

## 5. Publications

- P1. A. Hamza, I. Mayer: Overlap Repulsion with Löwdin's Pairing Theorem. *Int.J.Quantum Chem.* **82**, 53 (2001)
- P2. A. Hamza, I. Mayer: Overlap Repulsion with Löwdin's Pairing Theorem. II. The Leading Term. *Int.J.Quantum Chem.* **83**, 105 (2001)
- P3. A. Hamza, Á. Vibók, G. Halász, I. Mayer: BSSE-Free SCF Theories: A Comment. *J. Mol. Struct. (Theochem)* **501**, 427 (2000)
- P4. I. Mayer, A. Hamza: Energy Decomposition in the Topological Theory of Atoms-in-Molecules and in the LCAO formalism: a Note. *Theor. Chem. Accounts* **105**, 365 (2001)
- P5. I. Mayer and A. Hamza, Program "APOST" Version 1.0, Budapest April 2000. Available via the Internet at the address <http://occam.chemres.hu/programs> or by „anonymous ftp” at the address (<ftp://kvk.chemres.hu>). (The program also performs bond order and valence analysis.)
- P6. A. Hamza, I. Mayer: Novel Energy Decomposition Schemes for Intermolecular Interactions. *Recent Research Developments in Quantum Chemistry*, in press
- P7. A. Hamza, Á. Vibók, G.-J. Halász, I. Mayer: Second Order Energy Components in the BSSE-Free Intermolecular Perturbation Theory. *Theor. Chem. Accounts* **107**, 38 (2001)
- P8. I. Mayer, A. Hamza: Note on the interatomic exchange energy components. *Int.J.Quantum Chem.*, accepted for publication
- P9. A. Hamza, I. Mayer: Physical Analysis of the Diatomic „Chemical” Energy Components. submitted



## Energy Partitioning Methods for Studying Molecular Systems

Theses of the Dissertation

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## 1. Introduction

There are several methods for studying molecular structures, their bonding properties and interaction. For a better understanding of the nature of the system under study, it may be useful to decompose the total energy into different types of physically meaningful terms. The history of the energy decomposition is rather in the field of studying intermolecular interactions than for the interactions of the atoms within a molecule. One of the reasons is that there were many controversies between the different interpretations of the hydrogen bond – which is a particular case of the intermolecular interactions. On the second hand the intermolecular interactions were treated mainly by perturbational theories, the results of which can be at least apparently decomposed into different contributions. In the early stages of the research the simple methods based on electrostatic interactions were adequate for describing hydrogen-bonded systems. According to this fact the presumption stating that the hydrogen-bond is basically determined by the electrostatic interaction became widely used. Later it was believed that other types of interactions (exchange, delocalization) are the relevant ones.

In the case of intermolecular interactions several perturbational methods have been developed with less-or-more understandable energy components up to the second order.

Within the molecule the interaction energy cannot be decomposed such naturally into the sum of “physical” components, therefore there are much less theoretical developments in this field.

In this work I present some new energy decompositions of inter- and intramolecular interactions; for both cases results of sample calculations are presented, too. In this way the Thesis consists of two parts: one devoted to the study of the interactions between the molecules another to that within the molecules.

## 2. Intermolecular interactions

In the case of intermolecular interactions usually a relatively simple level of theory is sufficient to get semiquantitative results for the potential surface. At the same time very accurate calculations are usually not adequate to gain any physical insight into the problem, because they result in too large and complicated sets of data. Therefore, a relatively simple but sufficiently accurate scheme is needed if one wishes to obtain not only numbers for the interaction energy, but also a comprehensive physical picture of the intermolecular interactions.

program and performed a number of calculations for different systems. It was found that the individual energy components can be considered additive at the large and intermediate distances.

- I have studied a simplified version of the CHA-PT2 – the orthogonal approximation, in which all the intermolecular overlap integrals are neglected. The results show that we must take into account the intermolecular overlap everywhere except the asymptotic region.
- I have prepared a program “APOST” devoted to intramolecular energy analysis at the SCF level by using the CECA scheme, i.e. by performing an approximate decomposition of the molecular energy into one- and two-center components.
- I have shown that the two-center part of the CECA energy can be decomposed into terms having well defined physical meaning: electrostatic, exchange, overlap and finite basis effects and performed their coding.
- Starting from the decomposition of the SCF energy into one- and two-center energy components valid in the “AIM” method and applying an appropriate mathematical mapping between the AIM and LCAO formalisms, I have re-derived the expressions of the CECA energy components.

## 4. Results

All the energy decomposition schemes introduced in this work are meant to provide a deeper understanding of the different molecular interactions. In the following I summarize the main results obtained:

- I have derived a closed energy formula of the intermolecular Heitler-London interaction energy by using Löwdin’s pairing theorem. This permitted to describe intermolecular interactions by taking into account the intermolecular overlap explicitly.
- I have rearranged the intermolecular energy formula to present it as the sum of different terms with well-defined physical meaning: the ”naive” electrostatic interaction, the Hartree-Fock exchange, finite-basis terms, ”true” overlap effects, and the changes of the intramolecular, electrostatic and exchange interactions due to the intermolecular overlap. I have prepared a Fortran code permitting to calculate the energy and its different components.
- We observed that in all calculations only one intermolecular overlap between the ”paired” molecular orbitals was significantly different from zero and all the others were by one or more orders of magnitude smaller. For that reason I have introduced the ”leading term” approximation, in which only this largest intermolecular overlap integral is conserved and the others are neglected. This approximation considerably simplifies the expression of the energy and of different physical terms, without causing an appreciable loss in the accuracy of the numerical calculations. I have tested this by actual calculations, too.
- I have studied in detail the form of the ”interacting orbitals” – the paired orbitals having the greatest intermolecular overlap. In full accord with the classical interpretation of the hydrogen bond, one of the paired orbitals can be assigned to the X-H bond of the proton donor, and another to the lone pair of the proton acceptor.
- I have compared the peculiarities of several BSSE-free theories at the SCF level, by performing some calculations on the DNS base pairs.
- I have performed the decomposition of the second order intermolecular interaction energy correction calculated in the framework of the BSSE-free CHA-PT2 perturbational theory into different physical terms: polarization, charge-transfer, dispersion and the combined polarization-charge transfer term. I have introduced the necessary modifications into the PT

In the case of hydrogen bonds the electron correlation is just a minor correction in most cases, therefore the dominating interactions appear already at the single determinant level. Moreover, one can utilize the fact that the molecules change only slightly during the H-bond formation, and one can obtain some important effects even by calculating the energy with the simplest determinant wave function. This energy is often called the ”Heitler-London (H-L) energy”, and corresponds to a first order energy of the intermolecular PT in which the unperturbed problem is given by the Hartree-Fock solutions of the free monomers. Because of the nonorthogonality of the monomer orbitals it is unfeasible to derive an explicit general expression for the H-L energy in terms of the original canonical orbitals of the monomers, and to perform an analysis of the different contributions present in the H-L energy by their use. In such a situation we proposed to use Löwdin’s pairing theorem which permits to achieve the maximal possible degree of orthogonality between the two molecules. The orbitals of the two molecules are subjected to two separate, unitary transformations which do not change the original wave functions of the monomers, but the partial orthogonality provided by these transformations is good enough to derive an explicit and general energy formula for the intermolecular interactions and to identify the physical significance of the different terms. Regrouping the expression of the interaction energy, it can be presented as a sum of terms with different physical meaning, each of which is expressed explicitly in terms of the paired molecular orbitals of the interacting molecules. The terms I have obtained in this way are: the ”naive” electrostatic interaction corresponding to the undisturbed charge distribution of the two molecules; the Hartree-Fock exchange calculated by neglecting the orbital overlap; finite basis terms originating from the deviation of the individual MO’s from the Hartree-Fock limit; overlap effects modifying the intramolecular energies as well as the electrostatic and exchange interactions; and true overlap effects containing intermolecular overlap integrals and intermolecular charge distributions in the one- or two-electron integrals.

Inspecting the results of calculations, I have found that one intermolecular overlap integral is always larger by one or more orders of magnitude than all the other ones. It was found therefore reasonable to consider an approximation in which all the overlaps are neglected, except the dominating one, introducing in this way a significant simplification of the intermolecular energy expression and of the individual energy components.

As a consequence, these orbitals are quite suitable for discussing the intermolecular interactions as they are capable of ”absorbing” most of the intermolecular overlap effects. My results show that they are mainly located in the region of space where the two molecules are at closest and are directed to each

other. They are in perfect accordance with the classical picture of the hydrogen bond: if one considers an X–H...Y bond, one of these “interacting” orbitals can be considered as an X–H bonding orbital of the proton donor X and another one as a lone pair orbital of the proton acceptor Y.

Beyond the HL approximation I have studied the interaction energy in the framework of the second order BSSE-free PT. For this case I have used a special version of the CHA-PT2, in which the zero-order Hamiltonian is the sum of the free monomer Fockians, and the second order energy contribution is given by the Hylleraas-type functional for a non-Hermitian unperturbed Hamiltonian. A characteristic feature of this PT is that it has a first order wave function each term of which can be attributed a well-defined physical meaning. The overall second order energy, however, is not the sum of the respective energy contributions due to the mixings caused by the intermolecular overlap.

In order to decompose the second order energy contribution I have calculated some “partial Hylleraas-functionals” each of which corresponds to one of the physically distinguishable terms of the first order wave function. The physical energy components obtained in this way are: polarization, charge-transfer, intramonomer-correlation, dispersion and the combined polarization-charge transfer effect. I have found that these terms are almost additive at intermediate and large intermolecular distances, but not at the smaller ones.

### 3. Intramolecular interactions

We are interested in getting a deeper understanding of the chemical bonds and of the non-bonded interactions from chemical and as well as from quantumchemical points of view. For a better understanding it is helpful to find bridges between these two languages. A new scheme called “Chemical Energy Component Analysis” (CECA)<sup>1</sup> has recently been introduced in our laboratory, which permits to perform an *a posteriori* analysis of the standard LCAO quantumchemical results. The main idea of this analysis is that – by using a projective integral expansion technique – the SCF energy of the molecule can be decomposed to a good approximation into a sum of one- and twoatomic contributions.

I have prepared a FORTRAN program named “APOST” which is able to calculate the CECA energy components and can be used to post-process the results of the calculations performed with the standard “Gaussian” quantum program package. APOST is an independent program, getting its input (speci-

fication of atoms, the basis set and the MO coefficients) from the “formatted checkpoint file” of the “Gaussian”.

The calculations performed for numerous systems show that even for moderate basis sets one can obtain relevant results from the chemical point of view.

I have performed an analysis of the diatomic component of the SCF energy, which permitted to decompose it into terms of different physical origin: electrostatics, exchange, overlap effects and some finite basis corrections, and performed their coding in an extended version of program “APOST”. The results permit to analyse the relative importance of the different energy components, and in particular indicate the leading role of the exchange contributions in the chemical bond formation.

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<sup>1</sup>I. Mayer, *Chem. Phys. Lett.* **332**, 381 (2000)