mechanics, but only in last twenty years developed enough to serve chemists, another approach to investigating molecular systems is based on the electron density ρ,

$$\rho(\mathbf{x}) = N \int \cdots \int \psi^*(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N) \psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N) \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N$$

The density functional theory (DFT), built around this function, strives for a functional that would provide the energy of a system in its electronic ground state given the electron density. Unfortunately, the exact formula have not been found so far albeit it does exist [4]. However, very good approximations

are known, and they are commonly and extensively used to predict various properties of molecules. Actually, it is these approximate functionals that are often meant when one refers to the DFT, not the theory itself.

The apparent advantage of this approach is that ρ is a function of only three variables, no matter how many electrons are in the system. Thus the DFT can be currently employed even in case of systems containing hundreds of atoms, such as proteins or the DNA.

The DFT has one major problem regarding the mentioned biomolecules. While it can currently deal very accurately with covalent or ionic bonding, the local nature of most functionals misses to great extent the interaction coming from long-range electron correlation. This kind of weak bonding, called *dispersion*, can be understood as an interaction of two zero-point fluctuating charge distributions. The fact is that the dispersion plays a crucial role in the formation of the tertiary and quaternary structures of the biomolecules, which are mainly responsible for their bioactivity. Another phenomenon called physisorption, very important in technology, exists also in a great part due to the dispersion forces. It is clear from these examples that a correct description of the dispersion is necessary to model properties and processes that are of great interest in chemistry today [5].

There are many ways how to introduce dispersion into the DFT. As with every correction method, their main quality is how close to the hypothetical exact correction they get. But there is another not so apparent aspect, often encountered in computational chemistry, and that is the *transferability* of a method. A large part of computational methods in chemistry rests upon parametrization, *i.e.* setting free parameters of the method so its results agree with some benchmark data. The method is said to have a good transferability if the parametrization does not depend on the particular used benchmark system. In other words, when the method is parametrized on one class of systems, it should also work well for other classes. This property tends to correlate with the number of free parameters in the method—the less, the better.

Probably the most popular dispersion corrected DFT method is the DFT-D by Grimme *et al.* [6] Its main advantage is the simplicity of implementation, one of disadvantages the number of free parameters—one for each pair of two elements. That is more than 4000 parameters for elements up to uranium. A different method proposed by Sun *et al.* is a local atomic potential (LAP) approach [7], where the dispersion is included via interaction of electrons with effective potentials centered on the nuclei. As all electrons are the same, one needs only one potential for each element to fully specify the method, thus leading to much lesser variability than in case of the DFT-D. This should inherently lead to better transferability.

The *aim of this work is to review the problem of dispersion in the DFT, and to fully utilize the idea of the LAP method and examine its behaviour.* In Chapter 1, the DFT is briefly described first, followed by a general discussion of intermolecular forces, from which a precise notion of the dispersion comes. Then, the behaviour of the DFT with regard to dispersion is illustrated on a few simple examples. Finally, several methods for correcting dispersion in the DFT are reviewed. In Chapter 2, the original LAP method is described in detail, followed by our own work which extends the idea. In Chapter 3, our implementation of the LAP correction is compared with other dispersion corrected DFT methods.

Chapter 1

Dispersion in the DFT

The density functional theory (DFT) deals with a problem how to obtain the energy of a system from its electron density. Dispersion is a kind of van der Waals (vdW) interactions which is rendered rather poorly in the current DFT. In this chapter, the DFT and dispersion are introduced in a proper mathematical way first. Then a section follows where the problem of dispersion in the DFT is illustrated pictorially on a simple example. Several other more or less developed methods for incorporating dispersion into the DFT are described at the end.

All quantities are assumed in the atomic units if not stated otherwise.

1.1 Density functional theory

As was mentioned in the introduction, the electronic eigenstates of a molecular system take the form of a product of the space part $|\psi\rangle$ and a spin part. The wave function is defined as

$$\psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \langle \mathbf{x}_1, \ldots, \mathbf{x}_N | \psi \rangle \tag{1.1}$$

where N is the number of electrons and $\mathbf{x}_i$ denotes the position of the ith electron.

A general state can have the space and spin parts inseparable, in which case our simple definition is inadequate, and the spin part must be also included in the wave function. But as our definition is sufficient for a discussion of the eigenstates and also more closely corresponds to the actual reality of the calculations, we intentionally omit the spin coordinates.

1.1.1 Electron density

The above wave function depends on $3N$ variables which results in poor scaling of the computational methods with the size of a system. A reduction in the number of variables can be carried out by simple integration,

$$\rho(\mathbf{x}) = N \int \cdots \int \psi^*(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)\psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)\mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N \qquad (1.2)$$

The resulting function ρ depending on three variables is called the electron density as it is a probability density of finding an electron in a point in space. When the electronic state is taken as an antisymmetrized product (Slater determinant) of one-electron states, $|\psi\rangle = |\phi_1 \ldots \phi_N\rangle$, $\phi_i(\mathbf{x}) = \langle x|\phi_i\rangle$, the electron density can be recast as

$$\rho(\mathbf{x}) = \sum_{i=1}^{N} \left|\phi_i(\mathbf{x})\right|^2 \qquad (1.3)$$

The electron density has several simple properties, especially when the external potential in the electronic Hamiltonian comes from several point charges (the nuclei). From the normalization of the wave function it follows that

$$\int \rho(\mathbf{x})\mathrm{d}\mathbf{x} = N \qquad (1.4)$$

The gradient of ρ is discontinuous at the position of the jth nucleus, $\mathbf{R}_j$, as the density behaves there like

$$\rho(\mathbf{x}) \sim \exp\left(-2Z_j|\mathbf{x} - \mathbf{R}_j|\right) \qquad (1.5)$$

where Z_j is the charge of the jth nucleus. Thus to obtain the nuclear charges, one simply has to evaluate

$$Z_j = \lim_{\alpha \to 0+} -\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\alpha} \ln \rho(\mathbf{R}_j + \alpha\mathbf{e}) \qquad (1.6)$$

where $\mathbf{e}$ is an arbitrary unit vector.

1.1.2 Hohenberg–Kohn theorems

From what was said until now it is not clear whether the DFT is just an effective or an exact theory. The answer to this question is ambivalent—it is potentially exact, but only effective in current implementation. The potential exactness is proved in two theorems by Hohenberg and Kohn.

The first theorem states that the electron density ρ bears all the information needed to compute the ground state energy E_0 of a system. The proof can be seen immediately. Since the number of electrons and positions and charges of the nuclei can be obtained from ρ (see Section 1.1.1), the Hamiltonian can be constructed and the Schrödinger equation can be solved to obtain E_0. This theorem already shows that the DFT can be exact but does not suggest that to calculate the energy from the electron density should be any easier than to calculate it by solving the Schrödinger equation—which brings us back to where we started.

However, there is the second theorem which states that there exists an energy functional that is minimized by the correct density in the set of densities integrated to the correct number of electrons. This already provides us with some advise on how to use the DFT. The following proof gives even more information.

The variational principle of the quantum mechanics states that

$$E_0 = \min_{\mathcal{H}} \langle \psi | \hat{H} | \psi \rangle \tag{1.7}$$

where the minimization is over the whole N-electron Hilbert space $\mathcal{H}$ and $\hat{H} = \hat{T} + \hat{U} + \hat{V}$ is the Hamiltonian consisting of the kinetic terms $\hat{T}$, the interaction $\hat{U}$ of electrons with each other and the external potential $\hat{V}$. This minimization can be carried out in two steps. $\mathcal{H}$ is divided into groups where each group contains only states that give the same electron density. The minimization is then carried out in each group first and afterwards between the minimizers of the groups. The external potential term can be recast using only ρ,

$$\langle \psi | \hat{V} | \psi \rangle = \int V(\mathbf{x}) \rho(\mathbf{x}) \mathrm{d}\mathbf{x} = V[\rho] \tag{1.8}$$

Therefore, it can be factored out from the first minimization, and the procedure can be written as

$$E_0 = \min_{\rho} \left(V[\rho] + \min_{\psi \Rightarrow \rho} \langle \psi | \hat{T} + \hat{U} | \psi \rangle \right) \tag{1.9}$$

The term in the parentheses is the energy functional from the second theorem. Its second part is the sought-after functional which is not known and the current DFT knows only approximations to it.

1.1.3   Exchange–correlation functional

The biggest problem preventing the DFT to be used by chemists was the kinetic energy term for a long time. Then Kohn and Sham came with the

following idea. Fictively, the electron-interacting term is set to zero ($\hat{U} = 0$) while $\hat{V}$ is modified in such a way that ρ does not change. As the electrons do not interact now, the problem is separable to one-electron equations and easily solved. The resulting Kohn–Sham orbitals $\left|\phi_i^{\mathrm{KS}}\right\rangle$ then serve to calculate the approximate Kohn–Sham kinetic energy T_{KS} as

$$T_{\mathrm{KS}}[\rho] = \sum_{i=0}^{N} \left\langle \phi_i^{\mathrm{KS}} \middle| -\tfrac{1}{2}\nabla^2 \middle| \phi_i^{\mathrm{KS}} \right\rangle \tag{1.10}$$

It is worth reminding that T_{KS} is a functional of ρ as the orbitals depend on ρ.

Assuming for a while that the electron cloud is just a static cloud of charged dust, the Coulombic interaction J would be

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \tag{1.11}$$

and it is actually a good first approximation to $U[\rho]$.

Thus, the expression for E_0 can be rewritten as

$$E_0 = T_{\mathrm{KS}}[\rho] + V[\rho] + J[\rho] + E_{\mathrm{XC}}[\rho] \tag{1.12}$$

where E_{XC} is the *exchange–correlation* functional which contains everything that is not known—the correction to the kinetic energy, the error from counting the interaction of an electron with itself in J (self-interaction), the exchange energy coming from the antisymmetry of the wave function, and the correlation energy resulting from the fact that the electrons avoid each other due to the Coulombic forces which is not present in the charged dust model. It is this potential for which there can be found numerous approximate formulas in the literature.

One of the simplest approximations is the local density approximation (LDA), where E_{XC} is taken to be the same as for the homogeneous electron gas in the homogeneous sea of positive charge. The idea behind the LDA is that locally, the density is always homogeneous. The generalized gradient approximation (GGA) goes one step further and the formulas of this type contain also $\nabla\rho$. Its these latter GGA-type functionals that are extensively used by chemists to predict molecular properties with good results.

1.2 Dispersion

In this work, we are mainly concerned with the interaction of neutral, closed-shell molecules in their electronic ground states. In this special, yet very important case, the qualitative picture is always the same, and we will describe it in this section.

A common concept in discussion of the interaction energy is the interaction curve $E(R)$—the dependence of the energy E on the distance R of the centres of mass of two molecules (for a given relative orientation), while it is assumed that $E(\infty) = 0$. This concept arises from the use of Born–Oppenheimer approximation which separates the molecular Schrödinger equation into the electronic and nuclear part.

1.2.1 Electron exchange

When the two molecules are close to each other and there is a significant overlap of their electron densities, the main role in the interaction energy is played by the electron exchange. The electrons can no more be identified with either of the molecules, they are shared. As the electronic orbitals have to be orthogonal to each other and this is destroyed by the overlap, they have to change which (in case of closed shells) leads to the increase in energy. Curiously, it is the same exchange energy which leads to the formation of a covalent bond in case of open shells, such as two hydrogen atoms. This shows that the exchange energy is in size comparable to the chemical bonding and thus much stronger than any weak bonding we will discuss further.

The electron densities have an exponential decay, hence their overlap grows exponentially with decreasing distance. This in turn leads to an approximate exponential dependence of the exchange energy. Therefore, in longer distances, it can be safely neglected.

1.2.2 Long-range interactions

When the two molecules are far apart from each-other, the exchange of electrons is insignificant and one can assign the electrons to either the first or the other molecule. The application of a standard Rayleigh–Schrödinger perturbation theory is then straightforward as the whole situation can be treated without considering the antisymmetry. To be more specific, one takes all the kinetic and intramolecular interaction terms as the unperturbed Hamiltonian and the intermolecular terms as the perturbation. If the exchange was to be considered, the antisymmetry of the wave function would have to be included which results in the symmetry-adapted perturbation theory (SAPT).

After evaluating the expressions of the PT, it turns out that the various orders correspond to physically well-defined interactions. The first order is a purely classical electrostatic interaction—the interaction of two clouds of charged dust with the same charge density as the molecules. As one deals with long distances here, the interaction can be readily rewritten in terms of multipole expansions. This implies that in case of non-polar molecules,

this kind of interaction is very weak (leading quadrupole–quadrupole term), and it is just zero in case of spherically symmetrical atoms, such as noble-gas atoms.

The formula for the second order reads

$$E^{(2)} = -\sum_{n=1}^{\infty} \sum_{k=0}^{n} \frac{\left| \left\langle \psi_k^A \psi_{n-k}^B \middle| \hat{V} \middle| \psi_0^A \psi_0^B \right\rangle \right|^2}{\left(E_k^A - E_0^A \right) + \left(E_{n-k}^A - E_0^B \right)} \tag{1.13}$$

where $\left| \psi_i^{A,B} \right\rangle$ are the electronic eigenstates of the molecule A and B, $E_i^{A,B}$ are the corresponding energies and $\hat{V}$ is the intermolecular perturbation Hamiltonian [8]. It consists of two kinds of physically distinct interactions—induction and dispersion.

A mathematical distinction comes from dividing the summation into two parts,

$$\sum_{k=0}^{n} = \sum_{k \in \{0,n\}} + \sum_{k=1}^{n-1} \tag{1.14}$$

The first part can be understand as an interaction of a permanent multipole (one molecule is always in the ground state in the expression) and an induced multipole—hence induction. This interaction is significant when one of the molecules is polar (has a dipole moment). The other part is made up of terms where both molecules are in excited states and thus is a pure quantum effect. It is called *dispersion,* and it is a dominant interaction in systems lacking permanent dipole moments.

It can be shown that the multipole expansion of dispersion is of the form

$$E_{\text{disp}}^{(2)}(R) = -\sum_{n=6}^{\infty} \frac{C_n}{R^n} \tag{1.15}$$

where C_n are called the dispersion coefficients. The first R^{-6} term corresponds to the induced dipole–dipole interaction.

1.3 Benzene–argon system

To illustrate the topics of previous sections, we present here a system consisting of a benzene molecule and an argon atom positioned above it. It is depicted in Figure 1.2. It is a simple model of adsorption of argon on a graphene surface. Since a benzene molecule has a zero dipole moment (the quadrupole moment is nonzero) and an argon atom is spherically symmetrical, the only significant vdW interaction is dispersion. Therefore, it is a suitable example for our discussion.
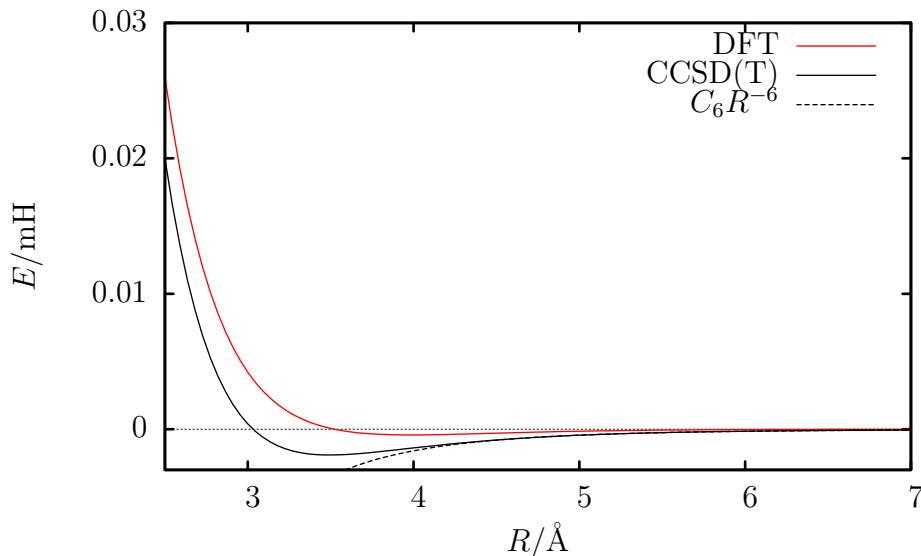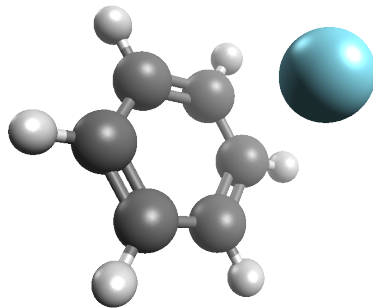
Figure 1.1. Interaction energy E of benzene with argon. R is the distance between an argon atom and the center of the benzene ring. The Perdew–Burke–Ernzerhof (PBE) functional is used for DFT calculations [9].

The interaction curve is presented in Figure 1.1. The coupled clusters method with single, double and perturbative triple excitations, abbreviated CCSD(T), can be considered as practically exact in this case. Going from the infinity, one can see a correct asymptotic R^{-6} behaviour up to $R = 4\,\text{Å}$ and an exponential repulsion coming from the overlap of the electron densities which begins at about $3\,\text{Å}$. The combination of these two phenomena results in a minimum located between 3 and $4\,\text{Å}$.

Figure 1.2. Benzene molecule with an argon atom positioned above.

The DFT picture is obviously quite different. There is almost no attractive interaction and the repulsion starts a few tenths of an ångström earlier. In other words, the standard DFT is wrong in this case.

One important lesson can be taught from this example. The problem of the DFT does not have to lie just in the wrong asymptotic behaviour, but also in a wrong electron density of the fragments, which could result in different distances where the repulsion begins to take effect.

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1.4 Adding dispersion to the DFT

There are many ways of incorporating dispersion to the DFT. Here, we present a few popular methods, going from pure *ab initio* to pure empirical.

Prior to the description of individual methods, several general trends will be discussed first. As was already mentioned, the missing dispersion interaction is not the only fact that affects the position and depth of the van der Waals minimum in the interaction curve—the error in the density of the fragments is also an important factor: (i) the radius of the electron density determines how close the fragments can approach each other before the electron exchange repulsion takes over; (ii) the overall charge distribution determines (via the multipole expansion) the long-range electrostatic interaction and (iii) also the polarizabilities which in turn determine the size of dispersion interaction. Thus even a hypothetical dispersion-corrected method that would give perfect results for DFT calculations performed on exact densities can give poor results in case of not-so-exact densities obtained from the DFT. This suggests that while *ab initio* methods can provide great transferability, they cannot be extremely accurate when used with present (non-exact) DFT functionals. On the contrary, empirical methods are not supposed to have superb transferability, but they can account even for the errors introduced by wrong DFT densities.

1.4.1 Symmetry-adapted perturbation theory

A general way to treat any weak interaction is to use the perturbation theory. It was already introduced to classify the various intermolecular interactions, but it can also serve to actually calculate them. In case of molecular systems, it has to be modified to take into account correctly the electron exchange coming from the wave function antisymmetry, hence symmetry-adapted perturbation theory (SAPT).

The use of the DFT to calculate the unperturbed molecular orbitals and orbital energies of fragments is computationally advantageous as compared to the Hartree–Fock (HF) method, because the electron correlation in fragments is treated by the exchange-correlation potential while it has to be dealt with by a special correlation term in case of the HF-based SAPT. This results in computational savings of two orders [10].

There are at least two principal problems with the SAPT(DFT) method. Specific to its DFT flavour is the problem of orbital energies. While these have a clear physical meaning in case of the HF method (Koopmans's theorem), it is much less understandable in case of the Kohn–Sham orbitals.

For example, it is well known that the HOMO–LUMO separation is often severely underestimated in the DFT. As these orbital energies are used in the SAPT formulas, this problem transfers into the SAPT.

The second, general problem of the SAPT is that it works on the assumption that there are two distinct sets of electrons, each belonging to one fragment, which does not hold when the electron exchange starts to take place. Therefore, the accuracy of the SAPT lessens as the fragments approach each other.

The SAPT is obviously an *ab initio* method and it should be also stressed that it differs from the following methods by giving explicitly the interaction energy, as compared to a more common supramolecular scenario, where the interaction energy is calculated as

$$E_{\text{interaction}} = E(\text{AB}) - E(\text{A}) - E(\text{B}) \qquad (1.16)$$

1.4.2   Van der Waals density functional

A hypothetical exact DFT functional would correctly describe dispersion as it is just a part of electron correlation. It is the local nature of the current functionals that causes absence of dispersion. The most straightforward way to correct the DFT is thus adding some non-local term to a density functional. We will discuss this topic in this section.

The simplest form of a non-local term describing dispersion is

$$E_{\text{non-local}}[\rho] = \tfrac{1}{2} \iint \rho(\mathbf{x}) \mathcal{K}(\mathbf{x}, \mathbf{x}') \rho(\mathbf{x}') \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \qquad (1.17)$$

where $\mathcal{K}$ depends non-locally on $|\mathbf{x} - \mathbf{x}'|$ and locally on ρ. An analytical formula for $\mathcal{K}$ has been found by a following approach. An exact DFT formula for the correlation energy is provided by the idea of adiabatic connection (gradually switching on the inter-electron interaction). This formula is useless for practical calculation, however, by imposing some simplifications it can be recast into a usable form. It is first divided into a short- and long-range part. The long-range non-local part is treated by several simplifying assumptions and requirement of a correct asymptotic behaviour. This results in the formula for $\mathcal{K}$. The short-range part is evaluated under the LDA. The theory is carefully built in such a way that it approaches a correct limit when considering a uniform density. Also, the saturation of the dispersion interaction at short distances of the fragments arises naturally in the theory. Overall, this method is also fully *ab initio* [11].

The vdW-DFT is still in development by its authors and promises very accurate results. A significant improvement could come from using the GGA

rather then LDA, although it is argued that by separating the long-range part, the LDA is more valid than in the standard DFT.

1.4.3 Pseudopotential approaches

The idea behind this class of methods is quite simple. Rather than considering the electron–electron interaction as described by (1.17), one of the integrations is actually performed a priori under the assumption that the electron density of an atom does not change substantially in various chemical environments.[1] While a reasonable assumption, the resulting simpler methods lose the *ab initio* advantage and have to be parametrized against some benchmark. This inherently results in a worsened transferability.

One additional advantage of this type of methods comes from a common use of pseudopotentials (PP) in DFT calculations. These functions are used to represent the effect of core electrons on the valence ones without the need to explicitly include them into calculations. This approach saves a great deal of computational time and also enables a simple inclusion of relativistic effects. Therefore, the PPs are implemented in most commercial quantum-chemical programs, and they can be easily employed to correct for dispersion too.

Two methods presented below differ in the assumed form of the half-integrated formula (1.17). The dispersion-corrected atom-centered potential (DCACP) approach takes the form of a popular class of analytic PPs, and calibrates its several parameters against interaction curves calculated at the Møller–Plesset perturbation theory to the second order (MP2) level [12]. On the contrary, the authors of the local atomic potentials (LAP) method proposed their own simple functional form [7].

The results of both methods are similar—they give very accurate results for the benchmark systems and there are some deviations in other cases. But neither of these methods was thoroughly tested to make any clearer conclusions.

1.4.4 Atom–atom corrections

The final step towards a completely effective method is to perform both integrations in (1.17) a priori. This results in a set of simple pairwise atom–atom potentials, one for each pair of atoms. Again, the methods differ in the form they use for these effective potentials.

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[1]The methods are not originally formulated in this way, but they emerge as such naturally in our discussion.

The methods are simple to use as they can be applied after performing the quantum-mechanical calculation. Their greatest disadvantage comes from a very complicated parametrization.

DFT–CC

In this approach, the potentials are constructed numerically on a grid so there are no limitations coming from the use of a particular analytical form. The data used for construction are coupled clusters (hence CC in the name) interaction curves of benchmark systems. These have to be chosen in such a way that in every step of parametrization, there is just one unknown potential (*e.g.*, C–C in case of parametrization on a benzene dimer), while the other ones (C–H, H–H) are already known [13].

A great advantage and disadvantage at the same time of this method is that it does not correct just for dispersion but actually for everything that is wrong in the DFT, even errors that do not behave according to (1.17). Thus when used on a set of chemically similar systems (*e.g.*, going from benzene to bigger PAHs), it yields superb results, but the performance worsens when used on a broader set of systems.

DFT-D

This is probably now the most popular method for including dispersion into the DFT. The effective potentials consist here from a R^{-6} function and a damping function to avoid singularity at $R = 0$. Every atom–atom pair requires one real parameter and these are optimized simultaneously on a huge number of systems and various quantities [6]. While the asymptotic behaviour has a physical meaning, the ad-hoc damping function is chosen arbitrarily and actually has a great effect on the positions of the vdW energy minima. This makes the method hardly tractable—it improves the results statistically, but in any particular case its behaviour is unpredictable if one does not have vast experiences with it.

Chapter 2

Local Atomic Potentials

In the previous chapter, several methods for adding dispersion into the DFT were briefly introduced. In this chapter, the local atomic potentials (LAP) approach will be described in detail first, followed by our modifications and implementation of the method. At the end, its general properties are discussed prior to some test calculations which are a subject of the following chapter.

2.1 Original formulation of the method

The idea behind is as follows. The electron density is mainly concentrated around the nuclei. The density of core electrons of an atom does not change much in various environments, and the density of valence electrons redistributes significantly but its overall magnitude remains similar (this is not quite true in ionic compounds). The approximation in the LAP approach is to assume that the electron density in the vicinity of an atom is always the same and to integrate over it in (1.17) prior to the actual calculation,

$$
\begin{aligned}
E_{\text{dispersion}}[\rho] &= \int \left(\sum_{\substack{\text{atoms}}} \int_{\substack{i\text{th} \\ \text{atom}}} \tfrac{1}{2} \rho(\mathbf{x}') \mathcal{K}(\mathbf{x}, \mathbf{x}') \mathrm{d}\mathbf{x}' \right) \rho(\mathbf{x}) \mathrm{d}\mathbf{x} \\
&= \int \sum_{\substack{\text{atoms}}} v^{(i)}(\mathbf{x}) \rho(\mathbf{x}) \mathrm{d}\mathbf{x} = \sum_{\substack{\text{atoms}}} \int v^{(i)}(\mathbf{x}) \rho(\mathbf{x}) \mathrm{d}\mathbf{x} \quad (2.1)
\end{aligned}
$$

For every element, there is a different v. As in case of two point charges, where one can evaluate the interaction either via the second charge in the potential of the first charge or vice versa or via both and then divide by two, even in case of LAPs one can either evaluate the density over potentials

on all atoms (as in Eq. 2.1) or constrain the evaluation to the density of one fragment over the potentials of the second fragment. In the latter case, the potentials must be twice as large in magnitude. This property results simply from the symmetry of the interaction. At least, this is what the theory suggests. However, in reality, the error in the DFT is far from being pure dispersion and the symmetry is broken. Therefore, it is better to put the potentials on all atoms which partially compensates for this flaw.

The LAPs are not generated by actual integration, but rather they are obtained by optimizing the corrected energies against some benchmark data. Here, the method ceases to be *ab initio*. As one cannot reasonably optimize a general three-dimensional function, one has to assume some form of the LAP. It was suggested to assume a radial symmetry, and an analytical form of the LAP was proposed,
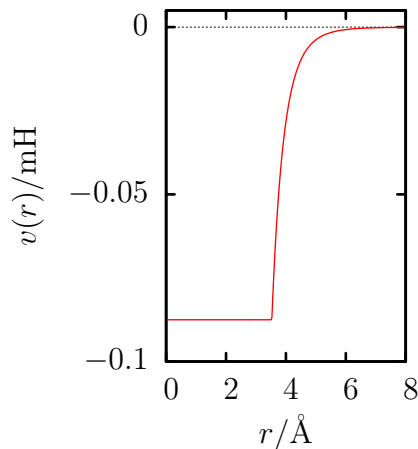
$$v(r) = \begin{cases} -c_0/r^n & r > r_{\text{cut}} \\ -v_{\text{const}} & r < r_{\text{cut}} \end{cases} \quad (2.2)$$

where r is the radial distance from a nucleus and c_0, n, r_{cut}, v_{const} are parameters. The potential is required to be continuous so there are three degrees of freedom in total.

Figure 2.1. The original LAP for carbon ($c_0 = 4.5{\times}10^3$, $n = 9$, $v_{\text{const}} = 0.175{\times}10^{-3}$ in Rydberg atomic units).

The parameters were obtained by requiring the interaction curves of some simple dimer systems to be as close as possible to the CCSD(T) curves. The dimers of H_2, C_2H_2, N_2 and O_2 were used to generate LAPs for H, C (Figure 2.1), N and O. The revised PBE (revPBE) functional was used for DFT calculations as this one is known to give almost no binding for vdW systems, making it a good starting point for corrections.

The LAPs are implemented by adding them to a local part of core pseudopotentials. Thus the correction is included self-consistently, and the final electron density is slightly different from the one obtained without the use of LAPs.

The test of the method with an emphasis on transferability was performed by calculating the binding energies of 148 weakly bonded complexes from a benchmark database. The results were presented as averages and statistical deviations, and while they showed that the method improves the binding en-

ergy deviations several times (in a statistical manner), they hardly provided a satisfactory insight into the behaviour of the method.

2.2 Our modifications

An obvious imperfection in the original formulation of the method is the analytical form of the potential for which no explanation is given. Our initial motivation was thus to improve the optimization process in such a way that a more general class of functions can be used. Finally, we have arrived at the following schema.

As a first modification, the correction is not treated self-consistently, but rather calculated on the final electron densities. The form of the potential is a step function, *i.e.* a stepwise constant function, defined by a finite set of intervals and values of the function on these intervals. These two modifications transform the complicated problem of optimizing the parameters of a non-linear function into a simple linear optimization problem.

First, a grid $\{r_k\}_{k=1}^n$, $r_k = r_1 + (k-1)b$ is chosen on which the potential is sampled, where r_1, b are parameters of the grid. Let χ_k be an indicator function of the interval $(r_k - b/2, r_k + b/2)$, *i.e.* it is one on that interval and zero elsewhere. The potential v is then given by numbers $\{v_k\}$,

$$v(r) = \sum_{k=1}^n v_k \chi_k(r) \tag{2.3}$$

The dispersion energy can be calculated as

$$E_{\text{disp}} = \sum_{\text{atoms}} \int v(\mathbf{x})\rho(\mathbf{x})\mathrm{d}\mathbf{x}$$

$$= \sum_{\text{atoms}} \sum_{k=1}^n v_k \int_{r_k-b/2}^{r_k+b/2} \int \rho(r,\Omega)r^2\mathrm{d}\Omega\mathrm{d}r = \sum_{\text{atoms}} \sum_{k=1}^n v_k \Gamma_k \tag{2.4}$$

where Γ_k must be found by integration over the electron density.

The coefficients v_k are found by requiring that the corrected interaction curve matches the one calculated by the CCSD(T) method, $E_{\text{CC}}(R)$. Typically, one does calculate the interaction energy only for several interfragment distances $\{R_i\}_{i=1}^N$. To be able to carry out the optimization, there has to be just one unknown potential at a time in the system. The DFT interaction energy with added dispersion from the already known potentials will be denoted $E_{\text{DFT}}(R)$, while the final energy with dispersion added also from the searched for potential will be just $E(R)$.

To search for v_k, the matrix $\mathbf{C}$ is constructed, which encodes the contributions of the individual potential intervals to the *interaction* energy,

$$C_{ik} = E_{\text{disp}}^{(AB-A-B)}\big(R_i, v(r) = \chi_k(r)\big) \tag{2.5}$$

Now given $\{v_k\}$, the correction for dispersion is calculated simply as

$$E_{\text{disp}}(R_i) = \sum_k C_{ik} v_k \tag{2.6}$$

The $\{v_k\}$ that give the right correction are then found by solving a set of linear equations

$$\sum_k C_{ik} v_k = E_{\text{CC}}(R_i) - E_{\text{DFT}}(R_i) \tag{2.7}$$

which can be solved exactly if $N = n$ and in a least-square sense if $N > n$. The latter means that the quantity ξ is minimized by the solution,

$$\xi = \sum_i \big(E_{\text{DFT}}(R_i) + E_{\text{disp}}(R_i) - E_{\text{CC}}(R_i)\big)^2 \tag{2.8}$$

Up until now, the procedure has been quite straightforward. Next, one would simply employ the known algebraic formulas to obtain the solution for $\{v_k\}$. However, it turns out that $\mathbf{C}$ is usually ill-conditioned and the exact solutions tend to wildly oscillate. If constrained to only positive or negative values, a typical solution has only one non-zero v_k. Thus, some approximate solution has to be introduced with a reasonable behaviour. We have employed an iterative approach, where in each step, the gradient of ξ with respect to v_k is calculated numerically,

$$g_k = \frac{\xi\big(\{\ldots, v_k + \Delta v, \ldots\}\big) - \xi\big(\{\ldots, v_k, \ldots\}\big)}{\Delta v} \tag{2.9}$$

where Δv is some sufficiently small number. The potential is then updated,

$$v_k := v_k - d g_k \tag{2.10}$$

where d is a damping factor. The procedure is repeated until a desired target ξ_{t} is reached. Note that if the target was set infinitesimally small, this would converge to an exact solution. The method was thoroughly tested to be independent on particular values of n or N.

Our modified version of the LAP method brings a few advantages over the original one. As it does not require any particular form of the potential, it employs the full capability of the method itself. Thus whatever results we get, they cannot be improved in the LAP scheme. This is ensured by requiring ξ to be sufficiently small after the optimization.

2.2.1 Implementation

Our current implementation differs from the above procedure in one aspect. We do not evaluate the dispersion correction as a difference between the total correction and corrections for fragments, but rather put the potentials only on one fragment, evaluate it over the density of the other one and thus obtain directly the interaction correction. The density is calculated for the isolated fragment, *i.e.* not in interaction with the first one. This is justified by the fact, that vdW interactions almost do not change the electron density on fragments.

The reason to the above simplification is that the integration over the density is carried out on a grid in a real space. By integrating only over one fragment, the grid can be much finer and the results contain less of numerical noise. Even so, the used grid is not fine enough to smoothly reproduce the rapid growth of the electron density at the nuclei. This could be circumvented by using a locally radial, not a rectangular grid. This could be implemented in feature if the LAP method turned out to be useful.

The interfaces between various quantum-chemistry programs and the LAP method were coded in *Octave*. It is an interpreted high-level language developed for convenient scientific programming [14]. It is not as fast as translated languages such as *Fortran* or *C*, but it provides much smoother development of programs.

Chapter 3

Test calculations

The primary testing of the method was performed on the hydrogen dimer. However, the LAP approach is effectively identical to the DFT–CC method for monoatomic systems, and so these preliminary results just confirmed there are no flaws in the technical part of the method and its implementation.

The statistical testing of transferability, via means of averaged binding energy deviations, does not provide much insight into the method. We chose a different approach, employing similarity of some elements. An extensively studied class of vdW systems comprises small molecules adsorbed on graphene (one isolated sheet of graphite). Among them, adsorbed noble gases are particularly governed by dispersion. The simplest meaningful model for graphene is a benzene molecule. Therefore, we have studied its interaction with a helium, neon, argon and krypton atom. Such a system was already introduced in the previous chapter and can be seen in Figure 1.2.

First, we have calculated the interaction curves of dimers of noble gases, which provided the noble gas LAPs. Then, we proceeded to the benzene–noble gas systems. Here, we have again calculated the interaction curves, applied the correction from the noble gas LAPs, and obtained the LAPs for carbon atoms from these corrected curves. The hydrogen atoms were not considered as they are in a greater distance from the noble gas atom than the carbon atoms, they have only one electron, and as they have the same symmetry as the carbon atoms, a significant part of their small effect can be covered by the carbon LAPs.

3.1 Technical details

For all interaction energies, we correct for the basis set superposition error (BSSE) by calculating the energies of individual fragments in the basis of both fragments.

The CC interaction curves are calculated at the complete basis set (CBS) limit. This is done by calculating the interaction energies using several Dunning-type basis sets which were designed in such a way that the calculated energy consistently improves with their growing size [15]. These results are then extrapolated to infinity. The extrapolation employs the energies from following methods: (i) the Møller–Plesset perturbation theory with aug-cc-pVnZ basis sets for $n = 2, 3, 4$ (MP2/AVnZ)[1], (ii) the Hartree-Fock method with aug-cc-pVnZ basis sets for $n = 3, 4, 5$ (HF/AVnZ), and (iii) the CCSD(T) method with the aug-cc-pVDZ basis set (CCSD(T)/AVDZ). For $n > 2$, the resolution of identity approximation was used—a numerical method that replaces four-centric integrals in the calculations by three-centric ones. All these energies were calculated with the program *Molpro* [16].

The formula used for extrapolation of the interaction energy is

$$E_{\mathrm{MP2/AV}n\mathrm{Z}}(n) - E_{\mathrm{HF/AV}n\mathrm{Z}}(n) = E_{\mathrm{MP2/CBS,corr}} - \frac{\varepsilon}{n^3} \qquad (3.1)$$

where the CBS correlation energy $E_{\mathrm{MP2/CBS,corr}}$ and ε are parameters which are found using the HF and MP2 energies for $n = 3, 4$. The CCSD(T)/CBS energy is then calculated as

$$E_{\mathrm{CCSD(T)/CBS}} = E_{\mathrm{HF/AV5Z}} + E_{\mathrm{MP2/CBS,corr}} \\ + (E_{\mathrm{CCSD(T)/AVDZ}} - E_{\mathrm{MP2/AVDZ}}) \qquad (3.2)$$

where it is assumed that the HF/AV5Z energies are practically converged, and that the difference between the MP2 and CCSD(T) methods is constant for different basis sets. This formula was shown to give good results in numerous cases [17].

As for the DFT calculations, we tested the behaviour of the LAP method for two different density functionals—the already mentioned PBE functional, and a combination of the Burke [18] exchange functional and the Lee–Yang–Parr [19] correlation functional (BLYP). Both are reasonably *ab-initio* and has been used extensively. The BLYP functional is known to give purely repulsive interaction for vdW systems, while the PBE functional tends to

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[1]Usually, letters D (double), T (triple) and Q (quadruple) are used instead of the numbers.
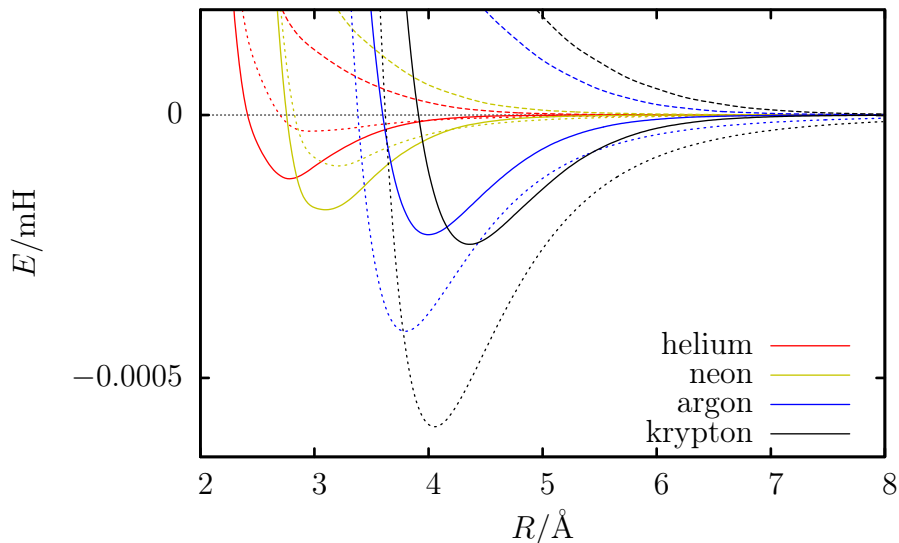
Figure 3.1. Interaction curves of noble gas dimers. The solid lines are CCSD(T)/CBS energies, the dotted and dashed lines are PBE and BLYP/aug-cc-pVQZ energies respectively.

give a small attractive interaction. The aug-cc-pVQZ basis set with the RI approximation was employed. The program *Gaussian* was used [20].

The numerical parameters of the LAP method were set as $d = 10^{-2}$ and $\xi_t = 10^{-4} \times \xi_0$, where ξ_0 is the initial ξ.

3.2 Results

The calculated interaction curves for noble gas dimers are depicted in Figure 3.1. While the grouping of helium and neon, and of argon and krypton as for the distance where the exchange takes over is present in all three methods, everything else is not. The BLYP functional gives purely repulsive curves as expected, while the PBE functional actually gives too strong interaction for He and Ne, and too weak for Ar and Kr. Thus the trend of increasing interaction down the group is rendered correctly, but the absolute values are completely wrong. The corrected interaction curves are not shown as they would look identical to the CC curves when put in a graph (they differ by less than 1%).

The LAPs for the noble gases obtained from the curves are shown in Figures 3.2 and 3.3. While they are mainly negative for the BLYP functional (repulsive curves), the behaviour of PBE LAPs is less homogeneous. Clearly,
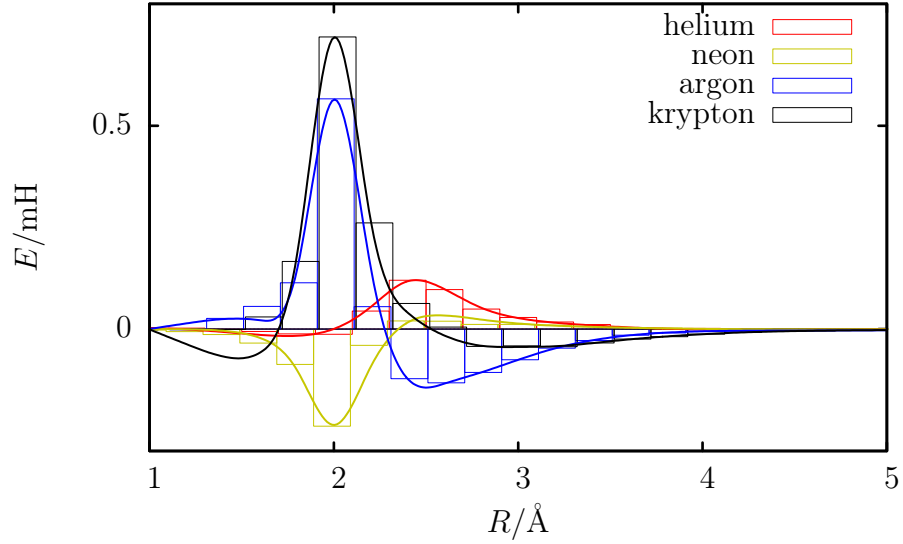
Figure 3.2. Noble gas atoms LAPs generated for the PBE functional from dimer interaction curves. The bars show the potential as it is used in calculations, the solid lines are general interpolated curves.
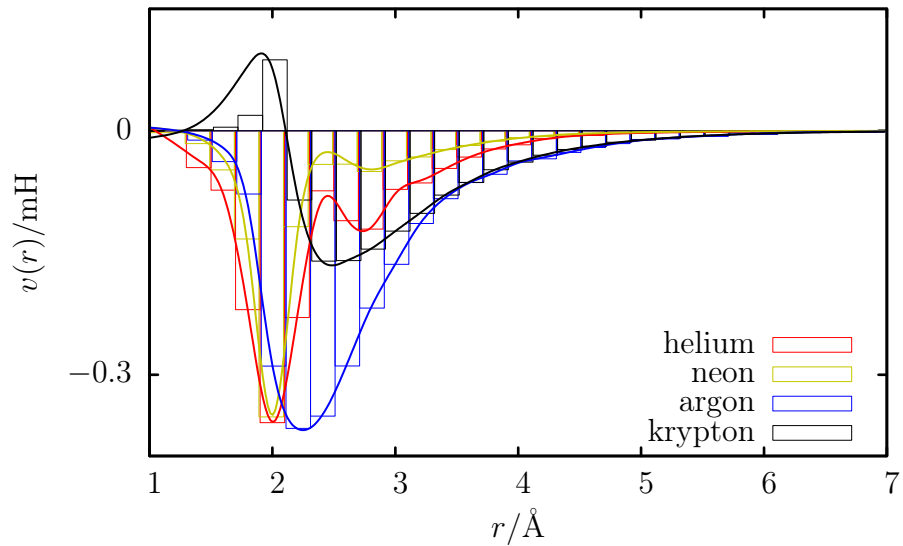
Figure 3.3. Noble gas atoms LAPs generated for the BLYP functional from dimer interaction curves. The bars show the potential as it is used in calculations, the solid lines are general interpolated curves.
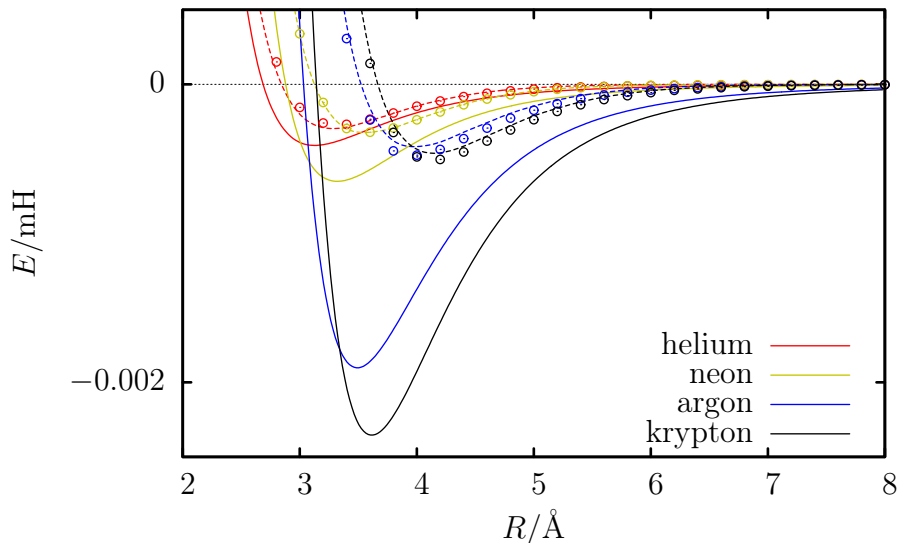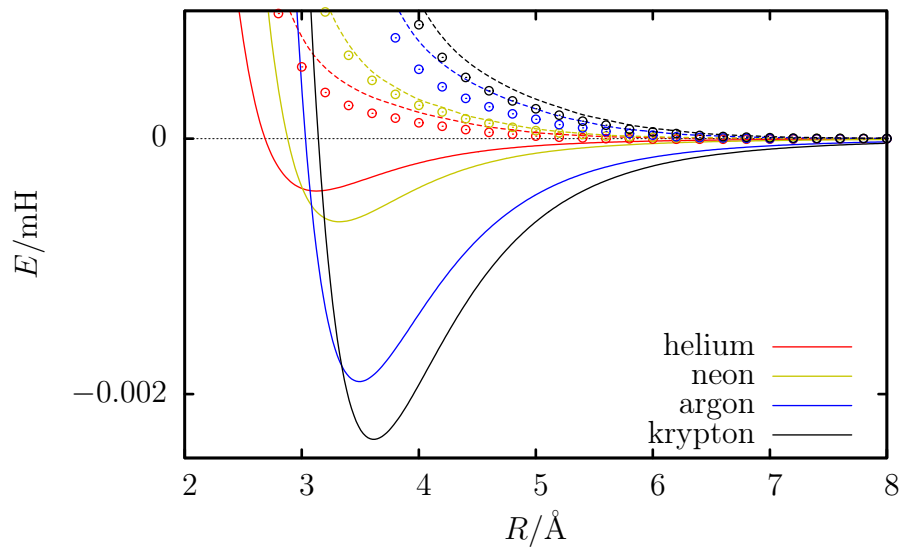
Figure 3.4. Interaction curves of systems benzene–noble gas. The solid lines are CCSD(T)/CBS energies, the dashed lines are PBE/aug-cc-pVQZ energies, and the circles are PBE energies after correction by the LAPs on noble gas atoms.

the LAPs depend on the choice of the potential very significantly.

The benzene–noble gas interaction curves are depicted in Figures 3.4 (PBE) and 3.5 (BLYP). It can be seen that the LAPs on noble gas atoms do not correct the curves substantially. This is caused by a much different density of the benzene molecule compared to the noble gas atoms. The overall picture is similar to the dimer case—the trends are correct in the DFT, but that is all. It is also noteworthy that the interaction does not scale linearly with the number of electrons as would be the case if $\mathcal{K}$ from (1.17) did not depend on the densities and the error accounted for by the LAP would be just missing dispersion.

The indications are then confirmed by the obtained LAPs in Figures 3.6 and 3.7. If the LAP method was perfectly transferable, the potentials in each graph would be all the same. Since they are not, some of the approximations used when constructing the LAP method have to be wrong.

Some trends in the LAPs are visible. As the size of the atom increases, so thus the part of space in which the electron density is non-negligible, and the potentials are thus broader. Also, the amount of correction, which can be roughly seen as an area under the curve, decreases down the group, showing that the interaction per electron decreases. This could be explained by the fact, that the core electrons are shielded and their fluctuations are not so well correlated, thus not contributing to dispersion interaction.

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Figure 3.5. Interaction curves of systems benzene–noble gas. The solid lines are CCSD(T)/CBS energies, the dashed lines are BLYP/aug-cc-pVQZ energies, and the circles are BLYP energies after correction by the LAPs on noble gas atoms.
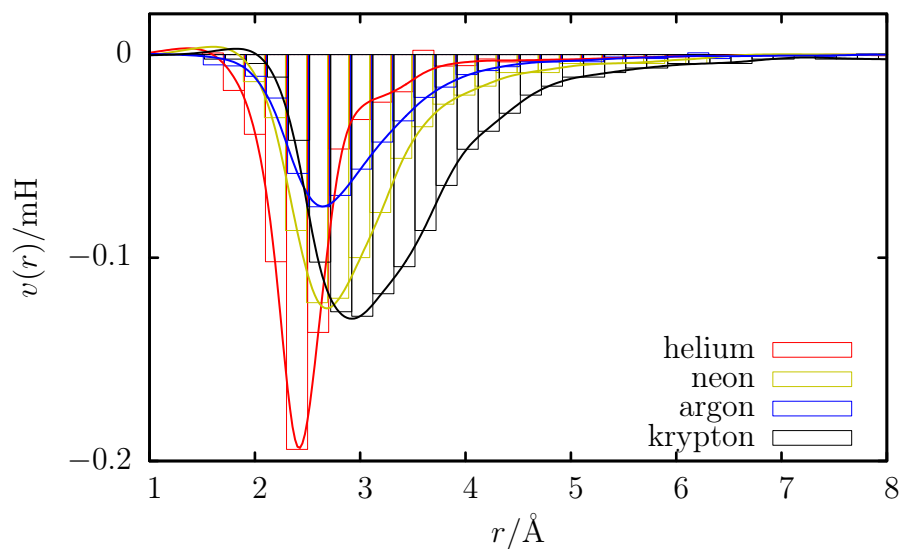
Figure 3.6. Carbon atom LAPs generated for the PBE functional from benzene–noble gas interaction curves. The bars show the potential as it is used in calculations, the solid lines are general interpolated curves.
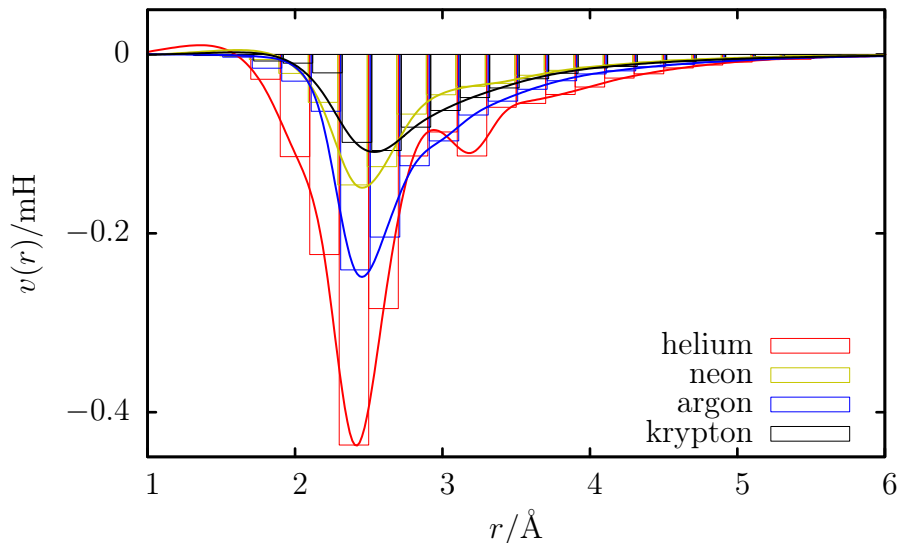
Figure 3.7. Carbon atom LAPs generated for the BLYP functional from benzene–noble gas interaction curves. The bars show the potential as it is used in calculations, the solid lines are general interpolated curves.

3.3 Discussion

Our results show that the LAP method is not as promising as it was proposed to be. This can be caused by several reasons which will be discussed here.

The main assumption of the LAP approach is that it corrects for dispersion interaction. If this condition is not met, the resulting correction scheme does not make much sense. As was already mentioned in Chapter 1, a large part of the error can come from a misplaced exponential decay of the electron density, resulting in wrong vdW radii and incorrect beginning of the exchange repulsion. This kind of error does not scale with the number of electrons at all and thus the LAP scheme which does so cannot work in this case. Specifically for our test systems, the error coming from the wrong decay of the π-electron density on the benzene molecule would be constant for all elements.

Another possible reason for the failure is that $\mathcal{K}$ actually depends significantly on the electron densities, reflecting the shielding of core electrons or some other effects. This would violate the approximation that one of the integrations in (1.17) can be done *a priori*.

Why the LAP method improves the results statistically despite these evident flaws can be seen easily. The potentials are all negative, so they always add some interaction which is almost always missing when modelling vdW

systems with the DFT. So any negative LAP is actually bound to improve the results. This insight shows that the statistical evaluation gives very little information about the performance of methods correcting dispersion in the DFT.

Our potentials do not look at all like the one originally proposed (Figure 2.1). While ours have a minimum and go to zero at the nucleus, the original ones are constant at the nucleus. But this difference can be understood when one considers on which electron density is this part of the potential applied— the density of the very nucleus the LAP is centered on. The resulting energy correction is then present in the total energy as well as in the fragment energy and cancel each other. Thus this part of the potential has actually no effect on the interaction energies. Another way how to look at this is that the functioning of the LAP method is partly encoded in the distribution of molecular electron densities and the method itself, while the particular form of the LAP contains a significant amount of redundant information.

It should be also pointed out, that the DFT–CC method was shown to have very good transferability. This suggests that the problem of dispersion is a complicated one and the greater amount of parameters better covers for this complexity as compared to the simpler LAP scheme.

Conclusions

The aim of this thesis was to review the problem of dispersion in the DFT and to investigate the behaviour of the LAP method for its correction, most importantly its transferability. This was motivated by a growing interest in molecular systems governed by dispersion. The work has been divided into three parts.

In Chapter 1, we gave a brief introduction to the DFT and to the classification of intermolecular forces based on the perturbation theory. We show on a simple system, that the problem of determining the binding distance and energy does not necessarily lie just in the missing dispersion interaction. Finally, several methods trying to incorporate dispersion into the DFT are reviewed, the local atomic potential (LAP) approach among them.

In Chapter 2, the original proposition and formulation of the LAP method is established first. Its main drawback is a severe restriction on the form of the dispersion potential—a simple arbitrary analytic function. We developed a few simple modifications of the method which linearize the problem. This enables to construct the potentials without any assumptions of their form, defining them by values on a discrete grid, which provides several advantages: (i) the benchmark coupled clusters curves can be matched exactly, and (ii) the behaviour of the LAP method can be understood with greater clarity.

In Chapter 3, the test calculations on systems consisting of a benzene molecule and a noble gas atom are presented. They should provide the critical information about transferability, since the dispersion potentials constructed on different noble gases should be identical. So we construct them and show that they are actually quite different. By evolving the method in the previous chapter, we can rest assured that this result is not caused by any constraints on the potential form, but it is rather the method itself which fails.

This thesis presents a systematic study of the behaviour of the LAP method. It gave us an initial theoretical insight into the topic of dispersion in the DFT and suggested that the LAP approach is probably a blind alley.

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