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Theoretical investigation of the potential energy, dipole moment and polarizability surfaces of the CH_4-N_2 and C_2H_4-C_2H_4 van der Waals complexes

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Abstract

In the present thesis both *ab initio* and analytical calculations were carried out for the potential energy, dipole moment and polarizability surfaces of the weakly bound van der Waals complexes CH_4-N_2 and C_2H_4-C_2H_4 for a broad range of intermolecular separations and configurations in the approximation of the rigid interacting molecules. For *ab initio* calculations the CCSD(T), CCSD(T)-F12 and less computationally expensive methods such as MP2, MP2-F12, SAPT, DFT-SAPT were employed (for all methods the aug-cc-pVTZ basis set was used). The BSSE correction was taken into account during the calculations. The analytical calculations were performed in the framework of the classical long-range approximation. A model accounting the exchange effects in the range of small overlap of the electron shells of interacting molecules has been suggested to describe the dipole moment of the CH_4-N_2 van der Waals complexes in analytical form for large intermolecular separations including the range of potential wells. In this model the total dipole moment is considered to be the sum of exchange, induction and dispersion contributions.

Keywords: *ab initio*, van der Waals, CH_4-N_2 complex, ethylene dimer, potential energy, dipole moment, polarizability.

Résumé

Dans cette thése, des calculs *ab initio* et analytiques ont été effectués pour déterminer les surfaces d'énergie potentielle, de moment dipolaire et de polarisabilité des complexes de van der Waals faiblement liés CH_4-N_2 et C_2H_4-C_2H_4, pour une large gamme de distances intermoléculaires et de configurations, dans l'approximation des molécules en interaction rigides. Pour les calculs *ab initio*, la méthode CCSD(T), CCSD(T)-F12, ainsi que les méthodes moins couteuses MP2, MP2-F12, SAPT et DFT-SAPT ont été employées (pour toutes les méthodes, la base aug-cc-pVTZ a été utilisée). La correction BSSE a été prise en compte dans les calculs. Les calculs analytiques ont été réalisés dans le cadre de l'approximation classique aux grandes distances. Un modèle prenant en compte les effets d'échange dans la région des petits recouvrements des nuages électroniques des molécules en interaction a été suggérée pour décrire le moment dipolaire du complexe de van des Waals CH_4-N_2 sous une forme analytique, pour les grandes distances intermoléculaires incluant la région des puits de potentiel. Dans ce modèle, le moment dipolaire total est considéré comme résultant de la somme des contributions d'échange, d'induction et de dispersion.

Les mots-clés: *ab initio*, van der Waals, complex CH_4-N_2, dimère d'éthylène, énergie potentielle, moment dipolaire, polarizabilité.

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Introduction

Introduction

Van der Waals complexes play an important role for understanding the nature of weak intermolecular interactions. Van der Waals forces are important for supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, astrophysics and condensed matter physics. A molecular description of condense phase properties relies on the full characterization of pairwise interactions, as well as on the knowledge of many-body forces. Van der Waals complexes of closed-shell species, atoms, and molecules have traditionally served as an important source of information on pair interactions to theoreticians and experimentalists alike [1].

The electric properties of van der Waals systems such as dipole moment and polarizability are of great importance for different applications. They directly reflect the electron density distribution of the system, influencing a significative amount of molecular (or intermolecular) properties. They influence on many optical or spectroscopical properties, such as the refraction index, absorption constant in optical spectroscopy, optical activity, non linear optical phenomena, etc. It is clear that it is important to obtain high quality values for these properties in order to give useful parameters for the modelling of systems under investigation both at micro and macro level.

The present work is dedicated to the theoretical investigation of the potential energy and dipole moment surfaces of the CH_4-N_2 and C_2H_4-C_2H_4 complexes, and to the polarizability surfaces of the methane-nitrogen complex.

OVERVIEW

The present thesis is represented as follows:

- The first Part consists of Chapter 1 that is dedicated to the introduction to the *ab initio* methods, basis sets and different corrections of the errors that arise during the calculation. Also, the finite-field method is described for the case of dipole moment and the polarizability calculations.
- Part II includes Chapter 2, which is dedicated to the presentation of the theory of intermolecular interactions and electric properties. The long-range classical approximation.
- Part III consists of Chapters 3, 4 and 5 devoted to the *ab initio* and analytical calculations of the potential energy surface, dipole moment and polarizability surfaces of the CH_4-N_2 van der Waals complex.
- Part IV includes Chapters 6 and 7 that are dedicated to the theoretical investigation of the potential energy and dipole moment surfaces of ethylene dimer: *ab initio* and analytical calculations.
- Part V gives the Conclusions.
- Part VI gives the Appendixes.

First part

Ab initio methods

Chapter 1

Ab initio Methods

At present, due to the big progress in development of new methods and increasing of computational resources, computational chemistry is widely used. Among others one should mark out *ab inito* methods of calculation. The term *ab initio* was first used in quantum chemistry by Robert Parr and coworkers, including David Craig in a semiempirical study on the excited states of benzene (see, for example, Ref. [2]). This term from Latin is translated as "from the beginning", "from the first principles". It means that the equations of quantum mechanics are solved directly from the first principles without any empirical parameters. The only necessary information is the atoms and their position in the appropriate coordinate system. But it should be mentioned of course, that there are different approximations used for solving differential equations, evaluating the integrals, etc. One of the major approximations is the Born-Oppenheimer approximation. The heavy nuclei move more slowly than the light electrons. Therefore, the wave function of a molecule can be broken into its electronic and nuclear (vibrational, rotational) components.

1.1 Hartree-Fock approximation

The Hartree-Fock (HF) or Self-Consistent Field (SCF) method is the starting point for the most of *ab initio* quantum chemistry methods (for more details on *ab nitio* methods see, for, example, [3,4]). It is an approximated method for ground-state wave function and ground-state energy determination of a many-electron system. Within the HF method the antisymmetric wave function is approximated by a single Slater determinant (SD): an antisymmetrized product of one-electron wave functions (spin-orbitals). This method is based on the mean-field approximation. This approximation implies that interelectron coulomb repulsion is accounted for by means of an average integration of the repulsion term, i.e. the interaction of one electron with the others are accounted for as the interaction of this electron with an average field induced by other electrons. The electron correlation (interaction between electrons) for the electrons of opposite spin is completely neglected. A certain amount of electron correlation is already considered within the HF approximation, found in the electron exchange term describing the correlation between electrons with parallel spin.

For the ground-state closed-shell system ($N = 2n$, N - number of electrons, n - number of orbitals), the Hartree-Fock equations can be obtained from the variational principle. The variational principle implies that an average energy of a system

$$\bar{E}(\Phi) = \langle\Phi|H|\Phi\rangle/\langle\Phi|\Phi\rangle \tag{1.1}$$

as a functional of Φ (wavefunction) has a set of extremums. We assume that the wavefunction Φ is orthonormilized ($\langle\Phi \mid \Phi\rangle = 1$). If Φ and E satisfy the Shrodinger equation $H\Phi = E\Phi$, then

$$\delta\bar{E}(\Phi) = 0, \quad \bar{E}(\Phi) = E. \tag{1.2}$$

The Hamiltonian for the N-electron system (Nn - number of nuclei) is written as follows:

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{a=1}^{Nn}\sum_{i=1}^{N}\frac{Z_a}{R_{ia}} + \sum_{i<j}^{N}\frac{1}{r_{ij}} + \sum_{a<b}^{Nn}\frac{Z_a Z_b}{R_{ab}}. \tag{1.3}$$

As the HF method is based on variational principle, the energies in this approximation equal or lie above the exact energy of the system.

The wave function of the type of a Slater determinant (Φ) for the ground state is an antisymmetrized determinant constructed using the one-electron orthogonal normalized spin-orbitals ($\langle\chi_i|\chi_j\rangle = \delta_{ij}$):

$$\Phi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_N(2) \\ \dots & \dots & \dots & \dots \\ \chi_1(N) & \chi_2(N) & \dots & \chi_N(N) \end{vmatrix}. \tag{1.4}$$

A spin-orbital χ_i(j) is expressed as a product of a spin one-electron function, α(j) or β(j), by a purely spatial one-electron function (orbital), φ_i(j). The use of this determinant satisfies the Pauli principle - the wave function for fermions (electron is a fermion) should be antisymmetric with respect to the permutation of two particles. The permutation of electrons is equivalent to the permutation of columns of determinant, which changes its sign. One more advantage of using Slater determinant is that it decomposes the wave function into one-electron wave functions. That is why for solving many-electron Schrödinger equation it decomposes to some simpler one-electron equations. The solution of each one-electron equation gives one-electron wave function which is called orbital, and the energy called orbital energy.

In the general case acting with the N-electron Hamiltonian on a Slater determinant-like wave function, the expression for the expected energy for the closed shell system will be:

$$\langle\Phi|H|\Phi\rangle = 2\sum_{i}^{N/2} H_i + \sum_{ij}^{N/2}(2J_{ij} - K_{ij}), \tag{1.5}$$

where

$$H_i = \int \chi_i^*(1) h_i \chi_i(1) dq_1, \tag{1.6}$$

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_a^{Nn} \frac{Z_a}{R_{ia}}, \tag{1.7}$$

$$J_{ij} = \int \chi_i^*(1)\chi_j^*(2)\frac{1}{r_{12}}\chi_i(1)\chi_j(2) dq_1 dq_2, \tag{1.8}$$

$$K_{ij} = \int \chi_j^*(1)\chi_i^*(2)\frac{1}{r_{12}}\chi_i(1)\chi_j(2) dq_1 dq_2. \tag{1.9}$$

The integral H_i is called *core integral*, which is the sum of the kinetic energy of an electron with χ_i orbital and its potential energy of attraction to the nuclei. It is multiplied by 2, because there are two electrons in each orbital. The two-electron integral J_{ij} is called *coulomb integral*, which is the averaged energy of electrostatic repulsion of electrons on orbitals χ_i and χ_j. For the same reason it is also multiplied by two. At last the integral K_{ij} is called *exchange integral.* Let us clarify the physical meaning of the *exchange integral.* By the Pauli exclusion principle two electrons with the same spin can not have the same spatial coordinates. Consequently in this case the effective average distance between electrons is bigger, and the energy of electrostatic repulsion is smaller by the magnitude of exchange energy. So the exchange integral partly takes into account the electron correlation, though the correlation due to the coulomb repulsion of pairs of electrons with different spins stay unaccounted for the Hartree-Fock method. It is also convenient to define the coulomb and exchange operators in terms of their action on an arbitrary spin-orbital χ_i:

$$J_j(1)\chi_i(1) = \chi_i(1) \int dq_2 |\chi_j(2)|^2 \frac{1}{r_{12}}, \tag{1.10}$$

$$K_j(1)\chi_i(1) = \chi_j(1) \int dq_2 \chi_j^*(2)\chi_i(2) \frac{1}{r_{12}}. \tag{1.11}$$

The solution of variational problem with the wave function of the type (Eq. 1.4) allows to find the best wave function of this form. To solve this problem one should solve the Hartree-Fock equations (the equations for finding the orbitals), which can be written as eigenvalue equations of Fock operator F for spin-orbitals:

$$F\chi_m(i) = \varepsilon_m \chi_m(i), \tag{1.12}$$

where ε_m is the energy of the χ_m spin-orbital, and the Fock operator

$$F = H + \sum_i^{N/2} (2J_i - K_i). \tag{1.13}$$

From the Hartree-Fock equations it is obvious, that

$$H_i + \sum_{j}^{N/2} (2J_{ij} - K_{ij}) = \varepsilon_i. \tag{1.14}$$

The total energy of the N-electron closed-shell system equals to the sum of total energies of all electrons without the energy of internucleus repulsion:

$$E = 2\sum_{i}^{N/2} \varepsilon_i - \sum_{i,j}^{N/2} (2J_{ij} - K_{ij}). \tag{1.15}$$

For calculating molecular orbitals in *ab initio* methods a linear combination of atomic orbitals (LCAO) method is used. In the method of LCAO-MO (Molecular Orbital as a LCAO) a molecular orbital is written as follows:

$$\varphi_i = \sum_{\mu=1}^{M} C_{\mu i} g_\mu, \tag{1.16}$$

where $C_{\mu i}$ are the expansion coefficients and $\{g_\mu\}$ is a set of atomic orbitals (atomic orbitals are expressed in terms of basis sets).

The calculations in the HF method begin with choosing the reference orbital coefficients $C_{\mu i}^{(0)}$. The initial function with these reference coefficients is used for the calculation of the energy and for a new set of orbital coefficients, which can be used for new set of coefficients. This process is iterative till the energies and orbital coefficients will not change from one iteration to the other in the limit of a given accuracy (convergence of calculation). Solutions of equations on the last step of iterations is «self-consistent with the field of potential», which are determined by the coulomb and exchange operators. This kind of field is called self-consistent (SCF) and the method Hartree-Fock is called method of self-consistent field.

Variations in HF procedure is the way of constructing orbitals dependent on the form of Slater determinant. If all electrons in the molecule are coupled, then one can use the same spatial orbital function for the electron spins α and β in each pair of them. And in this case the energies of the electrons α and β will be the same. A system with $2n$ electrons with n orbitals is a closed shell system. This method is called restricted the Hartree-Fock method (RHF). If there is no coupling between orbital motion and spin, the α and β orbitals parts of the spin-orbitals can be chosen to be equal.

There exist two methods for constructing HF wave functions of molecules with uncoupled electrons. The first method is based on using completely individual sets of orbitals for α and β electrons (the state of each electron is described by its own spin-orbitals). This method is called unrestricted Hartree-Fock method (UHF). It means that coupled electrons will be spatially distributed in different ways. Very often this leads to errors in calculations, which is called spin contamination. Depending on the system spin contamination can lead either to negligible or to big errors.

The other way of constructing wave functions for open-shell systems is the restricted HF method for open shells (ROHF). There are two sets of the wave functions: one for closed shells (core consists of $2n_c$ electrons) (ϕ_c) and the other one for open shells (ϕ_o). In this case there will be no spin contamination. Let us consider the N-electron open-shell system. We will use indexes k, l to label core orbitals, and indexes m, n to label open-shell orbitals; the indexes i, j label the orbitals of both types. The orbitals are normalized and orthogonal: $\langle\phi_i|\phi_j\rangle = \delta_{ij}$. Full wave function ϕ is presented in the form of the linear combination of all antisymmetrized determinants that are constructed from both sets of functions (ϕ_c, ϕ_o).

The expected value of the energy can be written as [5]:

$$E = 2\sum_k H_k + \sum_{k,l}(2J_{kl} - K_{kl}) + f\big[2\sum_m H_m + f\sum_{mn}(2aJ_{mn} - bK_{mn}) + 2\sum_{km}(2J_{km} - K_{km})\big], \quad (1.17)$$

where a, b and f are the numeric parameters depending upon the electronic configuration and considered state of the system. The partial occupation number f of the open shell equals to the ratio of the number of occupied spin-orbitals and the number of external spin-orbitals ($0 < f < 1$). The first two sums in Eq. 1.17 are the energy of the closed shells of the core, the next two sums are the energy of open shell and the last sum is the interaction energy of open shell and core.

Let us define the coulomb integrals J_c and J_o for closed and open shells, the total coulomb integral J_T and analogous exchange integrals K_c, K_o and K_T:

$$J_c = \sum_k J_k, \qquad J_o = f\sum_m J_m, \qquad J_T = J_c + J_o, \quad (1.18)$$
$$K_c = \sum_k K_k, \qquad K_o = f\sum_m K_m, \qquad K_T = K_c + K_o.$$

The Hermitian coulomb and exchange associated operators related to the spin-orbitals ϕ_i have the form:

$$L_i\phi = \langle\phi_i|J_o|\phi\rangle\phi_i + \langle\phi_i|\phi\rangle J_o\phi_i, \quad (1.19)$$
$$M_i\phi = \langle\phi_i|K_o|\phi\rangle\phi_i + \langle\phi_i|\phi\rangle K_o\phi_i,$$

and associated with close shells, open shells and total Coulomb and exchange integrals:

$$L_c = \sum_k L_k, \qquad L_o = f\sum_m L_m, \qquad L_T = L_c + L_o, \quad (1.20)$$
$$M_c = \sum_k M_k, \qquad M_o = f\sum_m M_m, \qquad M_T = M_c + M_o.$$

The spin-orbitals satisfy the relations:

$$F_c\phi_c = \varepsilon_c\phi_c, \qquad F_o\phi_o = \varepsilon_o\phi_o. \quad (1.21)$$

After mathematical transformations we obtain that Fock operators F_c and F_o are identical and have the form

$$F = H + 2J_T - K_T + 2\alpha(L_T - J_o) - \beta(M_T - K_o). \quad (1.22)$$

Here $\alpha = (1-a)/(1-f)$ and $\beta = (1-b)/(1-f)$. Thus, spin-orbitals satisfy the following equations:

$$F\phi_c = \varepsilon_c\phi_c, \qquad F\phi_o = \varepsilon_o\phi_o. \tag{1.23}$$

After the diagonalization, spin-orbitals ϕ_c and ϕ_o become the solutions of one Hartree-Fock equation

$$F\phi_i = \varepsilon_i\phi_i. \tag{1.24}$$

The set of ϕ_i is equivalent but not identical to the sets ϕ_c and ϕ_o (for eigen values ε_i - analogously, they are equivalent but not identical to the sets ε_c and ε_o).

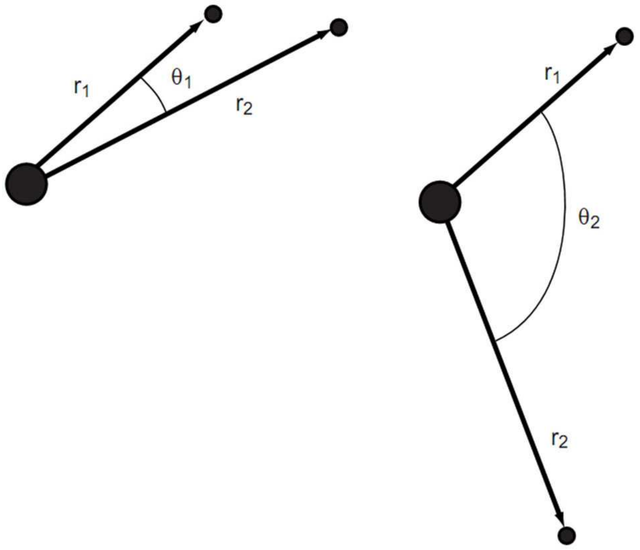
Therefore, total energy of the open-shell system without internucleus repulsion has the form:

$$E = \sum_k (H_k + \varepsilon_k) + f\sum_m (H_m + \varepsilon_m) - f\sum_{km}(2\alpha J_{km} - \beta K_{km}) - f^3\sum_{mn}(2\alpha J_{mn} - \beta K_{mn}). \tag{1.25}$$

1.2 Correlation

One of the limitations of the HF method is that it does not take into account the correlation of electrons. This means that this method takes into account only averaged interaction of electrons but not the real interelectron interaction. In the HF method the probability of finding the electron in some place near to atom is determined by distance from the nucleus but not by the distance between different electrons, as show in Fig. 1.1. Physically this is not right, but this is a mean field approximation which is included in the HF method.

FIG. 1.1 - *Two positions of the electrons near the nucleus, which have the same probability in the HF calculations and different - in the calculations accounting for the electron correlation.*



By using a sufficiently big basis set, the HF wave functions are able to consider about 99% of total energy, but the remaining 1% often appears to be very important for description of chemical phenomena. This 1% of the total energy is called the correlation energy. Because

HF solutions give the most part of the total energy, the methods which consider electron correlation use the HF wave functions as an initial approximation and after correcting them take into account correlation.

The HF method determines trial one-determinant wave function (in the given basis set). For improving of the HF solutions, a new wave function should be tested, which contains more than one Slater Determinant. The characteristic many-determinant trial wave function can be written as:

$$\Psi = a_0\Phi_{HF} + \sum_{i=1} a_i\Phi_i, \tag{1.26}$$

where the coefficient a_0 is close to 1. There are different ways to calculate coefficient a_i in electron correlation methods, and coefficient a_0 is determined from the normalization condition.

If we have N electrons and M basis functions then for the RHF case we will obtain $N/2$ occupied Molecular Orbitals (MO) and $M - N/2$ not occupied (virtual) MO. Usually (especially in the case of minimal basis set) there always will be more virtual MO than occupied ones. SD determines $N/2$ by spatial MO multiplied by two spin functions for obtaining N spin orbitals. By replacing MOs which are occupied in the HF determinant by MOs which are unoccupied, a whole series of determinants may be generated. These can be denoted according to how many occupied HF MOs have been replaced by unoccupied MOs, i.e. Slater determinants, which are singly, doubly, triply, etc. (maximum N excited electrons) excited with respect to the HF determinant). These determinants are often called Singles (S), Doubles (D), Triples (T), Quadruples (Q) etc (Fig. 1.2).

The total number of possible determinants depends on the size of basis set, as many virtual MO, as much exited determinants can be constructed. If all possible determinants are considered in the given basis set, then all correlation of electrons will be considered (in the given basis set). For infinite basis set the Schrödinger equation is exactly solvable. It should be mentioned here that the exact value in this context is not equivalent to the experimental value, because it is considered that the nuclei have infinitely big masses (Born-Oppenheimer approximation), and the relativistic effects are neglected.

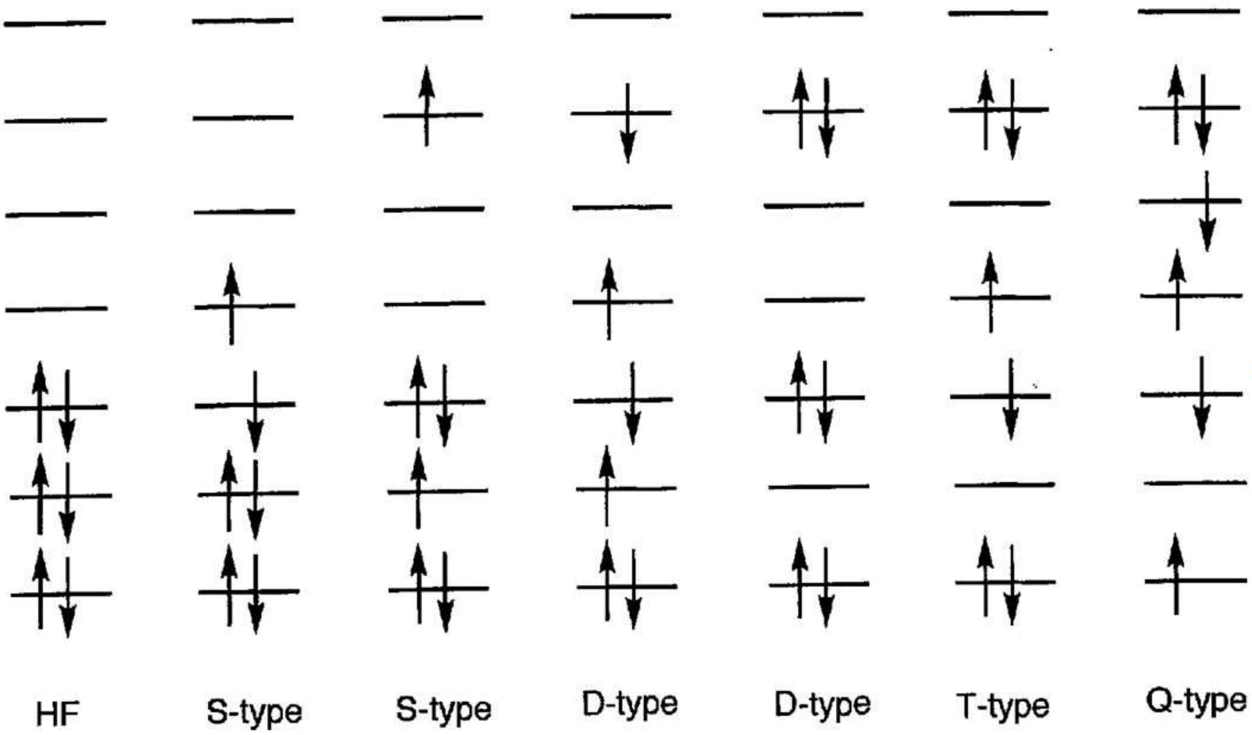
The main methods, which take into account electron correlation are: Møller-Plesset Perturbation theory (MPn, where n is the power of correction), Multi-configuration self-consistent field (MCSCF), Configuration Interaction (CI) and also Coupled Cluster(CC) method. In our study we have used only the MP2 and CCSD(T) methods.

1.2.1 Møller-Plesset perturbation theory

This theory is based on the Many-body perturbation theory (MBPT) of Rayleigh-Schrödinger. Due to the small correlation energy in comparison with the total energy the theory of perturbation can be used. As a zero-th approximation is taken HF Hamiltonian H_0 (for this solution is known) and correlation is included in Hamiltonian as a perturbation V:

$$H = H_0 + \lambda V. \tag{1.27}$$

FIG. 1.2 - *Excited determinants obtained from the reference HF determinant.*



Here λ-is a parameter ($0 < \lambda < 1$), which determines the strength of perturbation (let it be equal to one). In this case we obtain the Schrödinger equation

$$(H^0 + V)\Psi_i = E_i\Psi_i, \tag{1.28}$$

and its solutions are the Taylor series

$$E_i = \lambda^0 E_i^{(0)} + \lambda^1 E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots , \tag{1.29}$$

$$\Psi_i = \lambda^0 \Psi_i^{(0)} + \lambda^1 \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} + \cdots , \tag{1.30}$$

where $E_i^{(k)}$ and $\Psi_i^{(k)}$ are the corrections of the k-th order to the energy and wavefunction. We can express $\Psi_i^{(k)}$ as a linear combination of eigenfucntions of the non-perturbed Hamiltonian H_0:

$$\Psi_i^{(k)} = \sum_n c_n^{(k)} \Psi_n^{(0)}. \tag{1.31}$$

Using the equation $\langle\Psi|\Psi_i^{(0)}\rangle = 1$ we can find the energies of the 0-th and 1-st order:

$$E_i^{(0)} = \langle\Psi_i^{(0)}|H_0|\Psi_i^{(0)}\rangle, \qquad E_i^{(1)} = \langle\Psi_i^{(0)}|V|\Psi_i^{(0)}\rangle. \tag{1.32}$$

The coefficients $c_n^{(1)}$ for the 1-st order is the following

$$c_n^{(1)} = \frac{\langle\Psi_n^{(0)}|V|\Psi_i^{(0)}\rangle}{E_i^{(0)} - E_n^{(0)}}. \tag{1.33}$$

The wavefucntion corrected up to the 1st order has the form

$$\Psi_i = \Psi_i^{(0)} + \sum_{n\neq i} \frac{\langle \Psi_n^{(0)} | V | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_n^{(0)}} \Psi_n^{(0)}. \tag{1.34}$$

Let us consider the Møller-Plesset approach. The zero-th order Hamiltonian H_0 and perturbation V have the forms

$$H_0 = \sum_i F_i = \sum_i^N (h_i + \nu^{HF}) = \sum_i^N (h_i + \sum_j^N (J_{ij} - K_{ij})) = \sum_i^N h_i + 2\langle V_{ee} \rangle, \tag{1.35}$$

$$V = \sum_{i<j}^N \frac{1}{r_{ij}} - \sum_i^N \nu^{HF}, \tag{1.36}$$

where

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_a^{Nn} \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} \tag{1.37}$$

and $\langle V_{ee} \rangle$ is an average value of interelectronic repulsion. The wavefunction Ψ_0 is the eigenfunction of the Fock operator:

$$H_0 \Psi_0 = E_0^{(0)} \Psi_0. \tag{1.38}$$

Thus, the energy of non-perturbed system is the following

$$E_0^{(0)} = \sum_i^N \varepsilon_i. \tag{1.39}$$

The 1-st order correction to the energy has the form

$$E_0^{(1)} = \langle \Phi_0^{(0)} \mid V \mid \Phi_0^{(0)} \rangle = \langle \Psi_0^{(0)} | \sum_{i<j}^N \frac{1}{r_{ij}} | \Psi_0^{(0)} \rangle - \langle \Psi_0^{(0)} | \nu^{HF} | \Psi_0^{(0)} \rangle = -\frac{1}{2} \sum_{i,j}^N (J_{ij} - K_{ij}) = -\langle V_{ee} \rangle. \tag{1.40}$$

Thus, the sum of the zero-th and 1-st order energies gives the HF energy:

$$E_0 = E_0^{(0)} + E_0^{(1)} = \sum_i^N \varepsilon_i - \frac{1}{2} \sum_{i,j}^N (J_{ij} - K_{ij}) = E_{HF}. \tag{1.41}$$

The first correction to the HF energy appears only at the 2-nd order perturbation theory (MP2). Second order correction to the energy has the form

$$E_0^{(2)} = \sum_{i\neq 0} \frac{|\langle \Psi_i^{(0)} | V | \Psi_0^{(0)} \rangle|^2}{E_0^{(0)} - E_i^{(0)}}. \tag{1.42}$$

Consideration of single excitation states at summing gives (indexes i, j correspond to occupied orbitals and indexes a, b correspond to virtual orbitals)

$$\begin{gathered} \langle \Psi_0^{(0)} \mid V \mid \Psi_i^a \rangle = \langle \Psi_0^{(0)} \mid H - \sum_j^N F_j \mid \Psi_i^a \rangle = \\ \langle \Psi_0^{(0)} \mid H \mid \Psi_i^a \rangle - \langle \Psi_0^{(0)} \mid F_j \mid \Psi_i^a \rangle = \langle \Psi_0^{(0)} \mid H \mid \Psi_i^a \rangle - \varepsilon_a \langle \Psi_0^{(0)} \mid \Psi_i^a \rangle. \end{gathered} \tag{1.43}$$

The first term in the expression due to the Brillouin's theorem equal to zero and the second term equal to zero because of orthonormality of the Fock wave functions. Contribution of double excited states represented as

$$E_0^{(2)} = \sum_{i<j}^{occ}\sum_{a<b}^{vir} \frac{\langle \Psi_0^{(0)} \mid V \mid \Psi_{ij}^{ab}\rangle\langle \Psi_{ij}^{ab} \mid V \mid \Psi_0^{(0)}\rangle}{E_0^{(0)} - E_{ij}^{ab}} \tag{1.44}$$

$$= \sum_{i<j}^{occ}\sum_{a<b}^{vir} \frac{|(ia|jb)|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \tag{1.45}$$

where $(ia|jb)$ is a two-electron integral.

The MP2 method is the simplest method taking into account electron correlations. Comparatively, the MP4 the MP3 methods are not so used. The accuracy of MP4 is almost the same as the CISD (CI with singles and doubles). Calculations with MP5 methods take very long computational time and they are not so common.

1.2.2 Coupled Cluster Theory

The methods of perturbation theory add all kinds of corrections (S, D, T, Q etc.) to the sample wave function to a given order(2, 3, 4 etc.). The idea of Coupled Cluster methods is to include all corrections of a given type to infinite order.
The coupled cluster wave function is written as

$$\Psi_{CC} = e^T\Psi_0,$$

$$e^T = 1 + T + \frac{1}{2}T^2 + \frac{1}{3}T^3 + ... = \sum_{k=0}^{\infty}\frac{1}{k!}T^k, \tag{1.46}$$

where the cluster operator T is given by

$$T = T_1 + T_2 + T_3 + ...T_N. \tag{1.47}$$

The T$_i$ operator acting on a HF reference wave function generates all i-th excited Slater determinants:

$$T_1\Psi_0 = \sum_{i}^{occ}\sum_{a}^{vir} t_i^a\Psi_i^a, \tag{1.48}$$

$$T_2\Psi_0 = \sum_{i<b}^{occ}\sum_{a<b}^{vir} t_{ij}^{ab}\Psi_{ij}^{ab}. \tag{1.49}$$

The expansion coefficients t are called *amplitudes.* From Eqs. 1.46-1.47 exponential operator can be written

$$e^T = 1 + T_1 + (T_2 + \frac{1}{2}T_1^2) + (T_3 + T_2T_1 + \frac{1}{6}T_1^3) \tag{1.50}$$
$$+(T_4 + T_3T_1 + \frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{24}T_1^4) + \cdots .$$

The first term in Eq. 1.51 generates the reference HF and the second - all singly excited states. The first parenthesis generates all doubly excited states, which may be considered as connected (T_2) or disconnected (T_1^2). The second parenthesis generates all triply excited states, which again may be either "true" (T_3) or "product" triples (T_2T_1,T_1^3). The quadruply excited states can similarly be viewed as composed of five terms, a true quadruple and four product terms. Physically a connected type such as T_4 corresponds to four electrons interacting simultaneously, while a disconnected term such as T_2^2 corresponds to two non-interacting pairs of interacting electrons.

With CC wave function the Schrödinger equation has the form

$$He^T\Psi_0 = Ee^T\Psi_0. \tag{1.51}$$

Multiplying from the left by Ψ_0^* and integrating, we obtain

$$\langle\Psi_0 \mid He^T \mid \Psi_0\rangle = E_{CC}\langle\Psi_0 \mid e^T\Psi_0\rangle = E_{CC}\langle\Psi_0 \mid (1 + T_1 + T_2 + ...)\Psi_0\rangle, \tag{1.52}$$

$$E_{CC} = \langle\Psi_0 \mid He^T \mid \Psi_0\rangle. \tag{1.53}$$

Expanding the exponential operator e^T and using that fact, that Hamiltonian contains only one- and two-electron operators, we get

$$\begin{aligned} E_{CC} &= \langle\Psi_0 \mid H \mid (1 + T_1 + T_2 + \frac{1}{2}T_1^2 + \ldots)\Psi_0\rangle \\ &= \langle\Psi_0 \mid H \mid \Psi_0\rangle + \langle\Psi_0 \mid H \mid\ T_1\Psi_0\rangle + \langle\Psi_0 \mid H \mid\ T_2\Psi_0\rangle + \frac{1}{2}\langle\Psi_0 \mid H \mid\ T_1^2\Psi_0\rangle + \ldots \\ &= E_0 + \sum_i^{occ}\sum_i^{vir} t_i^a\langle\Psi_0 \mid H \mid \Psi_i^a\rangle + \sum_{i<j}^{occ}\sum_{a<b}^{vir}(t_{ij}^{ab} + t_i^at_j^b - t_i^bt_j^a)\langle\Psi_0 \mid H \mid \Psi_{ij}^{ab}\rangle + \cdots . \end{aligned} \tag{1.54}$$

When using HF orbitals for constructing the Slater determinants, the first matrix elements are zero (according to the Brillouin's theorem) and the second matrix elements are just two-electron integrals over MOs:

$$E_{CC} = E_0 + \sum_{i<j}^{occ}\sum_{a<b}^{vir}(t_{ij}^{ab} + t_i^at_j^b - t_i^bt_j^a)(\langle\phi_i\phi_j \mid \phi_a\phi_b\rangle - \langle\phi_i\phi_j \mid \phi_b\phi_a\rangle) + \cdots . \tag{1.55}$$

The coupled cluster correlation energy is therefore determined completely by the singles and doubles amplitudes and the two-electron MO integrals. In this CC method the wave function is a linear combination of some determinants. The CC method has different expansion orders named as CCSD, CCSDT and so on. The method designated as CCSD(T) is the one where the triple excitations are accounted not directly but as the perturbation. This method allows to account for 99% of correlation energy and at present it is one of the most popular methods applied to small molecules. It is difficult to carry out calculations for systems with a big number of particles due to big computational time and limited computational resources. If all possible excitations were taken into account, we would obtain the total correlation energy.

1.2.3 Explicitly Correlated F12 Methods

In the last years there had been a rapid development of explicitly correlated methods that use Slater-type geminals (STG's) as two-particle basis functions. Let us speak about the so-called "F12 methods". These methods were first developed, investigated, and applied in the framework of the second-order Møller-Plesset perturbation theory, i. e. at the MP2-F12 level [10]. One of the limitations in *ab initio* quantum chemistry is the slow convergence of electron correlation energies with respect to the basis set size. The reason of this is that the wave function cusp for $r_{12} > 0$ and, more importantly, the correlation hole for intermediate values of r_{12} are poorly represented by expansions of the wave function in terms of orbital products (Slater determinants), thus such wave functions poorly account for the short-range electron correlation. This situation can be improved by using explicitly correlated wave functions, that is, wave functions that depend explicitly on the interelectronic distances r_{ij}. The introduction of such terms into the wave function greatly accelerates basis set convergence. The choice of the correlation factor is much more important than any other approximation. Short-ranged correlation factors such as $exp(-\beta r_{12})$ were found to give very much improved results as compared to the linear r_{12} factor. Methods that are based on such short-ranged correlation factors are now referred to as F12 methods. In 2007 a new explicitly correlated CCSD(T)-F12 approximation was presented and tested in Ref. [11]. These methods proved to be more accurate and faster than conventional CCSD(T) method with the same basis set [11]. The correlation plays an important role in van der Waals interactions, thus these methods could be successfully applied for solving problems of weakly-bound complexes.

1.2.4 Symmetry-Adapted Perturbation Theory (SAPT)

One of the promising methods that can be applied to the calculation of the potential energy of complexes is the Symmetry-Adapted Intermolecular Perturbation Theory [12]. This method allows to account for the exchange (repulsive) interactions at short range separations in addition to the long-range (attractive) interactions. The developers of the method (mainly people in Warsaw Quantum Chemistry Group) came to the conclusion that symmetrized Rayleigh-Schrödinger perturbation theory (RSPT) was the most viable of the different variants of SAPT [13]. The idea of the symmetrized RSPT is the introduction of antisymmetrizer A^{AB}. After the symmetrization the polarization expansion for the wave function gives the correct asymptotic expansion for the exact (unnormalized) wave function:

$$\Psi = A^{AB}\Phi^0_{pol} + \sum_{n-1}^{N} A^{AB}\Phi^{(n)}_{pol} + O(R^{-k(N+1)}), \tag{1.56}$$

where Φ^0_{pol} is a zeroth-order wavefunction that does not have the correct, Pauli-allowed permutation symmetry; $\Phi^{(n)}_{pol}$ is the n-th order polarization wavefunction; $k = 2$ if at least one of the interacting molecules has a net charge and $k = 3$ if both molecules are neutral. Hence, the interaction energy expression (SRS - Symmetrized Rayleigh Schrödinger) is the following:

$$E_{SRS} = \frac{< \Phi^{(0)}_{pol} | V^{AB} | A^{AB} \Phi^{(0)}_{pol} >}{< \Phi^{(0)}_{pol} | A^{AB} \Phi^{(0)}_{pol} >}. \tag{1.57}$$

In SAPT approach the total interaction energy is calculated as a sum of individual first and second order terms: $E^{(1)}_{pol}$ (electrostatic), $E^{(2)}_{ind}$ (induction), $E^{(2)}_{disp}$ (dispersion) and their respective exchange terms $E^{(1)}_{exch}$, $E^{(2)}_{exch-ind}$ and $E^{(2)}_{exch-disp}$. The exchange contributions arise due to electron exchange between the monomers when the molecules are close to each other and are sometimes denoted as Pauli repulsion. Since all above terms are accessible through density matrices and static and dynamic density-density response functions of the monomers, in principle no calculation of the dimer wavefunction is required. Therefore, SAPT is free from the BSSE which occurs in the supermolecular approach.

The SAPT method can use single-determinant wavefunction for the monomers both from HF and Kohn-Sham DFT calculations. It is of crucial importance to account for the intramolecular correlation effects of the individual SAPT terms since HF theory often yields poor first- and second-order electrostatic properties. While this can be done using many-body perturbation theory a more efficient way is to use static and time-dependent DFT theory. This variant of SAPT, termed as DFT-SAPT, has in contrast to HF-SAPT (further, we will call HF-SAPT just SAPT) the feature that the polarisation terms ($E^{(1)}_{pol}$, $E^{(2)}_{ind}$, $E^{(2)}_{disp}$) are potentially exact. The DFT-SAPT could give highly accurate interaction energies comparable to high-level supermolecular many-body perturbation or coupled cluster theory. However, one should carry-out test (SAPT) calculations on several geometries of the complex under investigation in order to find out if these methods are applicable to the complex under investigation. The SAPT method can be applied only to the closed-shell systems.

Remark on DFT

Density functional theory (DFT) is a quantum mechanical theory used to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces. Its incomplete treatment of dispersion can adversely affect the accuracy of DFT (at least when used alone and uncorrected) in the treatment of systems which are dominated by dispersion. The major difference between DFT and Molecular Orbital theory is the following: DFT optimizes an electron density while Molecular Orbital theory optimizes a wavefunction.

The electron density ρ, integrated over all space, gives the total number of electrons N, i.e.

$$N = \int \rho(\mathbf{r}) d\mathbf{r}. \tag{1.58}$$

The density determines the external potential, which determines the Hamiltonian, which determines the wavefunction. And, of course, with the Hamiltonian and wavefunction in hand, the energy can be computed. In 1965 Kohn and Sham found that it would be considerably simpler if only the Hamiltonian operator were one for non-interacting system of electrons. Such Hamiltonian can be expressed as a sum of one-electron operators, has eigenfunctions that are Slater determinants of the individual one-electron eigenfunctions, and has eigenvalues that are simply the sum of the one-electron eigenvalues [6]. Then, the main thing is to take as a starting point a fictitious system of non-interacting electrons that have for their overall ground-state density the same density as some real system of interest where the electrons do interact. Next, we divide the energy functional into the components:

$$E[\rho(\mathbf{r})] = T_{ni}[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})], \tag{1.59}$$

where the terms on the r.h.s. refer, respectively, to the kinetic energy of the non-interacting electrons, the nuclear-electron interaction, the classical electron-electron repultion,the correction to the kinetic energy deriving from the interacting nature of the electrons. and all non-classical corrections to the electron-electron repulsion energy.

Note, that for a non-interacting system of electrons the kinetic energy is just the sum of the individual electronic kinetic energies. Within an orbital expression for the density, the total energy (Eq. 1.59) may be rewritten as

$$\begin{aligned} E[\rho(\mathbf{r})] = \sum_i^N \Big(\langle \chi_i | -\frac{1}{2}\nabla_i^2 | \chi_i \rangle) - \langle \chi_i | \sum_k^{nuclei} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} | \chi_i \rangle \Big) \\ + \sum_i^N \langle \chi_i | \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{\mathbf{r}_i - \mathbf{r}'} d\mathbf{r}' | \chi_i \rangle + E_{xc}[\rho(\mathbf{r})], \end{aligned} \tag{1.60}$$

where N is the number of electrons and we have used that the density for a Slater-determinant wavefunction (which is an exact eigenfunction for the non-interacting system) is simply

$$\rho = \sum_{i=1}^N \langle \chi_i | \chi_i \rangle. \tag{1.61}$$

If we undertake in the usual fashion to find the orbitals χ that minimize E in Eq. 1.61, we find that they satisfy the pseudoeigenvalue equations

$$h_i^{KS} \chi_i = \varepsilon_i \chi_i, \tag{1.62}$$

where the Kohn-Sham (KS) one-electron operator is defined as

$$h_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} + \int \frac{\rho(\mathbf{r}')}{\mathbf{r}_i - \mathbf{r}'} d\mathbf{r}' + V_{xc}, \tag{1.63}$$

and V_{xc} is a so-called functional derivative. As for determination of the KS orbitals, we express them within a basis set of functions ϕ, and we determine the individual orbital coefficients by solution of a secular equation entirely analogous to that employed for HF theory, except for the elements $F_{\mu\nu}$ are replaced by elements $K_{\mu\nu}$ defined by

$$K_{\mu\nu} = \langle\phi_\mu| - \frac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} + \int \frac{\rho(\mathbf{r}')}{\mathbf{r}_i - \mathbf{r}'} d\mathbf{r}' + V_{xc}|\phi_\nu\rangle. \tag{1.64}$$

The functional dependence of E_{xc} on the electron density is expressed as an interaction between the electron density and an "energy density" ε_{xc} that is dependent on the electron density:

$$E_{xc}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r}. \tag{1.65}$$

The energy ε_{xc} is always treated as a sum of individual exchange and correlation contributions. The main thing is to find correct functional ε_{xc}.

1.3 Basis sets

In *ab initio* calculations, MO (Molecular Orbitals) are used as a linear combinations of atomic orbitals [14]:

$$\Psi_i = \sum_i^M c_{\nu i}\phi_\nu, \tag{1.66}$$

where Ψ_i is i-th molecular orbital, c_{ji} is expansion coefficient, M is a number of molecular orbitals, and ϕ_ν is ν-th atomic orbital (solution for one-electron Schrödinger equation) or "basis function". As a basis functions the STOs (Slater type orbitals) can be used:

$$\varphi(r,\theta,\phi;\zeta,l,m,n) = N\frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1}e^{-\zeta r}Y_l^m(\theta,\phi), \tag{1.67}$$

where ζ is the exponent, n - principal quantum number of the valence orbital; l and m are the angular momentum quantum numbers, and N is the normalization constant. As a basis functions one can also use the GTOs (Gaussian type primitives or primitive functions of Gaussian type)(further, we will talk only about the GTOs). They are written as:

$$g(\alpha,l,m,n;x,y,z) = Ne^{-\alpha r^2}x^l y^m z^n. \tag{1.68}$$

Here N is a normalization constant; α is called "exponent"; x, y, z are Cartesian coordinates; l, m, n are the integral exponents on Cartesian coordinates (not the quantum numbers). Here are examples of basis sets:

$$\begin{aligned}
1s &= Ne^{-\alpha r^2}, \\
2p_x &= Ne^{-\alpha r^2}x, \\
2p_y &= Ne^{-\alpha r^2}y, \\
2p_z &= Ne^{-\alpha r^2}z, \\
3d_{xx} &= Ne^{-\alpha r^2}x^2, \\
3d_{xy} &= Ne^{-\alpha r^2}xy, \\
3d_{xz} &= Ne^{-\alpha r^2}xz, \\
3d_{yy} &= Ne^{-\alpha r^2}y^2, \\
3d_{yz} &= Ne^{-\alpha r^2}yz, \\
3d_{zz} &= Ne^{-\alpha r^2}z^2, \\
4f_{xxx} &= Ne^{-\alpha r^2}x^3, \\
4f_{xxy} &= Ne^{-\alpha r^2}x^2y, \\
4f_{xxy} &= Ne^{-\alpha r^2}xyz, \\
4f_{xyz} &= Ne^{-\alpha r^2}xyz.
\end{aligned}$$

For s-functions the normalization constant is $N = (\frac{2\alpha}{\pi})^{3/4}$, for p-function $N = (\frac{128\alpha^5}{\pi^3})^{1/4}$, for d-function with repeated indices $N = (\frac{2048\alpha^7}{9\pi^3})^{1/4}$ and for d-function with different indices $N = (\frac{2048\alpha^7}{\pi^3})^{1/4}$. The general formula for the normalization constant is the following [15]:

$$N = \left(\frac{2\alpha}{\pi}\right)^{3/4} \frac{(4\alpha)^{\frac{l+m+n}{2}}}{\sqrt{(2l-1)!!(2n-1)!!(2m-1)!!)}}. \tag{1.69}$$

The sum of exponents related to Cartesian coordinates $L = (l + m + n)$ are used also as the orbital quantum number for atoms: for the s-function $L = 0$, for the p-function $L = 1$ etc.

Gaussian primitives are usually obtained from atomic calculations. For this reason exponents are varied till obtaining the minimal energy. For constructing MO these primitives are used. This linear combination (contraction) is the basis function. As an example, for 1s orbital of the Hydrogen atom one can use the combination of s-functions:

$$\begin{aligned}
\phi_{1s} = {} & 0.50907N_1e^{-0.123317r^2} + 0.47449N_2e^{-0.453757r^2} \\
& +0.13424N_3e^{-2.01330r^2} + 0.01906N_4e^{-13.3615r^2}.
\end{aligned} \tag{1.70}$$

Here N_i is the normalization constant for a given primitive. This primitives in Eq. 1.70 can be separated into two contractions:

$$\phi_1 = N_1e^{-0.123317r^2},$$

$$\phi_2 = N(0.47449N_2e^{-0.453757r^2} + 0.13424N_3e^{-2.01330r^2} + 0.01906N_4e^{-13.3615r^2}), \tag{1.71}$$

where N is a normalization constant for all construction. In this case 4 primitives are contracted to obtain the basis functions (this contraction is denoted (4s)→[2s] or (4s)/[2s]). The way of choosing contractions depends on the system under consideration.

Usually basis sets are included in program software. However, at present the developments are going on in the field of basis sets. One of the most popular base, where one can find the basis sets for all atoms of the periodic table in format required for arbitrary software, is EMSL Basis set Exchange [16]. Here is the example of basis set 6-311G for carbon ((11s,5p)/[4s,3p]) taken from EMSL:

Shell	exponent	s - coefficient	p - coefficient
S			
	4563.2400000	0.00196665	
	682.0240000	0.0152306	
	154.9730000	0.0761269	
	44.4553000	0.2608010	
	13.0290000	0.6164620	
	1.8277300	0.2210060	
SP			
	20.9642000	0.1146600	0.0402487
	4.8033100	0.9199990	0.2375940
	1.4593300	-0.00303068	0.8158540
SP			
	0.4834560	1.0000000	1.0000000
SP			
	0.1455850	1.0000000	1.0000000

The primitives are represented as exponents and coefficients, starting from the biggest value. It should be pointed out, that primitives in this example are normalized, because the s- and p-coefficients for the basis sets equal to 1. From this example, it is obvious, that the orbital for the 2p$_x$ can be written as:

$$\phi_{2p_x} = 0.040xe^{-20.964r^2} + 0.238xe^{-4.803r^2} + 0.816xe^{-1.459r^2} + xe^{-0.483r^2} + xe^{-0.146r^2}. \tag{1.72}$$

There is also one more way of writting the basis set which characterizes how many contractions has been used, for example TZV (triple-zeta valence). It means that there are 3 valent contractions as in basis set 6-311G.

Polarization functions

Polarization functions are necessary for considering the displacement of the center of charge, for example in highly polar molecules. They give to the wavefunction a big flexibility (account of orbital polarization in molecule). The use of these functions allows to find more accurate geometries and vibrational frequencies. For this purpose the functions with the higher quantum number are included into the basis set: d-functions for heavy atoms and p-functions for hydrogen.

Diffuse functions

Very often the so-called diffuse functions are added to basis sets. Diffuse functions are primitives with a small value of exponent, that is why they describe the wavefunction far away from the nucleus. Diffuse functions are used for anions, possessing big electron density distribution. Also, these functions are very useful for the description of interactions at large separations, such as van der Waals interactions.

Example

Let us consider the notation of the basis set of Dunning [17] aug-cc-pVTZ: ”aug” means including diffuse functions, ”cc”-tells about correlation-consistent basis set (the functions are optimized for better work in correlation calculations), ”p” means that the basis set includes polarization functions, and ”VTZ” means, that valent orbitals are described by three contractions. For the basis sets of Pople (see, for example, [18]) there exists another notation. The polarization functions are included in a given way: 6-311G* or 6-311G** (or 6-311G(dp,p)). One star implies additional d-functions (or d- and p- functions) for heavy atoms, and two stars mean additional p-functions for hydrogen. Diffuse functions are designated as ”+”: 6-311$^+$G or 6-311^{++}G. One plus corresponds to the inclusion of diffuse functions for atoms except hydrogen, and two pluses - diffuse functions are added for all atoms.

1.4 Basis Set Superposition Error (BSSE)

The Basis Set Superposition Error (BSSE) was reported for the first time by Kestner [19] for the Helium dimer and by Jansen and Ros [20] in 1969, for the protonation of carbon monoxide, although the term BSSE was introduced by Liu and McLean in 1973 [21]. But it is still being studied and reviewed.

BSSE is present in all molecular electronic structure calculations in which orbitals are approximated by expansion in terms of analytic basis functions centered on different points (usually the nuclei) that are dependent on the geometry of the system being studied. The error arises when two chemical fragments, A and B, approach to form the AB supermolecule. The description of fragment A within the complex can be improved by the functions of fragment B and vice versa, while such extension is not possible in the calculation of the isolated fragments. Consequently, in the process $A + B \to AB$, the total energy decreases by two factors; the stabilization of the system due to the fragments interaction and the improvement in the individual atomic description. This second effect (BSSE) is an artifact, which causes an unphysical overestimation of the interaction energy. These errors have been mainly discussed in studies of weak interactions, such as van der Waals interactions, and more recently in studies of intramolecular interactions [22, 23]. However, let us recall that A and B fragments can be atoms as well as polyatomic species, that is, the BSSE is also present in every chemical bond, as well as it is in weakly bounded dimers.

The conventional way to correct for BSSE is based on the Boys - Bernardi [24] (counterpoise (CP)) scheme. Using the CP correction scheme one has to recalculate the monomers in the basis of the whole supermolecule for every geometrical arrangement. For example, in the case of two interacting monomers A and B, the uncorrected interaction energy (ΔE) can be calculated as

$$\Delta E = E_{AB}(AB) - E_A(A) - E_B(B), \tag{1.73}$$

where $E_{AB}(AB)$ is the total energy of the complex and $E_A(A)$ and $E_B(B)$ are the total energies of the monomers. In the following, we will use subscripts to denote the molecular species in the energy expressions, while the letters in parentheses refer to the (composite) basis used in the calculation. For example, $E_A(A)$ is the energy of monomer A calculated by using its own basis set. The CP-corrected interaction energy can be defined as

$$\Delta E^{CP} = E_{AB}(AB) - E_A(AB) - E_B(AB). \tag{1.74}$$

Using Eqs. 1.73 and 1.74, one can define the BSSE content of the interaction energy as

$$\delta^{BSSE} = \Delta E - \Delta E^{CP} = E_A(AB) - E_A(A) + E_B(AB) - E_B(B). \tag{1.75}$$

Using Eq. 1.75, one can define the CP-corrected total potential energy surface (PES) of a dimer as

$$E^{CP} = E_{AB}(AB) - \delta^{BSSE} = E_{AB}(AB) + E_A(A) - E_A(AB) + E_B(B) - E_B(AB). \tag{1.76}$$

According to Eq. 1.76, one has to calculate five different total energies at every geometrical arrangement of the system to determine a CP-corrected PES. Of course, Eq. 1.76 can be generalized to the case of an arbitrary number of subsystems, but the number of energy calculations necessary to determine the PES increases enormously with the number of monomers [25].

1.5 Basis Set Incompleteness Error (BSIE)

It is known that in electronic structure calculations the basis sets are not complete. But it is of interest to calculate the interaction energy in the CBS (Complete Basis Set) limit (corrected for the BSIE). If to use the CBS extrapolation for the BSSE-uncorrected energies, there is generally no monotonic convergence as is observed for BSSE-corrected ones [26]. But when we consider the energy values obtained successively, the convergence is rather systematic. Therefore, in the present work the BSSE-corrected energies were employed to obtain the CBS limit. Moreover, for the good convergence of energies to the CBS limit we have to use also rather large basis sets. For this purpose the aug-cc-pVXZ (X = 2(D), 3 (T), 4 (Q), 5, etc.) basis sets of

Dunning [17] can be employed in our investigation. There are the CBS extrapolation schemes of Feller [27]

$$E_X^{HF} = E_{CBS}^{HF} + Bexp(-\alpha X), \tag{1.77}$$

Truhlar [28]

$$\begin{aligned} E_X^{HF} &= E_{CBS}^{HF} + AX^{-\alpha}, \\ E_X^{corr} &= E_{CBS}^{corr} + BX^{-\beta}, \\ E_{CBS}^{tot} &= E_{CBS}^{HF} + E_{CBS}^{corr}, \end{aligned} \tag{1.78}$$

Martin [29]

$$E_{CBS}^{tot} = \frac{(X+3/2)^4}{(X+3/2)^4-(X+1/2)^4}E_{X+1}^{tot} - \frac{(X+1/2)^4}{(X+3/2)^4-(X+1/2)^4}E_X^{tot}, \tag{1.79}$$

and Helgaker [30]

$$\begin{aligned} E_X^{HF} &= E_{CBS}^{HF} + Bexp(-\alpha X), \\ E_X^{corr} &= E_{CBS}^{corr} + AX^{-3}, \\ E_{CBS}^{tot} &= E_{CBS}^{HF} + E_{CBS}^{corr}. \end{aligned} \tag{1.80}$$

Here X is the cardinal number of the correlation-consistent aug-cc-pVXZ basis set; E_X^{HF} , E_X^{corr} and E_X^{tot} are the Hartree-Fock, correlation and total energy, accordingly; B, A and α are the parameters to be optimized. The subscripts "X" and "CBS" correspond to the energy calculated using aug-cc-pVXZ basis set and the energy obtained in the complete basis set limit. It should be noted that Helgaker's extrapolation scheme is a three-point one for the Hartree-Fock energy and a two-point for the correlation energy. The calculation was carried out for the Hartree-Fock energy and it was found that α is constant for the given sequence of X. For X = 2, 3, 4 α=α_1 and for X = 3, 4, 5 α=α_2. So we reduced the number of points for the extrapolation of the HF energy to two. The notation for the Helgaker's extrapolation scheme, for example, "X = (3), 4, 5" means that α for the extrapolation of the Hartree-Fock energy was previously calculated with aug-cc-pVXZ (X = 3, 4, 5) basis sets (α=α_2) and the correlation energy was extrapolated using energies calculated with aug-cc-pVXZ (X = 4, 5) basis sets.

It should be pointed out that such extrapolation schemes to the CBS limit can be also applied for the accurate calculations of bond lengths and angles [26].

1.6 Finite-field method

The energy of an uncharged molecule being perturbed by a weak general static electric field can be written in terms of the components of the field as [32, 33]:

$$E(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, \ldots) = E^0 - \mu_\alpha F_\alpha - \frac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta} - \frac{1}{15}\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma} - \frac{1}{105}\Phi_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta} + \cdots \tag{1.81}$$

$$-\frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{3}A_{\alpha,\beta\gamma}F_\alpha F_{\beta\gamma} - \frac{1}{6}C_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} - \frac{1}{15}E_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta} + \cdots$$

$$-\frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \frac{1}{6}B_{\alpha,\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} + \cdots - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \cdots ,$$

where F_α, $F_{\alpha\beta}$, etc. are the field, field gradient, etc. at the origin. E^0, μ_α, $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$ and $\Phi_{\alpha\beta\gamma\delta}$ are the energy and permanent dipole, quadrupole, octopole and hexadecapole moments of the free molecule. The second, third and fourth-order properties are the dipole polarizability $\alpha_{\alpha\beta}$, the first $\beta_{\alpha\beta\gamma}$ and the second $\gamma_{\alpha\beta\gamma\delta}$ hyperpolarizabilities, dipole-quadrupole $A_{\alpha,\beta\gamma}$, dipole-octopole $E_{\alpha,\beta\gamma\delta}$, quadrupole $C_{\alpha\beta,\gamma\delta}$ and dipole-dipole-quadrupole $B_{\alpha\beta,\gamma\delta}$ polarizabilities. The greek subscripts denote Cartesian components and the repeated subscripts imply summation over x, y, and z.

Dipole moment

In order to evaluate the dipole moment the finite-field method (implemented in Gaussian 03 [34], Molpro [35], etc.) described by Cohen and Roothaan [37] was employed.

In the presence of only the field F_α (the component of the filed F in the α-direction) the Eq. 1.81 is significantly simplified:

$$E(F_\alpha) = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\alpha}F_\alpha^2 - \frac{1}{6}\beta_{\alpha\alpha\alpha}F_\alpha^3 - \frac{1}{24}\gamma_{\alpha\alpha\alpha\alpha}F_\alpha^4 + \cdots . \tag{1.82}$$

There are several techniques to obtain the dipole moment. The first technique is based on the solving the system of linear equations (Eq. 1.82) for the set of different fields F_α. The second technique is the one proposed by G. Maroulis [38]:

$$\mu_\alpha = \frac{256D_\alpha(F_\alpha) - 40D_\alpha(2F_\alpha) + D_\alpha(4F_\alpha)}{180F_\alpha}, \tag{1.83}$$

where

$$D_\alpha = (E(-F_\alpha) - E(F_\alpha))/2.$$

This formula eliminates the contribution of higher-order (hyper)polarizabilities and is more accurate.

And the third technique is obtained by simply taking the first derivative of the energy $E(F_\alpha)$ (Eq. 1.82) by the external field F_α using the finite-differences [39](the central approximation). As a result we get the following 2-point expression (with errors of order F_α^2) for the dipole moment components:

$$\mu_\alpha = \frac{E(F_\alpha) - E(-F_\alpha)}{2F_\alpha}, \tag{1.84}$$

and the 5-point stencil formula (with errors of order F_α^4)is the following:

$$\mu_\alpha = \frac{-E(2F_\alpha) + 8E(F_\alpha) - 8E(-F_\alpha) + E(-2F_\alpha)}{12F_\alpha}. \tag{1.85}$$

Polarizability

The polarizability is the second derivative of the interaction energy by the external field F_α.

The calculation formulas can be also obtained using the finite-difference method. The 3-point finite difference approximation (with errors of order F_α^2) gives

$$\alpha_{\alpha\alpha} = -\frac{E(F_\alpha) - 2E(0) + E(-F_\alpha)}{F_\alpha^2} \tag{1.86}$$

and

$$\alpha_{\alpha\beta} = -\frac{E(F_\alpha, F_\beta) - E(F_\alpha, -F_\beta) + E(-F_\alpha, F_\beta) + E(-F_\alpha, -F_\beta)}{4F_\alpha F_\beta}.$$

The formulas with errors of order F_α^4 are the following:

$$\alpha_{\alpha\alpha} = -\frac{-E(2F_\alpha) + 16E(F_\alpha) - 30E(0) + 16E(-F_\alpha) - E(-2F_\alpha)}{12F_\alpha^2}, \tag{1.87}$$

$$\begin{aligned}
\alpha_{\alpha\beta} = -\frac{1}{600F_\alpha F_\beta}\Big[& -63\{E(F_\alpha, -2F_\beta) + E(2F_\alpha, -F_\beta) + E(-2F_\alpha, F_\beta) + E(-F_\alpha, 2F_\beta)\} \\
& +63\{E(-F_\alpha, -2F_\beta) + E(-2F_\alpha, -F_\beta) + E(F_\alpha, 2F_\beta) + E(2F_\alpha, F_\beta)\} \\
& +44\{E(2F_\alpha, -2F_\beta) + E(-2F_\alpha, 2F_\beta) - E(-2F_\alpha, -2F_\beta) - E(2F_\alpha, 2F_\beta)\} \\
& +74\{E(-F_\alpha, -F_\beta) + E(F_\alpha, F_\beta) - E(F_\alpha, -F_\alpha) - E(-F_\alpha, F_\beta)\}\Big].
\end{aligned}$$

There is also the expression proposed by G. Maroulis in [38] for the $\alpha_{\alpha\alpha}$ component that eliminates the contribution of the higher-order (hyper)polarizabilities:

$$\alpha_{\alpha\alpha} = \frac{1024S_\alpha(F) - 80S_\alpha(2F) + S_\alpha(4F)}{360F_\alpha^2}, \tag{1.88}$$

where

$$S_\alpha = (2E(0) - E(F_\alpha) - E(-F_\alpha))/2.$$

It should be pointed out that both for the dipole moment and polarizability of interacting molecules, one should account for the BSSE correction. This means that the single point energy calculations with different applied fields should be carried out with the BSSE correction.

The choice of the applied homogeneous field should be done very carefully. For this purpose one should carry out a series of calculations with different amplitudes of the external field F. From these calculations we can find out the range of the amplitudes of the field where the property under the investigation doesn't change significantly with the change of the amplitude F. The field from this range only can be used for the further calculation of the dipole moment. Sometimes for different properties different amplitudes of the external field should be applied.

1.7 Frequency-dependent (hyper)polarizabilities

The response of molecules to static and dynamic (time- or frequency-dependent) perturbations, e.g. external electric fields, is of great importance for a variety of fields. For example, the frequency-dependent polarizability, describing the linear response to an electric field, determines optical properties such as refractive indices, dielectric constants, Verdet constants, and Raman intensities, as well as dispersion coefficients of long-range intermolecular interaction [40]. In particular the expression for the dipole expectation value can be used to define the permanent dipole moment and the polarizability and hyperpolarizabilities:

$$\mu_\alpha = \mu_\alpha^{(0)} + \alpha_{\alpha\beta}F_\beta + \beta_{\alpha\beta\gamma}F_\beta F_\gamma + \cdots . \tag{1.89}$$

The notation can be established by writting the formulas for the first three molecular response functions [41]:

$$\begin{aligned} \mu_\alpha^{(1)} &= \alpha_{\alpha\beta}(-\omega,\omega)F_\beta, \qquad (1.90)\\ \mu_\alpha^{(2)} &= \beta_{\alpha\beta\gamma}(-\omega_3;\omega_1,\omega_2)F_\beta F_\gamma,\\ \mu_\alpha^{(3)} &= \gamma_{\alpha\beta\gamma\delta}(-\omega_4;\omega_1,\omega_2,\omega_3)F_\beta F_\gamma F_\delta. \end{aligned}$$

The time-dependent field components are here taken to be the complex forms

$$\mathbf{F}(t) = \mathbf{F}\mathtt{exp}(-\omega_p t), \qquad p = 1,2,3... \tag{1.91}$$

which combine in the nonlinear interaction to give an induced dipole component at the sum frequency, $\sum \omega_p$. The negative sign indicates an "output" frequency.

The most direct approach to the calculation of the time-dependent polarizabilities is to apply standard time-dependent perturbation theory to the evolution of the wavefunction in the time-dependent Schrödinger equation. The wavefunction is formally expanded in terms of the complete set of molecular eigenfunctions (ground Ψ_0 and excited states Ψ_n) and the solutions are obtained in terms of matrix elements of the perturbation between these states and the corresponding eigenvalues [41]. For example, the polarizability is a linear response function to an oscillating electric field $F_\beta exp^{-i\omega t}$ and is defined by the following expression:

$$\alpha_{\alpha\beta}(\omega) = \sum_{n\neq 0}\Big(\frac{\langle\Psi_0|\mu_\alpha|\Psi_n\rangle\langle\Psi_n|\mu_\beta|\Psi_0\rangle}{\hbar\omega + E_0 - E_n} + \frac{\langle\Psi_0|\mu_\beta|\Psi_n\rangle\langle\Psi_n|\mu_\alpha|\Psi_0\rangle}{-\hbar\omega + E_0 - E_n}\Big), \tag{1.92}$$

where the summation is over all discrete and continuous spectra (the sum-over-states method). The main task here is to find a set of excitation energies $E_n - E_0$ and matrix elements $\langle\Psi_0|\mu_\alpha|\Psi_n\rangle$. The frequencies ω should be far from any absorption frequencies.

1.8 Summary

In general, *ab initio* methods give good qualitative and quantitative results and can provide better accuracy of calculations with decreasing of the size of system under investigation. The advantage of *ab initio* methods is that they do not use any empirical parameters. We can distinguish the following law of increasing accuracy (for the methods described above) using a middle size basis set:

$$HF << MP2 < MP4 \simeq CCSD < SAPT \leq CCSD(T) \approx CCSD(T) - F12 < CCSDT$$

However, it should be pointed out that this convergence is nonmonotonic. Here are the main sources of errors in *ab initio* calculations:

1. Basis set superposition error (can be removed using CP-correction scheme)
2. Error due to the incompleteness of the basis set (this error can be removed using CBS extrapolation schemes)
3. Not full correlation (but CCSD(T) allows to account $\sim 99\%$ of correlation energy)

It should be pointed out that *ab initio* methods are of high computational cost. They require a lot of time, big computational memory, CPU and disk storage.

Second part

Classical long-range approximation

Chapter 2

General consideration

2.1 Potential energy

Throughout this Part the formulas are expressed in atomic unit system ($e = m_e = \hbar = 1/4\pi\varepsilon_0 = 1$, $c = 1/\alpha$). Let us consider a pair of two interacting molecules, A and B. If they are far from each other, then we can neglect the electron exchange and, thus, the Hamiltonian of the system becomes the sum of the Hamiltonian $H_0 = H_0^A + H_0^B$ of free molecules and the interaction Hamiltonian H', which is a perturbation to H_0 [31, 32]:

$$\begin{aligned} H' = \sum_{i_A, i_B} e_{i_A} e_{i_B} R^{-1}_{i_A i_B} &= q^B \phi^B - \mu^B_\alpha F^B_\alpha - \frac{1}{3}\Theta^B_{\alpha\beta} F^B_{\alpha\beta} - \cdots \\ &= q^A \phi^A - \mu^A_\alpha F^A_\alpha - \frac{1}{3}\Theta^A_{\alpha\beta} F^A_{\alpha\beta} - \cdots , \end{aligned} \tag{2.1}$$

where the greek subscripts denote Cartesian components and the repeated subscripts imply summation over x, y, and z; $R_{i_A i_B}$ is the distance from the element of charge e_{i_A} in molecule A to e_{i_B} in molecule B; q^B, μ^B and Θ^B are the charge ($q^B = \sum_{i_B} e_{i_B}$), dipole and quadrupole moment operators for the B molecule; ϕ^B is the electric potential at the origin of molecule B due to the instantaneous charge distribution of molecule A, and

$$\begin{aligned} F^B_\alpha &= -\nabla_\alpha \phi^B, \\ F^B_{\alpha\beta} &= \nabla_\alpha F^B_\beta = -\nabla_\alpha \nabla_\beta \phi^B \end{aligned} \tag{2.2}$$

are the field and the filed gradient operators. When an external field $\mathbf{F}^0$ is applied to a pair of nonoverlapping molecules A and B, the local field acting on B is the superposition of $\mathbf{F}^0$ and the field from the charge distribution of the A molecule. For example, the field F^B_α at the B molecule produced by the A molecule has the form:

$$F^B_\alpha = F^0_\alpha - q^A T_\alpha + \mu^A_\beta T_{\alpha\beta} - \frac{1}{3}\Theta^A_{\beta\gamma} T_{\alpha\beta\gamma} + \frac{1}{15}\Omega^A_{\beta\gamma\delta} T_{\alpha\beta\gamma\delta} - \frac{1}{105}\Phi^A_{\beta\gamma\delta\varepsilon} T_{\alpha\beta\gamma\delta\varepsilon} + \cdots . \tag{2.3}$$

The gradients of the field

$$\begin{aligned}F^B_{\alpha\beta} &= F^0_{\alpha\beta} - q^A T_{\alpha\beta} + \mu^A_\gamma T_{\alpha\beta\gamma} - \frac{1}{3}\Theta^A_{\gamma\delta} T_{\alpha\beta\gamma\delta} + \frac{1}{15}\Omega^A_{\gamma\delta\varepsilon} T_{\alpha\beta\gamma\delta\varepsilon} - \frac{1}{105}\Phi^A_{\gamma\delta\varepsilon\varphi} T_{\alpha\beta\gamma\delta\varepsilon\varphi} + \cdots \, , \\ F^B_{\alpha\beta\gamma} &= F^0_{\alpha\beta\gamma} - q^A T_{\alpha\beta\gamma} + \mu^A_\delta T_{\alpha\beta\gamma\delta} - \frac{1}{3}\Theta^A_{\delta\varepsilon} T_{\alpha\beta\gamma\delta\varepsilon} + \frac{1}{15}\Omega^A_{\delta\varepsilon\varphi} T_{\alpha\beta\gamma\delta\varepsilon\varphi} + \cdots \, , \\ F^B_{\alpha\beta\gamma\delta} &= F^0_{\alpha\beta\gamma\delta} - q^A T_{\alpha\beta\gamma\delta} + \mu^A_\varepsilon T_{\alpha\beta\gamma\delta\varepsilon} - \frac{1}{3}\Theta^A_{\varepsilon\varphi} T_{\alpha\beta\gamma\delta\varepsilon\varphi} + \cdots \, , \\ F^B_{\alpha\beta\gamma\delta\varepsilon} &= F^0_{\alpha\beta\gamma\delta\varepsilon} - q^A T_{\alpha\beta\gamma\delta\varepsilon} + \mu^A_\varphi T_{\alpha\beta\gamma\delta\varepsilon\varphi} + \cdots \, , \end{aligned} \quad (2.4)$$

where Ω^A and Φ^A are the octupole and hexadecapole moments of the free A molecule; $T_{\alpha\beta\gamma...\nu} = \nabla_\alpha\nabla_\beta\nabla_\gamma...\nabla_\nu R^{-1}$ is a tensor symmetric in all subscripts, and if there are repeated subscripts the $\boldsymbol{T}$ equals to zero. Note, that $\boldsymbol{T} \equiv \boldsymbol{T}^{AB}$=(-1)$^n\, \boldsymbol{T}^{BA}$, where n is the order of the tensor. The $\boldsymbol{T}$ tensor of order n is proportional to $R^{-(n+1)}$, where R is the module of the vector $\boldsymbol{R}$ directed from the molecule A to the molecule B:

$$T = R^{-1},$$

$$T_\alpha = -R_\alpha R^{-3},$$

$$T_{\alpha\beta} = (3R_\alpha R_\beta - R^2\delta_{\alpha\beta})R^{-5},$$

$$T_{\alpha\beta\gamma} = -3(5R_\alpha R_\beta R_\gamma - R^2(R_\alpha\delta_{\beta\gamma} + R_\beta\delta_{\gamma\alpha} + R_\gamma\delta_{\alpha\beta}))R^{-7},$$

$$\begin{gathered}T_{\alpha\beta\gamma\delta} = 3(35R_\alpha R_\beta R_\gamma R_\delta - 5R^2(R_\alpha R_\beta\delta_{\gamma\delta} + R_\alpha R_\gamma\delta_{\beta\delta} + R_\alpha R_\delta\delta_{\beta\gamma} + R_\beta R_\gamma\delta_{\alpha\delta} \\ +R_\beta R_\delta\delta_{\alpha\gamma} + R_\gamma R_\delta\delta_{\alpha\beta}) + R^4(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}))R^{-9},\end{gathered}$$

$$\begin{gathered}T_{\alpha\beta\gamma\delta\nu} = -15(63R_\alpha R_\beta R_\gamma R_\delta R_\nu - 7R^2(R_\beta R_\gamma R_\delta\delta_{\alpha\nu} + R_\alpha R_\delta R_\nu\delta_{\beta\gamma} + R_\beta R_\delta R_\nu\delta_{\alpha\gamma} \\ +R_\gamma R_\delta R_\nu\delta_{\alpha\beta} + R_\alpha R_\gamma R_\delta\delta_{\beta\nu} + R_\alpha R_\beta R_\delta\delta_{\gamma\nu} + R_\alpha R_\beta R_\gamma\delta_{\delta\nu} + R_\nu R_\beta R_\gamma\delta_{\alpha\delta} + R_\nu R_\alpha R_\gamma\delta_{\beta\delta} \\ +R_\nu R_\alpha R_\beta\delta_{\gamma\delta}) + R^4(R_\gamma\delta_{\alpha\delta}\delta_{\beta\nu} + R_\beta\delta_{\alpha\delta}\delta_{\gamma\nu} + R_\gamma\delta_{\alpha\nu}\delta_{\beta\delta} + R_\alpha\delta_{\gamma\nu}\delta_{\beta\delta} + R_\beta\delta_{\alpha\nu}\delta_{\gamma\delta} \\ +R_\alpha\delta_{\beta\nu}\delta_{\gamma\delta} + R_\alpha\delta_{\delta\nu}\delta_{\beta\gamma} + R_\delta\delta_{\beta\nu}\delta_{\alpha\gamma} + R_\gamma\delta_{\delta\nu}\delta_{\alpha\beta} + R_\delta\delta_{\alpha\nu}\delta_{\beta\gamma} + R_\beta\delta_{\delta\nu}\delta_{\alpha\gamma} \\ +R_\delta\delta_{\gamma\nu}\delta_{\alpha\beta} + R_\nu\delta_{\alpha\delta}\delta_{\beta\gamma} + R_\nu\delta_{\beta\delta}\delta_{\alpha\gamma} + R_\nu\delta_{\gamma\delta}\delta_{\alpha\beta}))R^{-11},\end{gathered}$$

$$\begin{gathered}T_{\alpha\beta\gamma\delta\nu\varepsilon} = 15(693R_\alpha R_\beta R_\gamma R_\delta R_\nu R_\varepsilon - 63R^2(R_\beta R_\gamma R_\delta R_\nu\delta_{\varepsilon\alpha} + R_\alpha R_\gamma R_\delta R_\nu\delta_{\varepsilon\beta} \\ +R_\alpha R_\beta R_\delta R_\nu\delta_{\varepsilon\gamma} + R_\alpha R_\beta R_\gamma R_\nu\delta_{\varepsilon\delta} + R_\alpha R_\beta R_\gamma R_\delta\delta_{\varepsilon\nu} + R_\varepsilon R_\beta R_\gamma R_\delta\delta_{\alpha\nu} + R_\varepsilon R_\alpha R_\delta R_\nu\delta_{\beta\gamma} \\ +R_\varepsilon R_\beta R_\delta R_\nu\delta_{\alpha\gamma} + R_\varepsilon R_\gamma R_\delta R_\nu\delta_{\alpha\beta} + R_\varepsilon R_\alpha R_\gamma R_\delta\delta_{\beta\nu} + R_\varepsilon R_\alpha R_\beta R_\delta\delta_{\gamma\nu} + R_\varepsilon R_\alpha R_\beta R_\gamma\delta_{\delta\nu} \\ +R_\varepsilon R_\nu R_\beta R_\gamma\delta_{\alpha\delta} + R_\varepsilon R_\nu R_\alpha R_\gamma\delta_{\beta\delta} + R_\varepsilon R_\nu R_\alpha R_\beta\delta_{\gamma\delta}) + 7R^4(R_\gamma R_\delta\delta_{\alpha\nu}\delta_{\varepsilon\beta} + R_\beta R_\delta\delta_{\alpha\nu}\delta_{\varepsilon\gamma} \\ +R_\beta R_\gamma\delta_{\alpha\nu}\delta_{\varepsilon\delta} + R_\delta R_\nu\delta_{\beta\gamma}\delta_{\alpha\varepsilon} + R_\alpha R_\nu\delta_{\beta\gamma}\delta_{\varepsilon\delta} + R_\alpha R_\delta\delta_{\beta\gamma}\delta_{\varepsilon\nu} + R_\delta R_\nu\delta_{\alpha\gamma}\delta_{\varepsilon\beta} + R_\beta R_\nu\delta_{\alpha\gamma}\delta_{\varepsilon\delta} \\ +R_\beta R_\delta\delta_{\alpha\gamma}\delta_{\varepsilon\nu} + R_\delta R_\nu\delta_{\alpha\beta}\delta_{\varepsilon\gamma} + R_\gamma R_\nu\delta_{\alpha\beta}\delta_{\varepsilon\delta} + R_\gamma R_\delta\delta_{\alpha\beta}\delta_{\varepsilon\nu} + R_\gamma R_\delta\delta_{\beta\nu}\delta_{\varepsilon\alpha} + R_\alpha R_\delta\delta_{\beta\nu}\delta_{\gamma\varepsilon}\end{gathered}$$

$$
\begin{aligned}
&+R_\alpha R_\gamma \delta_{\beta\nu}\delta_{\delta\varepsilon} + R_\beta R_\delta \delta_{\gamma\nu}\delta_{\alpha\varepsilon} + R_\alpha R_\delta \delta_{\gamma\nu}\delta_{\varepsilon\beta} + R_\alpha R_\beta \delta_{\gamma\nu}\delta_{\varepsilon\delta} + R_\beta R_\gamma \delta_{\delta\nu}\delta_{\alpha\varepsilon} + R_\alpha R_\gamma \delta_{\delta\nu}\delta_{\varepsilon\beta} \\
&+R_\alpha R_\beta \delta_{\delta\nu}\delta_{\gamma\varepsilon} + R_\beta R_\gamma \delta_{\alpha\delta}\delta_{\nu\varepsilon} + R_\nu R_\gamma \delta_{\alpha\delta}\delta_{\beta\varepsilon} + R_\nu R_\beta \delta_{\alpha\delta}\delta_{\gamma\varepsilon} + R_\alpha R_\gamma \delta_{\beta\delta}\delta_{\nu\varepsilon} + R_\nu R_\gamma \delta_{\beta\delta}\delta_{\alpha\varepsilon} \\
&+R_\nu R_\alpha \delta_{\beta\delta}\delta_{\gamma\varepsilon} + R_\alpha R_\beta \delta_{\gamma\delta}\delta_{\nu\varepsilon} + R_\nu R_\beta \delta_{\gamma\delta}\delta_{\alpha\varepsilon} + R_\nu R_\alpha \delta_{\gamma\delta}\delta_{\beta\varepsilon} + R_\varepsilon R_\gamma \delta_{\alpha\delta}\delta_{\beta\nu} + R_\varepsilon R_\beta \delta_{\alpha\delta}\delta_{\gamma\nu} \\
&+R_\varepsilon R_\gamma \delta_{\alpha\nu}\delta_{\beta\delta} + R_\varepsilon R_\alpha \delta_{\gamma\nu}\delta_{\beta\delta} + R_\varepsilon R_\beta \delta_{\alpha\nu}\delta_{\gamma\delta} + R_\varepsilon R_\alpha \delta_{\beta\nu}\delta_{\gamma\delta} + R_\varepsilon R_\alpha \delta_{\delta\nu}\delta_{\beta\delta} + R_\varepsilon R_\delta \delta_{\alpha\nu}\delta_{\beta\gamma} \\
&+R_\varepsilon R_\beta \delta_{\delta\nu}\delta_{\alpha\gamma} + R_\varepsilon R_\delta \delta_{\beta\nu}\delta_{\alpha\gamma} + R_\varepsilon R_\gamma \delta_{\delta\nu}\delta_{\alpha\beta} + R_\varepsilon R_\delta \delta_{\gamma\nu}\delta_{\alpha\beta} + R_\varepsilon R_\alpha \delta_{\beta\nu}\delta_{\gamma\delta} + R_\varepsilon R_\nu \delta_{\alpha\delta}\delta_{\beta\gamma} \\
&+R_\varepsilon R_\nu \delta_{\beta\delta}\delta_{\alpha\gamma} + R_\varepsilon R_\nu \delta_{\gamma\delta}\delta_{\alpha\beta}) - R^6(\delta_{\alpha\delta}\delta_{\beta\nu}\delta_{\varepsilon\gamma} + \delta_{\alpha\delta}\delta_{\gamma\nu}\delta_{\beta\varepsilon} + \delta_{\alpha\nu}\delta_{\beta\delta}\delta_{\gamma\varepsilon} + \delta_{\gamma\nu}\delta_{\beta\delta}\delta_{\alpha\varepsilon} \\
&+\delta_{\alpha\nu}\delta_{\gamma\delta}\delta_{\beta\varepsilon} + \delta_{\beta\nu}\delta_{\gamma\delta}\delta_{\alpha\varepsilon} + \delta_{\delta\nu}\delta_{\beta\gamma}\delta_{\alpha\varepsilon} + \delta_{\alpha\nu}\delta_{\beta\gamma}\delta_{\delta\varepsilon} + \delta_{\delta\nu}\delta_{\alpha\gamma}\delta_{\beta\varepsilon} + \delta_{\beta\nu}\delta_{\alpha\gamma}\delta_{\delta\varepsilon} + \delta_{\delta\nu}\delta_{\alpha\beta}\delta_{\gamma\varepsilon} \\
&+\delta_{\gamma\nu}\delta_{\alpha\beta}\delta_{\delta\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\gamma}\delta_{\nu\varepsilon} + \delta_{\beta\delta}\delta_{\alpha\gamma}\delta_{\nu\varepsilon} + \delta_{\gamma\delta}\delta_{\alpha\beta}\delta_{\nu\varepsilon}))R^{-13}. \qquad (2.5)
\end{aligned}
$$

Here $\delta_{\alpha\beta}$ is the Kronecker symbol, R_α is the α-component of the vector $\boldsymbol{R}$.

The interaction Hamiltonian can be written as a multipole series:

$$
\begin{aligned}
H' = Tq^A q^B + T_\alpha(q^A\mu_\alpha^B - q^B\mu_\alpha^A) + T_{\alpha\beta}(\frac{1}{3}q^A\Theta_{\alpha\beta}^B + \frac{1}{3}q^B\Theta_{\alpha\beta}^A - \mu_\alpha^A\mu_\beta^B) \\
+T_{\alpha\beta\gamma}(\frac{1}{15}q^A\Omega_{\alpha\beta\gamma}^B - \frac{1}{15}q^B\Omega_{\alpha\beta\gamma}^A - \frac{1}{3}\mu_\alpha^A\Theta_{\beta\gamma}^B + \frac{1}{3}\mu_\alpha^B\Theta_{\beta\gamma}^A) + T_{\alpha\beta\gamma\delta}(\frac{1}{9}\Theta_{\alpha\beta}^A\Theta_{\gamma\delta}^B + \cdots) + \cdots . \qquad (2.6)
\end{aligned}
$$

Using the perturbation theory one can obtain the energy of the pair of molecules being in the states $\psi_{n_A}^0$ and $\psi_{n_B}^0$ (unperturbed states):

$$
\begin{aligned}
E^{AB} &= E_{n_A}^0 + E_{n_B}^0 + \langle\psi_{n_A}^0\psi_{n_B}^0|H'|\psi_{n_A}^0\psi_{n_B}^0\rangle \\
&-\Sigma'\frac{|\langle\psi_{n_A}^0\psi_{n_B}^0|H'|\psi_{j_A}^0\psi_{j_B}^0\rangle|^2}{(E_{j_A}^0 - E_{n_A}^0) + (E_{j_B}^0 - E_{n_B}^0)} + \cdots . \qquad (2.7)
\end{aligned}
$$

Here $E_{n_A}^0$ and $E_{n_B}^0$ are the energies of free molecules A and B in the states $\psi_{n_A}^0$ and $\psi_{n_B}^0$; Σ' is the summation over all unperturbed states $\psi_{j_A}^0$ and $\psi_{j_B}^0$. The first-order perturbed energy is called the *electrostatic* energy:

$$
\begin{aligned}
E_{elec}^{AB} = \langle\psi_{n_A}^0\psi_{n_B}^0|H'|\psi_{n_A}^0\psi_{n_B}^0\rangle = -\mu_\alpha^{A(0)}F_\alpha^A - \frac{1}{3}\Theta_{\alpha\beta}^{A(0)}F_{\alpha\beta}^A \\
-\frac{1}{15}\Omega_{\alpha\beta\gamma}^{A(0)}F_{\alpha\beta\gamma}^A - \frac{1}{105}\Phi_{\alpha\beta\gamma\delta}^{A(0)}F_{\alpha\beta\gamma\delta}^A - \frac{1}{945}\Xi_{\alpha\beta\gamma\delta\varepsilon}^{A(0)}F_{\alpha\beta\gamma\delta\varepsilon}^A - \cdots , \qquad (2.8)
\end{aligned}
$$

where $\mu_\alpha^{A(0)} = \langle\psi_{n_A}^0|\mu_\alpha^A|\psi_{n_A}^0\rangle$, $\Theta_{\alpha\beta}^{A(0)} = \langle\psi_{n_A}^0|\Theta_{\alpha\beta}^A|\psi_{n_A}^0\rangle$ etc. are the permanent dipole, quadrupole etc. moments of the molecule A. If we put in Eq. 2.8 the expressions 2.3 for the electrostatic energy we get:

$$
\begin{aligned}
E_{elec}^{AB} = Tq^A q^B + T_\alpha(q^A\mu_\alpha^B - q^B\mu_\alpha^A) + T_{\alpha\beta}(\frac{1}{3}q^A\Theta_{\alpha\beta}^B + \frac{1}{3}q^B\Theta_{\alpha\beta}^A - \mu_\alpha^A\mu_\beta^B) \\
+T_{\alpha\beta\gamma}(\frac{1}{15}q^A\Omega_{\alpha\beta\gamma}^B - \frac{1}{15}q^B\Omega_{\alpha\beta\gamma}^A - \frac{1}{3}\mu_\alpha^A\Theta_{\beta\gamma}^B + \frac{1}{3}\mu_\alpha^B\Theta_{\beta\gamma}^A) \\
+T_{\alpha\beta\gamma\delta}(\frac{1}{9}\Theta_{\alpha\beta}^A\Theta_{\gamma\delta}^B + \cdots) + \cdots . \qquad (2.9)
\end{aligned}
$$

The second-order perturbed energy in Eq. 2.7 includes both induction and dispersion energy. The sets of excited unperturbed states $\psi^0_{j_A}\psi^0_{n_B}$ and $\psi^0_{n_A}\psi^0_{j_B}$, in which the matrix elements of H' are diagonal in n_B and n_A, produce the *induction* energy E^{AB}_{ind}, and the remaining excited states produce the *dispersion* energy E^{AB}_{disp}. Thus,

$$E^{AB}_{ind} = -\sum_{j_A \neq n_A} \frac{|\langle \psi^0_{n_A}\psi^0_{n_B}|H'|\psi^0_{j_A}\psi^0_{n_B}\rangle|^2}{(E^0_{j_A} - E^0_{n_A})} - \sum_{j_B \neq n_B} \frac{|\langle \psi^0_{n_A}\psi^0_{n_B}|H'|\psi^0_{n_A}\psi^0_{j_B}\rangle|^2}{(E^0_{j_B} - E^0_{n_B})} = E^A_{ind} + E^B_{ind}. \quad (2.10)$$

The induction energy of the uncharged molecule A being perturbed by the weak, static electric field of the other molecule B can be written in terms of the components of the field and field gradients as [32, 33]:

$$\begin{aligned} E^A_{ind} = &-\frac{1}{2}\alpha^A_{\alpha\beta}F^A_\alpha F^A_\beta - \frac{1}{3}A^A_{\alpha,\beta\gamma}F^A_\alpha F^A_{\beta\gamma} - \frac{1}{15}E^A_{\alpha,\beta\gamma\delta}F^A_\alpha F^A_{\beta\gamma\delta} - \frac{1}{105}D^A_{\alpha,\beta\gamma\delta\varepsilon}F^A_\alpha F^A_{\beta\gamma\delta\varepsilon} \\ &-\frac{1}{945}H^A_{\alpha,\beta\gamma\delta\varepsilon\varphi}F^A_\alpha F^A_{\beta\gamma\delta\varepsilon\varphi} - \cdots - \frac{1}{6}C^A_{\alpha\beta,\gamma\delta}F^A_{\alpha\beta}F^A_{\gamma\delta} - \frac{1}{45}K^A_{\alpha\beta,\gamma\delta\varepsilon}F^A_{\alpha\beta}F^A_{\gamma\delta\varepsilon} \\ &-\frac{1}{315}N^A_{\alpha\beta,\gamma\delta\varepsilon\varphi}F^A_{\alpha\beta}F^A_{\gamma\delta\varepsilon\varphi} - \cdots - \frac{1}{6}\beta^A_{\alpha\beta\gamma}F^A_\alpha F^A_\beta F^A_\gamma - \frac{1}{6}B^A_{\alpha\beta,\gamma\delta}F^A_\alpha F^A_\beta F^A_{\gamma\delta} \\ &-\frac{1}{30}M^A_{\alpha\beta,\gamma\delta\varepsilon}F^A_\alpha F^A_\beta F^A_{\gamma\delta\varepsilon} - \frac{1}{210}G^A_{\alpha\beta,\gamma\delta\varepsilon\varphi}F^A_\alpha F^A_\beta F^A_{\gamma\delta\varepsilon\varphi} - \cdots \\ &-\frac{1}{24}\gamma^A_{\alpha\beta\gamma\delta}F^A_\alpha F^A_\beta F^A_\gamma F^A_\delta - \cdots . \end{aligned} \quad (2.11)$$

The second, third and fourth-order properties are the dipole polarizability $\alpha_{\alpha\beta}$, the first $\beta_{\alpha\beta\gamma}$ and the second $\gamma_{\alpha\beta\gamma\delta}$ hyperpolarizabilities, dipole-quadrupole $A_{\alpha,\beta\gamma}$, dipole-octopole $E_{\alpha,\beta\gamma\delta}$, dipole-hexadecapole $D_{\alpha,\beta\gamma\delta\varepsilon}$, quadrupole $C_{\alpha\beta,\gamma\delta}$, quadrupole-octupole $K_{\alpha\beta,\gamma\delta\varepsilon}$, quadrupole-hexadecapole $N_{\alpha\beta,\gamma\delta\varepsilon\varphi}$, dipole-dipole-quadrupole $B_{\alpha\beta,\gamma\delta}$, dipole-dipole-octupole $M_{\alpha\beta,\gamma\delta\varepsilon}$ and dipole-dipole-hexadecapole $G_{\alpha\beta,\gamma\delta\varepsilon\varphi}$ polarizabilities (see APPENDIX I for expessions for several polarizabilities and hyperpolarizabilities). These molecular (hyper)polarizabilities describe the distortion of the molecule by the external electric field and field gradient. The tensors $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ and $\Theta_{\alpha\beta}$ are totally symmetric (that is, they are unaffected by interchanging suffixes), $A_{\alpha,\beta\gamma}$ is symmetric with respect to β and γ, $E_{\alpha,\beta\gamma\delta}$ is symmetric with respect to β, γ and δ, and $B_{\alpha\beta,\gamma\delta}$ and $C_{\alpha\beta,\gamma\delta}$ in the pairs $\alpha\beta$ and $\gamma\delta$ (we can change β and α in one pair, and γ and δ in the other pair). Analogously one can find the symmetry rules for the rest of polarizabilities. The number of independent constants needed to describe the interaction energy with the external field is determined by the symmetry of the molecule (see APPENDIX II).

The contribution to the induction energy from two molecules can be written as:

$$E^{AB}_{ind} = (1 + \mathscr{P}^{AB})E^A_{ind},$$

where $\mathscr{P}^{AB}$ permutes labels A and B.

The remainder of the second-order perturbed energy in Eq. 2.7 is the dispersion energy, and

$$
\begin{aligned}
E^{AB}_{disp} &= \sum_{\substack{j_A \neq n_A \\ j_B \neq n_B}} \frac{|\langle \psi^0_{n_A}\psi^0_{n_B}|H'|\psi^0_{j_A}\psi^0_{j_B}\rangle|^2}{(E^0_{j_A}-E^0_{n_A})+(E^0_{j_B}-E^0_{n_B})} \\
&= -\sum_{\substack{j_A \neq n_A \\ j_B \neq n_B}} \left[T_{\alpha\beta}T_{\gamma\delta}\frac{\langle \psi^0_{n_A}\psi^0_{n_B}|\mu^A_\alpha\mu^B_\beta|\psi^0_{j_A}\psi^0_{j_B}\rangle\langle \psi^0_{j_A}\psi^0_{j_B}|\mu^A_\gamma\mu^B_\delta|\psi^0_{n_A}\psi^0_{n_B}\rangle}{(E^0_{j_A}-E^0_{n_A})+(E^0_{j_B}-E^0_{n_B})} \right. \\
&\quad +\frac{2}{3}T_{\alpha\beta}T_{\gamma\delta\varepsilon}\frac{\langle \psi^0_{n_A}\psi^0_{n_B}|\mu^A_\alpha\mu^B_\beta|\psi^0_{j_A}\psi^0_{j_B}\rangle\langle \psi^0_{j_A}\psi^0_{j_B}|\mu^A_\gamma\Theta^B_{\delta\varepsilon}-\mu^B_\gamma\Theta^A_{\delta\varepsilon}|\psi^0_{j_A}\psi^0_{j_B}\rangle}{(E^0_{j_A}-E^0_{n_A})+(E^0_{j_B}-E^0_{n_B})} \\
&\quad +\frac{1}{9}T_{\alpha\beta\gamma}T_{\delta\varepsilon\varphi}\frac{\langle \psi^0_{n_A}\psi^0_{n_B}|\mu^A_\alpha\Theta^B_{\beta\gamma}-\mu^B_\alpha\Theta^A_{\beta\gamma}|\psi^0_{j_A}\psi^0_{j_B}\rangle\langle \psi^0_{j_A}\psi^0_{j_B}|\mu^A_\gamma\Theta^B_{\varepsilon\varphi}-\mu^B_\gamma\Theta^A_{\varepsilon\varphi}|\psi^0_{j_A}\psi^0_{j_B}\rangle}{(E^0_{j_A}-E^0_{n_A})+(E^0_{j_B}-E^0_{n_B})} \\
&\quad \left. +\frac{2}{9}T_{\alpha\beta}T_{\gamma\delta\varepsilon\varphi}\frac{\langle \psi^0_{n_A}\psi^0_{n_B}|\mu^A_\alpha\mu^B_\beta|\psi^0_{j_A}\psi^0_{j_B}\rangle\langle \psi^0_{j_A}\psi^0_{j_B}|\Theta^A_{\gamma\delta}\Theta^B_{\varepsilon\varphi}|\psi^0_{j_A}\psi^0_{j_B}\rangle}{(E^0_{j_A}-E^0_{n_A})+(E^0_{j_B}-E^0_{n_B})} + \cdots \right]. \qquad (2.12)
\end{aligned}
$$

The expression 2.12 shows that dispersion energy varies as R^{-6} for large R, and there are also the contributions $\sim R^{-7}$, $\sim R^{-8}$ and so on.

In order to simplify the equation for dispersion energy (Eq. 2.12) one can use the approach of London [42], based on the Unsöld (or, average-energy) approximation for the energy denominators [43] of Eq. 2.12:

$$
\frac{1}{(E^0_{j_A}-E^0_{n_A})+(E^0_{j_B}-E^0_{n_B})} = \frac{U^AU^B(1+\Delta)}{(U^A+U^B)(E^0_{j_A}-E^0_{n_A})(E^0_{j_B}-E^0_{n_B})}, \qquad (2.13)
$$

where

$$
\Delta = \frac{[(U^A)^{-1}+(U^B)^{-1}]-[(E^0_{j_A}-E^0_{n_A})^{-1}+(E^0_{j_B}-E^0_{n_B})^{-1}]}{(E^0_{j_A}-E^0_{n_A})^{-1}+(E^0_{j_B}-E^0_{n_B})^{-1}}. \qquad (2.14)
$$

The approximation of London allows to express the dispersion energy in terms of the static polarizabilities of free molecules. For this purpose one should neglect Δ and set U^A and U^B equal to fixed energies related to the states $\psi^0_{n_A}$ and $\psi^0_{n_B}$. Taking this approximation into account, Eq. 2.12 is rewritten as follows:

$$
\begin{aligned}
E^{AB}_{disp} = -\frac{U^AU^B}{4(U^A+U^B)} &\Big[T_{\alpha\beta}T_{\gamma\delta}\alpha^A_{\alpha\gamma}\alpha^B_{\beta\delta} + \frac{2}{3}T_{\alpha\beta}T_{\gamma\delta\varepsilon}(\alpha^A_{\alpha\gamma}A^B_{\beta,\delta\varepsilon} - \alpha^B_{\alpha\gamma}A^A_{\beta,\delta\varepsilon}) \\
&+T_{\alpha\beta\gamma}T_{\delta\varepsilon\varphi}\Big(\frac{1}{3}\alpha^A_{\alpha\delta}C^B_{\beta\gamma,\varepsilon\varphi} + \frac{1}{3}\alpha^B_{\alpha\delta}C^A_{\beta\gamma,\varepsilon\varphi} - \frac{2}{9}A^A_{\alpha,\varepsilon\varphi}A^B_{\delta,\beta\gamma}\Big) \\
&-\frac{2}{9}T_{\alpha\beta}T_{\gamma\delta\varepsilon\varphi}A^A_{\alpha,\gamma\delta}A^B_{\beta,\varepsilon\varphi} + \cdots \Big]. \qquad (2.15)
\end{aligned}
$$

If $\psi^0_{n_A}$ and $\psi^0_{n_B}$ are the internal ground states of molecules A and B, then U^A and U^B may be set equal to the first ionization potentials or to the lowest allowed excitation energies of A and B.

One more approach to get the exact formula (and much more useful) for the dispersion energy was proposed by Casimir and Polder [44, 45]. In this approach the dispersion energy

(Eq. 2.12) can be expressed in terms of the polarizabilities at imaginary frequency $i\omega$:

$$\begin{aligned} E^{AB}_{disp} = -\frac{1}{2\pi}T_{\alpha\beta}T_{\gamma\delta}\int_0^{\infty}\alpha^A_{\alpha\gamma}(i\omega)\alpha^B_{\beta\delta}(i\omega)d\omega \\ -\frac{1}{3\pi}T_{\alpha\beta}T_{\gamma\delta\varepsilon}\int_0^{\infty}[\alpha^A_{\alpha\gamma}(i\omega)A^B_{\beta,\delta\varepsilon}(i\omega)\alpha^B_{\alpha\gamma}(i\omega)A^A_{\beta,\delta\varepsilon}(i\omega)]d\omega \\ -\frac{1}{6\pi}T_{\alpha\beta\gamma}T_{\delta\varepsilon\varphi}\int_0^{\infty}[\alpha^A_{\alpha\delta}(i\omega)C^B_{\beta\gamma,\varepsilon\varphi}(i\omega)+C^A_{\beta\gamma,\varepsilon\varphi}(i\omega)\alpha^B_{\alpha\delta}(i\omega)-\frac{2}{3}A^A_{\alpha,\varepsilon\varphi}(i\omega)A^B_{\delta,\beta\gamma}(i\omega)]d\omega \\ +\frac{1}{9\pi}T_{\alpha\beta}T_{\gamma\delta\varepsilon\varphi}\int_0^{\infty}A^A_{\alpha,\gamma\delta}(i\omega)A^B_{\beta,\varepsilon\varphi}(i\omega)d\omega+\cdots\ . \end{aligned} \tag{2.16}$$

It should be pointed out that the concept of polarizability at imaginary frequency is better to view merely as a mathematical construct.

In order to get the total energy of a pair of molecules one should carry out the summation

$$E^{AB} = E^A_0 + E^B_0 + E^{AB}_{elec} + E^{AB}_{ind} + E^{AB}_{disp}, \tag{2.17}$$

and the interaction energy of the pair of molecules is

$$\Delta E^{AB} = E^{AB}_{elec} + E^{AB}_{ind} + E^{AB}_{disp}. \tag{2.18}$$

All dispersion energy formulas (Eqs. 2.15-2.16) were obtained neglecting the effect of retardation of dispersion forces (valid for $kR \ll 1$, $k = \omega/c$). For $kR \gg 1$ with R increasing the leading term in dispersion energy goes as R^{-7} [46] (for the region $1/k \ll R \ll c/T$)

$$\Delta E^{AB}_{disp,ret} = -\frac{23c}{4\pi}\frac{\alpha^A(0)\alpha^B(0)}{R^7}. \tag{2.19}$$

At finite T there is an interplay of retardation and temperature effects. For the region $R \gg c/T$ the leading term in the dispersion energy has the form [46]

$$\Delta E^{AB}_{disp}(R,T) = -3k_BT\frac{\alpha^A(0)\alpha^B(0)}{R^6}, \tag{2.20}$$

where k_B is the Boltzmann constant.

Magnetic dispersion interactions.

Along with the electric interactions, the magnetic interactions also give contribution to the interaction energy. Below, we consider the major types of magnetic interactions. For the description of such interactions the perturbation theory is used with the interaction (perturbation) Hamiltonian written (for two interacting molecules in the ground electronic state) as [47]

$$H' = -\vec{\mu}^A\cdot\vec{F}^A - \vec{m}^A\cdot\vec{B}^A - \vec{\mu}^B\cdot\vec{F}^B - \vec{m}^B\cdot\vec{B}^B + \cdots\ , \tag{2.21}$$

where $\vec{m}$ is the magnetic dipole moment operator for corresponding molecule and $\vec{B}$ is the magnetic field operator. In the present work we will only evaluate the contribution of magnetic interactions to the dispersion energy (we will not consider the angular dependence of the tensors and will deal only with the isotropic values). The leading electric dipole interaction term will give the Casimir-Polder expression (Eq. 2.16), while the pure magnetic dipole coupling will give rise to the dispersion potential between two paramagnetically susceptible molecules. It is considerably smaller in magnitude than the electric dipole-dipole interaction and has the functional form:

$$\Delta E^{\chi-\chi} = -\frac{1}{\pi c^3 R^2}\int_0^\infty du u^4 e^{-2uR}\chi^A(iu)\chi^B(iu)\Big[1+\frac{2}{uR}+\frac{5}{u^2R^2}+\frac{6}{u^3R^3}+\frac{3}{u^4R^4}\Big], \tag{2.22}$$

where $u = i\omega/c$ and the isotropic magnetic dipole susceptibility at imaginary frequency is defined as

$$\chi(iu) = \frac{2}{3}\sum_n \frac{E_{n0}|\vec{m}_{0n}|^2}{E_{n0}^2+(\hbar cu)^2}. \tag{2.23}$$

Here $|\vec{m}_{0n}|$ is the transition magnetic dipole matrix element between the ground Ψ_0 and excited Ψ_n states of the corresponding molecule, $E_{n0} = E_n - E_0$.

Eq. 2.22 is valid for all intermolecular distances R beyond the overlap of electron shells. It is interesting to get the asymptotic behavior for this interaction energy in the far-zone (FZ) ($kR \gg 1$) limit and near-zone (NZ) ($kR \ll 1$) limits. Thus, the pure magnetic dipole correction to the London dispersion formula (Eq. 2.15) is expressed as

$$\Delta E_{NZ}^{\chi-\chi} = -\frac{2}{3c^2R^6}\sum_{n,s}\frac{|\vec{m}_{0n}^A|^2|\vec{m}_{s0}^B|^2}{(E_{n0}^A+E_{s0}^B)} \tag{2.24}$$

and

$$\Delta E_{FZ}^{\chi-\chi} = -\frac{23}{4\pi c^3R^7}\chi^A(0)\chi^B(0). \tag{2.25}$$

Dispersion potential between an electric dipole polarizable molecule A and a magnetic dipole polarizable molecule B is important when molecules with small electric dipole polarizability interact with species having a large magnetic dipole polarizability.

The additional interaction energy to the dispersion energy for freely tumbling A and B is in this case is expressed in form [47]

$$\begin{aligned}\Delta E^{\alpha-\chi} = &-\frac{2}{3c^2}\sum_{s,E_r>E_s}\alpha^A(k_{rs})|\vec{m}_{rs}^B|^2k_{rs}^6\Big[\frac{1}{k_{rs}^2R^2}+\frac{1}{k_{rs}^4R^4}\Big] \\ &-\frac{2}{3c^2}\sum_{q,E_p>E_q}\chi^B(k_{pq})|\vec{\mu}_{pq}^A|^2k_{pq}^6\Big[\frac{1}{k_{pq}^2R^2}+\frac{1}{k_{pq}^4R^4}\Big] \\ &+\frac{4}{9\pi c^3}\sum_{q,s}|\vec{\mu}_{pq}^A|^2|\vec{m}_{rs}^B|^2\int_0^\infty du u^6 e^{-2uR}\frac{k_{qp}k_{sr}}{(k_{qp}^2+u^2)(k_{sr}^2+u^2)}\Big[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\Big].\end{aligned} \tag{2.26}$$

Here magnetic dipole susceptibility is defined as

$$\begin{aligned}\chi_{\alpha\beta}(k) &= \sum_s\Big[\frac{\langle\Psi_0|m_\alpha|\Psi_s\rangle\langle\Psi_s|m_\beta|\Psi_0\rangle}{E_{s0}-\hbar ck}+\frac{\langle\Psi_0|m_\beta|\Psi_s\rangle\langle\Psi_s|m_\alpha|\Psi_0\rangle}{E_{s0}+\hbar ck}\Big] \\ &= \sum_s\frac{2E_{s0}\langle\Psi_0|m_\alpha|\Psi_s\rangle\langle\Psi_s|m_\beta|\Psi_0\rangle}{E_{s0}^2-(\hbar ck)^2}.\end{aligned} \tag{2.27}$$

The above formula works for all R beyond the overlap of electron shells. The following asymptotic limits can be considered: far-zone and near-zone limits. In these limits for molecules being in the ground electronic state the contribution to the dispersion energy takes the form [47]:

$$\Delta E_{NZ}^{\alpha-\chi} = \frac{2}{9c^4R^4}\sum_{q,s} E_{q0}^A E_{s0}^B \frac{|\vec{\mu}_{0q}^A|^2|\vec{m}_{s0}^B|^2}{E_{q0}^A + E_{s0}^B} \tag{2.28}$$

and

$$\Delta E_{FZ}^{\alpha-\chi} = \frac{7}{4\pi c R^7}\alpha^A(0)\chi^B(0), \tag{2.29}$$

where the isotropic electric dipole polarizability of the A molecule is

$$\alpha^A(0) = \frac{2}{3}\sum_n \frac{|\vec{\mu}_{0n}^A|^2}{E_{n0}^A}. \tag{2.30}$$

It should be noted, that the dispersion potential for this case is repulsive.

However, the results obtained are incomplete as we didn't account for the diamagnetic coupling term $(-1/2)\chi^B(\vec{B}^B)^2$. Let us consider the interaction between an electric dipole polarizable molecule A and a molecule B that is diamagnetic. In this case the interaction energy has the form [47, 48]

$$\Delta E^{\alpha-dia} = \frac{1}{9\pi c^2}\sum_n |\vec{\mu}_{0n}^A|^2\langle (q^B)^2\rangle^{00}\int_0^\infty du u^6 e^{-2uR}\frac{k_{0n}}{(k_{0n}^2+u^2)}\Big[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\Big], \tag{2.31}$$

where the electronic spatial extent for the B molecule

$$\langle (q^B)^2\rangle^{00} = \langle \Psi_0^B|(q^B)^2|\Psi_0^B\rangle. \tag{2.32}$$

This formula works for all R beyond charge overlaps. The asymptotic approximation yields the near-zone energy shift

$$\Delta E_{NZ}^{\alpha-dia} = -\frac{1}{18\pi c^2R^5}\sum_n |\vec{\mu}_{0n}^A|^2\langle (q^B)^2\rangle^{00}k_{n0} \tag{2.33}$$

and far-zone energy shift

$$\Delta E_{FZ}^{\alpha-dia} = -\frac{7}{24\pi c R^7}\alpha^A(0)\langle (q^B)^2\rangle^{00}. \tag{2.34}$$

Let us now consider the interaction between a diamagnetic species and a magnetic dipole susceptible body. In this case the energy shift is written as [48]

$$\Delta E^{dia-\chi} = \frac{1}{9\pi c^4}\sum_n \langle (q^A)^2\rangle^{00}|\vec{m}_{0n}^B|^2\int_0^\infty \frac{du u^6 e^{-2uR}}{(u^2+k_{n0}^2)}k_{n0}\Big[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\Big]. \tag{2.35}$$

The potential Eq. 2.35 is applicable for all inter-atomic/molecular separations beyond electron overlap. In the far-zone limit the energy has the form

$$\Delta E^{dia-\chi} = \frac{23}{24\pi c^3R^7}\langle (q^A)^2\rangle^{00}\chi^B(0). \tag{2.36}$$

The energy shift Eq. 2.35 vanishes for atoms in ground electronic state of S-type symmetry (for example, for alkali-metal atoms).

Moreover, the dispersion interaction energy between two diamagnetic molecules is given by [47,48]:

$$\Delta E^{dia-dia} = -\frac{23}{144\pi c^3 R^7}\langle (q^A)^2\rangle^{00}\langle (q^B)^2\rangle^{00}, \tag{2.37}$$

which has inverse $7th$ power law for all R.

Thus, the correction from the magnetic dispersion interactions to the London dispersion formula (Eq. 2.15) is a sum of the contributions

$$\Delta E^{mag} = \Delta E^{dia-dia} + \Delta E^{\chi-\chi} + \Delta E^{\alpha-dia} + \Delta E^{dia-\chi} + \Delta E^{\alpha-\chi}. \tag{2.38}$$

Relativistic corrections to the electric dipole interactions.

The relativistic effects are revealed not only at large intermolecular separations but at shorter distances. Meath and Hirschfelder [49,50] obtained the multipole expansion for all the terms of relativistic energy correction. The first terms of this expansion decrease more slowly with R than the first terms of the nonrelativistic expansion. For example, for interaction of two atoms in nondegenerate states, the expression for $kR \ll 1$ and with accuracy of the order of α^2 has the form [46]

$$\Delta E^{\alpha-\alpha}_{rel} = \alpha^2\Big[\frac{W_4}{R^4} + \frac{W_6}{R^6} + \cdots\Big], \tag{2.39}$$

where α is the fine structure constant, and the first coefficient W_4 is expressed in terms of oscillator strengths and transition frequencies

$$W_4 = \frac{1}{4}\sum_{n,m\neq 0}\frac{f^A_{n0}f^B_{m0}}{E^A_{n0}+E^B_{m0}}. \tag{2.40}$$

It should be noted, that the relativistic corrections are positive, which leads to the reduction of nonrelativistic dispersion attraction.

2.2 Dipole moment

In order to obtain the induced dipole moment of the A molecule being in the weak electric field of the B molecule one should take the first derivative of the energy E^{AB} (Eq. 2.17) by the external field F^0_α. The electrostatic interactions (Eq. 2.8) give the permanent dipole moment, the induction interactions (Eq. 2.47) give the contribution to the induction dipole moment $\mu^{ind,AB}_\alpha$. Therefore, the total dipole moment μ^{AB}_α is the sum of the permanent, induction and dispersion dipole moments:

$$\mu^{AB}_\alpha = \tilde{\mu}^A_\alpha + \tilde{\mu}^B_\alpha, \tag{2.41}$$

$$\tilde{\mu}^i_\alpha = \mu^{i(0)}_\alpha + \mu^{ind,i}_\alpha + \mu^{disp,i}_\alpha \equiv \mu^i_\alpha + \mu^{disp,i}_\alpha,$$

where $\mu^{i(0)}_\alpha$ is the permanent dipole moment of a free molecule i, $\mu^{ind,i}_\alpha$ and $\mu^{disp,i}_\alpha$ are the induction and dispersion contributions to the dipole moment of the i-th molecule. The dipole moment of the A molecule has the form (permanent and induction term):

$$\begin{aligned}\mu^A_\alpha = -\frac{\partial(E^A_{elec}+E^A_{ind})}{\partial F_\alpha} &= \mu^{A(0)}_\alpha + \mu^{ind,A}_\alpha = \mu^{A(0)}_\alpha + \alpha^A_{\alpha\beta}F^A_\beta + \frac{1}{3}A^A_{\alpha,\beta\gamma}F^A_{\beta\gamma} \\ &+\frac{1}{15}E^A_{\alpha,\beta\gamma\delta}F^A_{\beta\gamma\delta} + \frac{1}{105}D^A_{\alpha,\beta\gamma\delta\varepsilon}F^A_{\beta\gamma\delta\varepsilon} + \frac{1}{945}H^A_{\alpha,\beta\gamma\delta\varepsilon\varphi}F^A_{\beta\gamma\delta\varepsilon\varphi} + \cdots \\ &+\frac{1}{2}\beta^A_{\alpha\beta\gamma}F^A_\beta F^A_\gamma + \frac{1}{3}B^A_{\alpha\beta,\gamma\delta}F^A_\beta F^A_{\gamma\delta} + \cdots + \frac{1}{6}\gamma^A_{\alpha\beta\gamma\delta}F^A_\beta F^A_\gamma F^A_\delta + \cdots . \end{aligned} \tag{2.42}$$

For further consideration of the dipole moment, polarizability and hyperpolarizability we need also the expressions for the quadrupole moment

$$\Theta^A_{\alpha\beta} = -3\frac{\partial(E^A_{elec}+E^A_{ind})}{\partial F_{\alpha\beta}} = \Theta^{A(0)}_{\alpha\beta} + A^A_{\gamma,\delta\varepsilon}F^A_\gamma + \frac{1}{2}B^A_{\gamma\delta,\alpha\beta}F^A_\gamma F^A_\delta + C^A_{\alpha\beta,\gamma\delta}F^A_{\gamma\delta} + \cdots , \tag{2.43}$$

octupole

$$\Omega^A_{\alpha\beta\gamma} = 15\frac{\partial(E^A_{elec}+E^A_{ind})}{\partial F_{\alpha\beta\gamma}} = \Omega^{A(0)}_{\alpha\beta\gamma} + E^A_{\delta,\alpha\beta\gamma}F^A_\delta + \cdots , \tag{2.44}$$

hexadecapole

$$\Phi^A_{\alpha\beta\gamma\delta} = -105\frac{\partial(E^A_{elec}+E^A_{ind})}{\partial F_{\alpha\beta\gamma\delta}} = \Phi^{A(0)}_{\alpha\beta\gamma\delta} + D^A_{\varepsilon,\alpha\beta\gamma\delta}F^A_\varepsilon + \cdots , \tag{2.45}$$

and tetrahexacontapole

$$\Xi^A_{\alpha\beta\gamma\delta\varepsilon} = 945\frac{\partial(E^A_{elec}+E^A_{ind})}{\partial F_{\alpha\beta\gamma\delta\varepsilon}} = \Xi^{A(0)}_{\alpha\beta\gamma\delta\varepsilon} + H^A_{\varphi,\alpha\beta\gamma\delta\varepsilon}F^A_\varphi + \cdots \tag{2.46}$$

moments. Here the upper index (0) implies the permanent moment.

In order to obtain the induced dipole moment of the A molecule, we expand μ^A_α using equations for the field (Eq. 2.3), field gradient etc. Then the dipole, quadrupole etc. moments from Eq. 2.3 should be also expanded using Eqs. 2.42, Eq. 2.43, Eq. 2.44, Eq. 2.45 and Eq. 2.46. When necessary, we use expressions for the field and field gradients (Eqs. 2.3 and 2.4) twice. Thus, in the general case for neutral systems (both A and B molecules are uncharged) for $\mathbf{F}^0 = 0$ we have the induction dipole moment of the A molecule (this formula is partially reported in Ref. [33]):

$$\begin{aligned}\mu_\alpha^{ind,A} &= \alpha_{\alpha\beta}^A\mu_\gamma^{B(0)}T_{\beta\gamma}^{AB} + \frac{1}{3}\alpha_{\alpha\beta}^A\Theta_{\gamma\delta}^{B(0)}T_{\beta\gamma\delta}^{AB} - \frac{1}{3}A_{\alpha,\beta\gamma}^A\mu_\delta^{B(0)}T_{\beta\gamma\delta}^{AB} - \frac{1}{9}A_{\alpha,\beta\gamma}^A\Theta_{\delta\varepsilon}^{B(0)}T_{\beta\gamma\delta\varepsilon}^{AB} \\ &+\frac{1}{15}\alpha_{\alpha\beta}^A\Omega_{\gamma\delta\varepsilon}^{B(0)}T_{\beta\gamma\delta\varepsilon}^{AB} + \frac{1}{15}E_{\alpha,\beta\gamma\delta}^A\mu_\varepsilon^{B(0)}T_{\beta\gamma\delta\varepsilon}^{AB} + \frac{1}{105}\alpha_{\alpha\beta}^A\Phi_{\gamma\delta\varepsilon\varphi}^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi}^{AB} - \frac{1}{105}D_{\alpha,\beta\gamma\delta\varepsilon}^A\mu_\varphi^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi}^{AB} \\ &-\frac{1}{45}A_{\alpha,\beta\gamma}^A\Omega_{\delta\varepsilon\varphi}^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi}^{AB} + \frac{1}{45}E_{\alpha,\beta\gamma\delta}^A\Theta_{\varepsilon\varphi}^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi}^{AB} + \frac{1}{945}\alpha_{\alpha\beta}^A\Xi_{\gamma\delta\varepsilon\varphi\nu}^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi\nu}^{AB} \\ &-\frac{1}{315}A_{\alpha,\beta\gamma}^A\Phi_{\delta\varepsilon\varphi\nu}^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi\nu}^{AB} - \frac{1}{315}D_{\alpha,\beta\gamma\delta\varepsilon}^A\Theta_{\varphi\nu}^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi\nu}^{AB} + \frac{1}{225}E_{\alpha,\beta\gamma\delta}^A\Omega_{\varepsilon\varphi\nu}^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi\nu}^{AB} \\ &+\frac{1}{945}H_{\alpha,\beta\gamma\delta\varepsilon\varphi}^A\mu_\nu^{B(0)}T_{\beta\gamma\delta\varepsilon\varphi\nu}^{AB} + \frac{1}{2}\beta_{\alpha\beta\delta}^A\mu_\gamma^{B(0)}\mu_\varepsilon^{B(0)}T_{\beta\gamma}^{AB}T_{\delta\varepsilon}^{AB} + \alpha_{\alpha\beta}^A\mu_\gamma^{A(0)}\alpha_{\delta\varepsilon}^B T_{\beta\delta}^{AB}T_{\gamma\varepsilon}^{AB} \\ &+\frac{2}{3}\alpha_{\alpha\beta}^A\mu_\gamma^{A(0)}A_{\delta,\varepsilon\varphi}^B T_{\beta\varphi}^{AB}T_{\gamma\delta\varepsilon}^{AB} - \frac{1}{3}\alpha_{\alpha\beta}^A\Theta_{\gamma\delta}^{A(0)}\alpha_{\varepsilon\varphi}^B T_{\beta\varepsilon}^{AB}T_{\varphi\gamma\delta}^{AB} - \frac{1}{3}A_{\alpha,\beta\delta}^A\mu_\gamma^{A(0)}\alpha_{\varepsilon\varphi}^B T_{\gamma\varepsilon}^{AB}T_{\varphi\beta\delta}^{AB} \\ &+\frac{1}{3}\beta_{\alpha\beta\gamma}^A\mu_\delta^{B(0)}\Theta_{\varepsilon\varphi}^{B(0)}T_{\beta\delta}^{AB}T_{\gamma\varepsilon\varphi}^{AB} - \frac{1}{3}B_{\alpha\beta,\gamma\delta}^A\mu_\varepsilon^{B(0)}\mu_\varphi^{B(0)}T_{\beta\varepsilon}^{AB}T_{\gamma\delta\varphi}^{AB} + \cdots . \quad (2.47)\end{aligned}$$

The accurate dispersion contribution through the order R^{-7} to the dipole moment is written as:

$$\begin{aligned}\mu_\alpha^{disp,A} = -\frac{\partial E_{disp}^A}{\partial F_\alpha^0}\Big|_{\mathbf{F}^0=0} &= -\frac{1}{2\pi}\int_0^\infty d\omega\beta_{\alpha\beta\gamma}^A(0,i\omega,-i\omega)\alpha_{\delta\varepsilon}^B(i\omega)T_{\beta\delta}^{AB}T_{\gamma\varepsilon}^{AB} \\ &+\frac{1}{3\pi}\int_0^\infty d\omega B_{\alpha\beta,\gamma\delta}^A(0;i\omega,-i\omega)\alpha_{\varepsilon\varphi}^B(i\omega)T_{\beta\varepsilon}^{AB}T_{\varphi\gamma\delta}^{AB} + \cdots . \quad (2.48)\end{aligned}$$

Here $\beta_{\alpha\beta\gamma}(0,i\omega,-i\omega)$ and $B_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)$ are the first hyperpolarizability and a dipole-dipole-quadrople hyperpolarizability at imaginary frequencies; $B_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)$ has dipole indices α and β, quadrupole indices γ and δ, and the frequency $(-i\omega)$ is associated with the quadrupole indices. The contribution to the induction and dispersion dipole moments from both molecules is written as follows:

$$\mu_\alpha^{ind,AB} + \mu_\alpha^{disp,AB} = (1+\mathscr{P}^{AB})(\mu_\alpha^{ind,A} + \mu_\alpha^{disp,A}).$$

There is the same problem as with the dispersion energy: it is not easy to get the dynamic polarizabilities at imaginary frequencies $i\omega$. But there exist two "constant ratio" approximations (for example, [51, 52, 67, 68]), that allows to express the dispersion contribution to the dipole moment in terms of static (hyper)polarizabilities. This approximation is limited in accuracy because of the actual frequency dependence of the ratios. Let us consider the integral with $\beta_{\alpha\beta\gamma}(0,i\omega,-i\omega)$ in Eq. 2.48. The first "constant ratio" approximation (CRA1) gives the following formula:

$$\int_0^\infty \beta_{\alpha\beta\gamma}^{A,B}(0,i\omega,-i\omega)\alpha_{\delta\varepsilon}^{B,A}(i\omega)d\omega \cong S_{\beta\alpha}^{A,B}\int_0^\infty \alpha^{A,B}(i\omega)\alpha_{\delta\varepsilon}^{B,A}(i\omega)d\omega, \quad (2.49)$$

where the "constant ratio"

$$S_{\beta\alpha}^{A,B} = \frac{\beta^{A,B}(o,i\omega,-i\omega)}{\alpha^{A,B}(i\omega)} \quad (2.50)$$

doesn't depend on the ω, and the mean polarizability

$$\alpha^{A,B} = \frac{1}{3}(\alpha^{A,B}_{xx} + \alpha^{A,B}_{yy} + \alpha^{A,B}_{zz}). \tag{2.51}$$

One can evaluate the ratio by accounting for the approximation, that

$$S^{A,B}_{\beta\alpha} = \frac{\int_0^\infty \beta^{A,B}(0,i\omega,-i\omega)d\omega}{\int_0^\infty \alpha^{A,B}(i\omega)d\omega}. \tag{2.52}$$

In order to obtain $S^{A,B}_{\beta\alpha}$ one should use the Unsöld approximation [43], that gives the following expression for the (hyper)polarizabilities:

$$\begin{aligned}
\alpha_{\alpha\beta}(i\omega) &= \alpha_{\alpha\beta}(0)\frac{\Omega^2}{\Omega^2+\omega^2}, \\
\beta_{\alpha\beta\gamma}(0,i\omega,-i\omega) &= \beta_{\alpha\beta\gamma}(0,0,0)\frac{\Omega^2}{3}\frac{3\Omega^2+\omega^2}{(\Omega^2+\omega^2)^2}, \\
B_{\alpha\beta\gamma}(0,i\omega,-i\omega) &= B_{\alpha\beta,\gamma\delta}(0;0,0)\frac{\Omega^2}{3}\frac{3\Omega^2+\omega^2}{(\Omega^2+\omega^2)^2}.
\end{aligned} \tag{2.53}$$

Here Ω is the average excitation frequency for the molecule. Therefore, for the "constant ratio" $S^{A,B}_{\beta\alpha}$ we have

$$S^{A,B}_{\beta\alpha} = \frac{\beta^{A,B}_{\alpha\beta\gamma}(0,0,0)}{\alpha^{A,B}(0)}\frac{\int_0^\infty \frac{\Omega^2_{A,B}}{3}\frac{3\Omega^2_{A,B}+\omega^2}{(\Omega^2_{A,B}+\omega^2)^2}d\omega}{\int_0^\infty \frac{\Omega^2_{A,B}}{\Omega^2_{A,B}+\omega^2}d\omega}. \tag{2.54}$$

After taking the integrals over ω, Eq. 2.54 is rewritten as:

$$S^{A,B}_{\beta\alpha} = \frac{2}{3}\frac{\beta^{A,B}_{\alpha\beta\gamma}(0,0,0)}{\alpha^{A,B}(0)}. \tag{2.55}$$

The same can be done for the integral over ω with $B_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)$:

$$\int_0^\infty B^{A,B}_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)\alpha^{B,A}_{\varepsilon\varphi}(i\omega)d\omega \cong S^{A,B}_{B\alpha}\int_0^\infty \alpha^{A,B}(i\omega)\alpha^{B,A}_{\delta\varepsilon}(i\omega)d\omega, \tag{2.56}$$

where

$$S^{A,B}_{B\alpha} = \frac{2}{3}\frac{B^{A,B}_{\alpha\beta,\gamma\delta}(0;0,0)}{\alpha^{A,B}(0)}. \tag{2.57}$$

Taking Eqs. 2.49 and 2.56 into account, Eq. 2.48 is written as follows:

$$\begin{aligned}
\mu^{A,disp}_{\alpha} = &-\frac{1}{3\pi}\frac{\beta^{A}_{\alpha\beta\gamma}(0,0,0)}{\alpha^{A}(0)}T^{AB}_{\beta\delta}T^{AB}_{\gamma\varepsilon}\int_0^\infty \alpha^{A}(i\omega)\alpha^{B}_{\delta\varepsilon}(i\omega)d\omega \\
&+\frac{2}{9\pi}\frac{B^{A}_{\alpha\beta,\gamma\delta}(0;0,0)}{\alpha^{A}(0)}T^{AB}_{\beta\varepsilon}T^{AB}_{\varphi\gamma\delta}\int_0^\infty \alpha^{A}(i\omega)\alpha^{B}_{\varepsilon\varphi}(i\omega)d\omega.
\end{aligned} \tag{2.58}$$

Let us consider the second "constant ratio" approximation [68] (CRA2) (further, we will call it CRA2 as in original papers, in spite of the actual non dependence of ratios on ω), that gives the following relation for the integral with $\beta_{\alpha\beta\gamma}(0,i\omega,-i\omega)$ in Eq. 2.48:

$$\int_0^\infty \beta^{A,B}_{\alpha\beta\gamma}(0,i\omega,-i\omega)\alpha^{B,A}_{\delta\varepsilon}(i\omega)d\omega = \frac{I^{A,B}_{\beta\alpha}}{I_{\alpha\alpha}}\int_0^\infty \alpha^{A}(i\omega)\alpha^{B}(i\omega)d\omega = \frac{\pi}{3}\frac{I^{A,B}_{\beta\alpha}}{I_{\alpha\alpha}}C_6, \tag{2.59}$$

where

$$C_6 = \frac{3}{\pi}\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega, \tag{2.60}$$

and the "constant ratio"

$$\frac{I^{A,B}_{\beta\alpha}}{I_{\alpha\alpha}} = \frac{\int_0^\infty \beta^{A,B}_{\alpha\beta\gamma}(0, i\omega, -i\omega)\alpha^{B,A}_{\delta\varepsilon}(i\omega)d\omega}{\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega}. \tag{2.61}$$

Using Eqs. 2.53, we obtain the expression for the "constant ratio" $\frac{I^{A,B}_{\beta\alpha}}{I_{\alpha\alpha}}$ in the form [69]:

$$\frac{I^{A,B}_{\beta\alpha}}{I_{\alpha\alpha}} \cong \frac{\beta^{A,B}_{\alpha\beta\gamma}(0,0,0)\alpha^{B,A}_{\delta\varepsilon}(0)}{\alpha^A(0)\alpha^B(0)}\left[\frac{1+\frac{2}{3}\Delta_{1,2}}{1+\Delta_{1,2}}\right], \tag{2.62}$$

where

$$\Delta_1 = \frac{\Omega_B}{\Omega_A}, \Delta_2 = \frac{\Omega_A}{\Omega_B}. \tag{2.63}$$

Analogously one can get the expressions for the integrals with $B_{\alpha\beta,\gamma\delta}(0; i\omega, -i\omega)$:

$$\int_0^\infty B^{A,B}_{\alpha\beta,\gamma\delta}(0; i\omega, -i\omega)\alpha^{B,A}_{\varepsilon\varphi}(i\omega)d\omega = \frac{I^{A,B}_{B\alpha}}{I_{\alpha\alpha}}\frac{\pi}{3}C_6. \tag{2.64}$$

Here

$$\frac{I^{A,B}_{B\alpha}}{I_{\alpha\alpha}} \cong \frac{B^{A,B}_{\alpha\beta,\gamma\delta}(0;0,0)\alpha^{B,A}_{\varepsilon\varphi}(0)}{\alpha^A(0)\alpha^B(0)}\left[\frac{1+\frac{2}{3}\Delta_{1,2}}{1+\Delta_{1,2}}\right]. \tag{2.65}$$

Thus, assuming that $\Omega_A \cong \Omega_B$, the expression for the dispersion dipole moment contribution from the both molecules A and B takes on the form ($\alpha_{\alpha\beta}(0) \equiv \alpha$, $\beta_{\alpha\beta\gamma}(0,0,0) \equiv \beta_{\alpha\beta\gamma}$ and $B_{\alpha\beta,\gamma\delta}(0;0,0) \equiv B_{\alpha\beta,\gamma\delta}$):

$$\mu^{disp,AB}_\alpha = -\left[\beta^A_{\alpha\beta\gamma}\alpha^B_{\delta\varepsilon} + \beta^B_{\alpha\beta\gamma}\alpha^A_{\delta\varepsilon}\right]\frac{5T_{\beta\delta}T_{\gamma\varepsilon}C_6}{36\alpha^A\alpha^B} + \left[B^A_{\alpha\beta,\gamma\delta}\alpha^B_{\varepsilon\varphi} - B^B_{\alpha\beta,\gamma\delta}\alpha^A_{\varepsilon\varphi}\right]\frac{5T_{\beta\varepsilon}T_{\varphi\gamma\delta}C_6}{54\alpha^A\alpha^B}. \tag{2.66}$$

Having necessary properties of free molecules, it is not difficult to calculate the interaction-induced dipole moment using suggested formulas. As the components of the properties (polarizabilities, multipole moments, etc.) are dependent on the orientation of molecules, in general case, we have the dipole moment surface.

2.3 Polarizability

It should be pointed out that the methods of classical electrodynamics accounting for the induction and dispersion effects give a physically correct analytical description of the polarizability surface for interacting atomic-molecular systems at large intermolecular separations [53–63]. In the framework of the long-range approximation [31,32], *i.e.* when the molecules can be represented as point objects but with their anisotropic electric properties being maintained, the electric polarizability of two interacting molecules $\alpha^{AB}_{\alpha\beta}$ is written as:

$$\alpha^{AB}_{\alpha\beta} = \tilde{\alpha}^A_{\alpha\beta} + \tilde{\alpha}^B_{\alpha\beta} \equiv \alpha^{A(0)}_{\alpha\beta} + \alpha^{B(0)}_{\alpha\beta} + \alpha^{ind,A}_{\alpha\beta} + \alpha^{ind,B}_{\alpha\beta} + \alpha^{disp,A}_{\alpha\beta} + \alpha^{disp,B}_{\alpha\beta}, \tag{2.67}$$

where $\alpha_{\alpha\beta}^{A(0)}$ and $\alpha_{\alpha\beta}^{B(0)}$ are the permanent dipole polarizabilities of molecules A and B; $\alpha_{\alpha\beta}^{ind,A} + \alpha_{\alpha\beta}^{ind,B} \equiv \alpha_{\alpha\beta}^{ind,AB}$ and $\alpha_{\alpha\beta}^{disp,A} + \alpha_{\alpha\beta}^{disp,B} \equiv \alpha_{\alpha\beta}^{disp,AB}$ are the induction and dispersion terms of the polarizability of interacting molecules. Induction effects on the polarizability of A results from the field of the permanent moments and the static induced moments on B, while the dispersion contribution to the polarizability depends on the field due to spontaneous, quantum fluctuations in the charge densities of A and B.

The induction contribution to the polarizability of the A molecule $\alpha_{\alpha\beta}^{ind,A}$ being the part of the AB pair is found by differentiating E_{ind}^{A} by F_{α}^{0} and F_{β}^{0} with the use of Eq. 2.3 and subtracting the permanent polarizability of the A molecule:

$$\alpha_{\alpha\beta}^{A} = -\frac{\partial^2 E_{ind}^{A}}{\partial F_{\alpha}^{0} \partial F_{\beta}^{0}}\bigg|_{\mathbf{F}^0=0} = \alpha_{\alpha\beta}^{A(0)} + \alpha_{\alpha\beta}^{ind,A}. \tag{2.68}$$

Using analogous scheme for derivation the induction dipole moment of interacting molecules A and B, we obtain for the induction polarizability of the A molecule:

$$\begin{aligned}
\alpha_{\alpha\beta}^{ind,A} &= \alpha_{\alpha\gamma}^{A} T_{\gamma\delta}^{AB} \alpha_{\delta\beta}^{B} + \beta_{\alpha\beta\gamma}^{A} T_{\gamma\delta}^{AB} \mu_{\delta}^{B(0)} + \frac{1}{3}\alpha_{\alpha\gamma}^{A} T_{\gamma\delta\varepsilon}^{AB} A_{\beta,\delta\varepsilon}^{B} - \frac{1}{3} A_{\alpha,\gamma\delta}^{A} T_{\gamma\delta\varepsilon}^{AB} \alpha_{\varepsilon\beta}^{B} \\
&+\frac{1}{3}\beta_{\alpha\beta\gamma}^{A} T_{\gamma\delta\varepsilon}^{AB} \Theta_{\delta\varepsilon}^{B(0)} - \frac{1}{3} B_{\alpha\beta,\gamma\delta}^{A} T_{\gamma\delta\varepsilon}^{AB} \mu_{\varepsilon}^{B(0)} + \frac{1}{15}\alpha_{\alpha\gamma}^{A} T_{\gamma\delta\varepsilon\varphi}^{AB} E_{\beta,\delta\varepsilon\varphi}^{B} + \frac{1}{15} E_{\alpha,\gamma\delta\varepsilon}^{A} T_{\gamma\delta\varepsilon\varphi}^{AB} \alpha_{\varphi\beta}^{B} \\
&-\frac{1}{9} A_{\alpha,\gamma\delta}^{A} T_{\gamma\delta\varepsilon\varphi}^{AB} A_{\beta,\varepsilon\varphi}^{B} + \frac{1}{15}\beta_{\alpha\beta\gamma}^{A} T_{\gamma\delta\varepsilon\varphi}^{AB} \Omega_{\delta\varepsilon\varphi}^{B(0)} - \frac{1}{9} B_{\alpha\beta,\gamma\delta}^{A} T_{\gamma\delta\varepsilon\varphi}^{AB} \Theta_{\varepsilon\varphi}^{B(0)} \\
&+\frac{1}{15} M_{\alpha\beta,\gamma\delta\varepsilon}^{A} T_{\gamma\delta\varepsilon\varphi}^{AB} \mu_{\varphi}^{B(0)} + \frac{1}{105}\alpha_{\alpha\gamma}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} D_{\beta,\delta\varepsilon\varphi\nu}^{B} - \frac{1}{105} D_{\alpha,\gamma\delta\varepsilon\varphi}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} \alpha_{\nu\beta}^{B} \\
&-\frac{1}{45} A_{\alpha,\gamma\delta}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} E_{\beta,\varepsilon\varphi\nu}^{B} + \frac{1}{45} E_{\alpha,\gamma\delta\varepsilon}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} A_{\beta,\varphi\nu}^{B} + \frac{1}{45} M_{\alpha\beta,\gamma\delta\varepsilon}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} \Theta_{\varphi\nu}^{B(0)} \\
&-\frac{1}{105} G_{\alpha\beta,\gamma\delta\varepsilon\varphi}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} \mu_{\nu}^{B(0)} + \frac{1}{105}\beta_{\alpha\beta\gamma}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} \Phi_{\delta\varepsilon\varphi\nu}^{B(0)} - \frac{1}{45} B_{\alpha\beta,\gamma\delta}^{A} T_{\gamma\delta\varepsilon\varphi\nu}^{AB} \Omega_{\varepsilon\varphi\nu}^{B(0)} \\
&+\alpha_{\alpha\gamma}^{A} T_{\gamma\delta}^{AB} \alpha_{\delta\varepsilon}^{B} T_{\varepsilon\varphi}^{AB} \alpha_{\varphi\beta}^{A} + \alpha_{\alpha\gamma}^{A} T_{\gamma\delta}^{AB} \beta_{\delta\beta\varepsilon}^{B} T_{\varepsilon\varphi}^{AB} \mu_{\varphi}^{A(0)} + \beta_{\alpha\gamma\delta}^{A} T_{\gamma\varepsilon}^{AB} \mu_{\varepsilon}^{B(0)} T_{\delta\varphi}^{AB} \alpha_{\varphi\beta}^{B} \\
&+\beta_{\alpha\beta\gamma}^{A} T_{\gamma\delta}^{AB} \alpha_{\delta\varepsilon}^{B} T_{\varepsilon\varphi}^{AB} \mu_{\varphi}^{A(0)} + \cdots .
\end{aligned} \tag{2.69}$$

The dispersion contribution $\alpha_{\alpha\beta}^{disp,A}$ is determined by the shift in the dispersion energy E_{disp}^{A} for the pair in the presence of a static external field $\mathbf{F}^0$:

$$\alpha_{\alpha\beta}^{disp,A} = -\frac{\partial^2 E_{disp}^{A}}{\partial F_{\alpha}^{0} \partial F_{\beta}^{0}}\bigg|_{\mathbf{F}^0=0}. \tag{2.70}$$

The contribution of dispersion to the polarizability of the interacting molecules in the present work is calculated in the framework of the method [55] based on the fluctuation-dissipation theorem [64, 65]. In that case, restricting ourselves to the leading term $\sim R^{-6}$, the expression for the dispersion contribution takes the form [66]:

$$\alpha_{\alpha\beta}^{disp,A} = \frac{1}{2\pi} T_{\gamma\delta}^{AB} T_{\varepsilon\eta}^{AB} \int_0^\infty \alpha_{\eta\gamma}^{A}(i\omega) \gamma_{\delta\varepsilon\alpha\beta}^{B}(i\omega, 0, 0) d\omega, \tag{2.71}$$

where $\alpha_{\eta\gamma}(i\omega)$ and $\gamma_{\delta\varepsilon\alpha\beta}(i\omega, 0, 0)$ are the polarizability and second hyperpolarizability at the imaginary frequency $i\omega$.

The contribution to the induction and dispersion polarizabilities from two molecules has the form:

$$\alpha_{\alpha\beta}^{ind,AB} + \alpha_{\alpha\beta}^{disp,AB} = (1 + \mathscr{P}^{AB})(\alpha_{\alpha\beta}^{ind,A} + \alpha_{\alpha\beta}^{disp,A}).$$

Direct calculation of the dispersion contribution $\alpha_{\alpha\beta}^{disp,i}$ using Eq. 2.71 is impossible due to the absence of the $\gamma_{\delta\varepsilon\alpha\beta}(i\omega, 0, 0)$ values as functions of $i\omega$ for the majority of molecules. The dispersion contribution $\alpha_{\alpha\beta}^{disp,i}$ may be estimated, however, using "constant ratio" approximations CRA1 and CRA2 (in the framework of the method [55] based on the fluctuation-dissipation theorem [64, 65]) analogously to the dispersion dipole moment. The first approximation CRA1 gives the following relation:

$$\int_0^\infty \gamma_{\delta\varepsilon\alpha\beta}^{A,B}(i\omega, 0, 0)\alpha_{\eta\gamma}^{B,A}(i\omega)d\omega \cong S_{\gamma\alpha}^{A,B} \int_0^\infty \alpha^{A,B}(i\omega)\alpha_{\eta\gamma}^{B,A}(i\omega)d\omega, \tag{2.72}$$

where the "constant ratio" is assumed to be independent of ω:

$$S_{\gamma\alpha}^{A,B} = \frac{\gamma_{\delta\varepsilon\alpha\beta}^{A,B}(i\omega, 0, 0)}{\alpha^{A,B}(i\omega)}. \tag{2.73}$$

One of the ways to estimate this ratio is to use the following approximation

$$S_{\gamma\alpha}^{A,B} = \frac{\int_0^\infty \gamma_{\delta\varepsilon\alpha\beta}^{A,B}(i\omega, 0, 0)d\omega}{\int_0^\infty \alpha^{A,B}(i\omega)d\omega}. \tag{2.74}$$

This ratio is assumed, as in Ref. [59], to have the same relation to the static values of $\gamma_{\delta\varepsilon\alpha\beta}^{A,B}(0, 0, 0)$ and $\alpha^{A,B}(0)$ as in the Unsöld approximation [43]. In order to evaluate $S_{\gamma\alpha}^{A,B}$ one should use the Unsöld approximation for α and γ:

$$\begin{aligned} \alpha_{\alpha\beta}(i\omega) &= \alpha_{\alpha\beta}(0)\frac{\Omega}{\Omega^2 + \omega^2}, \\ \gamma_{\alpha\beta\gamma\delta}(i\omega, 0, 0) &= \gamma_{\alpha\beta\gamma\delta}(0, 0, 0)\frac{\Omega(6\Omega^4 + 3\Omega^2\omega^2 + \omega^4)}{6(\Omega^2 + \omega^2)^3}. \end{aligned} \tag{2.75}$$

Then, $S_{\gamma\alpha}^{A,B}$ takes the form:

$$S_{\gamma\alpha}^{A,B} = \frac{\gamma_{\delta\varepsilon\alpha\beta}^{A,B}(0, 0, 0)}{2\alpha^{A,B}(0)}. \tag{2.76}$$

Thus, accounting for Eq. 2.76 the expression 2.71 for the dispersion contribution $\alpha_{\alpha\beta}^{disp,AB}$ from the both molecules A and B can be rewritten as follows:

$$\alpha_{\alpha\beta}^{disp,AB} = \frac{1}{2}T_{\gamma\delta}^{AB}T_{\varepsilon\eta}^{AB}\Big[\frac{\gamma_{\delta\varepsilon\alpha\beta}^{A}(0, 0, 0)D_{\eta\gamma}}{\alpha^A(0)} + \frac{\gamma_{\delta\varepsilon\alpha\beta}^{B}(0, 0, 0)C_{\eta\gamma}}{\alpha^B(0)}\Big], \tag{2.77}$$

where

$$\begin{aligned} D_{\eta\gamma} &= \frac{1}{2\pi}\int_0^\infty \alpha^A(i\omega)\alpha_{\eta\gamma}^B(i\omega)d\omega, \\ C_{\eta\gamma} &= \frac{1}{2\pi}\int_0^\infty \alpha^B(i\omega)\alpha_{\eta\gamma}^A(i\omega)d\omega. \end{aligned} \tag{2.78}$$

Let us consider the second (CRA2), more correct approximation, that accounts for the frequency-dependent weighting of γ-tensor values for one molecule by the α of the other. It provides

$$\int_0^\infty \gamma^{A,B}_{\delta\varepsilon\alpha\beta}(i\omega,0,0)\alpha^{B,A}_{\eta\gamma}(i\omega)d\omega \cong \frac{I^{A,B}_{\gamma\alpha}}{I^{A,B}_{\alpha\alpha}}\int_0^\infty \alpha^{A,B}(i\omega)\alpha^{B,A}(i\omega)d\omega = \frac{\pi I^{A,B}_{\gamma\alpha}}{3I^{A,B}_{\alpha\alpha}}C_6, \tag{2.79}$$

where the "constant ratio"

$$\frac{I^{A,B}_{\gamma\alpha}}{I^{A,B}_{\alpha\alpha}} = \frac{\int_0^\infty \gamma^{A,B}_{\delta\varepsilon\alpha\beta}(i\omega,0,0)\alpha^{B,A}_{\eta\gamma}(i\omega)d\omega}{\int_0^\infty \alpha^{A}(i\omega)\alpha^{B}(i\omega)d\omega}. \tag{2.80}$$

Using the same Unsöld approximation (Eq. 2.75) we obtain the following expression

$$\frac{I^{A,B}_{\gamma\alpha}}{I^{A,B}_{\alpha\alpha}} = \frac{\gamma^{A,B}_{\delta\varepsilon\alpha\beta}(0,0,0)\alpha^{B,A}_{\eta\gamma}(0)}{6\alpha^A(0)\alpha^B(0)}\int_0^\infty \frac{\Omega_A\Omega_B(6\Omega^4_{A,B}+3\Omega^2_{A,B}\omega^2+\omega^4)}{\Omega_{A,B}(\Omega^2_{A,B}+\omega^2)^3(\Omega^2_{B,A}+\omega^2)}d\omega\Big/\int_0^\infty \frac{\Omega_A\Omega_B}{(\Omega^2_A+\omega^2)(\Omega^2_B+\omega^2)}d\omega, \tag{2.81}$$

which after integration is rewritten as

$$\frac{I^{A,B}_{\gamma\alpha}}{I^{A,B}_{\alpha\alpha}} = \frac{\gamma^{A,B}_{\delta\varepsilon\alpha\beta}(0,0,0)\alpha^{B,A}_{\eta\gamma}(0)(6+8\Delta_{1,2}+3\Delta^2_{1,2})}{6\alpha^A(0)\alpha^B(0)(1+\Delta_{1,2})^2}. \tag{2.82}$$

Assuming that $\Omega_A = \Omega_B$, constant ratio takes on the form:

$$\frac{I^{A,B}_{\gamma\alpha}}{I^{A,B}_{\alpha\alpha}} = \frac{17\gamma^{A,B}_{\delta\varepsilon\alpha\beta}(0,0,0)\alpha^{B,A}_{\eta\gamma}(0)}{24\alpha^A(0)\alpha^B(0)}. \tag{2.83}$$

Therefore, accounting for Eq. 2.83 the expression for the dispersion, contribution $\alpha^{disp,AB}_{\alpha\beta}$ from both molecules A and B is written as:

$$\alpha^{disp,AB}_{\alpha\beta} = \frac{17\pi T^{AB}_{\gamma\delta}T^{AB}_{\varepsilon\eta}C_6}{72\alpha^A(0)\alpha^B(0)}(\gamma^A_{\delta\varepsilon\alpha\beta}(0,0,0)\alpha^B_{\eta\gamma}+\gamma^B_{\delta\varepsilon\alpha\beta}(0,0,0)\alpha^A_{\eta\gamma}). \tag{2.84}$$

Further calculation of $\alpha^{disp,AB}_{\alpha\beta}$ is not difficult, as the imaginary frequency-dependent polarizabilities $\alpha(i\omega)$ are known for the majority of small molecules.

Third part

The CH_4-N_2 van der Waals complex

In gaseous media containing N_2 and CH_4 molecules there are both collisional and weakly bound van der Waals complexes. At present, collisional CH_4-N_2 complexes have been investigated in some experimental and theoretical [52, 70–76] works, but there is comparatively little information about the weakly bound van der Waals complexes [77, 78]. The CH_4-N_2 complex is of particular interest in astrophysical applications [79, 80]. For example, the most abundant compounds in the atmosphere of Saturn's satellite Titan are the N_2 (94 %) and CH_4 (2 – 5 %) molecules [72,73,76,81–88,88–92]. The low temperature of Titan (the temperature ranges from 70 to 100 K [83]) and relatively high pressure (1.5 bar) favor the formation of the CH_4-N_2 van der Waals complexes in stable configurations. In particular, van der Waals complexes CH_4-N_2 could manifest themselves in non-resolved diffuse contours of collision-induced absorption spectra of the molecules CH_4 and N_2. In the present work we consider the molecules CH_4 $({}^1A_1)$ and N_2 $({}^1\Sigma_g^+)$ in their ground electronic state.

Chapter 3

Potential energy

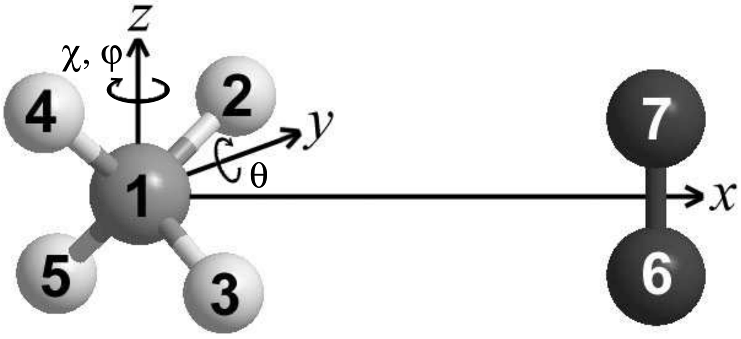
One of the most important characteristics of the complex is its potential energy surface (PES). Earlier, the PES of the CH_4-N_2 complex was investigated only in two works [77, 78]. In a pioneering work [77] this PES was obtained by self-consistent field calculations and Monte Carlo simulations. But it is worth noting that the basis sets employed are not large enough for the description of the interactions in van der Waals systems. Moreover, the basis set superposition error (BSSE) and the basis set incompleteness error (BSIE) were not taken into account. The calculations in Ref. [77] were carried out for 6 geometries of the complex and among them the most stable geometry was found. Recently, M. Shadman *et al.* [78] obtained a PES of the complex calculated at the second-order Møller-Plesset (MP2) level of theory with BSSE and BSIE corrections. The BSIE correction in this work was accounted by means of calculations with aug-cc-pVXZ (X = 2, 3, 4) [17] basis sets. But it should be noted that the aug-cc-pVQZ basis set gives results which are generally still too far from convergence for many weakly bound complexes. The MP2 method accounts for the electron correlation and is the most simple one required for the description of such systems. The calculations in Ref. [78] were carried out for a wide range of intermolecular distances R (5.0—20.0 a_0) for 12 geometries of the complex. The large step (0.5 a_0) used in the vicinity of equilibrium separation results in significant errors in the evaluation of the binding energy of the complex. In [78] the authors also found (among the investigated geometries) the geometry corresponding to the deepest potential well. But it draws attention that the stable configurations found in [78] and in [77] are different. It should be noted, that all these calculations [77, 78] were carried out in the approximation of rigid interacting molecules. But, in reality, the molecules in the complex undergo distortions while interacting with each other.

At present it is known, that the most suitable method for calculating the energy of complexes is the coupled cluster method with singles and double excitations and noniterative correction to triple excitations (CCSD(T)). But the MP2 method can also be used as a compromise between accuracy and computational costs. However, there are no calculations for this complex at the CCSD(T) level of theory. In this work we have carried out the PES calculations both at the MP2 and more advanced CCSD(T) levels of theory. The main object of investigation in this work is the van der Waals CH_4-N_2 complex and its stable configurations.

3.1 Coordinate system

In the present work, for the description of the complex a Cartesian coordinate system was used (see Fig. 3.1). The origin of this coordinate system is placed on the carbon atom of the methane molecule. The vector $\boldsymbol{R}$ is directed from the carbon atom to the center of N_2 bond length and has the components (R, 0, 0). The rotation of the methane (A) molecule in this coordinate system is determined by 3 Euler angles: 1) rotation of angle χ_A around the z-axis; 2) rotation of angle θ_A around the y-axis; 3) rotation of angle φ_A around the z-axis. The rotation of the nitrogen (B) molecule can be discribed by 2 additional Euler angles: 1) rotation of angle θ_B around the y-axis; 2) rotation of angle φ_B around the z-axis. The initial position of the molecules in the CH_4-N_2 complex, corresponding to the Euler angles $\chi_A = \theta_A = \varphi_A = \theta_B = \varphi_B = 0°$, is presented in Fig. 3.1. In this figure the axis of the N_2 molecule is parallel to the z-axis in the coordinate system of the complex and the CH_4 molecule has the standard orientation: the carbon atom is at the origin (0, 0, 0) and hydrogen atoms have the coordinates (c, c, c), (c,-c,-c), (-c,-c, c) and (-c, c,-c), where $c = r_{CH}/\sqrt{3}$.

FIG. 3.1 - *Coordinate system of the CH_4-N_2 complex*

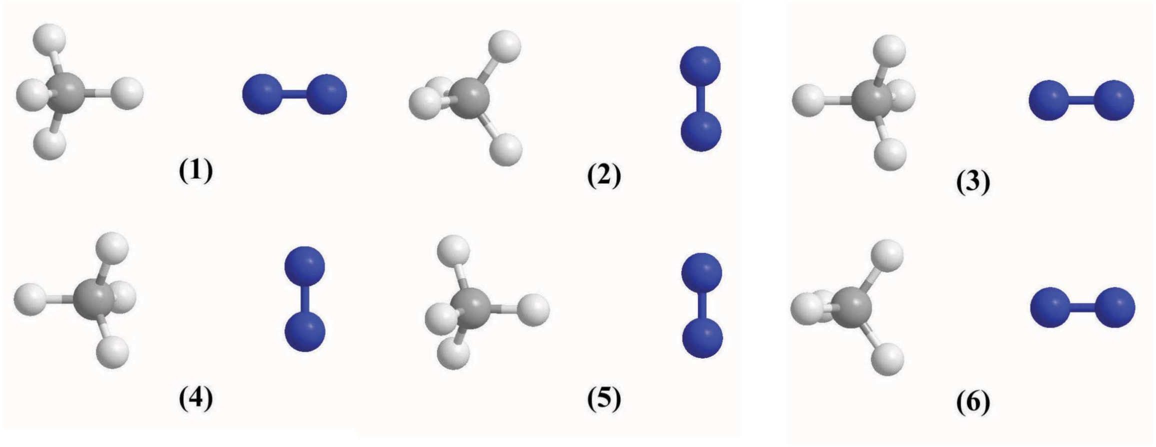


The geometries of the monomers CH_4 and N_2 were optimized at the CCSD(T) level of theory using the aug-cc-pVTZ correlation consistent basis set. The equilibrium bond lengths (r_e) and bond angles for the CH_4 molecule were found to be $r_{CH} = 2.0596\ a_0$ and $\theta_e = 109.4712°$ (the angle for a tetrahedral molecule) and the bond length for the N_2 molecule is $r_{NN} = 2.0864\ a_0$, which are in a good agreement with the values deduced from the experiment ($r_{CH} = 2.0498\ a_0$ [93], $r_{NN} = 2.0742\ a_0$ [94]).

3.2 Potential energy surface

The calculations were carried out for the set of configurations of the CH_4-N_2 complex (some general configurations are presented in Fig. 3.2) which can be characterized by 5 Euler angles $\chi_A, \theta_A, \varphi_A, \theta_B$ and φ_B. For these configurations the value of R has been varied within the range $5.67 - 189.0\ a_0$. This choice of distances covers both the long range attractive and short range repulsive regions of interaction in the CH_4-N_2 complex.

FIG. 3.2 - *Geometries of the CH_4-N_2 complex*



TAB. 3.1 - *Equilibrium distance R_e and interaction energy $\Delta E(R_e)$ for different configurations calculated at the CCSD(T)/aug-cc-pVTZ level of theory with BSSE correction. All angles are in Deg.*

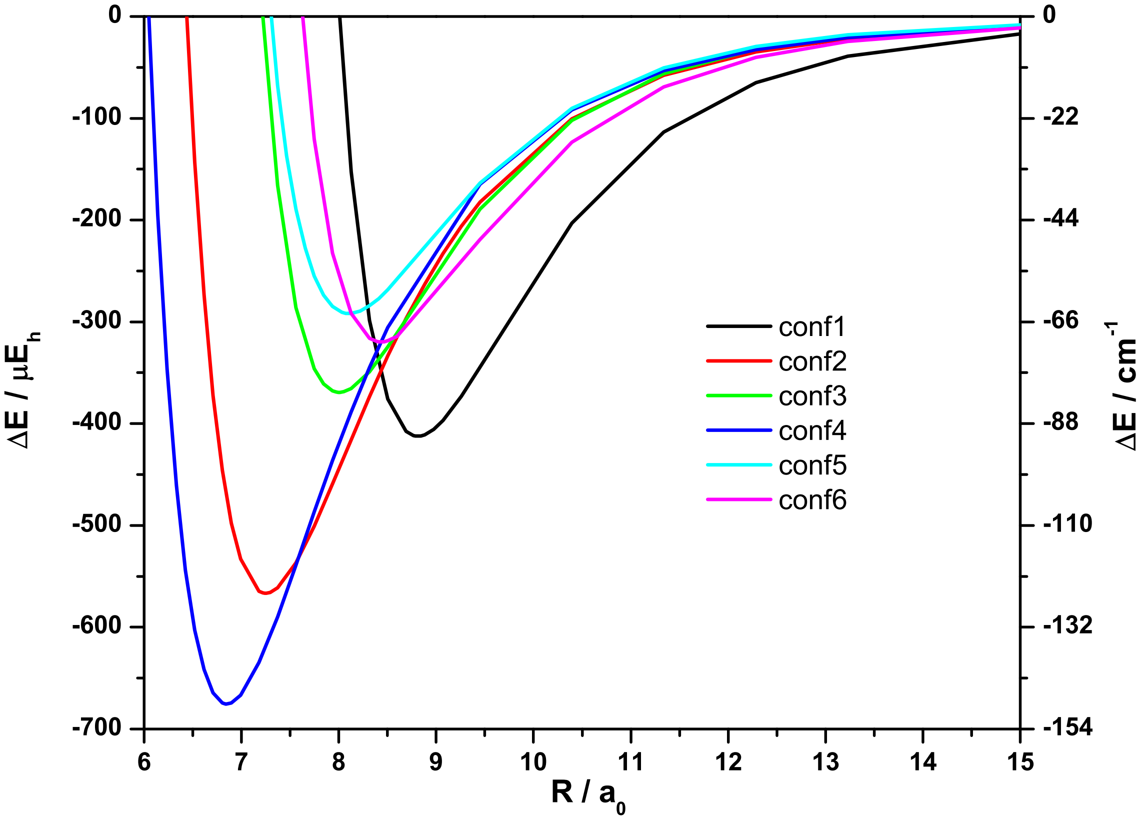
Configuration	χ_A	θ_A	φ_A	θ_B	φ_B	R_e, a_0	$\Delta E(R_e)$ (μE_h)
1	90	45	t	90	0	8.81	-412.251
2	0	45	90	0	0	7.26	-566.445
3	0	45	t	90	0	8.01	-369.226
4	0	45	t	0	0	6.84	-675.375
5	90	45	t	0	0	8.11	-291.741
6	0	45	90	90	0	8.43	-319.591

Here $t = (180/\pi)\arcsin(1/\sqrt{3})$.

In general, we have calculated 800 points on the PES at the CCSD(T) level of theory and 1000 points at the MP2 level (the coupled-cluster results are presented in Appendix V). The interaction energy ΔE as a function of the intermolecular distance R for 6 major configurations of the complex (Fig. 3.2) is plotted in Fig. 3.3. In Table 3.1 we present the equilibrium distance R_e and interaction energy $\Delta E(R_e)$ for these configurations calculated at the CCSD(T)/aug-cc-pVTZ level of theory with BSSE correction. It is seen from Fig. 3.3 and Table 3.1 that the potential well corresponding to the configuration 4 is the deepest one which is in a good agreement with [77]. But there is a discrepancy with the results from [78] where it was found that the deepest potential well corresponds to configuration 1-C, which can be obtained from configuration 4 by rotation of the N_2 molecule of angle 30° around the x-axis. Thus, to clarify the situation we have investigated the most stable configurations of the CH_4-N_2 complex in more detail (see next Section).

Moreover, some additional analytical calculations of the interaction energy surface of the

Fig. 3.3 - Ab initio *calculations at the CCSD(T)/aug-cc-pVTZ level of theory with BSSE correction of interaction energies of the* CH_4*-*N_2 *complex in different configurations (the numbers 1-6 are the numbers of the configurations from Fig. 3.2).*



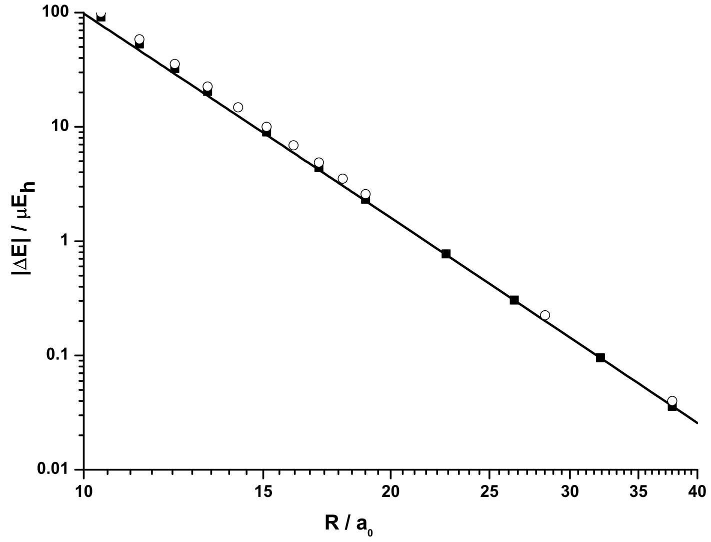
complex for large R have been carried out for the comparison of the *ab initio* theoretical methods used in this study. According to Eq. 2.8, 2.47 and 2.12 the contribution to the interaction energy ΔE of the complex CH_4-N_2 (taking the symmetry of molecules into account: $\Theta^A_{\alpha\beta} = \Omega^B_{\alpha\beta\gamma} = \beta^B_{\alpha\beta\gamma} = A^B_{\alpha,\beta\gamma} = D^B_{\alpha,\beta\gamma\delta\varepsilon} = 0$) at large intermolecular separations restricting ourselves to the order R^{-7} is determined by electrostatic and dispersion interactions:

$$\Delta E = E^{AB}_{elect} + E^{AB}_{disp}, \tag{3.1}$$

with the electrostatic energy

$$E^{AB}_{elec} = -\frac{1}{45} Q^B_{\alpha\beta} \Omega^A_{\gamma\delta\nu} T_{\alpha\beta\gamma\delta\nu} + \frac{1}{315} Q^B_{\alpha\beta} \Phi^A_{\gamma\delta\nu\varepsilon} T_{\alpha\beta\gamma\delta\nu\varepsilon} \tag{3.2}$$

FIG. 3.4 - *R-dependence of the interaction energy (in decadic logarithmic scale) of the CH_4-N_2 complex in configuration 4. Solid line - calculation using analytic formula (3.2); squares -* ab initio *calculation at the CCSD(T)/aug-cc-pVTZ level of theory with BSSE correction; circles -* ab initio *calculation at the MP2/aug-cc-pVTZ level of theory with BSSE correction.*



and dispersion energy

$$E_{disp}^{AB} = -\frac{1}{2\pi}T_{\alpha\beta}T_{\gamma\delta}\int_0^\infty \alpha_{\alpha\gamma}^A(i\omega)\alpha_{\beta\delta}^B(i\omega)d\omega$$
$$-\frac{U^AU^B}{6(U^A+U^B)}T_{\alpha\beta}T_{\gamma\delta\nu}(\alpha_{\alpha\gamma}^A A_{\beta,\delta\nu}^B - A_{\beta,\delta\nu}^A\alpha_{\alpha\gamma}^B). \tag{3.3}$$

The imaginary frequency-dependent polarizabilities were obtained from the values of excitation energies and oscillator strengths reported in Refs. [98] and [99] for the CH_4 and N_2 molecule, accordingly. The values of the molecular parameters used for the analytical calculation of the interaction energy ΔE by Eqs. 3.2 and 3.3 are listed in Table 8.2 (see Appendix IV). The leading terms in Eqs. 3.2 and 3.3 are $Q^B\Omega^A$ and $\alpha^A\alpha^B$ ($\sim R^{-6}$). Particularly, for configuration 4, which has the deepest potential well, the interaction energy of the CH_4-N_2 complex takes the form (R is in a_0):

$$\Delta E = -\frac{107.61E_h a_0^6}{R^6} + \frac{95.73E_h a_0^7}{R^7}. \tag{3.4}$$

The analysis of Eqs. 3.1–3.3 shows that the contribution of dispersion interaction to ΔE is the most important. More precisely, the contribution to the leading term in Eq. 3.4 of dispersion interaction is $-91.95E_h a_0^6/R^6$, while the contribution of electrostatic interaction is only $-15.66E_h a_0^6/R^6$. It should be noted that analytical Eqs. 3.1–3.3 describe very well the interaction energy of the complex at large R. Indeed, the analytically calculated averaged value of the dispersion coefficient $C_6 = 97.26\ E_h a_0^6$ is very close to the calculated one $C_6 = 96.92\ E_h a_0^6$ in Ref. [98]. The calculated *ab initio* interaction energies ΔE for configuration 4 at the CCSD(T) and MP2 levels of theory and the analytical ΔE are plotted in Fig. 3.4 in decadic logarithmic scale (log_{10}, only the scale is logarithmic, the values are the standard: $10 < R < 40\ a_0$, $0.01 < |\Delta E| < 100\ \mu E_h$). The coefficients C_6, C_7, etc. for the configuration 4 will be determined later using nonlinear least-square fitting (see Chapter 3.4). The figure 3.4 shows that the CCSD(T) level of theory provides better agreement with the theoretical dependance of the interaction energy at long-range intermolecular separation R than the MP2 one.

Moreover, there is an interest to check the SAPT method on the CH_4-N_2 complex, as it is less time and CPU consuming in comparison with the CCSD(T) method. The results of the calculations at the CCSD(T)(BSSE is accounted) and SAPT methods (both HF and DFT) with aug-cc-pVTZ basis set for configurations 1 and 4 are presented at Fig. 3.5. The Fig. 3.5 shows that HF-SAPT method better describes the whole interaction potential energy of the complex under investigation (for each task there are different grid points for the calculation) than the DFT-SAPT method (the most commonly used functional PBE0 and B3LYP were employed). This can be explained by the fact, that the use of the approximate exchange-correlation functionals for construction of the mono-electron potential in the DFT theory (employed as a starting point in DFT-SAPT calculations) gives no guarantee that the approximation used contains subtle effects for proper description of dispersion forces. There is a difference ($\sim$ 2-3 %) between the values obtained at the CCSD(T) and SAPT calculations. Therefore, if the accuracy of HF-SAPT calculations is acceptable for an arbitrary purpose, one can use these methods for the calculation of the whole PES of this complex. One of the advantages of the HF-SAPT method is that it provides the contribution of each type of interaction (E_{ind}, E_{disp}, etc.) separately. The induction and dispersion contributions to the energy for configuration 4 of the CH_4-N_2 complex calculated using the HF-SAPT method and analytical expressions Eqs. 3.2–3.3 are plotted at Fig. 3.6. A small discrepancy between the results obtained at the HF-SAPT method and using analytical expressions could be due to the fact that we have accounted in Eqs. 3.2–3.3 only for the terms up to R^{-7}, while the HF-SAPT method accounts also for higher-order terms.

Generally, the interaction energy not only depends on the intermolecular separations R but also on the mutual orientation of the CH_4 and N_2 molecules in the complex. Fig. (3.7) illustrates the dependence of the interaction energy of the complex on the angles θ_A and θ_B. While computing, all other geometric parameters were kept constant as in the equilibrium geometry 4.

3.3 Potential energy of the most stable configuration

In this Section, to solve the problem of finding the most stable configuration, we have accurately investigated the configuration 4 from Ref. [77] and the configuration 1-C from Ref. [78]. For this purpose we have carried out the calculations of the interaction energy of the CH_4-N_2 complex versus the angle τ (Fig. 3.2) of which the N_2 molecule rotates around x-axis in the CH_4-N_2 complex. The configurations of the complex obtained by rotation of the angle τ will be designated by C_τ. Note, that at $\tau = 0°$ we have the geometry 4 (or geometry C_0) and the rotation of N_2 of the angle $\tau = 30°$ corresponds to configuration 1-C (or geometry C_{30}). There is the following relation between the new angle τ and Euler angles: the rotation of angle τ corresponds to the rotation of Euler angles $\theta_B = \tau$ and $\varphi_B = 90°$.

TAB. 3.2 - *Interaction energies ΔE (in μE_h) calculated at the CCSD(T) level with aug-cc-pVTZ basis set with BSSE correction for configuration C_τ ($\tau = 0° - 30°$).*

R, a_0	τ (Deg)						
	0	5	10	15	20	25	30
6.43	-544.22	-544.21	-544.19	-544.15	-544.11	-544.08	-544.06
6.61	-641.73	-641.72	-641.70	-641.68	-641.65	-641.63	-641.61
6.71	-664.45	-664.44	-664.43	-664.41	-664.38	-664.37	-664.35
6.80	-674.40	-674.39	-674.38	-674.36	-674.34	-674.33	-674.31
6.90	-674.37	-674.37	-674.35	-674.34	-674.32	-674.31	-674.30
6.99	-666.58	-666.57	-666.56	-666.54	-666.53	-666.51	-666.51
7.18	-634.68	-634.68	-634.67	-634.66	-634.65	-634.63	-634.63
7.34	-589.71	-589.71	-589.70	-589.69	-589.67	-589.67	-589.68
7.56	-538.87	-538.87	-538.86	-538.85	-538.84	-538.84	-538.84
8.50	-305.27	-305.27	-305.27	-305.27	-305.27	-305.27	-305.27
9.45	-164.84	-164.84	-164.84	-164.84	-164.84	-164.85	-164.85
10.39	-91.51	-91.51	-91.51	-91.51	-91.51	-91.51	-91.51
11.34	-53.21	-53.21	-53.21	-53.21	-53.21	-53.21	-53.21
13.23	-20.45	-20.45	-20.45	-20.45	-20.45	-20.46	-20.46
15.12	-9.00	-9.00	-9.00	-9.00	-9.00	-9.00	-9.00
17.00	-4.37	-4.37	-4.37	-4.37	-4.37	-4.37	-4.37
18.90	-2.29	-2.29	-2.29	-2.29	-2.29	-2.29	-2.29

Calculations of ΔE for configuration C_τ (τ was varied from 0° to 30° by 5°) of the CH_4-N_2 complex at the MP2 and CCSD(T) levels of theory were carried out. The chosen range of angles τ is enough to describe the nonequivalent configurations of the complex in accordance with its symmetry. The calculated interaction energies ΔE at the CCSD(T) level of theory with the aug-cc-pVTZ basis set using the BSSE correction are presented in Table 3.2. The BSSE correction is the same for all configurations C_τ. It is seen from the table, that for all R and τ the difference in ΔE does not exceed 0.16 μE_h ($\sim$0.04 cm^{-1}) (the convergence of CCSD(T) calculations is $10^{-7}E_h$). As the difference in ΔE is less than any energy in the ground vibrational state of the CH_4-N_2 complex, all configurations C_τ should be considered as a family of the most stable configurations of the complex. From this point of view, configuration 4 from Ref. [77] and configuration 1-C from Ref. [78], which belong to the family of configurations C_τ, are both the most stable.

Note also that the difference in interaction energies for configuration 1-B (in our notation, configuration C_0) and configuration 1-C (or configuration C_{30}) obtained in Ref. [78] at $R = 6.5$ a_0 is 203.03 μE_h, which is in disagreement with our previous statement. That is why we have carried out additional calculations of the interaction energy of the CH_4-N_2 complex being in these configurations with the same geometric parameters and level of theory (MP2 level with BSSE and BSIE corrections) as in Ref. [78]. The results of the calculation are presented in Table 3.3. It is seen from the table that in this case the values of ΔE for the both configurations practically coincide for Martin's and Helgaker's methods accounting for BSIE when the larger basis set is used. The larger is the basis set, the closer are the extrapolated interaction energies using different extrapolation methods.

It should be noted that the same behavior of the interaction energy ΔE is obtained when calculating it with the use of analytical Eqs. 3.1–3.3. The analysis of these expressions shows that the coefficients in Eq. 3.4 are constant for all angles τ, and, as a result, analytical interaction energy does not depend on the angle τ.

One of the important criteria of the complex stability is its binding energy (BE). In order to accurately evaluate BE one should account for the BSSE, BSIE corrections and correction of the nonrigidity of the molecules in the complex. To obtain the BSIE correction, the calculations were carried out at the MP2 and CCSD(T) levels of theory (with BSSE correction) using four CBS extrapolation schemes Eqs. 1.77–1.80. The nonrigidity correction ΔE_{nr} was accounted by substracting the binding energy calculated in the CBS limit for configuration C_{30} with the rigid molecules from the BE in CBS limit for the fully optimized (at the MP2/aug-cc-pVTZ level of theory) configuration C_{30}. The parameters of the rigid and nonrigid complex being in configuration C_{30} are given in Table 3.4. The total binding energy of the complex can be calculated as follows:

$$\mathtt{BE} \;=\; \mathtt{BE}_r + \Delta\mathtt{BSIE}_r + \Delta\mathrm{E}_{nr}, \tag{3.5}$$

where BE_r is the binding energy of the complex with rigid molecules, calculated without the BSIE correction; $\Delta\mathrm{BSIE}_r$ is the BSIE correction for the case of rigid molecules; ΔE_{nr} is the correction on the nonrigidity of the molecules in complex to the BE. In Table 3.5 the contribution of different corrections to the total BE of the complex being in configuration C_{30} is presented. As it is seen from the Table 3.5, the BSSE correction gives the biggest contribution to the BE and the nonrigidity correction is higher than the BSIE one. Tables 3.3 and 3.5 show that the closest energies are obtained when Martin's and Helgaker's extrapolation schemes are used. But the convergence of the interaction energies to the CBS limit is better for the Helgaker's extrapolation scheme due to the separate extrapolation of the HF and correlation energies. Finally, the calculated values of BE at the MP2 level of theory with aug-cc-pVXZ (X = 3, 4, 5) basis sets are the following: -938.520 μE_h for Martin's extrapolation scheme (Eq. 1.79) and -942.373 μE_h for Helgaker's scheme (Eq. 1.80). These values can be improved by replacing $\mathrm{BE}_r^{CBS} = \mathrm{BE}_r + \Delta\mathrm{BSIE}_r$ in Eq. 3.5 calculated at the MP2 level of theory by BE_r^{CBS} calculated at the CCSD(T) level (with aug-cc-pVXZ basis set, where X = 2, 3, 4). Thus, the recommended values of the binding energy of the complex are: -820.536 μE_h for CBS extrapolation scheme of Martin and -827.143 μE_h for CBS extrapolation scheme of Helgaker.

It is also of interest to investigate the BSIE effect on the interaction energy $\Delta E(R)$ of the complex being in the most stable configuration, for example, for configuration 4. In the calculations, the BSIE correction was carried out using the CBS extrapolation schemes of Martin and Helgaker Eqs. 1.79–1.80 as we believe them to be more reliable. The results of the calculations at the MP2 and CCSD(T) levels of theory are presented at Fig. 3.8. We have investigated the convergence of interaction energies to the CBS limit for the MP2 (X = 2, 3, 4, 5) and CCSD(T) (X = 2, 3, 4) levels and found out that the CCSD(T) level with aug-cc-pVXZ up to X = 4 is enough for the evaluation of the interaction energy as there is good convergence to the CBS limit; as for the calculation at the MP2 level with aug-cc-pVXZ up to X = 5 there is high convergence to the CBS limit. The Fig. 3.8 shows that the CBS limit for the MP2 level is too far from the CBS limit for the CCSD(T) level of theory and it overestimates the interaction energy.

3.4 Analytical representation of the interaction potential of the most stable configuration

For some applications there is a particular interest in the analytical representation of the interaction energy ΔE. With the help of this analytical function one can easily calculate, for example, the second virial coefficient B_2. In the present work, for the most stable geometriy C_0, we used the simple but popular Lennard-Jones potential and the more correct modified Esposti-Werner potential [95]. In our work all parameters for these potentials were fitted using the Mathematica software [97] for nonlinear least-square fitting. The best-fit curve is often assumed to be that which minimizes the sum of squared residuals. This is the (ordinary) least squares approach. However, in cases where the dependent variable does not have constant variance a sum of weighted squared residuals may be minimized. Each weight should ideally be equal to the reciprocal of the variance of the observation, but weights may be recomputed on each iteration, in an iteratively weighted least squares algorithm. In Mathematica the weighted least squares are implemented.

The fitting was done for the Lennard-Jones potential

$$\Delta E(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right] \tag{3.6}$$

to 42 *ab initio* points, calculated at the CCSD(T)/aug-cc-pVTZ level of theory (with the BSSE and without the BSIE correction), with a satisfactory agreement. In Eq. 3.6 ϵ and σ are the depth of the the potential well and the effective interaction diameter (the distance at which the potential is zero), respectively. The fitting parameters are defined as $\sigma = 6.01868\ a_0$ and $\epsilon = 645.782\ \mu E_h$ (the estimated error variance in the fitting is $1.41 \cdot 10^{-3}$).

A better agreement was obtained by fitting to the same *ab initio* data for the Grimme-Esposti-Werner potential (we have combined the short-range potential of Esposti-Werner [95] and long-range potential of Grimme [96]):

$$\Delta E(R) = \exp^{-a(R-R_0)} \sum_{i=0}^{3} g_i R^i - s \frac{1}{1 + e^{-b(R-R_0)/R_0}} \sum_{i=6}^{10} \frac{C_i}{R^i}, \tag{3.7}$$

where s is a global scaling factor (in our work it is set to 1.28); R_0 is the sum of van der Waals radii of interacting species. In the approximation that we have point interacting molecules (we consider the long-range dispersion interactions neglecting the shape of the molecules), we have estimated the van der Waals radius $R_0^{A,B}$ for each molecule through the molecular polarizability:

$$R_0^{A,B} = \frac{3}{4\pi} (\alpha^{A,B})^{\frac{1}{3}}. \tag{3.8}$$

For the molecules CH_4 and N_2 we obtain $R_0^A = 3.44\ a_0$ and $R_0^B = 3.04\ a_0$.

All fitting parameters a, b, g_i and C_i obtained using Levenberg-Marquardt method for the suggested potential Eq. 3.7 are presented in Table 3.6. The estimated error variance in our fitting is $4.56 \cdot 10^{-9}$. We should point out that the fitting coefficient C_6=107.327 $E_h \cdot a_0^6$ is very close to the one calculated analytically using Eq. 3.3 (C_6=107.61 $E_h \cdot a_0^6$).

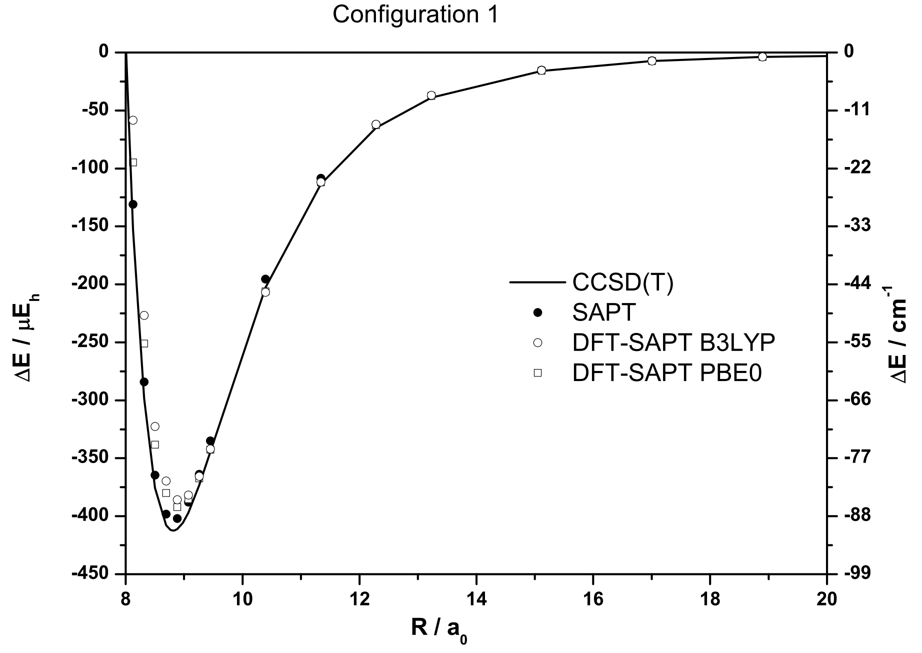
Fig. 3.9 illustrates the efficiency of the analytical interaction potentials Eqs. 3.6 and 3.7 in comparison with the *ab inito* interaction potential. It is seen that potential Eq. 3.7 better describes *ab initio* calculations.

3.5 Frequency calculations

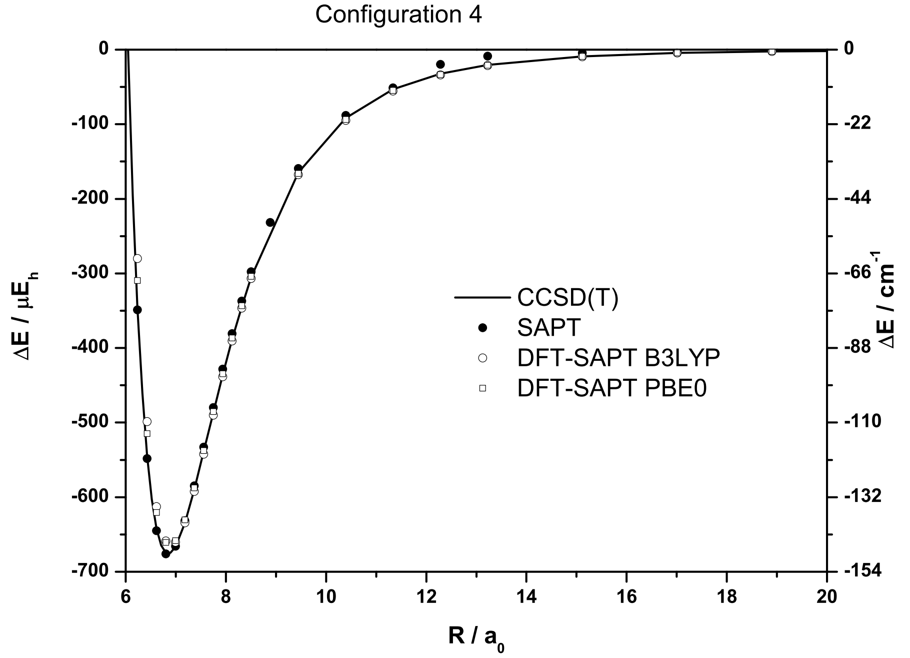
In this study we have calculated at the MP2/aug-cc-pVTZ level of theory the harmonic frequencies (Table 3.7) for a set of the most stable configurations C_τ. In Gaussian [34] harmonic vibrational frequencies are computed by determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates. This transformation is only valid at a stationary point. It is seen from Table 3.7 that the frequencies, except for the lowest one, are changing slightly for these configurations. Here, the modes from 1 to 5 are the intermolecular, the modes 6–10 and 12–15 are the vibrational modes for the CH_4 molecule and the 11th mode is the vibration of the N_2 molecule. As the symmetry of the CH_4 molecule in the complex becomes lower due to the deformations, its degenerate vibrational energy levels are splitted. For this reason all vibrational modes of CH_4 and N_2

molecules in the complex are IR active. In the CH_4-N_2 complex there are vibrational frequency shifts $\Delta\omega = \omega^{mon} - \omega^{com}$ (here, ω^{mon} and ω^{com} are the harmonic frequencies of the monomer and of the complex, respectively, calculated at the MP2/aug-cc-pVTZ level) which are presented in Table 3.8 for configuration 4. As follows from Table 3.8, there is a small tendency of the intramolecular vibrational frequencies of CH_4 and N_2 to a red shift. Analogous shift tendency is observed for all configurations C_τ. The fully automated code to build the anharmonic constants used in a second-order perturbative method of V. Barone [105] implemented in Gaussian 03 was employed to calculate the anharmonic frequencies of the CH_4-N_2 complex. The calculated anharmonic frequencies for the fundamental bands of the complex being in the geometry 4 are presented in Table 3.8. Due to the large error of intermolecular anharmonic frequency calculations, these frequencies are not given in Table 3.8. The calculated rotational constants are also presented in this table. It is noteworthy that the CH_4-N_2 complex is almost a prolate symmetric top as follows from the analysis of rotational constants. Indeed, the asymmetry parameter $K = (2B - A - C)/(A - C)$ = -0.99 almost equals to -1 which corresponds to a prolate symmetric top.

FIG. 3.5 - *R-dependence of the interaction energy of the CH_4-N_2 complex (a - configuration 1, b - configuration 4). Solid line - calculations at the CCSD(T)/aug-cc-pVTZ level of theory with BSSE correction; black circles - calculations at the SAPT/aug-cc-pVTZ level of theory; white squares - calculations at the DFT-SAPT/aug-cc-pVTZ level with PBE0 functional; white circles - calculations at the DFT-SAPT/aug-cc-pVTZ level with B3LYP functional.*

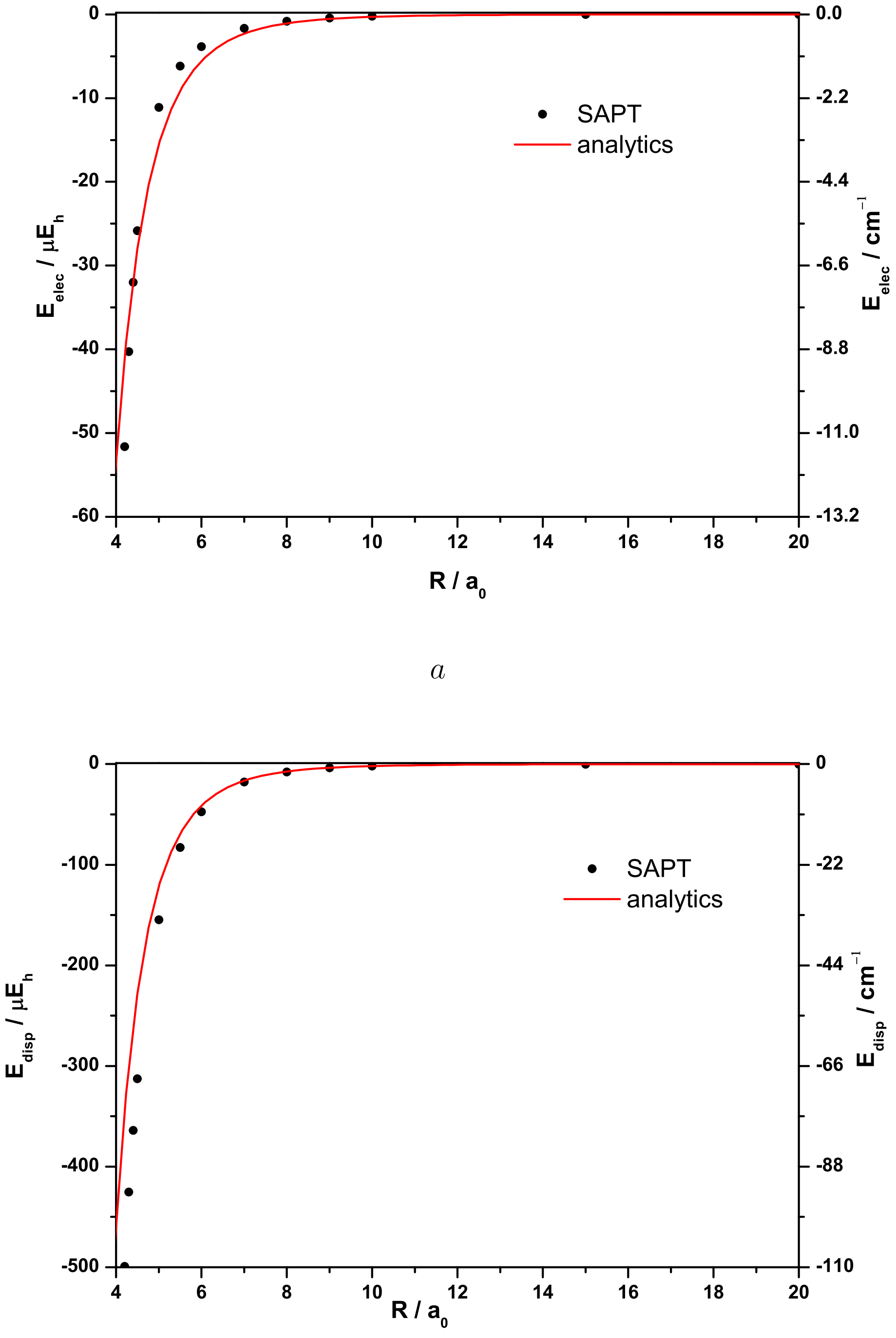


a



b

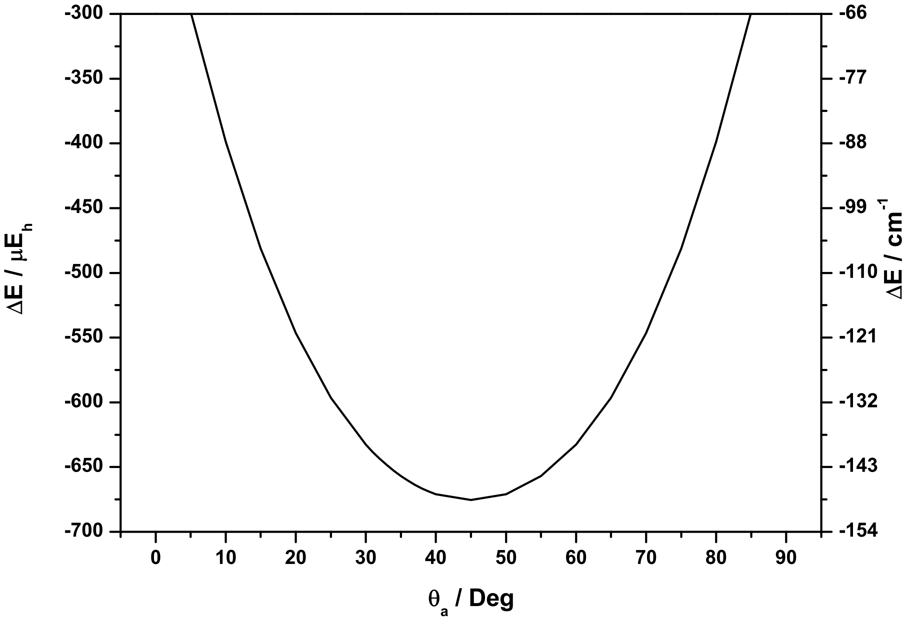
FIG. 3.6 - *Induction (E_{elec} - a) and dispersion (E_{disp} - b) contributions to the potential energy of the configuration 4 of the CH_4-N_2 van der Waals complex calculated at the HF-SAPT method and using analytical Eqs. 3.2–3.3. All values are in a.u.*



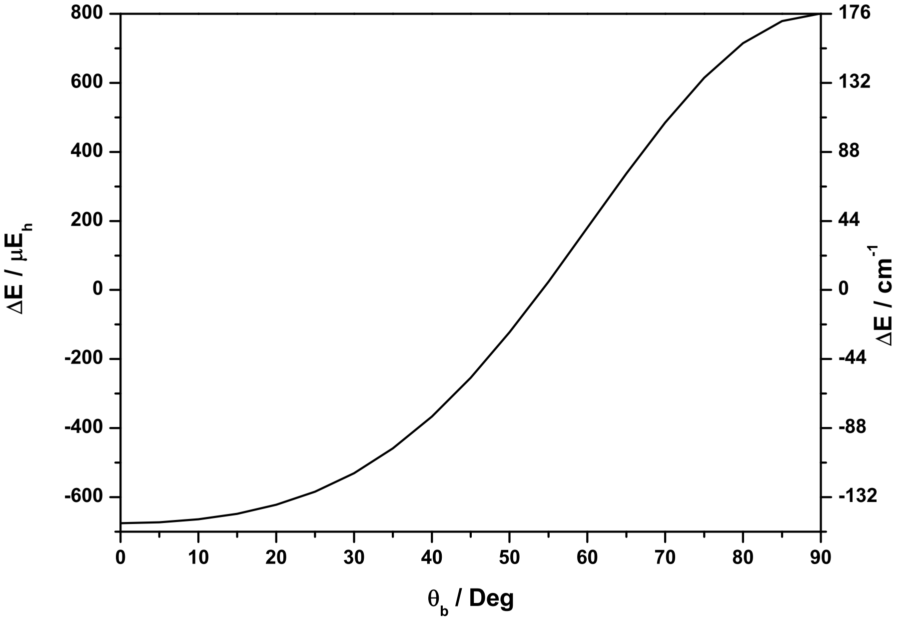
a

b

FIG. 3.7 - *θ_A-dependence (a) and θ_B-dependence (b) of the interaction energy of the CH_4-N_2 complex (the values of other Euler angles and distances r_{CH}, r_{NN}, R_e correspond to the equilibrium geometry 4).*



a



b

TAB. 3.3 - *Interaction energy ΔE_{CBS} (in μE_h) at $R = 6.5\ a_0$ with BSIE correction (see Eqs. 1.77–1.80) for configuration C_τ ($\tau = 0°$, $30°$)[†] of the CH_4-N_2 complex calculated at the MP2 level of theory with BSSE correction.*

τ (Deg)	ΔE_{CBS} (Feller)		ΔE_{CBS} (Truhlar)		ΔE_{CBS} (Martin)		ΔE_{CBS} (Helgaker)		ΔE_{CBS}
	$X = 2, 3, 4$	$X = 3, 4, 5$	$X = 2, 3, 4$	$X = 3, 4, 5$	$X = 3, 4$	$X = 4, 5$	$X = (2), 3, 4$	$X = (3), 4, 5$	Ref. [78]
0	-817.089	-833.279	-849.831	-848.826	-826.525	-836.776	-835.999	-842.480	-844.47
30	-817.215	-833.181	-849.970	-848.598	-826.642	-836.730	-836.278	-841.755	-1047.50

[†] The geometric parameters were chosen as in Ref. [78].

TAB. 3.4 - *Optimized bond lengths (in a_0) and angles (in Deg) for configuration C_{30} with and without nonrigidity of the molecules (the optimization has been carried out using the MP2/aug-cc-pVTZ level of theory with BSSE correction).*

Parameters	Nonrigid molecules	Rigid molecules
$r_{(C1-H2)}$	2.0534	2.0577
$r_{(C1-H3)}$	2.0577	2.0577
$r_{(C1-H4)}$	2.0577	2.0577
$r_{(C1-H5)}$	2.0526	2.0577
$r_{(N6-C1)}$	6.8259	6.8336
$r_{(N7-N6)}$	2.1057	2.0864
∠ H2-C1-H3	109.4347	109.4712
∠ H2-C1-H4	109.4347	109.4712
∠ H2-C1-H5	109.5013	109.4712
∠ H2-C1-N6	79.2385	79.3095
∠ C1-N6-N6	81.6445	81.2193
∠ H3-H2-C1-H4	109.6170	109.4712
∠ H3-H2-C1-H5	109.4199	109.4712
∠ H3-H2-C1-N6	66.4122	66.3350
∠ H2-C1-N6-N7	0.0000	0.0000

TAB. 3.5 - *The BE and contributions of the corrections to the BE (in μE_h) for configuration C_{30} of the CH_4-N_2 complex.*

Extrapolation Scheme	Total BE	$\mathrm{BE}_r{}^{\mathrm{a}}$	ΔBSSE	$\Delta\mathrm{BSIE}_r$	ΔE_{nr}
Feller [27]	-979.143	-776.818	374.011	-62.807	-139.519
Truhlar [28]	-1014.007	-776.818	374.011	-88.029	-149.160
Martin [29]	-938.520	-776.818	374.011	-76.126	-85.576
Helgaker [30]	-942.373	-776.818	374.011	-79.985	-85.570

TAB. 3.6 - *Fitted parameters for the Grimme-Esposti-Werner potential for configuration 4. All values are in a.u.*

a	1.17031	C_6	-107.327
b	28.0921	C_7	9139.9
g_0	0.0247961	C_8	-144612
g_1	-0.0081538	C_9	843213
g_2	0.000895235	C_{10}	$-1.68617 \cdot 10^6$
g_3	-0.0000371771		

FIG. 3.8 - *Interaction energies* ΔE *of the* CH_4*-*N_2 *complex for configuration 4. Black color - calculation at the CCSD(T) level of theory; red color - calculation at the MP2 level of theory; solid line - calculation using aug-cc-pVTZ basis set; circles - CBS extrapolation scheme of Martin (Eq. 1.79) with aug-cc-pVXZ (*$X = 2, 3$ *for the CCSD(T) level and* $X = 3, 4$ *for the MP2 one); triangles - CBS extrapolation scheme of Martin (Eq. 1.79) with aug-cc-pVXZ (*$X = 3, 4$ *for the CCSD(T) level and* $X = 4, 5$ *for the MP2 one); dash line - CBS extrapolation scheme of Helgaker (Eq. 1.80) with aug-cc-pVXZ (*$X = (2), 3, 4$*); squares - CBS extrapolation scheme of Helgaker (Eq. 1.80) with aug-cc-pVXZ (*$X = (3), 4, 5$*).*

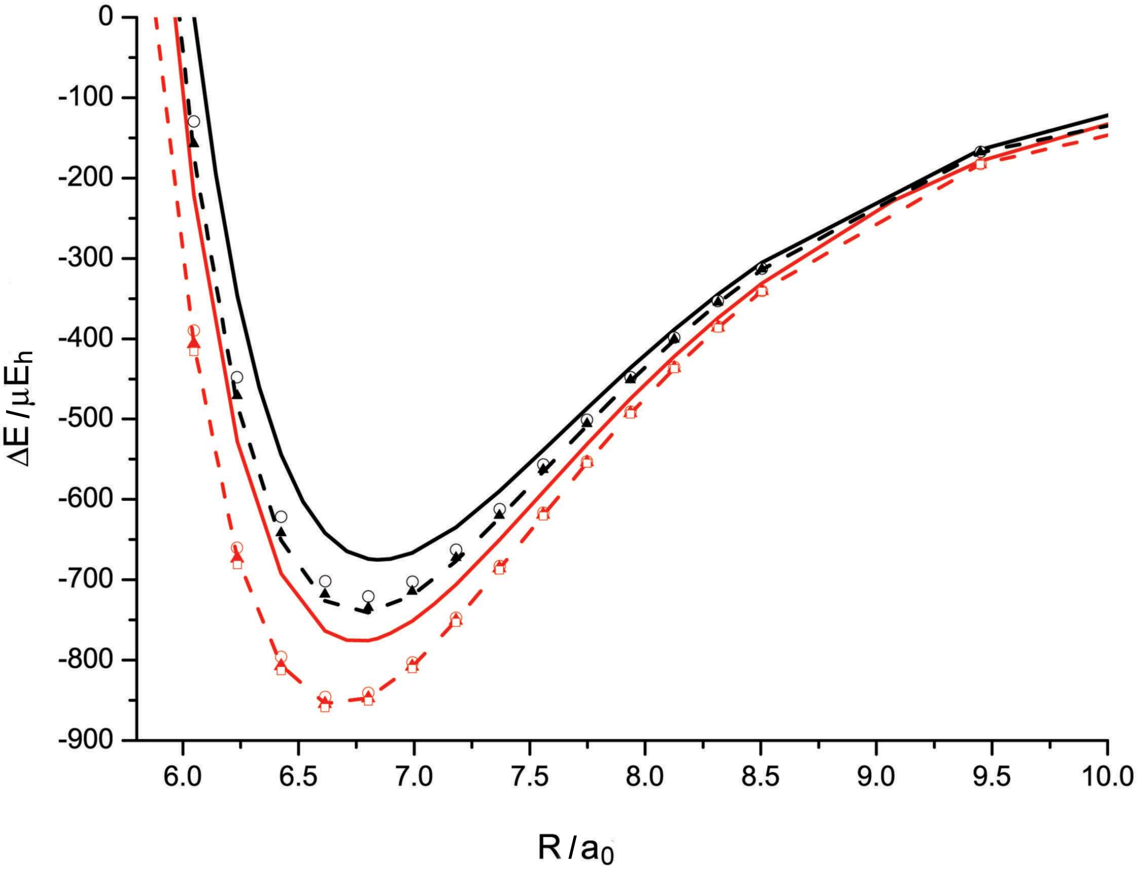
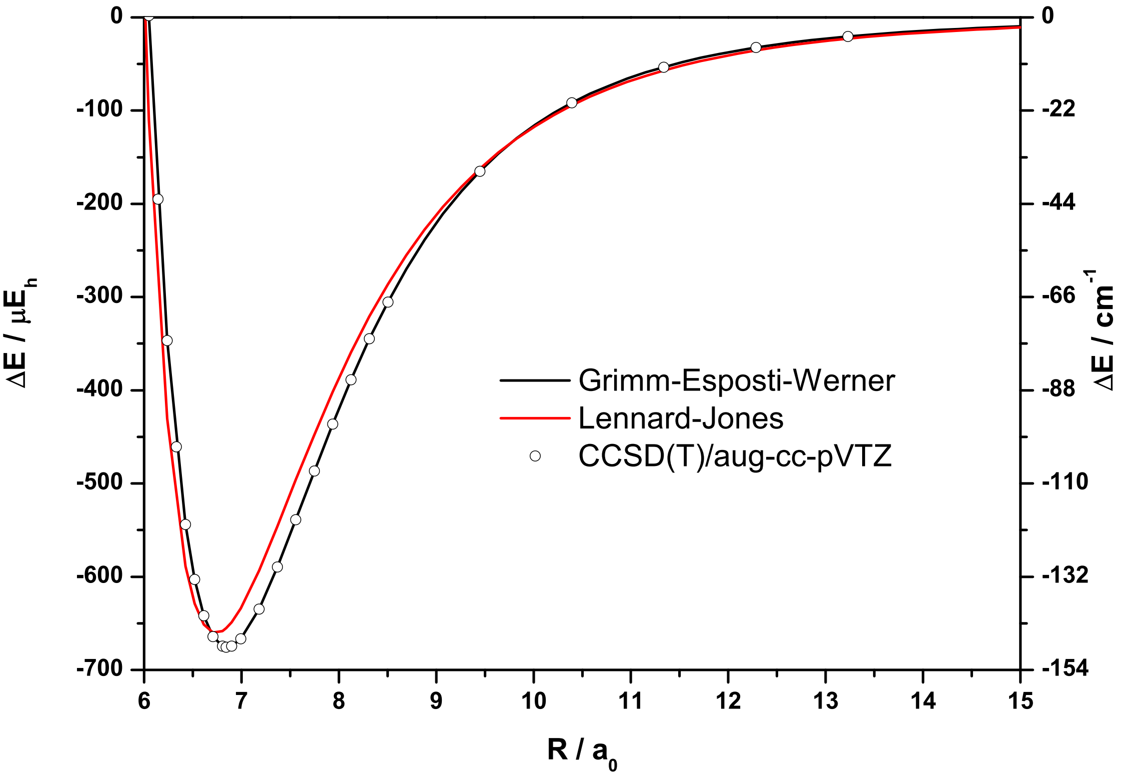


Fig. 3.9 - *R-dependence of the interaction energy of the CH_4-N_2 complex for the equilibrium configuration 4. Circles -* ab initio *calculation at the CCSD(T)/aug-cc-pVTZ level of theory with BSSE correction; red line - Lennard-Jonnes potential (Eq. 3.6); black line - Grimme-Esposti-Werner potential (Eq. 3.7).*



Tab. 3.7 - *Harmonic (ω) vibrational wave numbers (cm^{-1}) calculated at the MP2/aug-cc-pVTZ level with BSSE correction for the CH_4-N_2 complex being in configuration C_τ ($\tau = 0° \div 30°$).*

Normal Mode	τ (Deg)						
	0	5	10	15	20	25	30
1	19.6				7		9.5
2	23.3	26.2	25.8	28.6	26.6	26.3	28.2
3	48.2	50.8	50.8	54.0	50.6	50.6	54.3
4	65.7	67.3	66.3	70.2	66.8	66.8	74.4
5	71.8	75.3	76.0	79.9	77.6	76.4	78.5
6	1355.4	1355.4	1355.4	1355.5	1355.4	1355.4	1355.5
7	1356.0	1356.9	1355.9	1355.9	1355.9	1355.9	1356.0
8	1356.1	1356.1	1356.1	1356.1	1356.1	1356.1	1356.2
9	1587.7	1587.6	1587.6	1587.6	1587.7	1587.6	1587.6
10	1588.3	1588.4	1588.4	1588.4	1588.4	1588.4	1588.4
11	2185.0	2184.8	2184.9	2184.8	2184.8	2184.8	2184.8
12	3066.8	3067.0	3067.1	3067.0	3066.9	3067.0	3066.8
13	3201.6	3201.9	3202.0	3201.9	3201.9	3201.9	3201.4
14	3201.6	3202.1	3202.1	3202.0	3202.0	3202.0	3202.1
15	3204.0	3203.9	3204.0	3204.0	3203.8	3203.9	3203.8

TAB. 3.8 - *Harmonic* (ω) *and anharmonic* (ν) *vibrational wavenumbers, shifts* $\Delta\omega = \omega^{mon} - \omega^{com}$ *and rotational constants (A, B, C)*† *calculated at the MP2/aug-cc-pVTZ level with BSSE correction for configuration 4 of the* CH_4-N_2 *complex. All values are in* cm^{-1}. *In parenthesis we present the correspondence of the complex vibrational modes to the vibrational modes of the monomers.*

Mode	Sym.	ω	$\Delta\omega$	ν	A	B	C
1	A''	19.6			1.533416	0.106836	0.100632
2	A''	23.3			1.706804	0.109399	0.100219
3	A'	48.2			1.522507	0.096197	0.091039
4	A'	65.7			1.538965	0.094149	0.089516
5	A''	71.8			1.537200	0.094502	0.089132
6 (ν_4, CH_4)	A'	1355.4	0.6	1317.4	1.523007	0.106739	0.100339
7 (ν_4, CH_4)	A''	1356.0	0.0	1317.9	1.515098	0.106811	0.100339
8 (ν_4, CH_4)	A'	1356.1	-0.1	1317.4	1.516464	0.106803	0.100312
9 (ν_2, CH_4)	A''	1587.7	0.9	1549.5	1.528913	0.106856	0.100418
10 (ν_2, CH_4)	A'	1588.3	0.3	1549.3	1.528894	0.106879	0.100388
11 (ν, N_2)	A'	2185.0	1.9	2148.0	1.511501	0.107070	0.100509
12 (ν_1, CH_4)	A'	3066.8	2.8	2950.1	1.520032	0.106795	0.100339
13 (ν_3, CH_4)	A''	3201.6	3.4	3070.2	1.520209	0.106792	0.100334
14 (ν_3, CH_4)	A'	3201.6	3.4	3069.9	1.520202	0.106799	0.100345
15 (ν_3, CH_4)	A'	3204.0	1.0	3070.2	1.520327	0.106799	0.100344

†Rotational constants in the equilibrium geometry: A_e=1.420734, B_e=0.123238 and C_e=0.115954; in the ground state: A = 1.522647, B = 0.106818 and C = 0.100360 (cm^{-1}).

Chapter 4

Interaction-induced dipole moment

It is well known that any gas media consisting of nondipolar molecules absorb in IR and far IR spectra [7–9]. The nature of absorption is in the presence both of transient dipole moments of colliding molecules, and of the dipole moment of stable van der Waals complexes. For this reason dipole moments of interacting molecules are the object of numerous theoretical and experimental studies [106–118]. At present, there arises an interest to the CH_4-N_2 complex in connection with the study of nitrogen-methane atmosphere of Titan [79–92].

In spite of the importance of the CH_4-N_2 complex in investigations of properties of methane-nitrogen planetary atmospheres, this complex is poorly studied. At present, electric properties of the complex were studied in Refs. [52, 142]. In Ref. [52] the analytical investigation of the long-range collision-induced dipole moment surface taking into account the induction (up to R^{-6}) and dispersion (up to R^{-7}) contributions was carried out. In work [142] the investigations were carried out for the CH_4-N_2 complex at the CCSD(T)/aug-cc-pVTZ level of theory with the BSSE correction and within the framework of the long-range multipolar induction (partially up to R^{-6}) and dispersion (up to R^{-6}) interactions. The dipole moment surface suggested in Ref. [52], was employed for the description of collisional spectra of molecules CH_4 and N_2 in works [74, 75]. In these works it was shown that calculated absorption spectra for frequencies from 30 to 250 cm^{-1} agrees well with existing measurements [70, 71] but at the high frequencies > 250 cm^{-1} it shows substantial intensity defect.

In the present work we have carried out *ab initio* CCSD(T) calculations of the dipole moment surface for the wide range of intermolecular separations (6 - 40 a_0) including the range of potential wells for different configurations of the van der Waals complex CH_4-N_2. Also, we have improved the long-range model of the dipole moment surface [52] by fully including the induction terms up to R^{-7} and by accounting for the contributions from the effects of electron shell overlap of the interacting molecules.

4.1 Theoretical treatment

In the present work, for the calculation of the dipole moment of the complex CH_4-N_2 both *ab initio* and analytical methods were employed. The Cartesian coordinate system shown in Fig. 3.1 was used for description of the complex.

4.1.1 *Ab initio* calculations details

For the calculation of the electric properties of the weakly bound CH_4-N_2 van der Waals complex the MP2 and CCSD(T) levels of theory were employed using MOLPRO 2006.1 package [35]. For these calculations we have used the aug-cc-pVTZ basis set designed specially for correlated calculations. The BSSE was taken into account for all calculations of the dipole moment. In order to evaluate the dipole moment of the CH_4-N_2 complex the finite-field method was employed. In the present work the major calculations of the dipole moment were carried out using the following 2-point formula [39]:

$$\mu_\alpha = \frac{E(F_\alpha) - E(-F_\alpha)}{2F_\alpha}. \tag{4.1}$$

The calculation errors of the dipole moment μ_α in Eq. 4.1 were estimated by comparison with μ_α calculated using the more accurate formula of G. Maroulis [38] that eliminates the contribution of higher polarizabilities:

$$\mu_\alpha = \frac{256D(F_\alpha) - 40D_\alpha(2F_\alpha) + D_\alpha(4F_\alpha)}{180F_\alpha}, \tag{4.2}$$

where

$$D_\alpha = \frac{E(F_\alpha) - E(-F_\alpha)}{2}.$$

The results of the calculation have shown that for the chosen applied field strength of 0.001 $e^{-1}a_0^2E_h$ these errors do not exceed 10^{-5} ea_0.

4.1.2 Analytical calculations details

The electric dipole moment $\mu_\alpha^{AB} \equiv \mu_\alpha$ of two interacting molecules for the large intermolecular separations including the range of small overlap of electron shells of these molecules may be written in the form

$$\mu_\alpha = \mu_\alpha^{ind} + \mu_\alpha^{disp} + \mu_\alpha^{exch}, \tag{4.3}$$

where μ_α^{ind}, μ_α^{disp} and μ_α^{exch} are the induction, dispersion and exchange contributions to the dipole moment of interacting systems. Here, μ_α^{exch} includes contributions from different effects caused by small overlap of electron shells of interacting molecules.

In the case of interacting molecules CH_4 (T_d symmetry: $\Theta_{\alpha\beta} = 0$) and N_2 ($D_{\infty h}$ symmetry: $\Omega_{\alpha\beta\gamma} = 0$, $\beta_{\alpha\beta\gamma} = 0$, $A_{\alpha,\beta\gamma} = 0$, $D_{\alpha,\beta\gamma\delta\varepsilon} = 0$) the induction dipole moment through the order

R^{-7} is written as [33] (see Chapter II):

$$\mu_\alpha^{ind} = \frac{1}{3}\alpha^A_{\alpha\beta}\Theta^{B(0)}_{\gamma\delta}T_{\beta\gamma\delta} - \frac{1}{9}A^A_{\alpha,\beta\gamma}\Theta^{B(0)}_{\delta\varepsilon}T_{\beta\gamma\delta\varepsilon} + \frac{1}{15}\alpha^B_{\alpha\beta}\Omega^{A(0)}_{\gamma\delta\varepsilon}T_{\beta\gamma\delta\varepsilon}$$
$$+\frac{1}{105}\alpha^A_{\alpha\beta}\Phi^{B(0)}_{\gamma\delta\varepsilon\varphi}T_{\beta\gamma\delta\varepsilon\varphi} - \frac{1}{105}\alpha^B_{\alpha\beta}\Phi^{A(0)}_{\gamma\delta\varepsilon\varphi}T_{\beta\gamma\delta\varepsilon\varphi} + \frac{1}{45}E^A_{\alpha,\beta\gamma\delta}\Theta^{B(0)}_{\varepsilon\varphi}T_{\beta\gamma\delta\varepsilon\varphi}$$
$$-\frac{1}{315}A^A_{\alpha,\beta\gamma}\Phi^{B(0)}_{\delta\varepsilon\varphi\nu}T_{\beta\gamma\delta\varepsilon\varphi\nu} + \frac{1}{225}E^B_{\alpha,\beta\gamma\delta}\Omega^{A(0)}_{\varepsilon\varphi\nu}T_{\beta\gamma\delta\varepsilon\varphi\nu} + \frac{1}{3}\alpha^B_{\alpha\beta}\Theta^{B(0)}_{\gamma\delta}\alpha^A_{\varepsilon\varphi}T_{\beta\varepsilon}T_{\varphi\gamma\delta}$$
$$-\frac{1}{315}D^A_{\alpha,\beta\gamma\delta\varepsilon}\Theta^{B(0)}_{\varphi\nu}T_{\beta\gamma\delta\varepsilon\varphi\nu}. \tag{4.4}$$

The dispersion dipole moment μ_α^{disp} through the order R^{-7} is defined by the following expression [33, 52]:

$$\mu_\alpha^{disp} = -\frac{1}{2\pi}\int_0^\infty d\omega \beta^A_{\alpha\beta\gamma}(0,i\omega,-i\omega)\alpha^B_{\delta\varepsilon}(i\omega)T_{\beta\delta}T_{\gamma\varepsilon}$$
$$+\frac{1}{3\pi}\int_0^\infty d\omega\Big[B^B_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)\alpha^A_{\varepsilon\varphi}(i\omega) - B^A_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)\alpha^B_{\varepsilon\varphi}(i\omega)\Big]T_{\beta\varepsilon}T_{\varphi\gamma\delta}. \tag{4.5}$$

Due to the absence of the data on the imaginary frequency-dependent hyperpolarizabilities $\beta_{\alpha\beta\gamma}(i\omega,0)$ and $B_{\alpha\beta,\gamma\delta}(0,i\omega)$ both for CH_4 and N_2 molecules, we can only estimate the dispersion dipole moment μ_α^{disp} by replacing the integral over imaginary frequency in Eq. 4.5 by the expressions depending only on static properties. For this purpose one can use the 'CRA2' approximation (see, Chapter II):

$$\int_0^\infty B^{A,B}_{\alpha\beta,\gamma\delta}(0,i\omega)\alpha^{B,A}_{\varepsilon\varphi}(i\omega)d\omega = \frac{I^{A,B}_{B\alpha}}{I_{\alpha\alpha}}\frac{\pi}{3}C_6, \tag{4.6}$$

where the isotropic dispersion coefficient

$$C_6 = \frac{3}{\pi}\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega, \tag{4.7}$$

and the mean polarizability

$$\alpha^{A,B} = \frac{1}{3}(\alpha^{A,B}_{xx} + \alpha^{A,B}_{yy} + \alpha^{A,B}_{zz}). \tag{4.8}$$

Using the Unsöld approximation [43], the ratio $I^{A,B}_{B\alpha}/I_{\alpha\alpha}$ takes on the form [69]

$$\frac{I^{A,B}_{B\alpha}}{I_{\alpha\alpha}} = \frac{\int_0^\infty B^{A,B}_{\alpha\beta,\gamma\delta}(0,i\omega)\alpha^{B,A}_{\varepsilon\varphi}(i\omega)d\omega}{\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega} \cong \frac{B^{A,B}_{\alpha\beta,\gamma\delta}(0,0)\alpha^{B,A}_{\varepsilon\varphi}(0)}{\alpha^A(0)\alpha^B(0)}\Big[\frac{1+\frac{2}{3}\Delta_{1,2}}{1+\Delta_{1,2}}\Big], \tag{4.9}$$

where

$$\Delta_1 = \frac{\Omega_B}{\Omega_A}, \Delta_2 = \frac{\Omega_A}{\Omega_B}. \tag{4.10}$$

Here $\Omega_{A,B}$ is the average excitation frequency for the monomers A and B.

Analogously one can get the expressions for the first term in Eq. 4.5

$$\frac{\int_0^\infty \beta^{A,B}_{\alpha\beta\gamma}(i\omega,0)\alpha^{B,A}_{\delta\varepsilon}(i\omega)d\omega}{\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega} \cong \frac{\pi C_6\beta^{A,B}_{\alpha\beta\gamma}(0,0)\alpha^{B,A}_{\delta\varepsilon}(0)}{3\alpha^A(0)\alpha^B(0)}\Big[\frac{1+\frac{2}{3}\Delta_{1,2}}{1+\Delta_{1,2}}\Big]. \tag{4.11}$$

Thus, assuming $\Omega_A \cong \Omega_B$, the expression for the dispersion dipole moment (Eq. 4.5) takes on the form ($\alpha_{\alpha\beta}(0) \equiv \alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}(0,0) \equiv \beta_{\alpha\beta\gamma}$ and $B_{\alpha\beta,\gamma\delta}(0,0) \equiv B_{\alpha\beta,\gamma\delta}$):

$$\mu_{\alpha}^{disp} = -\frac{5\beta^{A}_{\alpha\beta\gamma}\alpha^{B}_{\delta\varepsilon}}{36\alpha^{A}\alpha^{B}} T_{\beta\delta}T_{\gamma\varepsilon}C_6 + \left(B^{A}_{\alpha\beta,\gamma\delta}\alpha^{B}_{\varepsilon\varphi} - B^{B}_{\alpha\beta,\gamma\delta}\alpha^{A}_{\varepsilon\varphi}\right)\frac{5T_{\beta\varepsilon}T_{\varphi\gamma\delta}C_6}{54\alpha^{A}\alpha^{B}}. \tag{4.12}$$

The analytical expression for exchange dipole moment μ_{α}^{exch} can be obtained using the asymptotic methods [119,120]. These methods may be applied in the range of R where a weak overlapping of the valence electron shells of interacting systems takes place. Such situation is typical for the ranges of R corresponding to potential wells of van der Waals complexes. The analytical expression for μ_{α}^{exch} are obtained for the case of two interacting atoms with the valence s-electrons. In this case, the exchange interaction of atoms is approximately considered as an exchange interaction of two valence electrons (by one from each atom). Then, the two-electron (one electron from atom A and one from atom B) wave function of atomic complex is written as follows:

$$\Psi(r_1, r_2, R) = c^{(1)}\psi^{(1)}(r_1, r_2, R) + c^{(2)}\psi^{(2)}(r_1, r_2, R), \tag{4.13}$$

where

$$\begin{aligned} \psi^{(1)}(r_1, r_2, R) &= \phi^{(A)}(r_1, R)\phi^{(B)}(r_2, R)\chi_I(r_1, r_2, R), \\ \psi^{(2)}(r_1, r_2, R) &= \phi^{(A)}(r_2, R)\phi^{(B)}(r_1, R)\chi_{II}(r_1, r_2, R). \end{aligned} \tag{4.14}$$

Here $\phi^{(A)}(r_1, R)$, $\phi^{(B)}(r_1, R)$ and $\phi^{(A)}(r_2, R)$, $\phi^{(B)}(r_2, R)$ are asymptotic atomic wave functions of the first and the second electron located near corresponding atom cores. Eqs. 4.13 and 4.14 are written in the coordinate system of the complex in which the interacting atoms are located on the axis connecting these atoms, and the center of the interatomic separation is taken as the origin of coordinates. In this coordinate system r_1 and r_2 are coordinates of the first and the second electron. The functions $\chi_I(r_1, r_2, R)$ and $\chi_{II}(r_1, r_2, R)$ accounting for the interaction of electrons with each other and with extraneous nuclei have complicated forms and are given in Ref. [120]. The asymptotic function $\phi(r, R)$ can be obtained from the asymptotic radial wave function of a valence electron of a neutral atom. This radial wave function in the coordinate system with the origin in the atom nuclear has the form Ref. [119]:

$$\phi(r) = A_0 r^{1/\beta - 1}\mathtt{exp}(-r\beta), \tag{4.15}$$

where $\beta^2/2$ is the atomic ionization potential and the value of the asymptotic coefficient A_0 depends on the electron distribution in the internal zone of the atom. The function $\phi(r, R)$ is obtained from the function $\phi(r)$ by transition from the atomic coordinate system to the coordinate system of the complex.

Then the exchange interaction contribution into the dipole moment for two interacting atoms may be represented as

$$\mu^{exch}(R) = \langle\psi^{(1)}(r_1, r_2, R)|\hat{\mu}|\psi^{(2)}(r_1, r_2, R)\rangle^{exch} = BR^{\delta}\mathtt{exp}(-\eta R), \tag{4.16}$$

where

$$\delta = \frac{1}{\beta_A} + \frac{1}{\beta_B} + \frac{1}{2(\beta_A+\beta_B)+1}, \tag{4.17}$$

$$\eta = \frac{3}{4}(\beta_A+\beta_B). \tag{4.18}$$

Here $\beta_A^2/2 = U^A$ and $\beta_B^2/2 = U^B$ are the ionization potentials of the atoms A and B at the ground electronic state and the parameter $B \equiv B(\beta_A, \beta_B, R)$ is the function weakly dependent on R in the region of small overlapping of their electron shells. The results obtained for atoms with the valence s-electrons can also be applied, after minimal changes, to interacting atoms having the valence electrons with nonzero orbital moment l. Indeed, according to Ref. [120], the coefficient A_0 in Eq. 4.15 for this case should be multiplied by $\sqrt{(2l+1)}$.

The results obtained above may be generalized for the case of small interacting molecules. In this case the model of exchange dipole moment for interacting atoms (Eq. 4.16) should be modified. First of all, the exchange dipole moment of interacting molecules generally has several non-zero components μ_α^{exch}. In the framework of considered model for interacting molecules we conserve the form of R-dependence for the exchange dipole moment components like the form for interacting atoms in Eq. 4.16 with β_A and β_B being the parameters expressed in terms of ionization potentials of molecules. This form is the same for all components and doesn't depend on the mutual orientation of molecules in the complex. The orientational dependence of μ_α^{exch} is introduced by B_α parameter, which is not dependent on R. Therefore, for the considered complex CH_4-N_2 the exchange dipole moment takes the form (μ_α, B_α, R, η and δ are in a.u.):

$$\mu_\alpha^{exch}(R, \chi_A, \theta_A, \varphi_A, \theta_B, \varphi_B) = B_\alpha(\chi_A, \theta_A, \varphi_A, \theta_B, \varphi_B) R^\delta \texttt{exp}(-\eta R), \tag{4.19}$$

where δ and η are defined by Eqs. 4.17 and 4.18. It should be noted, that the size of interacting molecules is accounted only by the B_α parameter.

Such approach was suggested and successfully applied for the calculation of exchange contribution to the polarizability of Ar-H_2 complex in Ref. [121].

4.2 Results and discussions

4.2.1 *Ab initio* and analytical dipole moment surface of the CH_4-N_2 complex

Ab initio calculations of the dipole moment components as a function of R were carried out for 58 configurations of the CH_4-N_2 complex with the interacting molecules considered as rigid. For these configurations the value of R has been varied within the range 6 - 40 a_0. The calculation results of dipole moments for the CH_4-N_2 complex using CCSD(T) level of theory with and without the BSSE correction are given in Appendix VI. The comparison of the values of the dipole moment calculated with and without the BSSE correction shows that the difference between them is less then 10^{-5} ea_0. Further, the values of the CP-corrected dipole moment will be used for the analysis throughout the thesis.

The mostly discussed in works [52,77,78,141,142] six configurations of the CH_4-N_2 complex, including the most stable configuration, are presented at Fig. 3.2. The geometric parameters (Euler angles χ_A, θ_A, φ_A, θ_B, and φ_B) for these configurations along with equilibrium distance and interaction energy $\Delta E(R_e)$ are given in Table 3.1. The *ab initio* calculations of the dipole moment components for these configurations at the MP2 and CCSD(T) levels of theory are presented at Fig. 4.1. For the MP2 calculations, R was varying from 5.7 to 8.5 by 0.2 a_0 and from 8.5 to 18.5 by 1 a_0. According to the symmetry of the complex the μ_x component exists for all six configurations of the complex, μ_y component appears only for the configurations possessing C_S symmetry, and there is no μ_z component at all. Fig. 4.1a shows that with the R decreasing the μ_x component for the configurations 1, 3 and 6 (the N_2 molecule lies along the x-axis) monotonically goes up and for the configuration 4 monotonically goes down. The functions $\mu_x(R)$ for the configurations 2 and 5 have more complicated behavior. The values of μ_y components are significantly smaller (by $\sim 10^2$) then the values of μ_x components. Fig. 4.1b shows that for the configuration 4 the function monotonically goes down and for the configuration 5 monotonically goes up when the molecules become closer in the complex. It should be pointed out, that the calculation results of the dipole moment of the complex at the MP2 and CCSD(T) levels of theory agree well: for example, at $R = 7.5$ a_0 for the μ_x component the absolute values of differences between calculations using these two methods for 6 major configurations is about $5{\cdot}10^{-4}$ ea_0 and for the μ_y component doesn't exceed $4{\cdot}10^{-5}$ ea_0.

TAB. 4.1 - *Coefficients for the calculation of exchange contribution to the CH_4-N_2 dipole moment* in a.u.*

Configuration	B_x	B_y
1	5.4669	-
2	0.4041	-
3	0.3720	-
4	0.1240	0.00746
5	1.5859	0.02739
6	0.2521	-

*$\mu_\alpha^{exch} = B_\alpha R^{3.20238}\mathtt{exp}(-1.53525R)$. Here μ_α^{exch}, R, B_α are in a.u.

The applicability of analytical description of the dipole moment of the CH_4-N_2 complex in the framework of the suggested model is illustrated in Fig. 4.2. In this figure the long-range calculations, analytical calculations with the exchange contribution and the CCSD(T) calculations of the dipole moment components of the CH_4-N_2 complex for configurations 3-5 are given. The molecular parameters used for analytical calculations are given in Table 8.2. The coefficient $C_6 = 96.94$ $E_h a_0^6$ for interacting molecules CH_4 and N_2 is taken from Ref. [98]. The exchange contribution to dipole moment in analytical form for considered configurations was found by fitting μ_α^{exch} (Eq. 4.19) to the difference between *ab initio* and long-range calculations in the range of potential well for each configuration. The obtained parameters for six configurations (Fig. 3.2) are presented in Table 4.1. Note, that the obtained values of the parameters B_α correspond to μ_α^{ind} and μ_α^{disp} used in this work (see, Eqs. 4.4 and 4.12). The Fig. 4.2 shows that this approach allows to describe well the dipole moment including the whole range of potential well of considered configurations of the CH_4-N_2 complex, while the long-range approximation provides good results for $R > 10\ a_0$. A noticeable divergence between *ab initio* calculations and analytical calculations carried out in the framework of the proposed model appears for small R outside of the well where overlapping of the valence electron shells of interacting molecules grows (i.e., $R < 7.4\ a_0$ for configuration 3, $R < 6.3\ a_0$ for configuration 4, and $R < 7.5\ a_0$ for configuration 5 [141]). Fig. 4.2 shows also that analytical calculation of the dipole moment of the complex without accounting for the exchange contribution leads to an incorrect (in some cases to dramatic) behavior of the dipole moment in a range $R < R_e$. It should be noted that there is also a good agreement between *ab initio* calculations and analytical calculations with μ_α^{exch} for configurations 1, 2 and 6 in the range of the potential well.

It is of interest to evaluate different long-range contributions to the dipole moment of the considered complex. For the first time, such analysis for the complex CH_4-N_2 has been done in Ref. [52] where the induction terms were accounted up to R^{-6} and dispersion terms up to R^{-7}. In the present work, the induction terms were accounted more completely (up to R^{-7}). As an example, the dipole moment contributions for configuration 4 of the complex CH_4-N_2 are presented in Fig. 4.3. The figure shows the dispersion contributions and the induction contributions gathered for each order of R. Fig. 4.3 demonstrates that the induction terms $\sim R^{-7}$ give noticeable contribution to the dipole moment, which is essential especially for μ_y. The total analytical description of the dipole moment of the CH_4-N_2 complex in the framework of considered model requires the knowledge of the angular dependence of $B_\alpha(\chi_A, \theta_A, \varphi_A, \theta_B, \varphi_B)$ in Eq. 4.19. In the present work, the possibility of the analytical description of μ_α is illustrated by the particular examples (rotation of the CH_4 molecule by angle φ_A, and rotation of the N_2 molecule by angle θ_B). The numerical values of coefficients B_α for 42 configurations of the complex (13 configurations obtained by rotation of angle θ_B by 15° from 0° to 180° with fixed coordinates of CH_4; 29 configurations obtained by rotation of angle φ_A from 0° to 360° with fixed coordinates of N_2) were obtained as described above for 6 configurations presented in Fig. 3.2.

Fig. 4.4 illustrates the dependence of the numerical values of coefficients B_α on the angle θ_B for the configurations of the CH_4-N_2 complex with fixed Euler angles $\chi_A = 0°$, $\theta_A = 45°$, $\varphi_A = (180/\pi)\arcsin(1/\sqrt{3})$ and $\varphi_B = 0°$. It is shown, that the numerical values of B_α form the smooth functions depending on the angle θ_B, which can be expanded in a series in terms of Legendre polynomial of low order. The analytical expressions for the coefficients B_α, obtained by fitting to the numerical values deduced from the *ab initio* calculation, have the forms (in a.u.):

$$B_x(\theta_B) = 0.2732 - 0.1601P_2^0(\cos\theta_B) + 0.0333P_4^0(\cos\theta_B) - 0.0227P_6^0(\cos\theta_B), \tag{4.20}$$

$$B_y(\theta_B) = 0.00696 + 0.01060P_2^0(\cos\theta_B) - 0.00718P_4^0(\cos\theta_B) - 0.00330P_6^0(\cos\theta_B), \tag{4.21}$$

$$B_z(\theta_B) = -0.1076P_2^1(\cos\theta_B) - 0.0307P_4^1(\cos\theta_B) - 0.0011P_6^1(\cos\theta_B), \tag{4.22}$$

where $P_l^m(\cos\theta_B)$ are the associated Legendre polynomials. It should be pointed out, that at $\theta_B = 0°$ the complex CH_4-N_2 is in configuration 4 and at $\theta_B = 90°$ in configuration 3, and the fitted values B_α in Eqs. 4.20-4.22 for these configurations ($B_x(0°) = 0.1237$, $B_x(90°) = 0.3728$ and $B_y(0°) = 0.00708$) are in a good agreement with the values in Table 4.1. It is obvious, that the functions B_α in Eqs. 4.20-4.22 are periodic functions with the period of 180° due to the fact, that the N_2 molecule is homonuclear.

Fig. 4.5 shows the dependence of the coefficients B_α on the angle φ'_A ($\varphi'_A = \varphi_A - 90°$) for the configurations of the CH_4-N_2 complex with fixed $\chi_A = 0°$, $\theta_A = 45°$, $\theta_B = 0°$, and $\varphi_B = 0°$. The angle φ'_A is introduced to show the symmetry properties of the complex (and the coefficients B_α, respectively) more clearly when the molecule CH_4 is rotated by the angle φ_A. For considered configurations of the CH_4-N_2 complex the coefficient has only x and y components and have the following properties: $B_x(180° - \varphi'_A) = B_x(180° + \varphi'_A)$, $B_y(180° - \varphi'_A) = -B_y(180° + \varphi'_A)$. The analytical expressions for these coefficients have the forms (in a.u.)

$$\begin{aligned} B_x(\varphi'_A) = {} & 0.6508 - 0.6558P_1^0(\cos\varphi'_A) - 0.0515P_2^0(\cos\varphi'_A) + 0.6386P_3^0(\cos\varphi'_A) \\ & -0.1913P_4^0(\cos\varphi'_A) - 0.0655P_5^0(\cos\varphi'_A) - 0.0778P_6^0(\cos\varphi'_A), \end{aligned} \tag{4.23}$$

$$\begin{aligned} B_y(\varphi'_A) = {} & -0.01062P_1^1(\cos\varphi'_A) - 0.03098P_2^1(\cos\varphi'_A) + 0.01854P_3^1(\cos\varphi'_A) \\ & -0.02633P_4^1(\cos\varphi'_A) - 0.00127P_5^1(\cos\varphi'_A) \\ & -0.00485P_6^1(\cos\varphi'_A) + 0.00185P_7^1(\cos\varphi'_A). \end{aligned} \tag{4.24}$$

It should be pointed out, that the coefficients B_α in Eqs. 4.23 and 4.24, unlike those in Eqs. 4.20 - 4.22, are periodic functions of φ'_A (and φ_A) with the period of 360°. Although Eqs. 4.23 and 4.24 have more complicated form in comparison with Eqs. 4.20 - 4.22, the coefficients $B_\alpha(\varphi'_A)$ (and $B_\alpha(\varphi_A)$, correspondingly) are also smooth functions. So, the considered particular cases of rotation of molecules in the complex show that the exchange contributions to the dipole moment of the complex CH_4-N_2 may be successfully obtained in analytical form.

4.2.2 Dipole moment of the most stable configuration

It is of interest to consider the dipole moment of the CH_4-N_2 complex being in the most stable configuration. As it was shown in Ref. [141], the CH_4-N_2 complex has a family of such configurations, for which interaction energies are practically equal (the difference is less than 0.16 μE_h). These configurations are obtained from configuration 4 by rotation of the N_2

molecule by angle τ over x axis at fixed equilibrium intermolecular separation $R_e = 6.8\ a_0$. The rotation of nitrogen molecule by angle τ corresponds to its rotation by angle θ_B at fixed angle $\varphi_B = 90°$.

The dipole moment calculations for the CH$_4$-N$_2$ complex were carried out for τ from 0° to 180° by 15° (13 configurations). For the calculations we have employed Eq. 4.2, that provides enough accuracy for the correct description of small changing in $\mu_\alpha(R,\tau)$. As a result, the analytical expressions for $\mu_\alpha(R,\tau)$ obtained in this work take the form (in a.u.)

$$\mu_x(R,\tau) = -\frac{27.67779}{R^4} - \frac{78.76850}{R^5} + \frac{379.8549}{R^6} + \frac{687.0685}{R^7} + B_x(\tau)f(R), \tag{4.25}$$

$$\mu_y(R,\tau) = -\Big(\frac{8.282}{R^5} + \frac{39.795}{R^6}\Big)(2\mathtt{cos}^2\tau - 1)$$
$$+\frac{57.053\mathtt{cos}^4\tau + 610.461\mathtt{cos}^2\tau - 326.625}{R^7} + B_y(\tau)f(R), \tag{4.26}$$

$$\mu_z(R,\tau) = -\Big(\frac{16.564}{R^5} + \frac{79.590}{R^6} + \frac{57.053\mathtt{cos}^2\tau - 696.041}{R^7}\Big)\mathtt{sin}\tau\mathtt{cos}\tau + B_z(\tau)f(R), \tag{4.27}$$

where

$$f(R) = R^{3.20238}\mathtt{exp}(-1.53525R) \tag{4.28}$$

and the fitting parameters $B_\alpha(\tau)$ were found from *ab initio* values of dipole moments of the CH$_4$-N$_2$ complex at R_e and can be written as follows

$$B_x(\tau) = 0.112522 + 0.000154\mathtt{cos}^2\tau(4\mathtt{cos}^2\tau - 3)^2, \tag{4.29}$$

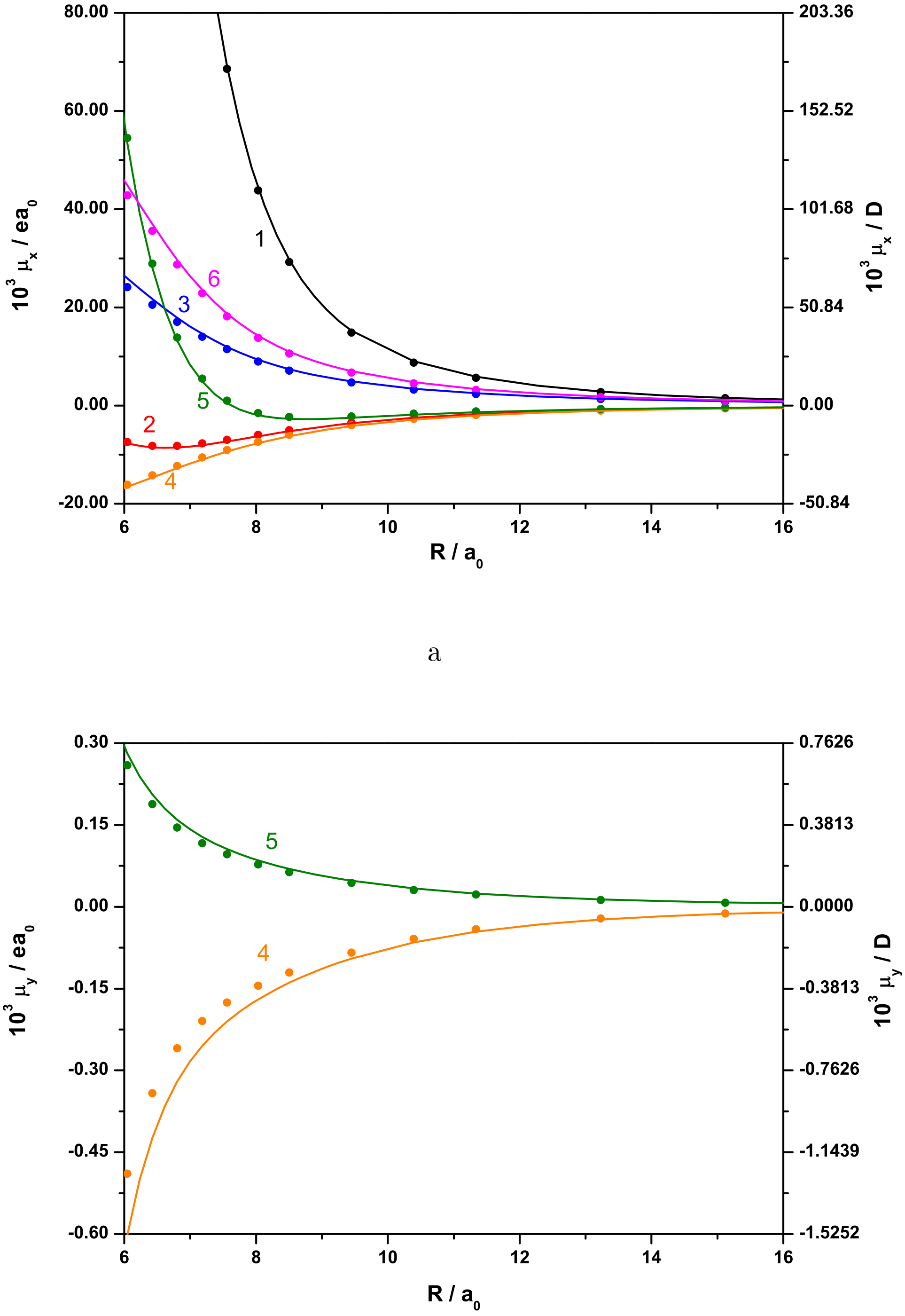
$$B_y(\tau) = -0.005913 + 0.000111\mathtt{cos}^2\tau + 0.022825\mathtt{cos}^4\tau - 0.008514\mathtt{cos}^6\tau, \tag{4.30}$$

$$B_z(\tau) = (0.019364 - 0.007734\mathtt{cos}^2\tau)\mathtt{sin}\tau\mathtt{cos}\tau. \tag{4.31}$$

The *ab initio* and analytical calculations (see, Eqs. 4.25 - 4.31) of $\mu_\alpha(R,\tau)$ at R_e are presented in Fig. 4.6. The analysis of results shows that a very weak dependence of μ_x on the angle τ (Fig. 4.6a) is defined only by the exchange contribution to the dipole moment, because the dispersion and induction contributions for this case are not dependent on angle τ. It should be noted, that the major contribution (96%) to μ_x is the induction one, the dispersion (16%) and exchange (12%) contributions have opposite signs and partially cancel out each other. The period of changing of $\mu_x(\tau)$ is equal to 60° and is governed by the symmetry of the complex. The dipole moment components $\mu_y(\tau)$ and $\mu_z(\tau)$ are significantly smaller then $\mu_x(\tau)$ and are defined both by induction and exchange contributions (the dispersion contribution is negligible). The functions $\mu_y(\tau)$ and $\mu_z(\tau)$ are both sign-changing periodic functions with period 180° (Fig. 4.6b,c).

Fig. 4.6d shows, that the modulus of the dipole moment $|\mu(\tau)| = \sqrt{\sum_\alpha \mu_\alpha^2(\tau)}$ of the CH$_4$-N$_2$ complex being in the most stable configurations is also weakly dependent on angle τ ($|\mu(\tau)| = 0.011961\ ea_0 \pm \Delta|\mu(\tau)|$ where the variations $\Delta|\mu(\tau)| < 0.000003\ ea_0$). It is obvious, that behaviour of the modulus $|\mu(\tau)|$ is similar to the behaviour of $\mu_x(\tau)$ component (see Fig. 4.6a,d). It is interesting to note, that a very weak dependence on the angle τ is also observed for the polarizability invariants of the complex CH$_4$-N$_2$ [142].

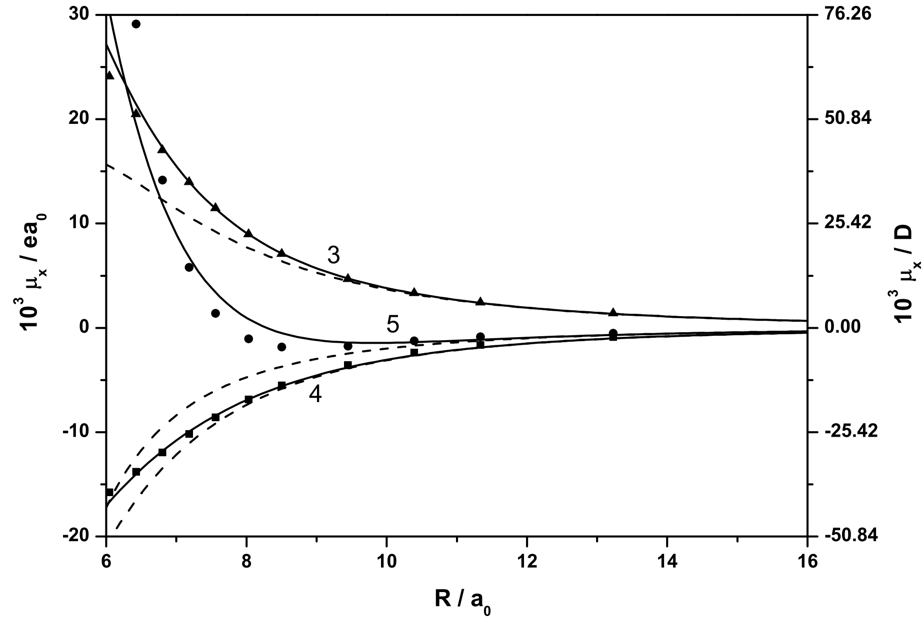
FIG. 4.1 - Ab initio *calculation of the dipole moment (a - μ_x, b - μ_y) for six configurations of the complex CH_4-N_2. Solid line - MP2 calculations; circles - CCSD(T) calculations. The numbers indicate the configurations.*



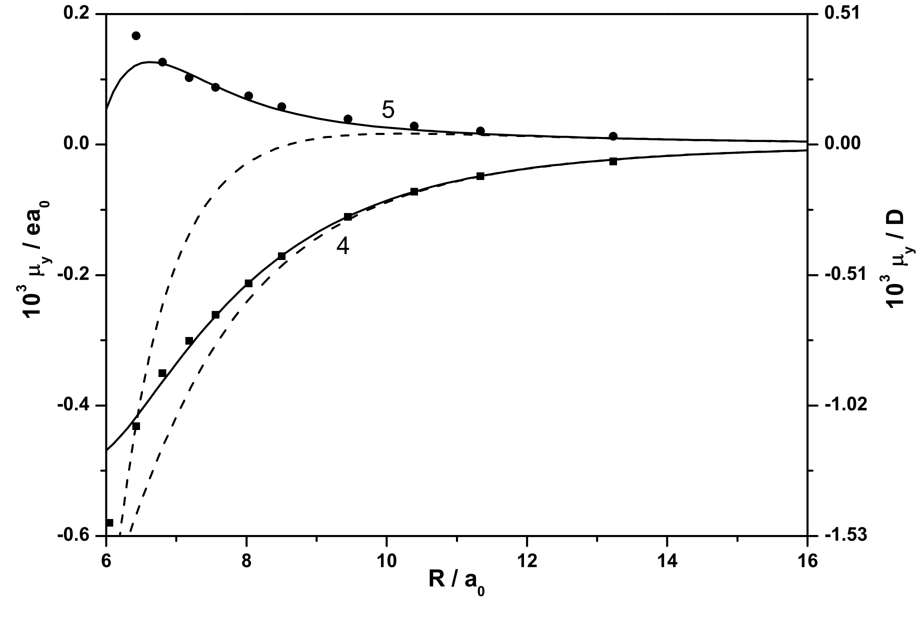
a

b

FIG. 4.2 - *Dipole moment components (a - μ_x, b - μ_y) for configurations 3, 4 and 5 of the complex CH_4-N_2. The numbers indicate the configurations. Solid lines - analytical calculations with the exchange contribution; dash lines - analytical calculations without the exchange contribution; CCSD(T) calculations: triangles - configuration 3; squares - configuration 4; circles - configuration 5.*

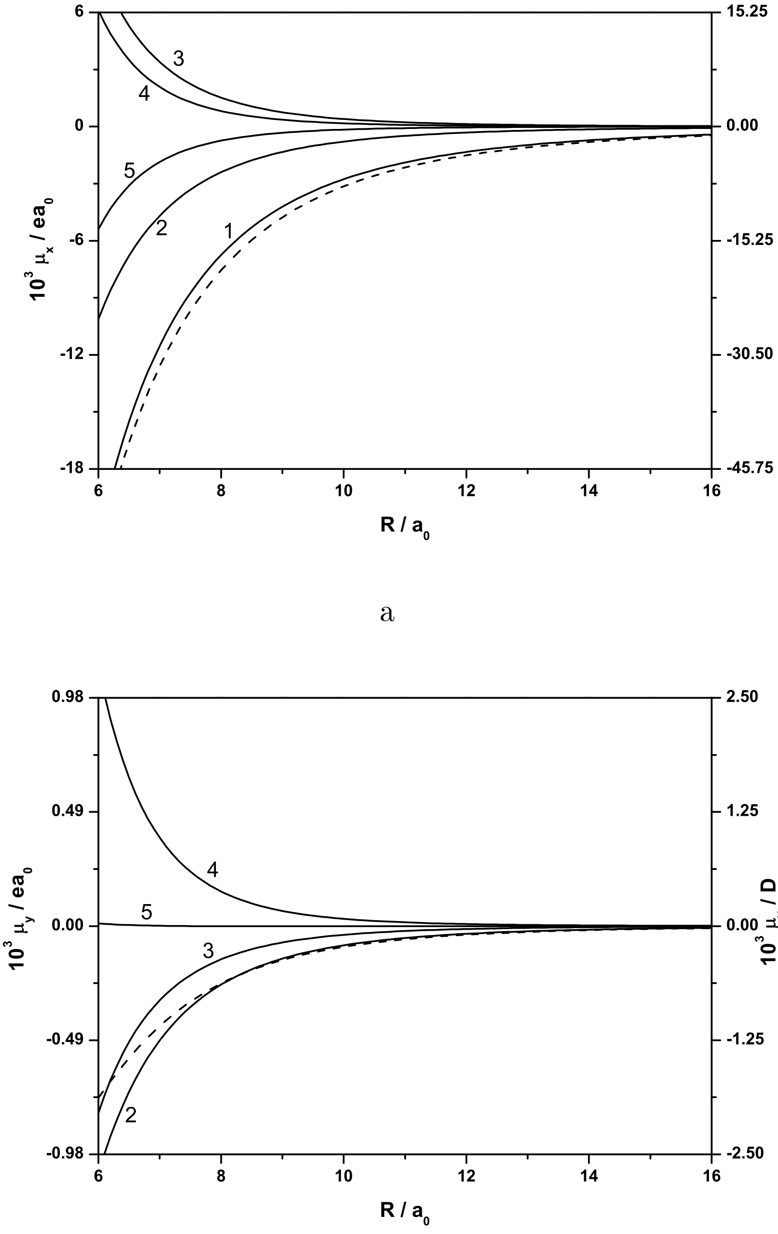


a



b

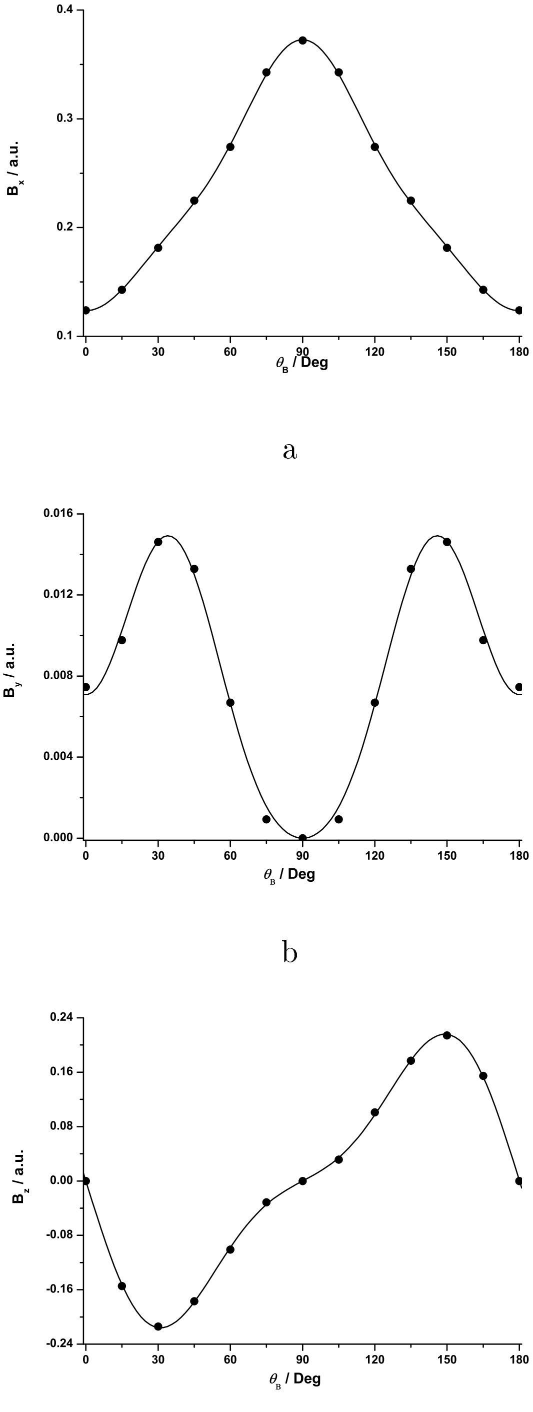
FIG. 4.3 - *Long-range contributions to the dipole moment components of the configuration 4 of the CH*$_4$*-N*$_2$ *complex (a -* μ_x*, b -* μ_y*). Solid lines: 1 - induction contribution of order* R^{-4} $(\alpha^A\Theta^B)$*, 2 - induction contributions of order* R^{-5} $(A^A\Theta^B+\alpha^B\Omega^A)$*, 3 - induction contributions of order* R^{-6} $(\alpha^A\Phi^B+\alpha^B\Phi^A+E^A\Theta^B)$*, 4 - induction contributions of order* R^{-7} $(E^B\Omega^A+\alpha^B\Theta^B\alpha^A+A^A\Phi^B+D^A\Theta^B)$*, 5 - dispersion contributions* $(\beta^A\alpha^B+B^A\alpha^B+B^B\alpha^A)$*. Dash lines - total long-range dipole moment.*



a

b

FIG. 4.4 - *Dependence of the coefficients B_α on the angle θ_B for the configurations of the CH_4-N_2 complex with fixed $\chi_A = 0°$, $\theta_A = 45°$, $\varphi_A = (180/\pi)arcsin(1/\sqrt{3})$ and $\varphi_B = 0°$ (all angles are in Deg). Points - values of B_α deduced from the* ab initio *calculation (see text); lines - analytical calculation by Eqs. 4.20-4.22.*

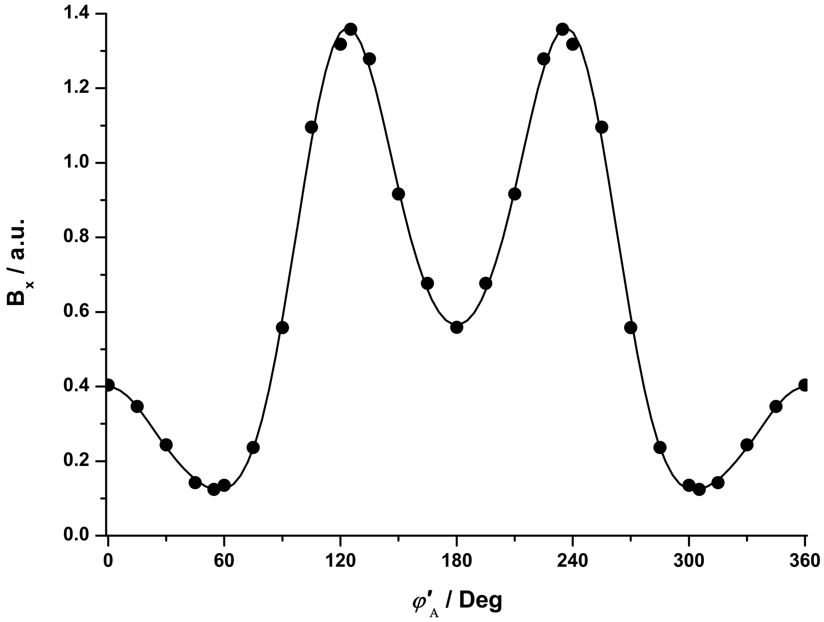


a

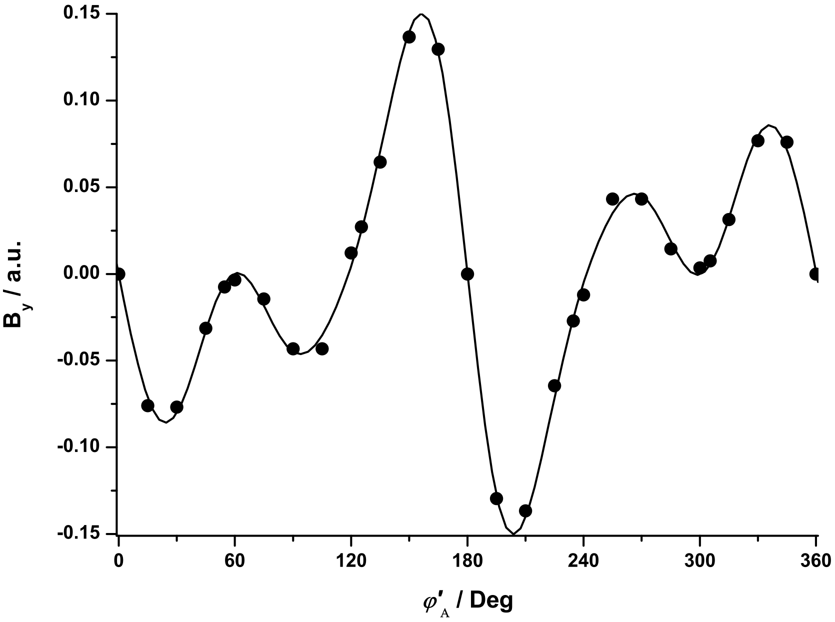
b

c

FIG. 4.5 - *Dependence of the coefficients* B_α *on the angle* φ'_A *for the configurations of the* CH_4-N_2 *complex with fixed* $\chi_A = 0°$, $\theta_A = 45°$, $\theta_B = 0°$ *and* $\varphi_B = 0°$ *(all angles are in Deg).*

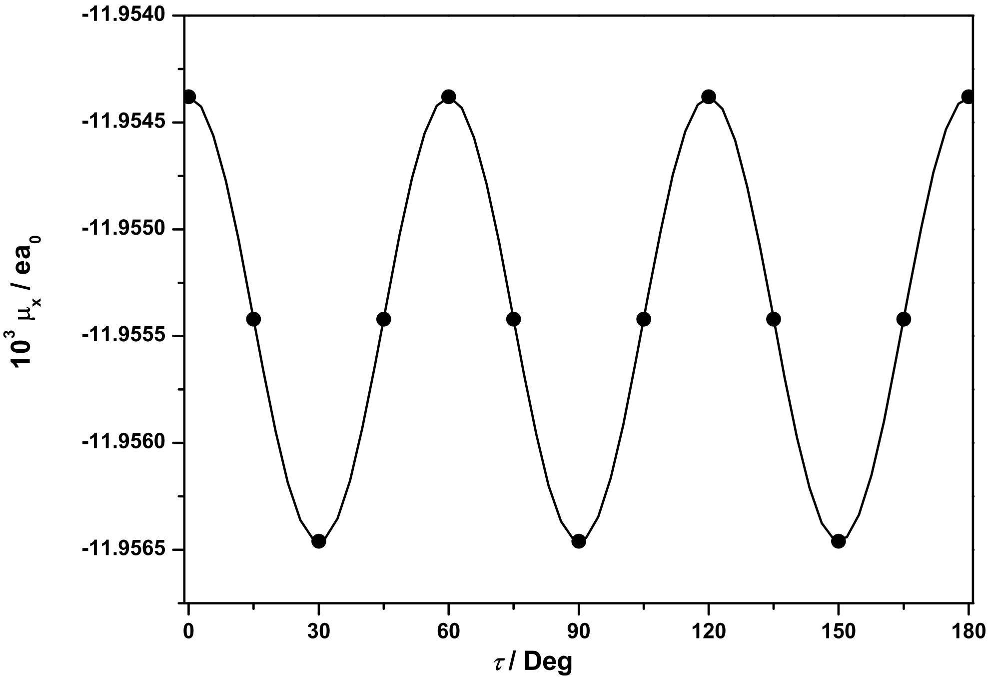


a

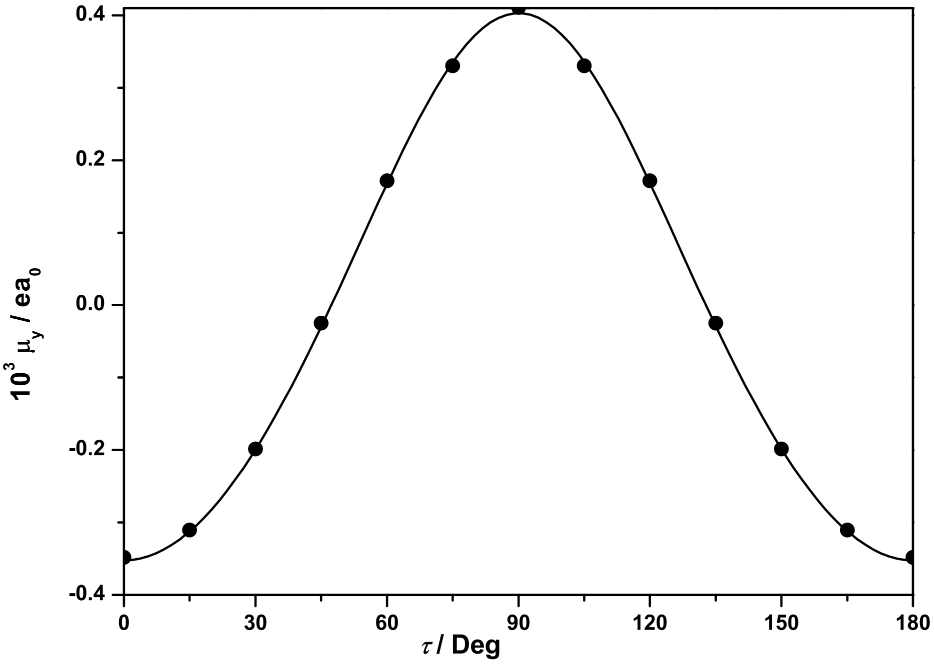


b

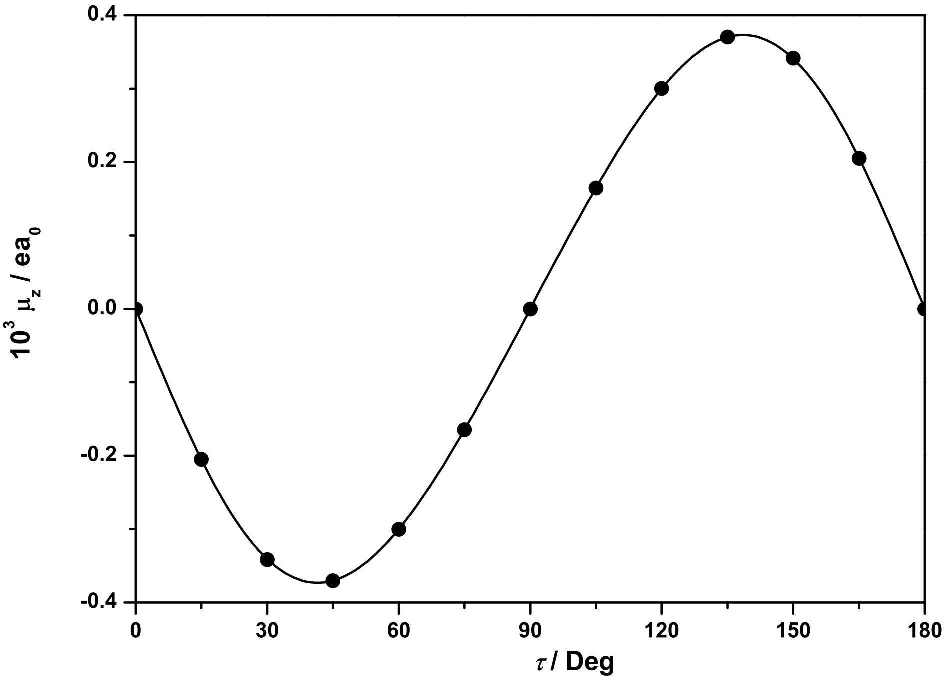
FIG. 4.6 - *Dependence of the dipole moment of the CH_4-N_2 complex (for the most stable configurations) on the angle* τ*: a -* $\mu_x(R_e,\tau)$*, b -* $\mu_y(R_e,\tau)$*, c -* $\mu_z(R_e,\tau)$*, d - modulus of the dipole moment* $|\mu(\tau)| = \sqrt{\sum_\alpha \mu_\alpha^2(\tau)}$.



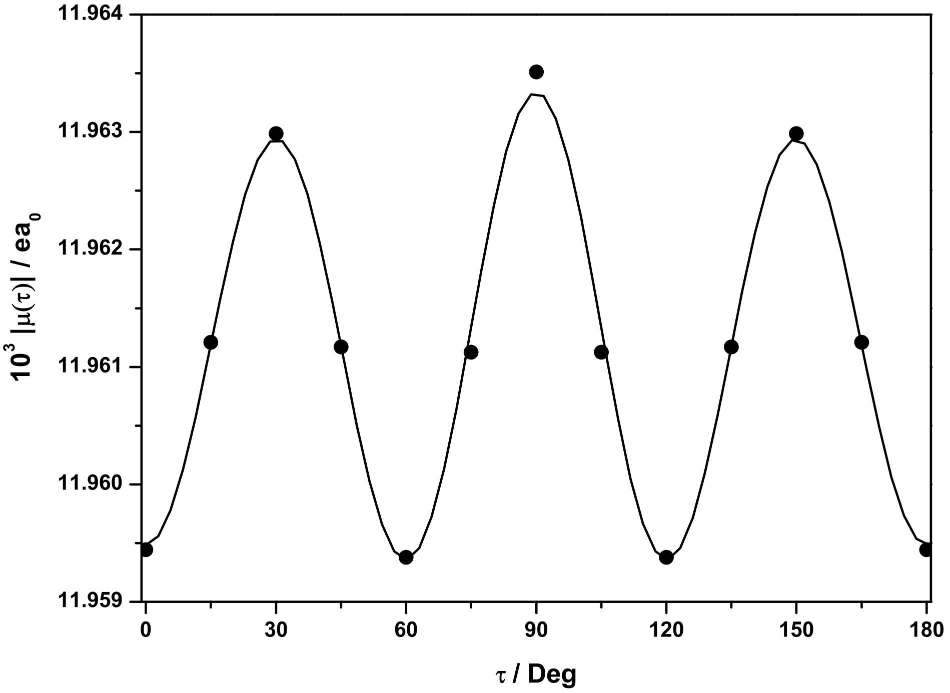
a



b


0.4
0.2
0.0
-0.2
-0.4
$10^3\ \mu_z$ / ea_0
0
30
60
90
120
150
180
τ / Deg

c


11.964
11.963
11.962
11.961
11.960
11.959
$10^3\ |\mu(\tau)|$ / ea_0
0
30
60
90
120
150
180
τ / Deg

d

Chapter 5

Static Polarizability

The polarizability tensor of interacting molecules plays an important role in molecular physics. The change of the polarizability of molecules due to their interaction contributes to the optical and dielectric properties of dense gas media and influences the properties of the Rayleigh and Raman scattering [31, 122, 123]. In this work, we consider the interacting molecules both as colliding molecules and as molecules which are parts of weakly-bound molecular complexes. At present, polarizability calculations for interacting molecules are carried out using both *ab initio* and classical electrodynamics methods.

The methods of classical electrodynamics, which account for multipole induction and dispersion effects, give a physically correct analytical description of the polarizability surface for interacting atomic-molecular systems at large intermolecular separations, when the interacting systems are well separated [53–63].

Ab initio methods allow to carry out polarizability calculations in a wider range of intermolecular separations, including those where the overlap effects of the electronic shells of atomic-molecular systems and charge transfers become essential. However, the majority of *ab initio* polarizability calculations for atomic-molecular systems are carried out for the equilibrium configurations of weakly-bound atomic-molecular complexes [124, 125]. The calculations of polarizability functions mostly concern pairs of interacting rare-gas atoms in their ground states (see, for example, [126–134]). There are comparatively few *ab initio* calculations of the polarizability surface for more complicated atomic-molecular systems [63, 135–140]. It should be also pointed out, that *ab initio* calculations have some disadvantages inherent in numerical methods: i) there are difficulties of methodological type which are related to the choice of the method and basis set for the achievement of high accuracy and reliability of the calculations; ii) polarizability surfaces can be calculated only in certain points; iii) there is a need of considerable computational resources.

It is thus reasonable to use both approaches as complementary ones for the investigation of the polarizability surface for interacting molecules.

In the present work, we have chosen to look at the poorly studied molecular complex CH_4-N_2, which is of particular interest for planetary applications (see, for instance, [87–91]). At present time, there are only few works devoted to the theoretical investigation of the potential energy surfaces and dipole moment surfaces of the CH_4-N_2 complex [52,77,78,141], and to the experimental investigation of the absorption spectra of this complex [70,71]. However, there are no works devoted to the polarizability surface of the CH_4-N_2 complex. In connection with this, in the present work, we have carried out polarizability calculations for the CH_4-N_2 complex in a wide range of intermolecular separations and mutual orientations of the interacting molecules.

5.1 Polarizability surface

Polarizability calculations for the CH_4-N_2 complex were carried out by means of the finite-field method based on finite differences [39]. The 3-point formula (with the errors of order F^2) used for the calculation of polarizability components is the following:

$$\alpha_{ii} = (2E^0 - E(F_i) - E(-F_i))/F^2, \tag{5.1}$$

where E^0 is the energy of a system in the absence of the external electric field and $E(F_i)$ is the energy in the presence of the external electric field $\mathbf{F}$ in i-direction.

In our study the polarizability components were calculated from the energy of the complex being in a weak homogeneous field of strength 0.001 $e^{-1}a_0^2E_h$. The energy calculations were carried out by use of Gaussian 03 [34] at the MP2 and CCSD(T) levels of theory with a correlation-consistent aug-cc-pVTZ basis set with the BSSE correction treated by counterpoise correction scheme of Boys and Bernardi [24].

The polarizability components for the monomers CH_4 and N_2 were calculated at the MP2 and CCSD(T) levels of theory using Eq. 5.1 and the expressions [38]

$$\alpha_{ii} = (1024S_i(F) - 80S_i(2F) + S_i(4F))/(360F^2), \tag{5.2}$$

$$S_i(F) = (2E^0 - E(F_i) - E(-F_i))/2,$$

which eliminate the contribution of the higher polarizabilities. The results of the calculation are presented in Table 5.1. The table shows that the calculated values of polarizability are in a good agreement with the ones obtained in Ref. [100,101] and that there is almost no difference (less then 0.05 %) between polarizability values calculated using Eq. 5.1 and Eq. 5.2. Further, we will use Eq. 5.1.

In the framework of the long-range approximation (see Eq. 2.67, Chapter 2) [31,32] the electric polarizability of two interacting molecules $\alpha_{\alpha\beta}^{AB}$ is written as:

$$\alpha_{\alpha\beta}^{AB} = \alpha_{\alpha\beta}^{A} + \alpha_{\alpha\beta}^{B} + \alpha_{\alpha\beta}^{ind} + \alpha_{\alpha\beta}^{disp}, \tag{5.3}$$

where $\alpha_{\alpha\beta}^{A}$ and $\alpha_{\alpha\beta}^{B}$ are the dipole polarizabilities of molecules A (CH_4) and B (N_2); $\alpha_{\alpha\beta}^{ind}$ and $\alpha_{\alpha\beta}^{disp}$ are the induction and dispersion terms of the polarizability of interacting molecules defined by Eqs. 2.69 and 2.71, accordingly. Thus, for the case of interaction of the CH_4 molecule (T_d

TAB. 5.1 - *Calculated in present work at the MP2 and CCSD(T) levels of theory using aug-cc-pVTZ basis set and literature molecular parameters (bond length, r, and polarizability components, α_{ii}) of the molecules CH_4 and N_2 (all values are in a.u.).*

Parameter	CH_4			N_2		
	Lit.	MP2	CCSD(T)	Lit.	MP2	CCSD(T)
r	2.0498^a		2.0596	2.0742^b		2.0864
α_{zz}	16.39^c	$16.6167^\dagger$	$16.5157^\dagger$	14.8425^d	$14.4198^\dagger$	$14.9640^\dagger$
		$16.6121^\ddagger$	$16.5111^\ddagger$		$14.4176^\ddagger$	$14.9597^\ddagger$
α_{xx}	16.39^c	$16.6168^\dagger$	$16.5158^\dagger$	10.2351^d	$10.1578^\dagger$	$10.2608^\dagger$
		$16.6121^\ddagger$	$16.5111^\ddagger$		$10.1568^\ddagger$	$10.2596^\ddagger$

[a] Reference [93].

[b] Reference [94].

[c] Reference [101].

[d] Reference [100].

† Calculated using Eq. 5.1 with the field strength of 0.005 $e^{-1}a_0^2E_h$.

‡Calculated using Eq. 5.2 with the field strength of 0.005, 0.01 and 0.02 $e^{-1}a_0^2E_h$.

symmetry) with the linear N_2 molecule ($D_{\infty h}$ symmetry), the induction term in Eq. 5.3 takes on the form:

$$\begin{aligned}\alpha_{\alpha\beta}^{ind} = {} & \alpha_{\alpha\beta}^{A} + \alpha_{\alpha\beta}^{B} + \alpha_{\alpha\gamma}^{A}T_{\gamma\delta}\alpha_{\delta\beta}^{B} + \alpha_{\alpha\gamma}^{B}T_{\gamma\delta}\alpha_{\delta\beta}^{A} + \frac{1}{3}\beta_{\alpha\beta\gamma}^{A}T_{\gamma\delta\varepsilon}\Theta_{\delta\varepsilon}^{B} - \frac{1}{3}A_{\alpha,\gamma\delta}^{A}T_{\gamma\delta\varepsilon}\alpha_{\varepsilon\beta}^{B} - \frac{1}{3}\alpha_{\alpha\gamma}^{B}T_{\gamma\delta\varepsilon}A_{\beta,\delta\varepsilon}^{A} \\ & + \frac{1}{15}\alpha_{\alpha\gamma}^{A}T_{\gamma\delta\varepsilon\varphi}E_{\beta,\delta\varepsilon\varphi}^{B} + \frac{1}{15}E_{\alpha,\gamma\delta\varepsilon}^{B}T_{\gamma\delta\varepsilon\varphi}\alpha_{\varphi\beta}^{A} + \frac{1}{15}E_{\alpha,\gamma\delta\varepsilon}^{A}T_{\gamma\delta\varepsilon\varphi}\alpha_{\varphi\beta}^{B} + \frac{1}{15}\alpha_{\alpha\gamma}^{B}T_{\gamma\delta\varepsilon\varphi}E_{\beta,\delta\varepsilon\varphi}^{A} \\ & - \frac{1}{9}B_{\alpha\beta,\gamma\delta}^{A}T_{\gamma\delta\varepsilon\varphi}\Theta_{\varepsilon\varphi}^{B} + \alpha_{\alpha\gamma}^{A}T_{\gamma\delta}\alpha_{\delta\varepsilon}^{B}T_{\varepsilon\varphi}\alpha_{\varphi\beta}^{A} + \alpha_{\alpha\gamma}^{B}T_{\gamma\delta}\alpha_{\delta\varepsilon}^{A}T_{\varepsilon\varphi}\alpha_{\varphi\beta}^{B} + \cdots . \qquad (5.4)\end{aligned}$$

In Eq. 5.4 we have fully accounted for the long-range multipolar induction contributions up to terms $\sim R^{-5}$ inclusive and terms $\sim R^{-6}$ caused by back induction effect due to dipole-induced-dipole interaction.

The direct calculation of the dispersion contribution $\alpha_{\alpha\beta}^{disp}$ using Eq. (2.71) is impossible due to the absence of the $\gamma_{\delta\varepsilon\alpha\beta}(i\omega, 0, 0)$ values as functions of $i\omega$ for the molecules under investigation. Thus, we used CRA1 for calculation the contribution of dispersion to the polarizability of the interacting molecules (Eq. 2.77). In that case, restricting ourselves to the leading term $\sim R^{-6}$, the expression for the dispersion contribution takes the form:

$$\alpha_{\alpha\beta}^{disp} = \frac{T_{\gamma\delta}\gamma_{\delta\varepsilon\alpha\beta}^{B}(0,0,0)T_{\varepsilon\eta}C_{\eta\gamma}}{2\alpha^{B}(0)} + \frac{T_{\gamma\delta}\gamma_{\delta\varepsilon\alpha\beta}^{A}(0,0,0)T_{\varepsilon\eta}D_{\eta\gamma}}{2\alpha^{A}(0)}, \qquad (5.5)$$

where

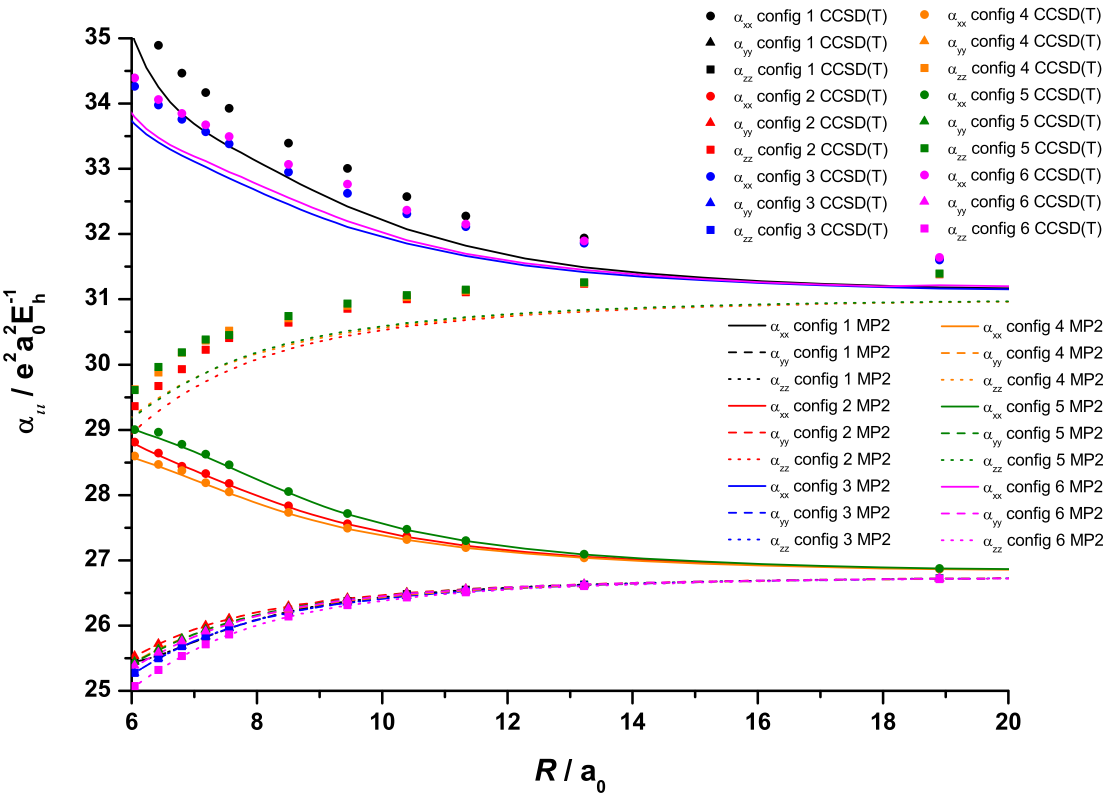
$$C_{\eta\gamma} = \frac{1}{2\pi}\int_0^\infty \alpha^{B}(i\omega)\alpha_{\eta\gamma}^{A}(i\omega)d\omega, \qquad (5.6)$$

$$D_{\eta\gamma} = \frac{1}{2\pi}\int_0^\infty \alpha^A(i\omega)\alpha^B_{\eta\gamma}(i\omega)d\omega.$$

Since the imaginary frequency-dependent polarizability for the molecules CH_4 and N_2 are known [98, 99], the further calculation of the $\alpha^{disp}_{\alpha\beta}$ is not difficult.

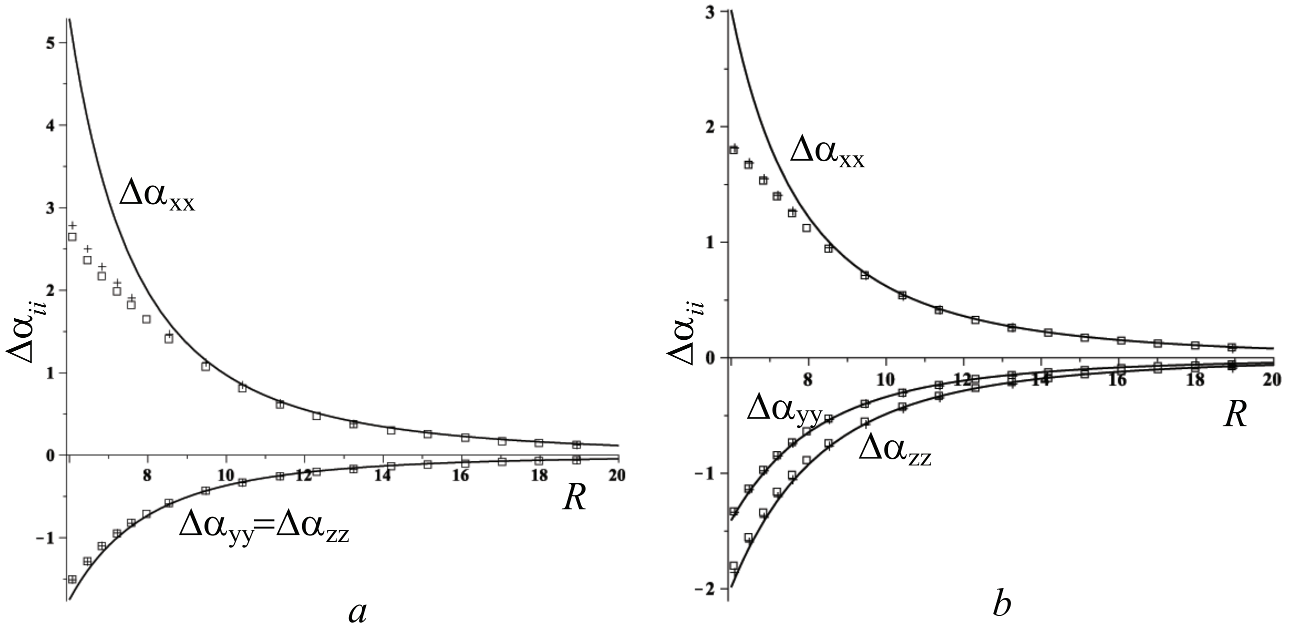
Multipole polarizabilities and moments in Eqs. 5.4-5.5 are dependent on the orientation of the interacting molecules, which can be defined by Euler angles χ_A, θ_A, φ_A, θ_B and φ_B, and as a result the polarizability of the pair of interacting molecules is the surface determined by these Euler angles and the intermolecular separation R.

FIG. 5.1 - *Polarizability components* α_{ii} *of the* CH_4-N_2 *complex calculated at the CCSD(T) and MP2 levels of theory with aug-cc-pVTZ basis set with the BSSE correction. All values are in a.u. Black color - conf. 1, red color - conf. 2, blue color - conf. 3, orange color - conf. 4, olive color - conf. 5, magenta color - conf. 6; Solid lines -* α_{xx} *(MP2), dash lines -* α_{yy} *(MP2), dot lines -* α_{zz} *(MP2); Rounds -* α_{xx} *(CCSD(T)), triangles -* α_{yy} *(CCSD(T)), squares -* α_{zz} *(CCSD(T)).*



Ab initio calculations of the polarizability tensor components as a function of R were carried out for six major configurations of the CH_4-N_2 complex (Fig. 3.2) with the interacting molecules considered as rigid. The geometrical parameters of the configurations are listed in Table 3.1. For the same configurations of the complex the polarizability calculations using analytical expressions Eqs. 5.3-5.5 were carried out. Input molecular data used in the work for analytical calculations are given in Table 8.2. For the calculation of the coefficients $C_{\eta\gamma}$ and $D_{\eta\gamma}$ (Eq. 5.5) the analytical pseudospectral dipole oscillator strength distributions for the molecules CH_4 [98] and N_2 [99] were used.

FIG. 5.2 - *Interaction polarizabilities $\Delta\alpha_{ii}$ of the CH_4-N_2 complex (a - configuration 3, b - configuration 4). All values are in a.u. Solid lines - analytical calculations, crosses - CCSD(T) calculations, boxes - MP2 calculations.*



Ab initio calculations results for the polarizability tensor components of the complex CH_4-N_2 are given in Fig. 5.1 and in Appendix VII. As expected, for the considered range of R the polarizability tensor components α_{xx} of the CH_4-N_2 complex for all configurations go up when the two molecules approach each other, while the components α_{yy} and α_{zz} go down. It is also can be seen that the polarizability of the complex is affected to a great extent by the orientation of the N_2 molecule relative to the x-axis (dependence on the θ_B angle) due to the big anisotropy of the polarizability tensor of the N_2 molecule. The dependence of the complex polarizability on the orientation of highly symmetric molecule CH_4 in the complex is significantly smaller and becomes noticeable only at small intermolecular separations. It draws attention that the values of polarizability calculated at the MP2 level of theory are underestimated for the configurations 1, 3 and 6. This can be explained by the fact that the value $\alpha_{zz}^{N2} + \alpha^{CH_4}$ calculated at the CCSD(T) level exceeds corresponding value calculated at the MP2 level of theory (see Table 5.1). It should be pointed out that for configurations 4 and 5 (symmetry C_s) the main axes of the polarizability tensor for the complex do not coincide with the coordinate system of the complex (Fig. 3.1), which leads to the appearance of the non-zero nondiagonal component α_{xy}. However, the values of α_{xy} for these configurations are very small

($\alpha_{xy} \sim 0.005\ e^2a_0^2E_h^{-1}$ at R=6.6 a_0) and go to zero at increasing R.

It is interesting to compare the results of *ab initio* calculations with the results of analytical polarizability calculations of the considered complex, carried out using Eqs. 5.3-5.5. It is convenient to carry out such comparison for the interaction polarizabilities $\Delta\alpha_{\alpha\beta}$ defined as:

$$\Delta\alpha_{\alpha\beta} = \alpha_{\alpha\beta}^{AB} - \alpha_{\alpha\beta}^{A} - \alpha_{\alpha\beta}^{B} \equiv \alpha_{\alpha\beta}^{AB}(R) - \alpha_{\alpha\beta}^{AB}(\infty). \tag{5.7}$$

The results of the calculation of $\Delta\alpha_{\alpha\beta}$ for two configurations of the complex, which are typical cases for the polarizability tensor, namely $\alpha_{xx}^{AB} \neq \alpha_{yy}^{AB} \neq \alpha_{zz}^{AB}$ and $\alpha_{xx}^{AB} \neq \alpha_{yy}^{AB} = \alpha_{zz}^{AB}$, are presented in Fig. 5.2. The analysis of Fig. 5.2 shows that the values $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$, calculated using both methods, are in a good agreement in the considered range of intermolecular separations. The values of $\Delta\alpha_{xx}$ agree well for $R > 10\ a_0$, and for shorter R the analytical values of $\Delta\alpha_{xx}$ noticeably exceed the results of *ab initio* calculations. There is an analogous situation with the other configurations of the complex CH_4-N_2.

The analytical polarizability description for the complex allows us to evaluate the contributions to $\Delta\alpha_{\alpha\beta}$ (and, accordingly, to $\alpha_{\alpha\beta}^{AB}$) of the different terms in Eqs. 5.3–5.4. As an example, the results of the calculations of these contributions to $\Delta\alpha_{\alpha\beta}$ for configuration 3 of the CH_4-N_2 complex are presented in Fig. 5.3. This figure shows that the major contribution to the polarizability of the complex is due to the terms such as $\alpha^A\alpha^B \sim R^{-3}$ (in Eq. 5.4), caused by dipole-induced-dipole interactions. It should be noticed that the contribution of these terms is the leading one for any configuration of the complex. The induction contribution of the terms $\sim R^{-4}(A^A\alpha^B)$ and $\sim R^{-5}(E^A\alpha^B, \alpha^AE^B$ and $B^A\Theta^B)$, and also the terms $\sim R^{-6}$ caused by back induction effect due to dipole-induced-dipole interaction $(\alpha^A\alpha^B\alpha^A + \alpha^B\alpha^A\alpha^B)$ are of comparable values. However, their role is different for the tensor components α_{ii}, and to a significant extent depends on the configuration of the complex. It should be noticed that there is a small value of the contribution of the induction term $\beta^A\Theta^B$ ($\sim R^{-4}$) to $\Delta\alpha_{ii}$, which is also typical for other configurations. The contribution of the terms α^{disp} (R^{-6}) caused by dispersion interactions is comparable in value with the contribution of the induction terms due to their partial mutual compensation.

It is also of interest to consider the polarizability tensor invariants for the CH_4-N_2 complex: the mean polarizability,

$$\alpha^{AB} = \frac{1}{3}(\alpha_{xx}^{AB} + \alpha_{yy}^{AB} + \alpha_{zz}^{AB}) \tag{5.8}$$

and the anisotropy of the polarizability tensor

$$\gamma^{AB} = \Big[\frac{1}{2}(\alpha_{xx}^{AB} - \alpha_{yy}^{AB})^2 + \frac{1}{2}(\alpha_{xx}^{AB} - \alpha_{zz}^{AB})^2 + \frac{1}{2}(\alpha_{zz}^{AB} - \alpha_{yy}^{AB})^2$$
$$+3(\alpha_{xy}^{AB})^2 + 3(\alpha_{xz}^{AB})^2 + 3(\alpha_{yz}^{AB})^2\Big]^{\frac{1}{2}}. \tag{5.9}$$

Ab initio values of the polarizability tensor invariants α^{AB} and γ^{AB} as functions of R for the six considered configurations of the CH_4-N_2 complex can be simply calculated using

Eqs. 5.8 and 5.9 with the help of the data from Appendix VII, assuming the contributions of the nondiagonal elements of the polarizability tensor of the complex to the anisotropy to be negligible. The comparison of *ab initio* and analytical calculations of the invariants α^{AB} and γ^{AB} can be carried out using the mean ($\Delta\alpha$) and the anisotropy ($\Delta\gamma$) of the interaction polarizability

$$\Delta\alpha = \alpha^{AB} - \alpha^{CH_4} - \alpha^{N_2} \tag{5.10}$$

and

$$\Delta\gamma = \gamma^{AB} - \gamma^{N_2}, \tag{5.11}$$

describing the contribution of intermolecular interactions to the invariants α^{AB} and γ^{AB}, where α^{CH_4}, α^{N_2} and γ^{N_2} are the mean polarizabilities and the anisotropy of the molecules CH_4 and N_2.

The calculation results of the interaction anisotropy $\Delta\gamma$ as a function of R for the six considered configurations of the CH_4-N_2 complex are presented in Fig. 5.4. It is noticeable that the form of the function $\Delta\gamma(R)$ is significantly dependent on the complex configuration. Thus, for configurations 1, 3 and 6 in the investigated range of intermolecular separations, the interaction anisotropy $\Delta\gamma(R)$ monotonically increases with decreasing R, which corresponds to the increasing of the polarizability anisotropy γ^{AB}. For configurations 2, 4 and 5 the behavior of function $\Delta\gamma(R)$ is more complicated, and the negative sign of $\Delta\gamma(R)$ implies the decreasing of γ^{AB} in comparison with the complex anisotropy $\gamma^{AB}(\infty) \equiv \gamma^{N_2}$. Fig. 5.4 also shows that *ab initio* calculations of the interaction anisotropy $\Delta\gamma$ agree well with the analytical calculations of these values in the whole considered range of R, and for $R \geq 10\ a_0$ this agreement is very good. Analytical calculations show that the leading contribution to the interaction anisotropy of the complex for $R \geq 10\ a_0$ gives the induction terms $\alpha^A\alpha^B(R^{-3})$, and for $R \leq 10\ a_0$ the substantial contribution to $\Delta\gamma$ gives the dispersion and induction terms of higher order, which can lead to the nonmonotonic behavior of $\Delta\gamma(R)$ (see, for example, Fig. 5.4*b*).

The mean interaction polarizability $\Delta\alpha$ for the CH_4-N_2 complex is considerably smaller than the interaction anisotropy $\Delta\gamma$ (Fig. 5.5). Fig. 5.5 shows that there is, as for $\Delta\gamma$, a good agreement between analytical and *ab initio* calculations of $\Delta\alpha$ for $R \geq 10\ a_0$ For $R < 10\ a_0$ the approximation used in the analytical calculation does not allow to describe correctly the function $\Delta\alpha(R)$ even qualitatively. It is noticeable that for configurations 2, 4 and 5 in the considered range of R, the sign of the function $\Delta\alpha(R)$ changes, *i.e.* there are intermolecular separations for which the different types of induction and dispersion contributions compensate each other. Thus, for example, the function $\Delta\alpha(R)$ for the configuration 5 is positive only in the range $8 < R < 11\ a_0$ The nature of the change of the sign for the function $\Delta\alpha(R)$ at $R \approx 11\ a_0$ is illustrated in Fig. 5.6. The figure shows that for $R > 11\ a_0$ the negative values of the function $\Delta\alpha(R)$ are defined by the induction terms $\alpha^A\alpha^B(\sim R^{-3})$ in Eq. 5.4. The change of sign of the function $\Delta\alpha(R)$ at the point $R \approx 11\ a_0$ is in total agreement with the classical theory (Eqs. (1)-(7)) and takes place mainly due to the dominance of the contribution from the terms $A^A\alpha^B(\sim R^{-4})$, $E^A\alpha^B(\sim R^{-5})$, $\alpha^A\alpha^B\alpha^A + \alpha^B\alpha^A\alpha^B(\sim R^{-6})$ and $\alpha^{disp}(\sim R^{-6})$ over the contribution from the terms $\alpha^A\alpha^B(\sim R^{-3})$ and $\alpha^A E^B(\sim R^{-5})$. It should be noticed that the terms $\beta^A\Theta^B(\sim R^{-4})$ and $B^A\Theta^B(\sim R^{-5})$ give no contribution to $\Delta\alpha(R)$ for all configurations of the CH_4-N_2 complex. The change of sign of the function $\Delta\alpha(R)$ at $R \approx 8\ a_0$ for configuration 5 and also at $R \approx 7\ a_0$ for configurations 2 and 4 (see Figs. 5.5 and 5.6) cannot be explained by the classical theory in the framework of the considered approximation. In order to explain such a behavior of the function $\Delta\alpha(R)$ in this range, there is probably a need to account for the induction and dispersion interactions of higher order and also for the exchange interaction.

5.2 Polarizability of the most stable configuration

It is interesting to consider the polarizability of the CH_4-N_2 complex being in the most stable configuration. In Ref. [141] (see Chapter Three) it is shown that the complex has not just one stable configuration, but a family of the most stable configurations, whose interaction energies differ by less than 0.16 μE_h. The family of these configurations can be obtained from configuration 4 by rotating the N_2 molecule around x-axis by an angle τ (see Fig. 3.2) at the equilibrium intermolecular separation $R_e = 6.84\ a_0$. It is obvious that the polarizability tensor components $\alpha^{AB}_{\alpha\beta}(R_e)$ are different for the different configurations of the family. However, the *ab initio* calculations of the polarizability tensor invariants $\alpha^{AB}(R_e)$ and $\gamma^{AB}(R_e)$ for this family of configurations, when the monomers CH_4 and N_2 in the complex are considered to be rigid, have shown that the values of the invariants almost coincide and are equal to $\alpha^{AB}(R_e) = 28.13\ e^2a_0^2E_h^{-1}$ and $\gamma^{AB}(R_e) = 3.82\ e^4a_0^4E_h^{-3}$. Calculated values $\alpha^{AB}(R_e)$ and $\gamma^{AB}(R_e)$ are less than the values of the invariants $\alpha^{AB}(\infty) = 28.34\ e^2a_0^2E_h^{-1}$ and $\gamma^{AB}(\infty) = 4.61\ e^4a_0^4E_h^{-3}$ for the noninteracting molecules CH_4 and N_2, which indicates the reduction of the mean polarizability and anisotropy of the polarizability tensor for the CH_4-N_2 complex at the formation of the more stable configurations. This leads to the reduction of the efficiency of light scattering (index of refraction $n \sim \alpha$), including rotational Raman scattering. Note that the calculated values $\alpha^{AB}(\infty)$ and $\gamma^{AB}(\infty)$ are in a good agreement with the values $\alpha^{CH_4} + \alpha^{N_2} = 28.16\ e^2a_0^2E_h^{-1}$ and $\gamma^{N_2} = 4.61\ e^4a_0^4E_h^{-3}$, which were obtained from the high-accuracy calculations of the molecules CH_4 and N_2 [100, 101] (see Table 8.2).

As far as, at the formation of the complex, the monomers CH_4 and N_2 are deformed (see [141]), it is of interest to estimate the change of the complex polarizability caused by the nonrigidity of the monomers. For this purpose we have carried out *ab initio* calculations of the polarizability tensor invariants $\widetilde{\alpha}^{AB}(R_e)$ and $\widetilde{\gamma}^{AB}(R_e)$ for the family of the most stable configurations of the CH_4-N_2 complex at full optimization of their geometries. The results of calculations have shown that accounting for the monomer nonrigidity practically does not affect on the mean polarizability $\alpha^{AB}(R_e)$, but noticeably increases (on $\sim 2.3\%$) the polarizability anisotropy $\gamma^{AB}(R_e)$ of the complex.

Ab initio calculated polarizability tensor invariants $\alpha^{AB}(R)$ and $\gamma^{AB}(R)$ for the family of the most stable configurations of the CH_4-N_2 complex can be expanded in a series in the vicinity of R_e (in a.u.):

$$\alpha^{AB}(R) = 28.105 + 0.208(R - 6.84) - 0.081(R - 6.84)^2, \tag{5.12}$$

$$\gamma^{AB}(R) = 3.801 + 0.091(R - 6.84) + 0.047(R - 6.84)^2. \tag{5.13}$$

The expressions obtained allow to estimate the derivatives of the polarizability tensor invariants for the CH_4-N_2 complex in the case of rigid interacting molecules CH_4 and N_2. Particularly, at $R_e = 6.84\ a_0$, the first derivatives $\partial\alpha^{AB}(R)/\partial R = 0.208\ e^2 a_0 E_h^{-1}$ and $\partial\gamma^{AB}(R)/\partial R = 0.091\ e^4 a_0^3 E_h^{-3}$ are of different sign and considerably differ in their absolute value.

5.3 Polarizability of free oriented interacting molecules CH_4-N_2

The analytical representation of the polarizability of interacting molecules allows us to simply calculate the polarizability of the free oriented interacting molecules CH_4 and N_2. For this purpose, the polarizabilities $\alpha^{AB}_{\alpha\beta}$ (Eqs. 5.3 - 5.5) should be averaged over Euler angles χ_A, θ_A, φ_A, θ_B and φ_B. In this case the polarizability tensor has only two independent components and has the form:

$$\overline{\alpha}^{AB}_{xx} = \alpha^A + \alpha^B + \frac{4}{R^3}\alpha^A\alpha^B + \frac{4}{R^6}\alpha^A\alpha^B(\alpha^A + \alpha^B) + \frac{22\alpha^A}{45R^6}(\alpha^B_{zz} - \alpha^B_{xx})^2 + \frac{7C_6^{AB}}{18R^6}\left(\frac{\overline{\gamma}^A}{\alpha^A} + \frac{\overline{\gamma}^B}{\alpha^B}\right) \tag{5.14}$$

and

$$\begin{aligned}\overline{\alpha}^{AB}_{yy} = \overline{\alpha}^{AB}_{zz} &= \alpha^A + \alpha^B - \frac{2}{R^3}\alpha^A\alpha^B + \frac{1}{R^6}\alpha^A\alpha^B(\alpha^A + \alpha^B)\\ &+ \frac{19\alpha^A}{45R^6}(\alpha^B_{zz} - \alpha^B_{xx})^2 + \frac{2C_6^{AB}}{9R^6}\left(\frac{\overline{\gamma}^A}{\alpha^A} + \frac{\overline{\gamma}^B}{\alpha^B}\right),\end{aligned} \tag{5.15}$$

where $\overline{\gamma}^A$ and $\overline{\gamma}^B$ are the mean hyperpolarizabilities of the methane and nitrogen molecules. The expressions for the mean hyperpolarizabilities $\overline{\gamma}^A$ and $\overline{\gamma}^B$ are written as

$$\overline{\gamma}^A = \frac{3}{5}(\gamma^A_{zzzz} + 2\gamma^A_{zxzx}), \tag{5.16}$$

$$\overline{\gamma}^B = \frac{1}{15}(3\gamma^B_{zzzz} + 12\gamma^B_{zxzx} + 8\gamma^B_{xxxx}). \tag{5.17}$$

In Eqs. 5.14 and 5.15 the isotropic dispersion coefficient C_6^{AB}

$$C_6^{AB} = \frac{3}{\pi}\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega \tag{5.18}$$

is simply related to the coefficients $C_{\eta\gamma}$ and $D_{\eta\gamma}$ from Eq. 5.5: $C_6^{AB} = 6C_{xx} = 6C_{yy} = 6C_{zz} = 2Dxx{+}2D_{yy}{+}2D_{zz}$. It is obvious that the polarizabilities $\overline{\alpha}_{ii}$ are defined only by the tensors $\alpha^{A,B}_{\alpha\beta}$ and $\gamma^{A,B}_{\delta\varepsilon\alpha\beta}$ of the interacting molecules CH_4 and N_2 and by the dispersion coefficient C_6^{AB}. The calculated value of the coefficient $C_6^{AB} = 97.26\ E_h{\cdot}a_0^6$ using Eq. 5.18 is in a good agreement with

$C_6^{AB} = 96.94\ E_h \cdot a_0^{-6}$ from work [98]. Note that Eqs. 5.14 and 5.15, when $\alpha_{xx}^B = \alpha_{zz}^B$, become the well known expressions for the polarizabilities of two interacting spherically symmetric atoms A and B [54, 55].

The analysis of Eqs. 5.14 and 5.15 shows that the dependence of the polarizability tensor components $\overline{\alpha}_{ii}^{AB}$ and the anisotropy of the polarizability tensor $\overline{\alpha}_{xx}^{AB} - \overline{\alpha}_{yy}^{AB}$ on the intermolecular separation is defined mainly by the terms $\sim R^{-3}$, and the R-dependence of the mean polarizability $\overline{\alpha}^{AB} = (\overline{\alpha}_{xx}^{AB} + 2\overline{\alpha}_{yy}^{AB})/3$ is defined by the terms $\sim R^{-6}$:

$$\overline{\alpha}^{AB} - \alpha^A - \alpha^B = \frac{2}{R^6}\alpha^A\alpha^B(\alpha^A + \alpha^B) + \frac{4\alpha^A}{9R^6}(\alpha_{zz}^B - \alpha_{xx}^B)^2 + \frac{5C_6^{AB}}{18R^6}\Big(\frac{\overline{\gamma}^A}{\alpha^A} + \frac{\overline{\gamma}^B}{\alpha^B}\Big). \tag{5.19}$$

The calculation has shown that the first term in the right part of Eq. 5.19 gives the leading contribution ($\sim$ 64 %), the dispersion interactions (the third term) give the contribution $\sim$ 35 %, and the contribution of the second term, which is defined by the anisotropy of the polarizability tensor of the N_2 molecule, is very small ($\sim$ 1 %).

5.4 Vibrational Raman spectrum

The computations were carried out with Gaussian03 [34] package at the MP2/aug-cc-pVTZ level of theory for monomers CH_4, N_2 and for complex CH_4-N_2 (configuration 4). The molecular geometries of these species were optimized followed by a frequency calculation. The automatic methods in Gaussian were used to compute the Raman activities for 90° scattering [143] (keyword: freq=Raman):

$$R_A = (45(\alpha')_k^2 + 7(\gamma')_k^2)/45, \tag{5.20}$$

where $(\alpha')_k^2$ is a square magnitude of derivative of the isotropic part polarizability tensor with respect to the k-th normal mode, and $(\gamma')_k^2$ is a square magnitude of derivative of the anisotropic part polarizability tensor with respect to the k-th normal mode and the derivatives are evaluated at zero displacement. It should be noted that R_A is proportional to the Raman intensity I.

In the Figs. 5.7-5.8 the Raman spectrum is presented for the CH_4-N_2 complex. At Fig. 5.8 all of the predicted anharmonic frequencies (see Table 3.8) corresponding to the frequencies of methane were scaled by 0.983 factor to fit the experimental data. As the MP2 method gives the harmonic frequency of the N_2 molecule that is far from the experimental one, we have corrected the harmonic frequency ω of N_2 and the harmonic frequency of the mode ν_{11} of the complex by factor 1.054 to fit the experimental value 2358.6 cm^{-1} [188]. For figures 5.7-5.8 the Lorentzians with 10 cm^{-1} width were used. Figures and Table 5.2 show that for all vibrational modes of the CH_4-N_2 complex R_A decreases by factors 0.7-0.98 in comparison with R_A for the vibrational modes of monomers CH_4 and N_2.

The Raman spectrum can be used to give additional information regarding the properties of Raman scattering. One of the important properties is the depolarization ratio ρ. The depolarization ratio ρ is defined as the ratio of the intensities I_y/I_x, where I_y and I_x are the

TAB. 5.2 - *Harmonic ω vibrational wavenumbers (in cm^{-1}) and Raman activities R_A (Å^4/AMU) calculated at the MP2/aug-cc-pVTZ level of theory with BSSE correction for configuration 4 of the CH_4-N_2 complex. In parenthesis we present the correspondence of the complex vibrational modes to the vibrational modes of the monomers.*

Mode	Sym.	$\omega^{complex}$	$R_A^{complex}$	$\omega^{monomer}$	$R_A^{monomer}$
1	A''	19.6	0.2787		
2	A''	23.3	0.9607		
3	A'	48.2	0.0463		
4	A'	65.7	0.0032		
5	A''	71.8	0.0123		
6 (ν_4, CH_4)	A'	1355.3694	0.0141	1356.0124	0.0188
7 (ν_4, CH_4)	A''	1356.0315	0.0136	1356.0124	0.0188
8 (ν_4, CH_4)	A'	1356.0581	0.0118	1356.0124	0.0188
9 (ν_2, CH_4)	A''	1587.6962	2.7775	1588.5680	2.8632
10 (ν_2, CH_4)	A'	1588.2845	2.8162	1588.5680	2.8632
11 (ν, N_2)	A'	2185.0729	14.6099	2186.8628	16.0198
12 (ν_1, CH_4)	A'	3066.7775	215.6018	3069.5665	224.5058
13 (ν_3, CH_4)	A''	3201.5411	35.6778	3204.9644	41.9746
14 (ν_3, CH_4)	A'	3201.5602	36.2711	3204.9644	41.9746
15 (ν_3, CH_4)	A'	3203.9712	44.2979	3204.9644	41.9746

components of intensity of scattered light in the plane perpendicular to the direction of scattered light propagation (along z-axis). Fig. 5.9 shows that polarization properties of Raman scattering are retained in the complex for vibrational frequencies corresponding to the frequencies of monomers CH_4 and N_2 (anisotropic Raman scattering: ν_2, ν_3 and ν_4 of the CH_4 molecule; isotropic Raman scattering: ν_1 of the methane molecule and ν of the dinitrogen molecule), which is in agreement with the symmetry of vibrations. Fig. 5.9 also shows that the Raman scattering for intermolecular vibrations (modes 1, 2, 4 and 5 from Table 5.2) has purely anisotropic nature ($\rho \approx 3/4$ for linearly polarized (the vector of the electric field of the incident light is directed along the y-axis) and $\rho \approx 6/7$ for unpolarized incident light), and the Raman scattering for the vibrational mode 3 (ν=48.2 cm^{-1}) is a mixture of the anisotropic and isotropic scattering. It should be noted that for collision Raman scattering the Raman line intensities could be larger than predicted ones for configuration 4.

FIG. 5.3 - *Interaction polarizabilities* $\Delta\alpha_{ii}$, *and induction and dispersion contributions to* $\Delta\alpha_{ii}$ *of the* CH_4-N_2 *complex for the configuration 3 (b, d - enlarged fragments). All values are in a.u. 1 -* $\Delta\alpha_{ii}$, *2 -* $\alpha^A\alpha^B$ *contributions, 3 -* $\beta^A\Theta^B$ *contribution, 4 -* $A^A\alpha^B$ *contributions, 5 -* $E^A\alpha^B$ *contributions, 6 -* $\alpha^A E^B$ *contributions, 7 -* $B^A\Theta^B$ *contribution, 8 -* $\alpha^A\alpha^B\alpha^A + \alpha^B\alpha^A\alpha^B$ *contribution, 9 -* α^{disp} *contribution.*

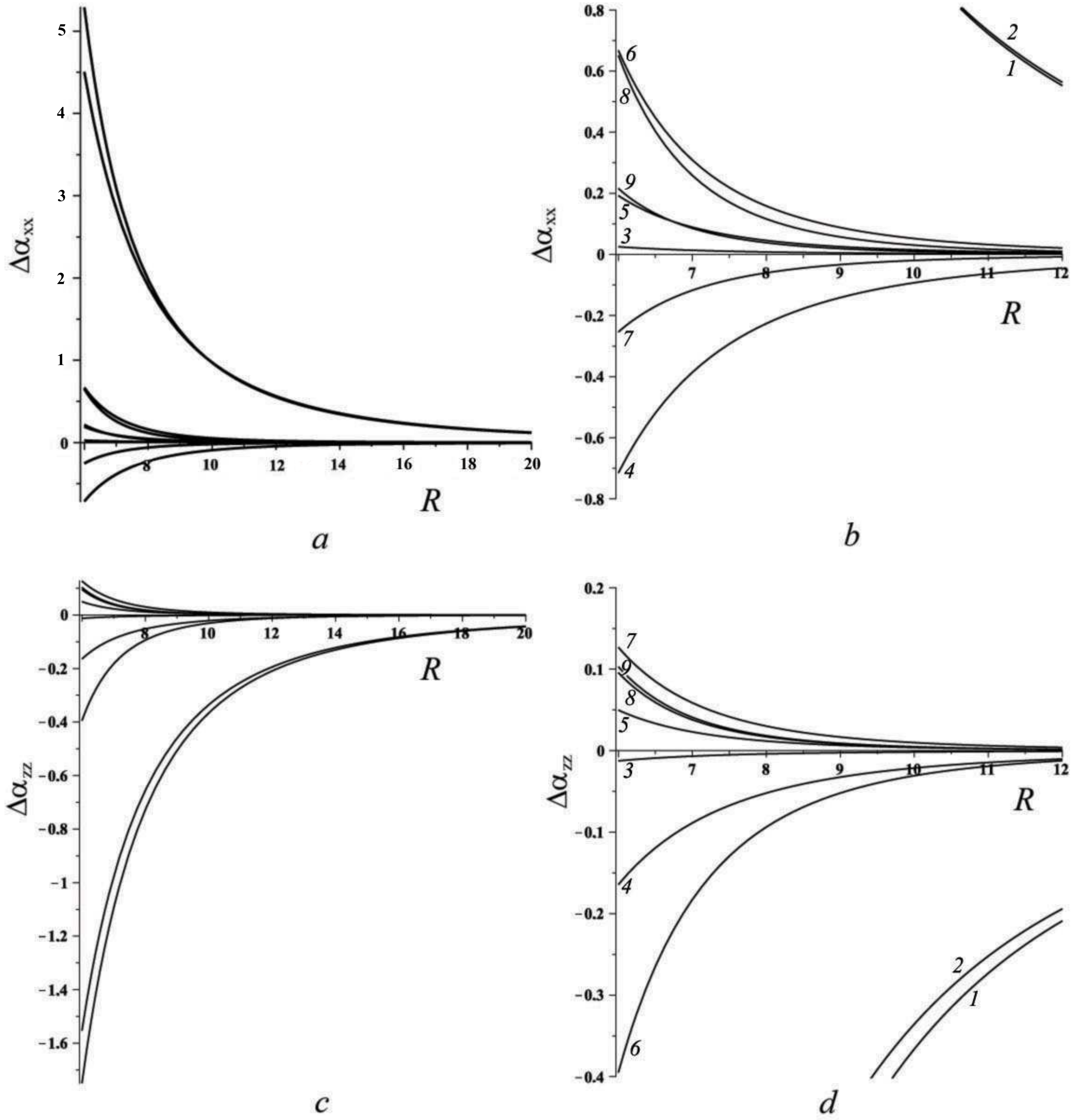


FIG. 5.4 - *Interaction anisotropy $\Delta\gamma$ for the CH_4-N_2 complex (a - configurations 1, 3 and 6; b - configurations 2, 4 and 5). All values are in a.u. Configurations 1 and 2: solid lines - analytical calculations, solid boxes - CCSD(T) calculations. Configurations 3 and 4: dash lines - analytical calculations, boxes - CCSD(T) calculations. Configurations 5 and 6: dot lines - analytical calculations, solid circles - CCSD(T) calculations.*

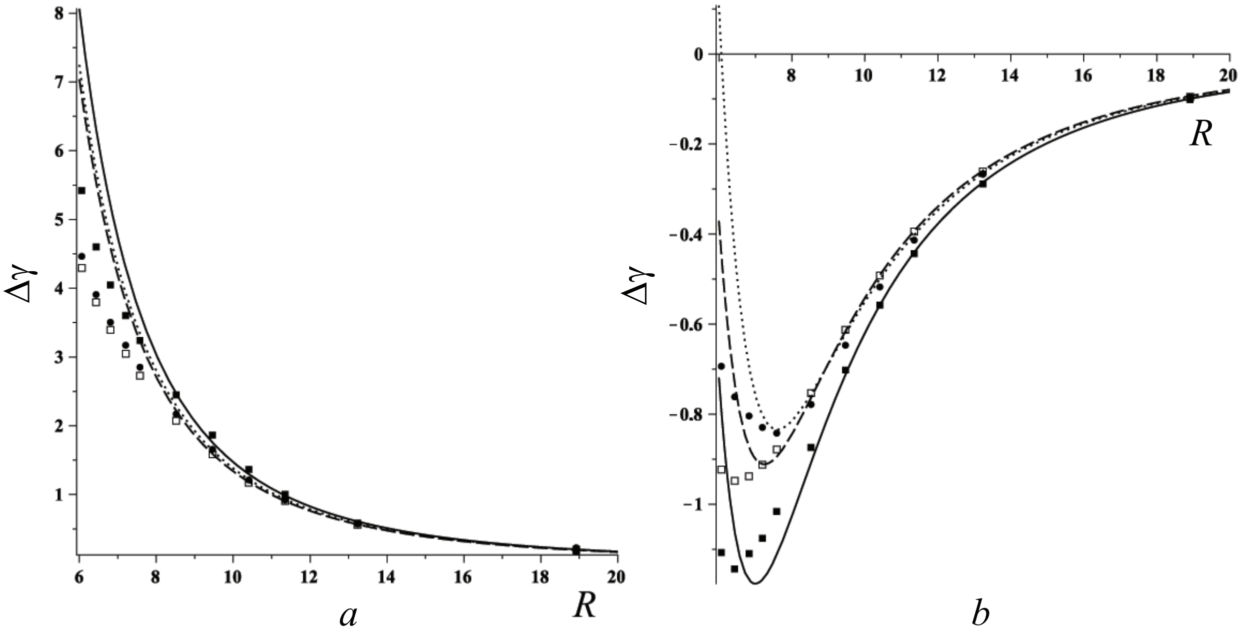


Fig. 5.5 - *The mean interaction polarizability $\Delta\alpha$ for the CH_4-N_2 complex for configurations 1–6. All values are in a.u. The numbers in the figure correspond to those of the configurations. Solid lines - analytical calculations, diamonds - CCSD(T) calculations for the configuration 1, solid circles - CCSD(T) calculations for the configuration 2, solid boxes - CCSD(T) calculations for the configuration 3, boxes - CCSD(T) calculations for the configuration 4, circles - CCSD(T) calculations for the configuration 5, solid diamonds - CCSD(T) calculations for the configuration 6.*

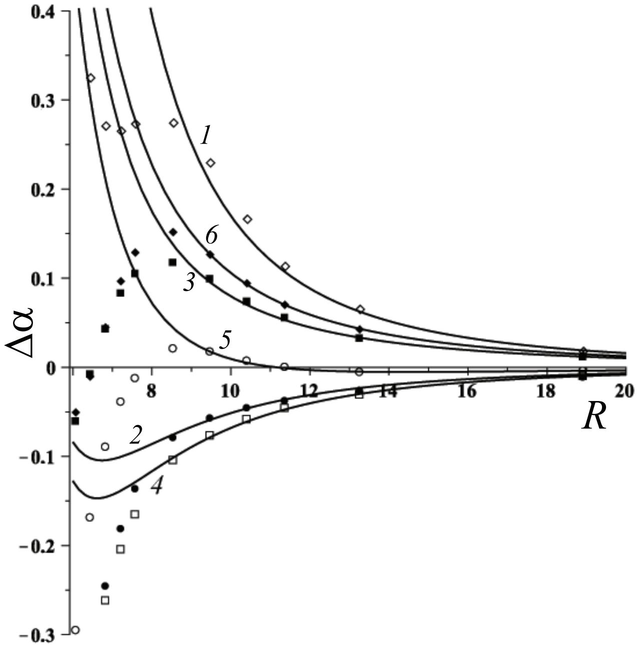


Fig. 5.6 - *Induction and dispersion contributions to* $\Delta\alpha$ *of the* CH_4*-*N_2 *complex for configuration 5 (on the right - enlarged fragment). All values are in a.u. 1 -* $\Delta\alpha$*, 2 -* $\alpha^A\alpha^B$ *contributions, 3 -* $A^A\alpha^B$ *contributions, 4 -* α^{disp} *contributions, 5 -* $\alpha^A E^B$ *contributions, 6 -* $\alpha^A\alpha^B\alpha^A + \alpha^B\alpha^A\alpha^B$ *contribution, 7 -* $E^A\alpha^B$ *contribution. Solid lines - analytical calculations, solid circles - CCSD(T) calculations, boxes - MP2 calculations.*

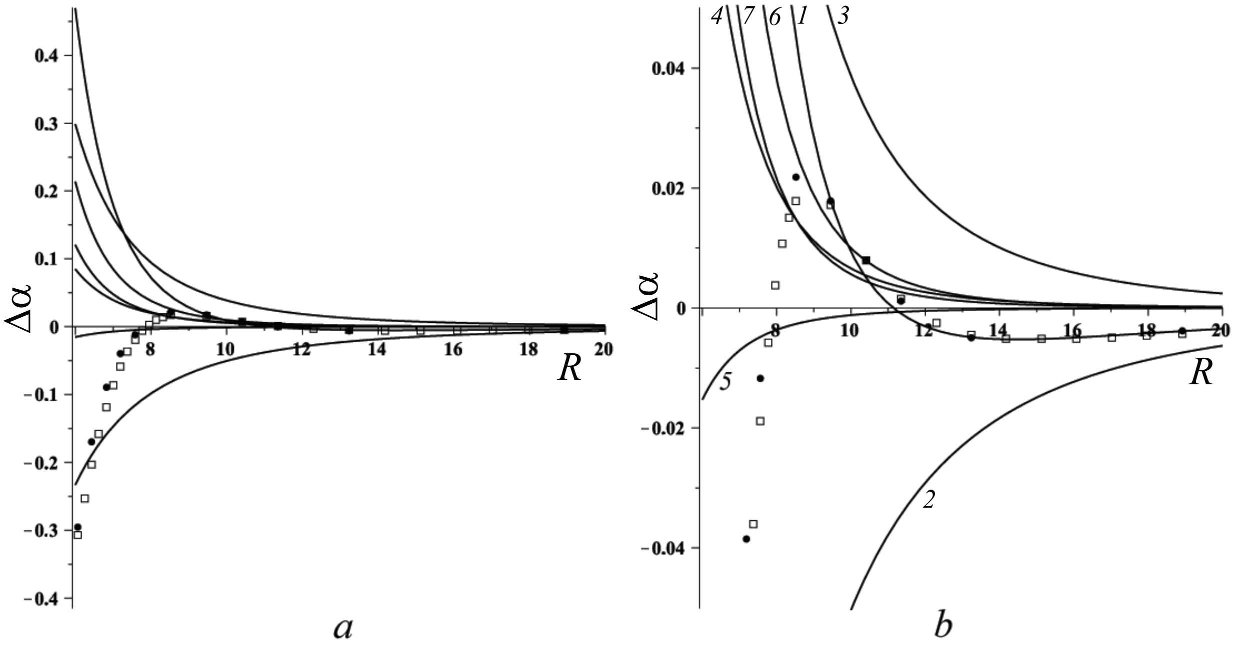
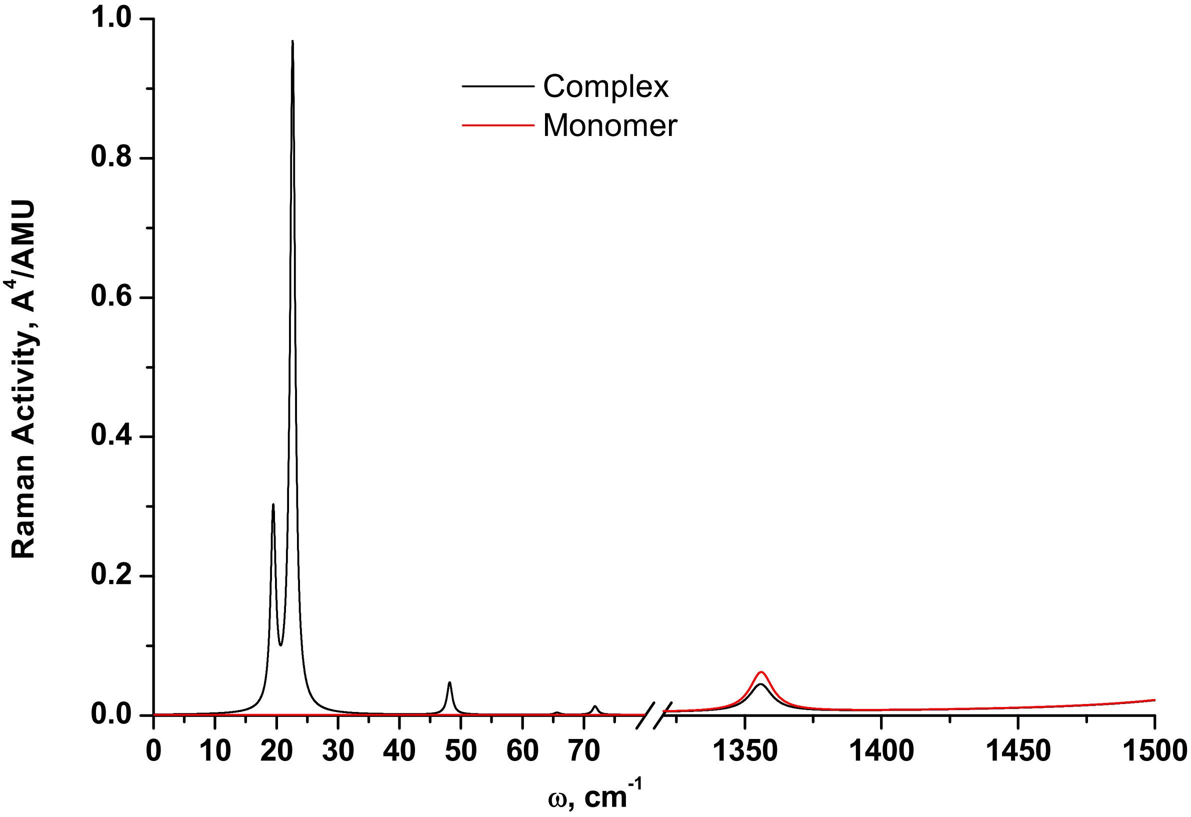
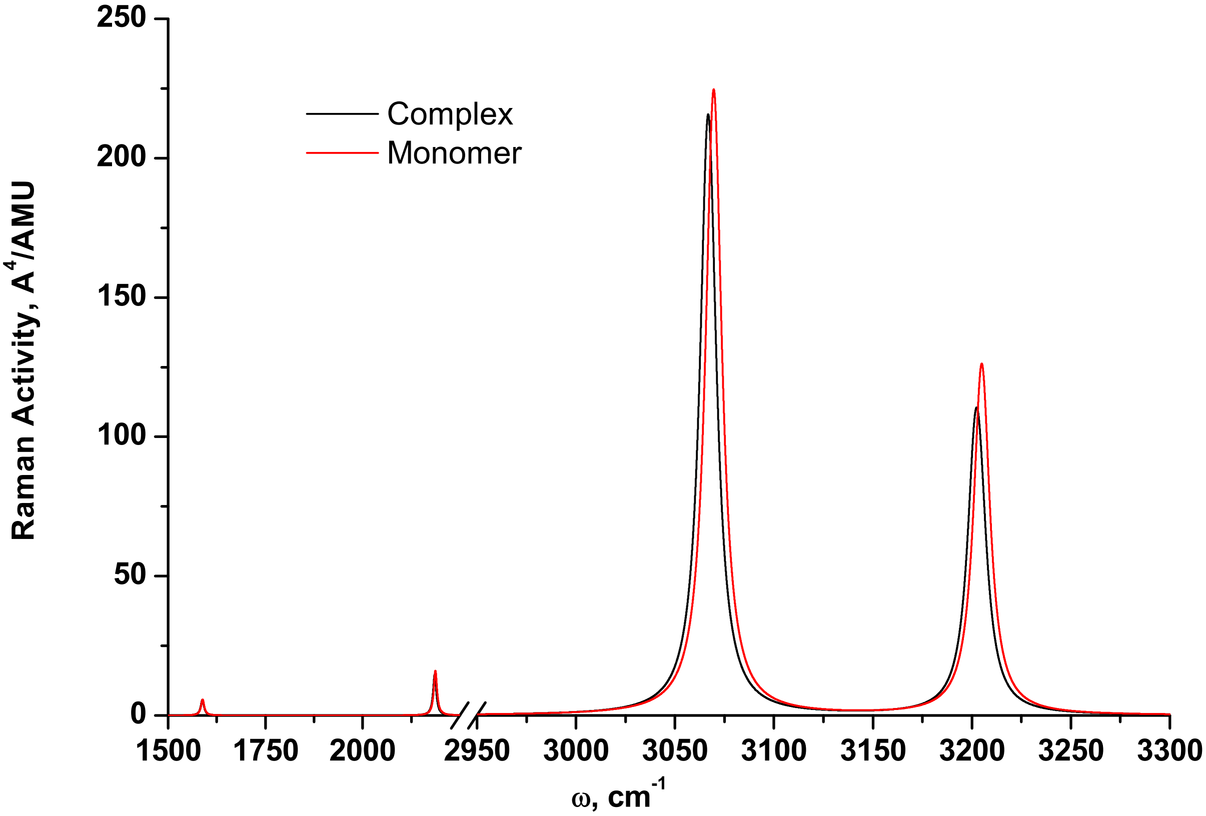


FIG. 5.7 - *Simulated Raman spectrum of the CH_4-N_2 complex calculated at the MP2/aug-cc-pVTZ level of theory for harmonic frequencies.*

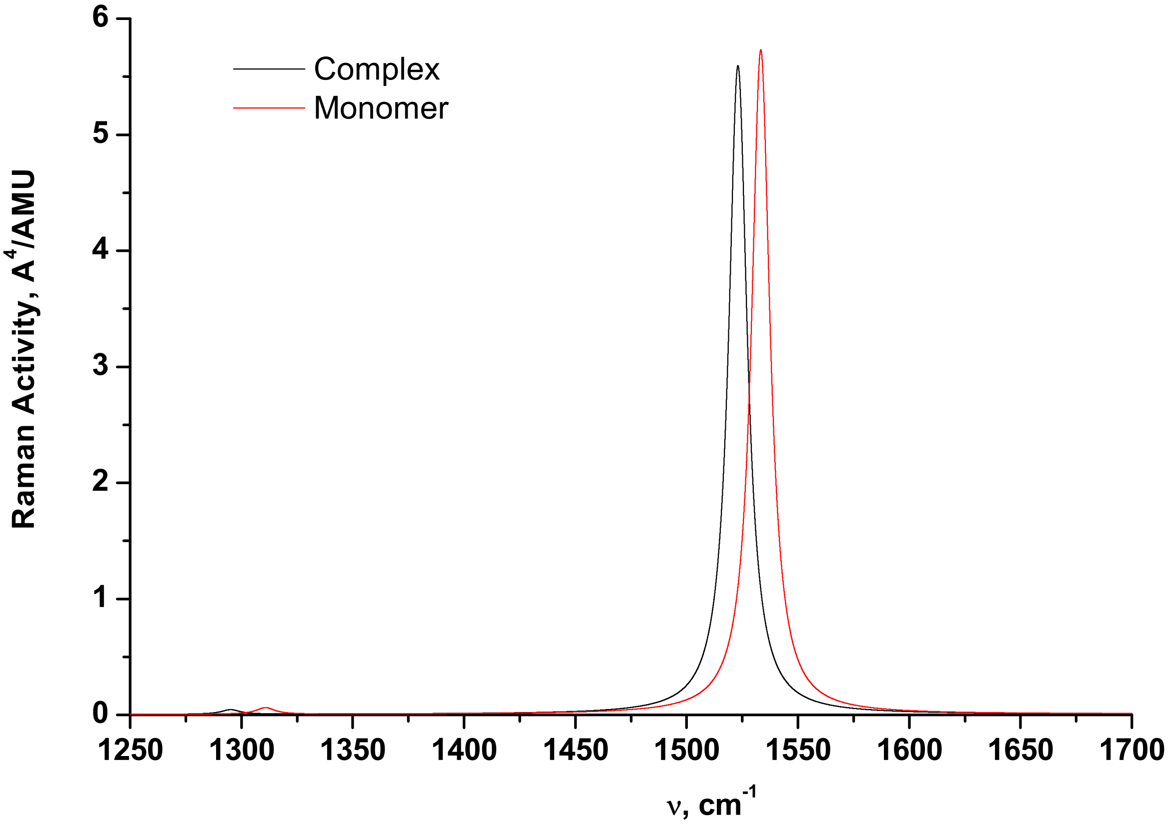


a



b

FIG. 5.8 - *Simulated Raman spectrum of the CH_4-N_2 complex calculated at the MP2/aug-cc-pVTZ level of theory for anharmonic frequencies (intermolecular modes are not presented) corresponding to the frequencies of the monomers CH_4 and N_2. Lorentzians with 10 cm^{-1} width were used.*



a

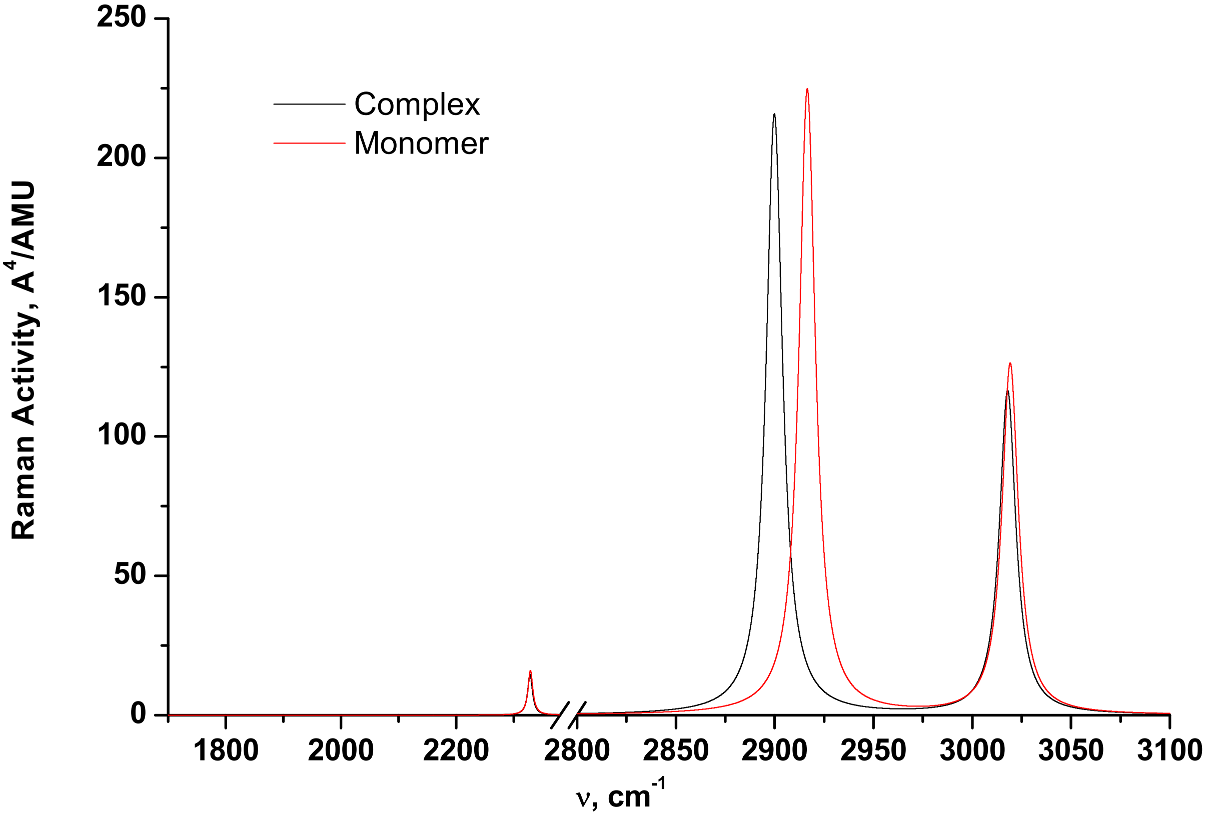
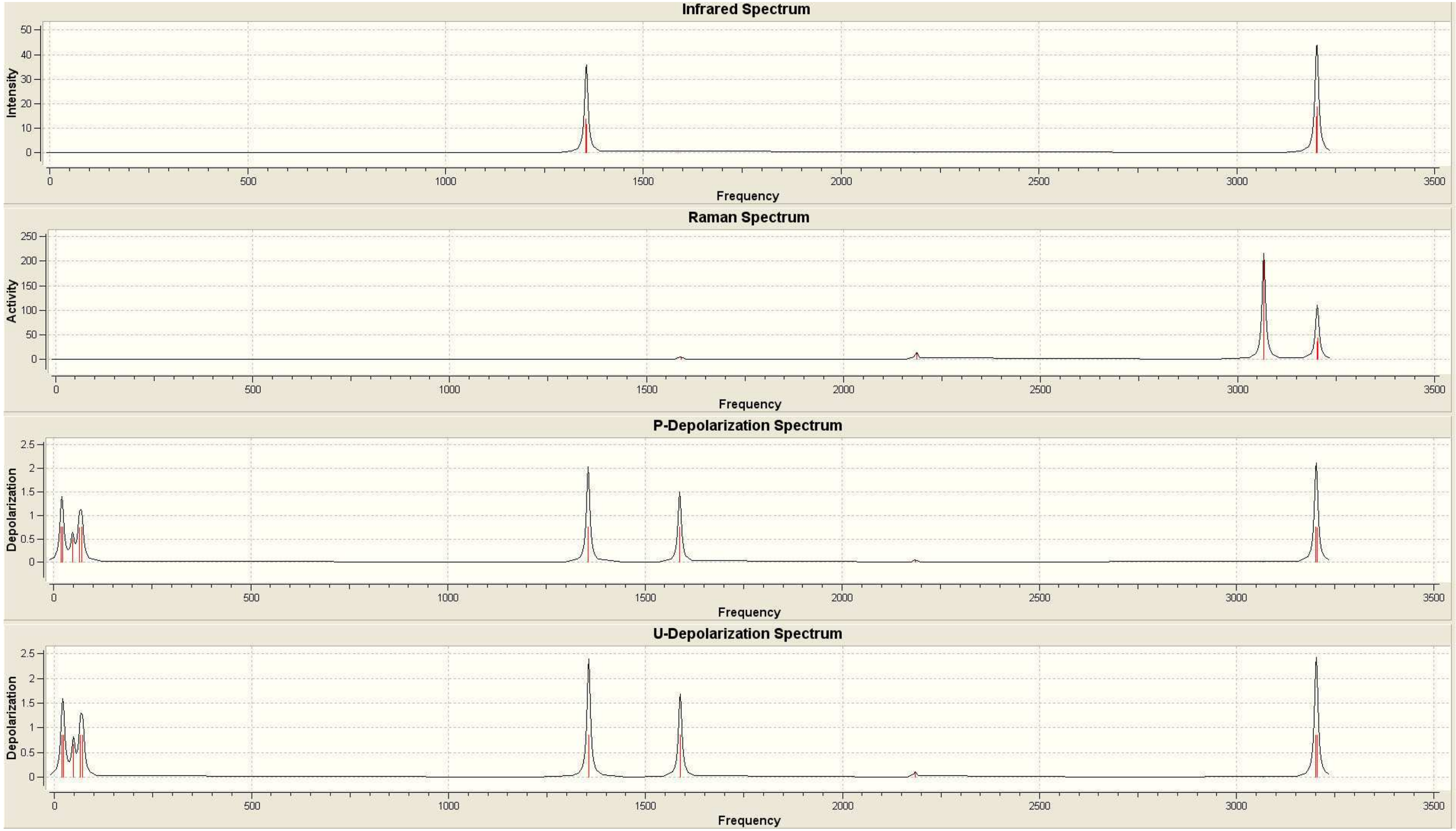


FIG. 5.9 - *Simulated Raman and IR spectrum (for harmonic frequencies) of the CH_4-N_2 complex calculated at the MP2/aug-cc-pVTZ level of theory (visualization using GaussView). The P-depolarization spectrum corresponds to the linearly polarized incident light, and the U-depolarization spectrum corresponds to the unpolarized (natural) incident light. Raman activity is in $\mathring{A}^4/AMU$, Infrared intensity is in km/mole.*



Fourth part

The C_2H_4-C_2H_4 van der Waals complex

Ethylene is a simple, unsaturated hydrocarbon. In spite of its chemical simplicity, C_2H_4 affects many diverse processes. Even in biology it is of great interest, for example, ethylene is a hormone that regulates a number of physiological and developmental events in plants [145].

Nonbonding interactions of π-electron systems have been intensively studied, since π-π interactions control several phenomena such as crystal packing of unsaturated hydrocarbon molecules, conformational preference of nucleic acids, and host-guest interactions of aromatic molecules. The ethylene dimer is the simplest π-π organic complex that can serve as a test object for nonbonding interaction theories.

Moreover, ethylene dimer as long as the methane-nitrogen complex is of particular interest for astrophysical applications. These complexes exist in the atmospheres of giant planets (Jupiter [146, 147], Saturn [148], Neptune and Uranus [149]) and Saturn's satellite Titan [80, 90, 92, 150, 151], and contribute to the IR absorption spectra of their atmospheres. In the present work we consider the interacting molecules C_2H_4 in their ground electronic state ^1A_g.

Chapter 6

Potential energy

Apparently, the history of quantum-mechanical calculations of the interaction energy of two ethylene molecules begins with the work of Hashimoto and Isobe in 1973 [152]. At the beginning the interaction energy calculations of the $(C_2H_4)_2$ van der Waals complex were performed at various levels of theoretical methods from semiempirical ones [152–157] to relatively simple variants of *ab initio* [158–163] methods. In these works the stability of different configurations of the ethylene dimer was investigated and the search of the most profound configuration was carried out. However, the first reliable interactions energies were calculated by Tsuzuki and Tanabe [164] in 1992 only. In this work the interaction potential energies of 12 orientations of ethylene dimer were calculated at the second-order Møller-Plesset (MP2) level of theory with the basis set 6-311G(2d,2p) accounting for the BSSE. The authors [164] have found the most stable configuration (D_{2d}) of ethylene dimer which agrees with the structure predicted from the analysis of infrared spectra of matrix isolated and solid ethylene [165]. In the sequel Tsuzuki et al. [166–168] have investigated the most profound configuration of $(C_2H_4)_2$ in more details using the modern theoretical *ab initio* methods with larger basis sets including the complete basis set (CBS) limit. As a result of these investigations the interaction energy of the most stable configuration of the ethylene dimer at MP2/CBS level of theory [168] at the equilibrium is $\Delta E^{MP2}(R_e)$ = -1.54 kcal/mol, which is 1.4 times larger than in [164]. Further, in Ref. [169] the authors obtained the value $\Delta E^{MP2}(R_e)$ = -1.62 kcal/mol, which was used for the interaction energy evaluation of the most stable configuration of $(C_2H_4)_2$ at the CCSD(T) level in the CBS limit. At present, the obtained value $\Delta E^{CCSD(T)}(R_e)$ = -1.51 kcal/mol [169] should be considered as the most accurate value of well depth of the most stable configuration of the ethylene dimer. Recently, the interaction energies of $(C_2H_4)_2$ were calculated in the framework of spin-component scaled second-order Møller-Plesset (SCS-MP2) method [170,171]. In the work [171] it was shown, that SCS-MP2 potential energy curves with obtained scaling parameters very well reproduce the corresponding CCSD(T) potential energy curves. We should point out, that in work [171] the potential energy calculations were carried out at the CCSD(T) level of theory for 6 configurations of $(C_2H_4)_2$, that is at present the most complete description of the potential energy of the ethylene dimer in the framework of high-level theory.

The other approach to the investigation of the potential energy surface of the $(C_2H_4)_2$

dimer was applied in Refs. [172–176] in the framework of analytical description of long range interactions between ethylene molecules in the multipole expansion. Such approach requires higher order multipole moments and polarizabilities, including imaginary frequency-dependent polarizabilities, and gives a physically correct analytical description of the potential energy surface for interacting molecules at large intermolecular separations. However, in the framework of this approach the well depths of different configurations of the $(C_2H_4)_2$ dimer can't be described correctly, because at such intermolecular separations the electron shells of interacting ethylene molecules begin to overlap and the long-range approximation is broken.

Our purpose is to carry out *ab initio* calculations at the CCSD(T) level of theory with relatively large correlation-consistent basis set and to investigate the applicability of the less demanding SAPT, DFT-SAPT, MP2 and explicitly-correlated methods CCSD(T)-F12 and MP2-F12 and analytical methods for the description of potential energy surface of the $(C_2H_4)_2$ van der Waals complex.

6.1 Coordinate system

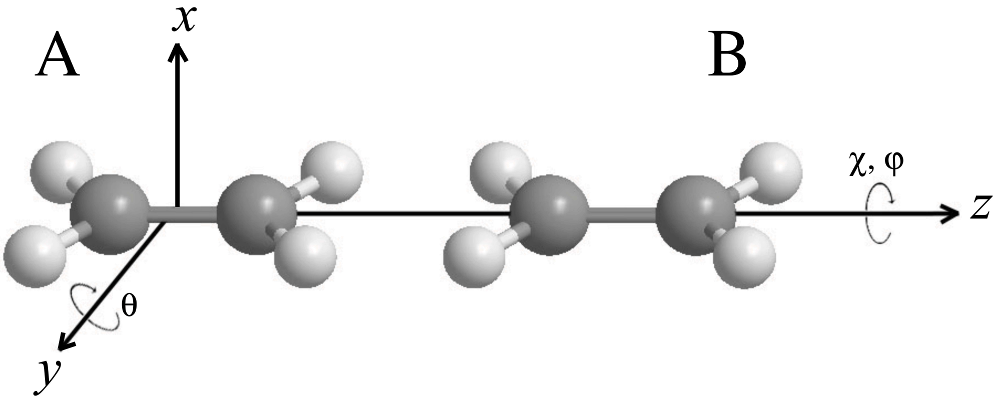
In the present work, for the description of the complex C_2H_4-C_2H_4 a Cartesian coordinate system was used (see Fig. 6.1). The C-C bond is in the yz-plane. The origin of this coordinate system is placed in the center of the C-C bond of the first (A) molecule. The vector $\boldsymbol{R}$ is directed from the origin to the center of C-C bond of the second (B) molecule and has the components (0, 0, R). The rotation of the i-th ethene molecule in this coordinate system is determined by 3 Euler angles: 1) rotation of angle χ_i around the z-axis; 2) rotation of angle θ_i around the y-axis; 3) rotation of angle φ_i around the z-axis. The initial position of the molecules in the C_2H_4-C_2H_4 complex, corresponding to the Euler angles $\chi_A = \theta_A = \varphi_A = \chi_B = \theta_B = \varphi_B = 0°$, is presented in Fig. 6.1.

The experimental r_0 (ground state) geometry of ethylene was used for all the calculations: the bond lengths and angles of ethylene $r_{CC} = 2.530\ a_0$ (1.339 Å), $r_{CH} = 2.050\ a_0$ (1.085 Å), $\alpha_{HCC} = 121.085$ and $\alpha_{HCH} = 117.83$ Deg were taken from ref. [177].

6.2 Potential energy surface

The calculations were carried out for 12 geometries (Fig. 6.2) of the C_2H_4-C_2H_4 complex in the approximation of rigid interacting molecules at the CCSD(T), MP2, MP2-F12, CCSD(T)-F12, SAPT and DFT-SAPT levels of theory with the correlation-consistent aug-cc-pVTZ (AVTZ) basis set. When calculating the energy at the CCSD(T), MP2, MP2-F12 and CCSD(T)-F12 levels of theory the BBSE correction was taken into account. It should be noted, that the SAPT and DFT-SAPT methods are BSSE free. The interaction energies $\Delta E(R)$ calculated at the CCSD(T) level of theory are shown at Fig. 6.3 (Table 8.4 in Appendix IX). The figure shows that the most profound geometry corresponds to configuration 2 with an interac-

FIG. 6.1 - *Coordinate system of the C_2H_4-C_2H_4 complex.*



tion energy of -2191.168 μE_h (480.9 cm^{-1}) at R_e = 7.181 a_0 (3.8 Å) which is consistent with the $\Delta E(R_e)$ = -2178 μE_h at R_e=7.086 a_0 (3.75 Å) (CCSD(T)/aug-cc-pVTZ) from Ref. [171]. The difference in values is due to the different bond lengths and angles used for the calculation. The authors of Ref. [171] used bond lengths (r_{CH} = 1.0810 Å and r_{CC} = 1.3332 Å) and angle (α_{HCC} = 121.33 Deg) optimized at the MP2/aug-cc-pVTZ level of theory.

The binding energy of the complex is a characteristic of its stability, thus the knowledge of its accurate value is very important because it could interpret and guide the experimental investigations. In the present work it was obtained in the CBS limit. For this purpose the extrapolation scheme of Helgaker et al. [30]

$$\begin{aligned} E_X^{HF} &= E_{CBS}^{HF} + B\texttt{exp}(-\alpha X), \\ E_X^{corr} &= E_{CBS}^{corr} + AX^{-3}, \\ E_{CBS}^{tot} &= E_{CBS}^{HF} + E_{CBS}^{corr}. \end{aligned} \tag{6.1}$$

was employed. The HF and correlation interaction energies were corrected for the BSSE. Since the ethylene dimer is a large system, the CCSD(T) calculations with a big cardinal number X (X = 4, 5, etc.) are very long and computationally expensive and extrapolation can only be performed at the MP2 level. However, the role of the higher-order correlation energy contributions can not be neglected and the interaction energies calculated at the CCSD(T) level of theory in the CBS limit were determined using the following scheme, proposed in Ref. [169]:

$$\Delta E_{CBS}^{CCSD(T)} = \Delta E_{CBS}^{MP2} + (\Delta E^{CCSD(T)} - \Delta E^{MP2})|_{aug-cc-pVTZ}. \tag{6.2}$$

The use of Eq. 6.2 is based on assumption that the difference between the CCSD(T) and MP2 interaction energies ($\Delta E^{CCSD(T)} - \Delta E^{MP2}$) depends only negligibly on the basis set size and can thus be determined with the medium basis set (we used the AVTZ basis set). The energies ΔE_{CBS}^{MP2} were obtained using Dunning's basis sets AVXZ (X = 3, 4). For calculating the ΔE_{CBS}^{HF} a 3-point extrapolation is needed. However, it was shown in Ref. [30] that parameter α is almost invariant and equals to 1.63, thus we fixed α = 1.63. Therefore, the energies with two basis

FIG. 6.2 - *Geometries of the C_2H_4-C_2H_4 complex.*

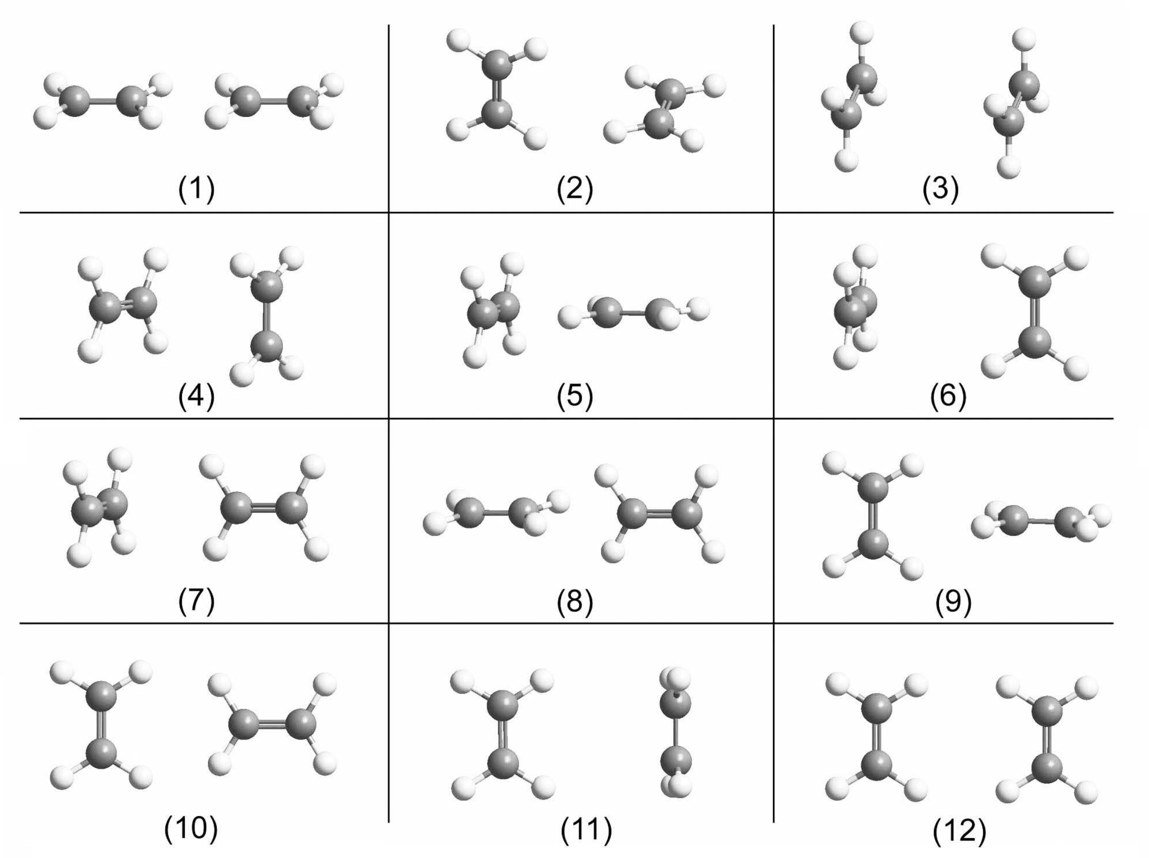
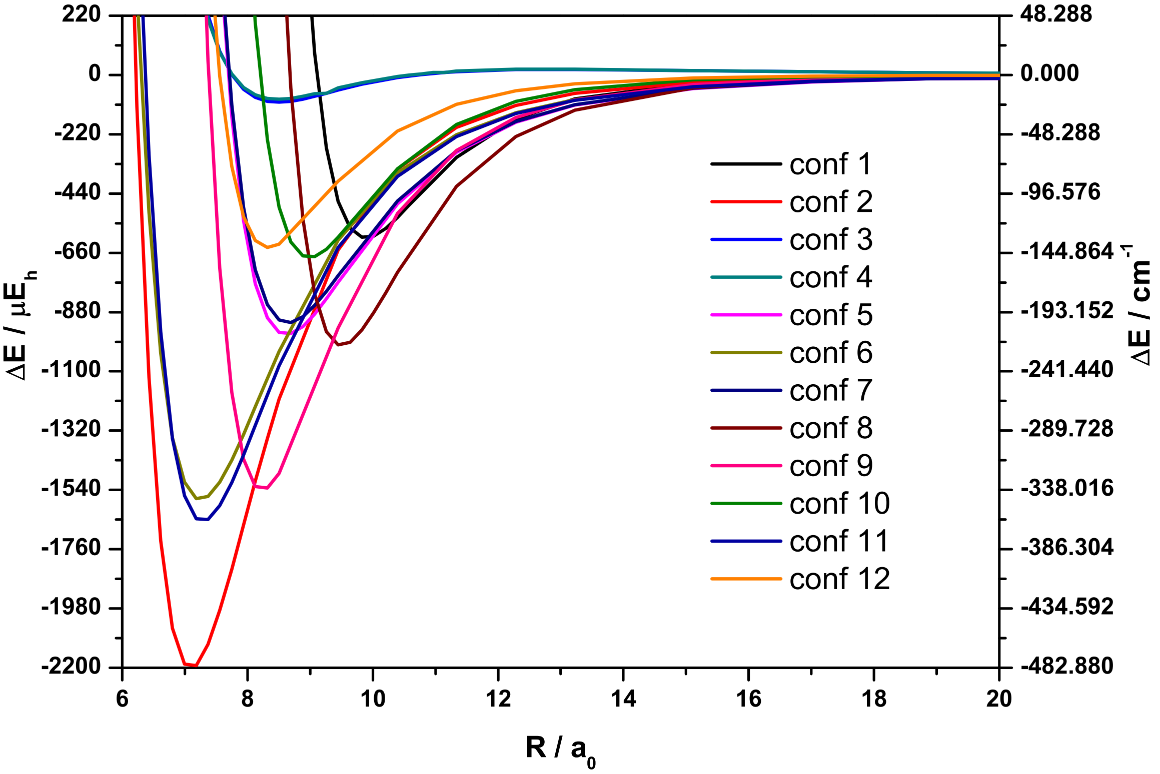


FIG. 6.3 - *Interaction energy* $\Delta E(R)$ (μE_h) *of the* C_2H_4-C_2H_4 *complex calculated at the CCSD(T)/aug-cc-pVTZ level of theory with the BSSE correction.*



sets are enough to carry out the extrapolation of the HF energies as well as the correlation energies. The results of the calculation are presented in the last column of the Table 6.1. The table shows that the BSIE is 7 - 25 % of the energy calculated using the AVTZ basis set. The largest contribution of the BSIE correction to the binding energy of the complex is for the configuration 3 and 4. These configurations are also noticeable because of their potential energy behavior (see Fig. 6.3 and 6.4): the energy has a very small potential well and for $R > 10.5\ a_0$ it is positive.

TAB. 6.1 - *Equilibrium distance R_e (in Å) and binding energy $\Delta E(R_e)$ for different configurations calculated at the CCSD(T)/AVTZ and CCSD(T)-F12/AVTZ levels of theory with the BSSE correction. In the last column there are presented the binding energies in CBS limit calculated at the CCSD(T) level using extrapolation scheme of Helgaker ($\Delta E_{CBS}(R_e)$). All angles are in Deg, energies are in μE_h.*

Conf.	Symm.	χ_A	θ_A	φ_A	χ_B	θ_B	φ_B	R_e	$\Delta E(R_e)$ CCSD(T)	$\Delta E(R_e)$ CCSD(T)-F12	$\Delta E_{CBS}(R_e)$ CCSD(T)
1	D_{2h}	0	0	0	0	0	0	5.2	-602.465	-638.187	-646.192
2	D_{2d}	90	90	90	90	0	90	3.8	-2191.168	-2323.555	-2356.714
3	D_{2h}	0	0	90	90	90	90	4.5	-100.906	-129.405	-135.979
4	D_{2d}	0	0	90	90	90	0	4.5	-90.037	-116.577	-126.153
5	C_{2v}	0	0	90	0	90	0	4.6	-959.821	-1011.151	-1028.653
6	C_{2v}	0	90	90	90	90	0	3.8	-1572.798	-1670.690	-1707.929
7	C_{2v}	0	0	90	0	90	90	4.6	-919.016	-968.161	-986.520
8	D_{2d}	0	0	0	0	0	90	5.0	-1001.250	-1064.007	-1077.743
9	C_{2v}	90	0	90	0	0	0	4.4	-1533.231	-1622.923	-1644.732
10	C_{2v}	90	0	90	0	0	90	4.8	-674.079	-706.381	-714.547
11	C_{2v}	90	0	90	90	0	0	3.9	-1649.328	-1734.829	-1767.935
12	D_{2h}	90	90	90	90	0	0	4.4	-639.834	-668.195	-681.133

In order to check whether it is possible to use the SAPT or DFT-SAPT methods (developed specially for complexes, less demanding) and explicitly correlated methods (MP2-F12 and CCSD(T)-F12) to calculate the potential energy surface of the ethylene dimer we have carried out the calculations at the CCSD(T), SAPT for all 12 configurations of the complex and DFT-SAPT, MP2, MP2-F12 and CCSD(T)-F12 calculations for the deepest (configuration 2) and the one of the less deep (configuration 3) configurations of the $(C_2H_4)_2$ van der Waals complex. All the calculations were carried out using the AVTZ basis set. The results of the calculations are shown at Fig. 6.4 (the values of interaction energy are also presented in Tables 8.4-8.6 in Appendix IX). It is obvious that the DFT-SAPT (both with PBE0 and B3LYP functionals) method provides results that are more correct than the SAPT, MP2 and MP2-F12 methods. However, the DFT-SAPT method is still not correct enough to describe the interactions of the complex under investigation. Therefore, the SAPT, MP2 and MP2-F12 methods proved to give non-reliable results for all 12 configurations of the ethylene dimer. A good agreement was obtained for the CCSD(T) and CCSD(T)-F12 methods. It should be noted that the CCSD(T)-F12/AVTZ level gives values of energy close to the CBS limit calculated at the CCSD(T) level (see Table 6.1) as well as MP2-F12 gives the values close to the CBS limit calculated at the MP2 level of theory.

Analytical calculations were carried out using the long-range approximation (Eq. 2.18):

$$\Delta E = E_{elec} + E_{ind} + E_{disp}, \tag{6.3}$$

where E_{elec}, E_{ind} and E_{disp} are the electrostatic, induction and dispersion contributions to the total interaction energy of the complex. For the case of the ethylene dimer ($\Omega_{\alpha\beta\gamma} = \beta_{\alpha\beta\gamma} = A_{\alpha,\beta\gamma} = 0$ due to the symmetry D_{2h}), limiting ourselves to the order of R^{-8}, we have

$$E_{elec} = \frac{1}{9} T_{\alpha\beta\gamma\delta} \Theta^A_{\alpha\beta} \Theta^B_{\gamma\delta} + \frac{1}{315} T_{\alpha\beta\gamma\delta\varepsilon\varphi} [\Theta^A_{\alpha\beta} \Phi^B_{\gamma\delta\varepsilon\varphi} + \Theta^B_{\alpha\beta} \Phi^A_{\gamma\delta\varepsilon\varphi}], \tag{6.4}$$

$$E_{ind} = -\frac{1}{18} T_{\alpha\gamma\delta} T_{\beta\varepsilon\varphi} [\alpha^A_{\alpha\beta} \Theta^B_{\gamma\delta} \Theta^B_{\varepsilon\varphi} + \alpha^B_{\alpha\beta} \Theta^A_{\gamma\delta} \Theta^A_{\varepsilon\varphi}], \tag{6.5}$$

$$\begin{aligned} E_{disp} = & -\frac{1}{2\pi} T_{\alpha\beta} T_{\gamma\delta} \int_0^\infty \alpha^A_{\alpha\gamma}(i\omega) \alpha^B_{\beta\delta}(i\omega) d\omega \\ & -\frac{1}{6\pi} T_{\alpha\beta\gamma} T_{\delta\varepsilon\varphi} \int_0^\infty [\alpha^A_{\alpha\delta}(i\omega) C^B_{\beta\gamma,\varepsilon\varphi}(i\omega) + C^A_{\beta\gamma,\varepsilon\varphi}(i\omega) \alpha^B_{\alpha\delta}(i\omega)] d\omega \\ & -\frac{1}{15\pi} T_{\alpha\beta} T_{\gamma\delta\varepsilon\varphi} \int_0^\infty [\alpha^A_{\alpha\gamma}(i\omega) E^B_{\beta,\delta\varepsilon\varphi}(i\omega) + E^A_{\beta,\delta\varepsilon\varphi}(i\omega) \alpha^B_{\alpha\gamma}(i\omega)] d\omega. \end{aligned} \tag{6.6}$$

Dispersion contribution (Eq. 6.6) was calculated in the present work using the London formula [32] within the Unsöld approximation [43]:

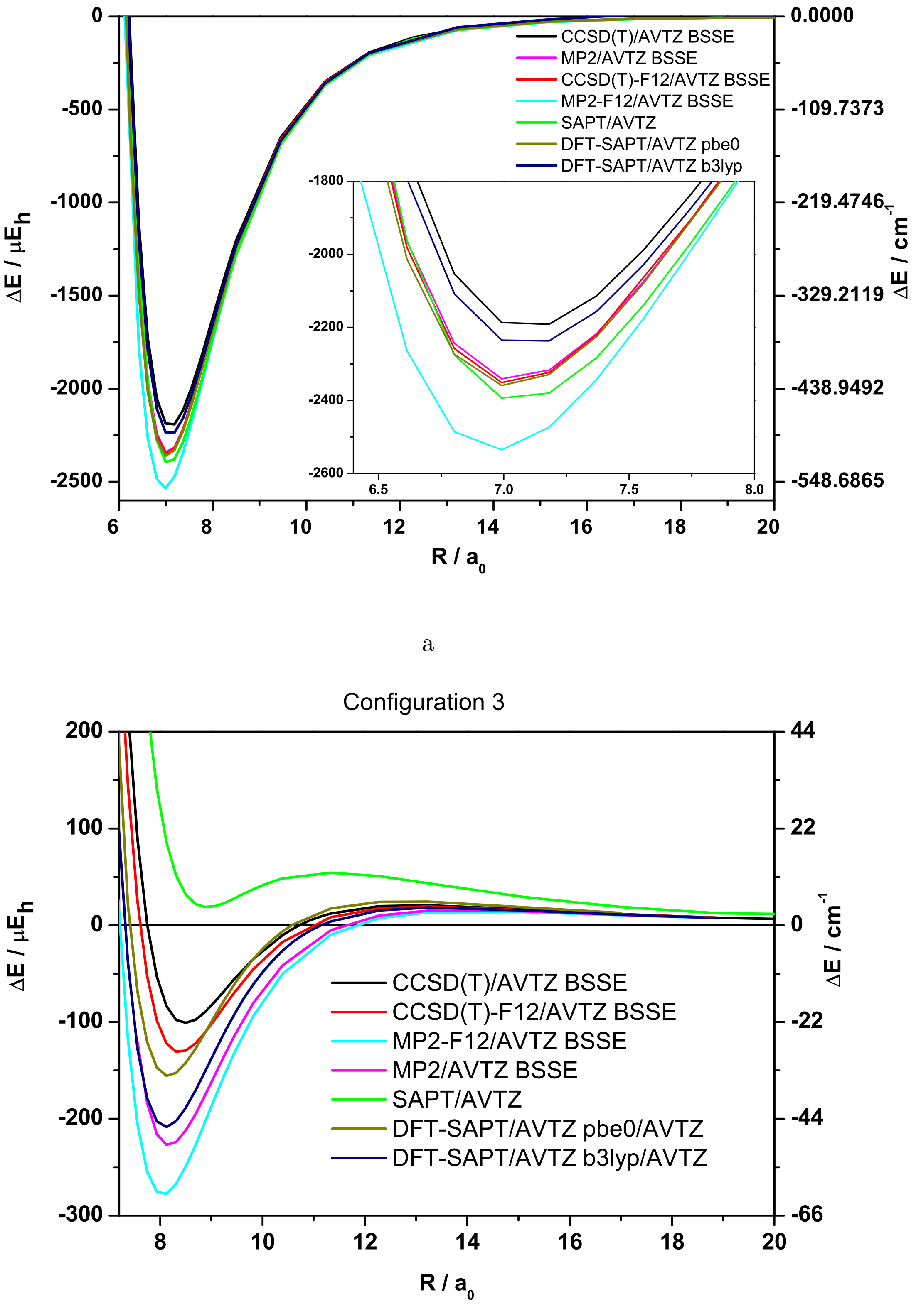
$$\begin{aligned} E^{London}_{disp} = & -\frac{U}{8} (T_{\alpha\beta} T_{\gamma\delta} \alpha^A_{\alpha\gamma} \alpha^B_{\beta\delta} + \frac{1}{3} T_{\alpha\beta\gamma} T_{\delta\varepsilon\varphi} [\alpha^A_{\alpha\delta} C^B_{\beta\gamma,\varepsilon\varphi} + C^A_{\beta\gamma,\varepsilon\varphi} \alpha^B_{\alpha\delta}] \\ & + \frac{2}{15} T_{\alpha\beta} T_{\gamma\delta\varepsilon\varphi} [\alpha^A_{\alpha\gamma} E^B_{\beta,\delta\varepsilon\varphi} + E^A_{\beta,\delta\varepsilon\varphi} \alpha^B_{\alpha\gamma}]) \end{aligned} \tag{6.7}$$

and using CRA2 (analogously to the CRA2 for dipole moment and polarizability calculations, described in Part II):

$$\begin{aligned} E^{CRA2}_{disp} = & -\frac{C_6}{6\alpha^2} \Big[T_{\alpha\beta} T_{\gamma\delta} \alpha^A_{\alpha\gamma} \alpha^B_{\beta\delta} + \frac{1}{3} T_{\alpha\beta\gamma} T_{\delta\varepsilon\varphi} (\alpha^A_{\alpha\delta} C^B_{\beta\gamma,\varepsilon\varphi} + \alpha^B_{\alpha\delta} C^A_{\beta\gamma,\varepsilon\varphi}) \\ & + \frac{2}{15} T_{\alpha\beta} T_{\gamma\delta\varepsilon\varphi} (\alpha^A_{\alpha\delta} E^B_{\beta,\gamma\varepsilon\varphi} + \alpha^B_{\alpha\delta} E^A_{\beta,\gamma\varepsilon\varphi}) \Big]. \end{aligned} \tag{6.8}$$

The values of the molecular parameters used for the analytical calculation of the interaction energy (Eq. 6.3) are listed in Table 8.3 in Appendix VIII. The leading terms in the electrostatic interaction energy of the complex are the terms $\Theta^A\Theta^B + \Theta^B\Theta^A$ ($\sim R^{-5}$). However, the dominant contribution to the interaction energy give the dispersion interactions (see Fig. 6.5 and Eq. 6.9).

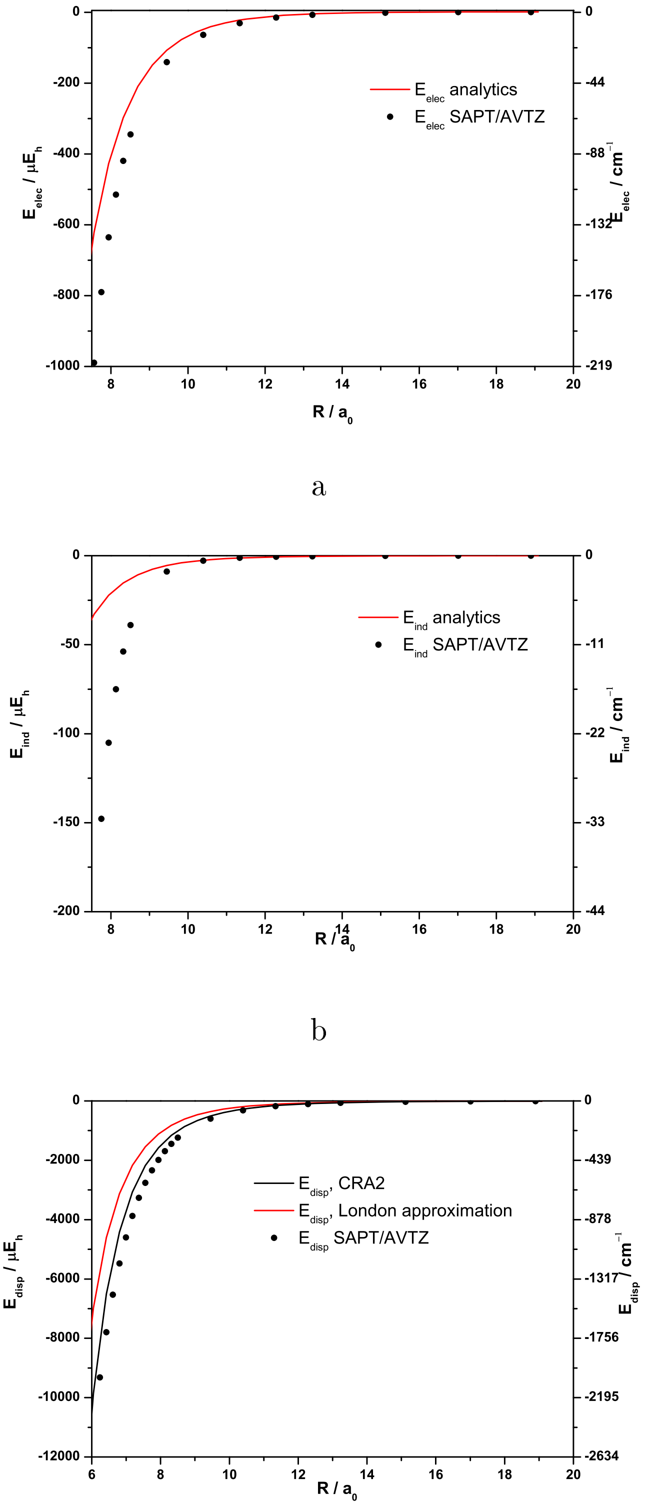
FIG. 6.4 - *Interaction energy $\Delta E(R)$ of the $(C_2H_4)_2$ complex (a - configuration 2, b - configuration 3). All the calculations were carried out with AVTZ basis set.*



a

b

Fig. 6.5 - *Contributions to the interaction energy $\Delta E(R)$ of the $(C_2H_4)_2$ complex being in configuration 2 (a - E_{elec}, b - E_{ind}, c - E_{disp}).*



a

b

c

As an example we present the results of the calculations using analytical formulas for configuration 2 (R is in a_0)

$$\begin{aligned} E_{elec} &= \frac{4.84 E_h a_0^5}{R^5} - \frac{1152.0 E_h a_0^7}{R^7}, \\ E_{ind} &= -\frac{351.0 E_h a_0^8}{R^8}, \\ E_{disp}^{CRA2} &= -\frac{272.98 E_h a_0^6}{R^6} - \frac{7630.78 E_h a_0^8}{R^8}, \\ E_{disp}^{London} &= -\frac{193.22 E_h a_0^6}{R^6} - \frac{5401.12 E_h a_0^8}{R^8} \end{aligned} \tag{6.9}$$

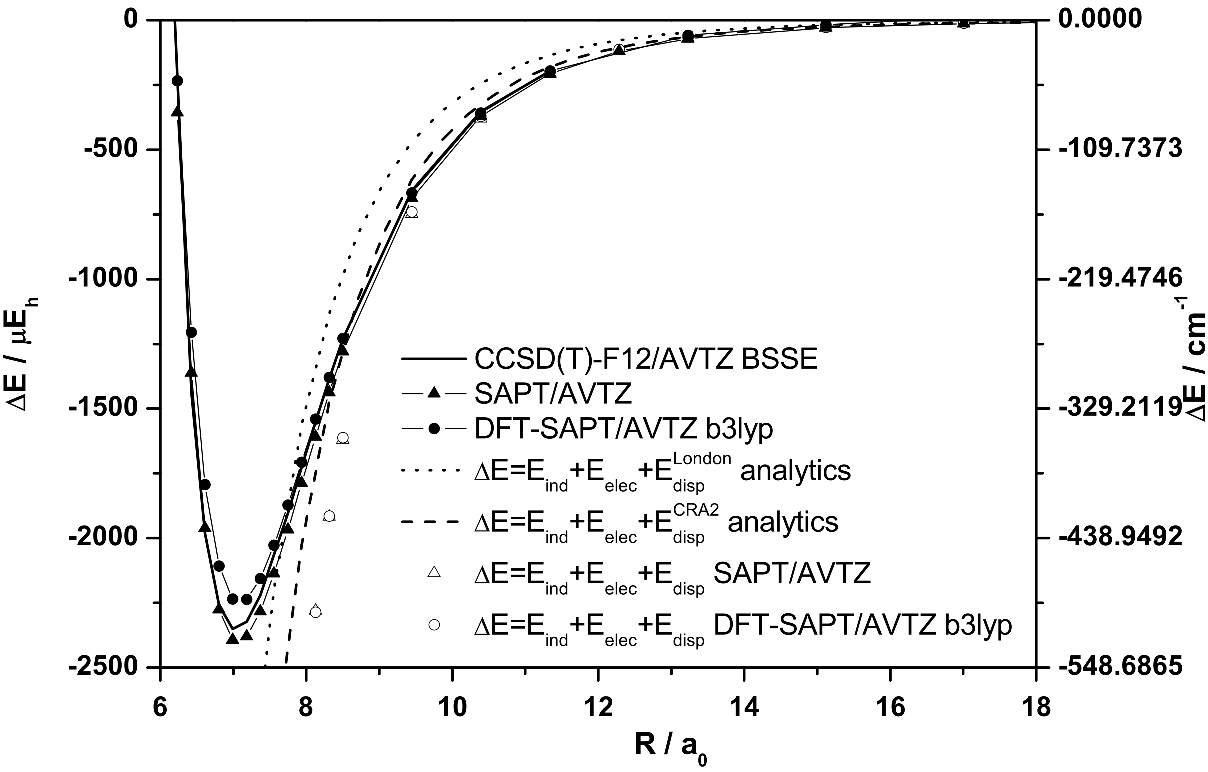
in Fig. 6.6. The analysis of the results shows that the analytical representation of the interaction energy by Eq. 6.3 with the dispersion contribution treated using CRA2 (Eq. 6.8) for the ethylene dimer is in a good agreement with the high-level *ab initio* calculations (CCSD(T)-F12/AVTZ with the BSSE correction) for the intermolecular separations $R > 11\ a_0$. The figure shows also that the London approximation (Eq. 6.8) underestimates the dispersion energy. Further, we will use the dispersion energy calculated using CRA2. In Fig. 6.6 the comparison of analytically calculated $\Delta E = E_{elec} + E_{ind} + E_{disp}$ with the same $\Delta E = E_{elec} + E_{ind} + E_{disp}$ obtained using DFT-SAPT and HF-SAPT methods says that the number of terms accounted in our expansion (Eq. 6.4-6.8) is enough for the description of interaction energy for long-range separations. The figure shows that DFT-SAPT and HF-SAPT methods provide practically the same values of $\Delta E = E_{elec} + E_{ind} + E_{disp}$ (the difference in values of energy calculated using these methods appeared to be in the exchange contribution). The Fig. 6.6 also shows that the contribution from the electron overlap effect (exchange contribution) become noticeable for $R < 11\ a_0$.

It is interesting to note that for configurations 3 and 4 the repulsive electrostatic terms $\Theta^A\Theta^B + \Theta^B\Theta^A$ give noticeable contribution to ΔE for large R, which leads to the positive interaction energy for $R > 10.5\ a_0$. Particularly, for configuration 3 the electrostatic, induction and dispersion contributions have the form (R is in a_0):

$$\begin{aligned} E_{elec} &= \frac{36.61 E_h a_0^5}{R^5} - \frac{1400.4 E_h a_0^7}{R^7}, \\ E_{ind} &= -\frac{1210.7 E_h a_0^8}{R^8}, \\ E_{disp}^{CRA2} &= -\frac{255.12 E_h a_0^6}{R^6} - \frac{4270.86 E_h a_0^8}{R^8}, \\ E_{disp}^{London} &= -\frac{180.58 E_h a_0^6}{R^6} - \frac{3022.95 E_h a_0^8}{R^8}. \end{aligned} \tag{6.10}$$

The interaction energy for configuration 3 is presented at Fig. 6.7. Like for configuration 2 the dispersion contribution is better described by CRA2.

FIG. 6.6 - *Interaction energy $\Delta E(R)$ of the $(C_2H_4)_2$ complex for configuration 2 (a - normal size, b - enlarged fragment).*



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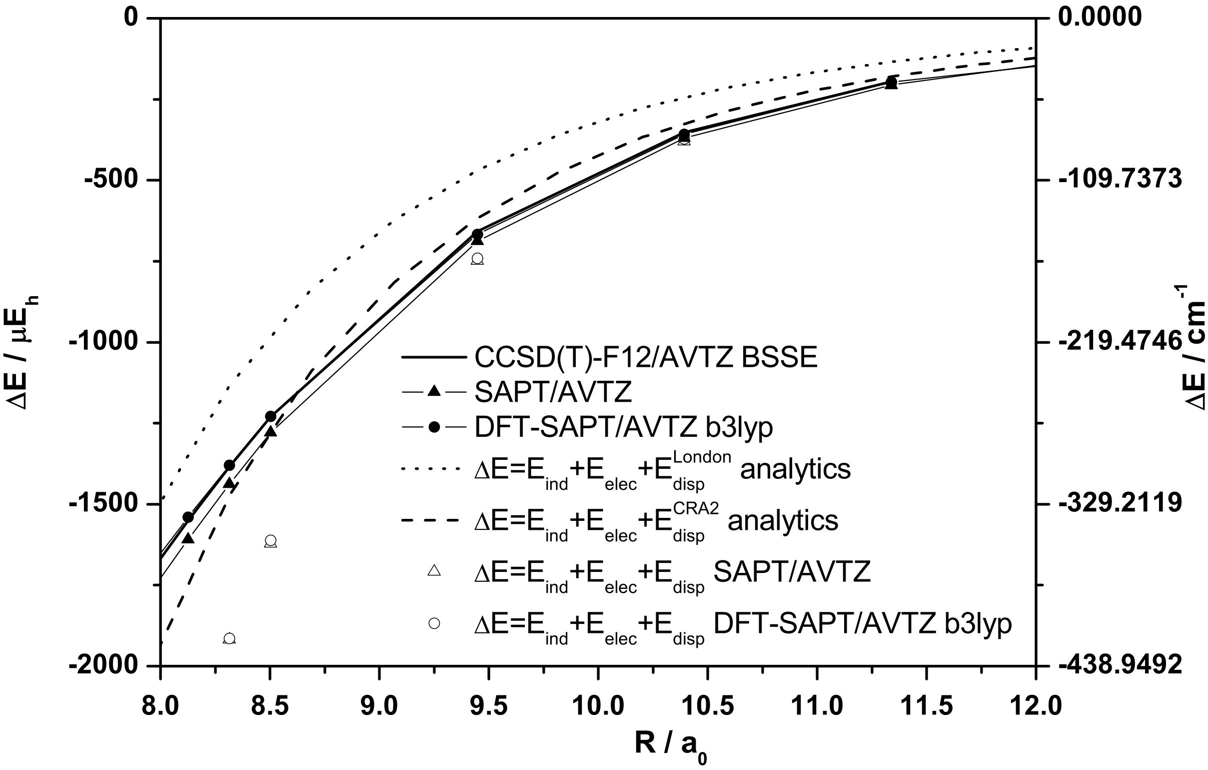
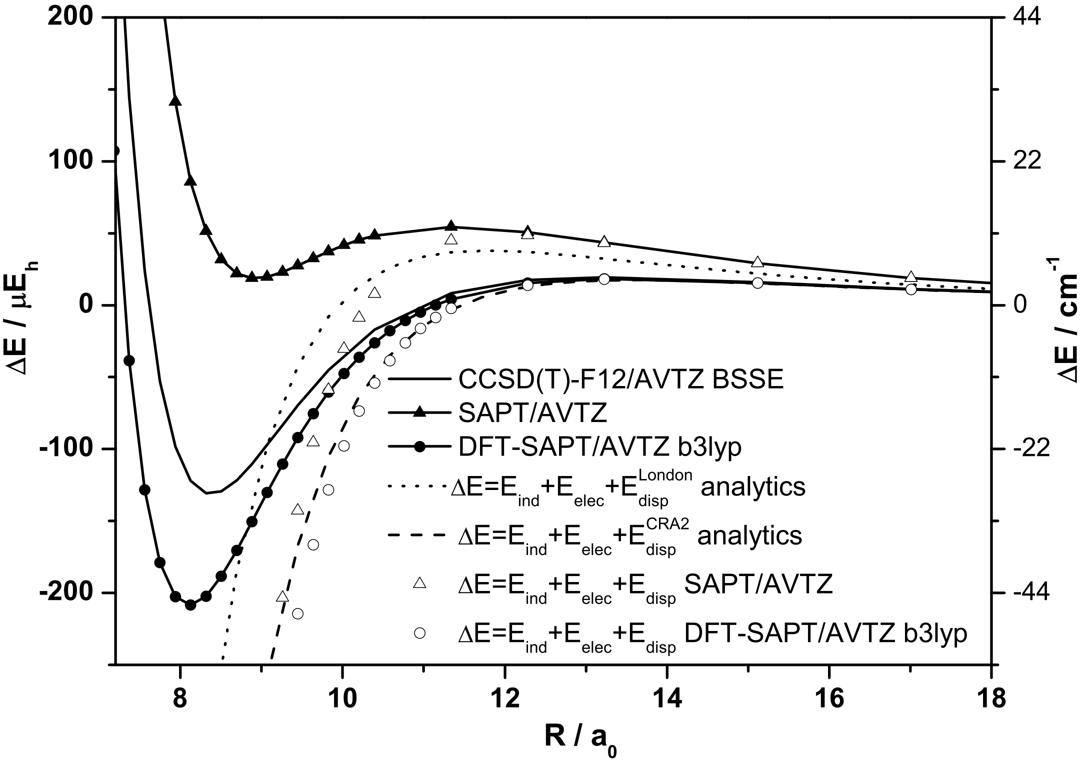


b

Fig. 6.7 - *Interaction energy $\Delta E(R)$ of the $(C_2H_4)_2$ complex for configuration 3.*



Magnetic corrections to the dispersion energy.

As the ethylene molecule has π-bonds, it is interesting to evaluate the contributions of magnetic interactions to the dispersion energy of the complex C_2H_4-C_2H_4. The evaluation of the terms in Eq. 2.38 and Eq. 2.39 for the region $kR \ll 1$ gives the results, presented in Table 6.2. The first column is the leading contribution in the London dispersion formula (Eq. 2.15). The table shows that the contribution of the magnetic interactions for the complex under investigation is negligible in comparison with the electric interactions.

TAB. 6.2 - *Leading contributions from different interactions to the dispersion energy of the ethylene dimer for $kR \ll 1$. All values are in a.u.*

$\Delta E^{\alpha-\alpha}$	$\Delta E^{\alpha-\chi}$	$\Delta E^{\alpha-dia}$	$\Delta E^{\chi-\chi}$	$\Delta E^{dia-dia}$	$\Delta E_{rel}^{\alpha-\alpha}$
$\dfrac{3\times10^{2}}{R^6}$	$\dfrac{5\times10^{-9}}{R^4}$	$-\dfrac{10^{-5}}{R^5}$	$-\dfrac{3\times10^{-4}}{R^6}$	$-\dfrac{2\times10^{-8}}{R^7}$	$\dfrac{10^{-3}}{R^4}$

Molecular parameters used for the calculation: $\langle q^2\rangle^{00}$=83.031 a.u. (calculated at the MP2/AVTZ level of theory), χ = 4.145739 a.u. [189], α and U are taken from Table 8.3.

Chapter 7

Interaction-induced dipole moment

Dipole moment of ethylene complexes gives rise to the absorption of gas media containing nonpolar ethylene molecules. In spite of particular interest in the ethylene dimer in astrophysics and chemistry, dipole moment of the ethylene dimer was studied very poorly. At present, there is no theoretical calculations of the dipole moment surface of ethylene dimer, and it is known only that the dipole moment of ethylene dimer being in the most stable configuration (D_{2d}) equals to zero. There are experimental works on collision-induced absorption in ethylene in the infrared region [180–183] that contain the information on the dipole moment surface of the interacting ethylene molecules. However, these spectra of collision-induced absorption were not employed for the investigation of the dipole moment of ethylene dimer, but for the evaluation of the quadrupole moment of ethylene molecule. Thus, our purpose is to carry out high-level *ab initio* and long-range analytical calculations (up to large order of R^{-7}) of the dipole moment of the $(C_2H_4)_2$ complex.

7.1 Dipole moment surface

The *ab initio* calculations were carried out for 6 configurations of the C_2H_4-C_2H_4 complex (configurations 5, 6, 7, 9, 10, and 11 presented in Fig. 3.2, other configurations do not possess the dipole moment) which can be characterized by 6 Euler angles $\chi_A, \theta_A, \varphi_A, \chi_B, \theta_B$ and φ_B. The geometric parameters for these configurations are presented in Table 6.1. For these geometries the value of R has been varied within the range 3.0 – 20.0 Å.

For the *ab initio* calculations the field strength of the 0.001 $e^{-1}a_0^2E_h$ was applied to the van der Waals complex $(C_2H_4)_2$. The calculations of the dipole moment surface were carried out at the explicitly correlated CCSD(T)-F12 [178] (that is claimed to give results using the AVTZ basis set that are better than conventional CCSD(T) with the AV5Z basis set [179]) and CCSD(T)/AVTZ levels of theory with the BSSE correction using Eq. 1.84:

$$\mu_\alpha = \frac{E(F_\alpha) - E(-F_\alpha)}{2F_\alpha}.$$

The *ab initio* calculations for the six configurations from Table 6.1 are presented at the Fig. (7.1) and in Table 8.7 (see Appendix X). The comparison of the values calculated with and without the BSSE correction shows that the BSSE correction gives small contribution to the dipole moment (the difference is about 0.002%), therefore, we haven't presented the dipole moment calculated without the BSSE in Appendix X. We will use the values of the dipole moment with the BSSE correction throughout this chapter.

Analytical calculations in the classic long-range approximation [32] of the interaction-induced dipole moment surface of the complex have been carried out for the comparison with *ab initio* calculations. Taking into account the symmetry of the C_2H_4 molecule (D_{2h} symmetry), for the $(C_2H_4)_2$ dimer the components of the dipole moment Eq. (2.41) take on the form:

$$\mu_\alpha = \mu_\alpha^{ind} + \mu_\alpha^{disp}, \tag{7.1}$$

where the induction dipole moment μ_α^{ind} ($\Omega_{\alpha\beta\gamma} = \beta_{\alpha\beta\gamma} = A_{\alpha,\beta\gamma} = 0$ due to the symmetry D_{2h})(through the order R^{-7}):

$$\begin{aligned}\mu_\alpha^{ind} &= \frac{1}{3}T_{\beta\gamma\delta}[\alpha^A_{\alpha\beta}\Theta^B_{\gamma\delta} - \alpha^B_{\alpha\beta}\Theta^A_{\gamma\delta}] + \frac{1}{105}T_{\beta\gamma\delta\varepsilon\varphi}[\alpha^A_{\alpha\beta}\Phi^B_{\gamma\delta\varepsilon\varphi} - \alpha^B_{\alpha\beta}\Phi^A_{\gamma\delta\varepsilon\varphi}] \\ &+\frac{1}{45}T_{\beta\gamma\delta\varepsilon\varphi}[E^A_{\alpha,\beta\gamma\delta}\Theta^B_{\varepsilon\varphi} - E^B_{\alpha,\beta\gamma\delta}\Theta^A_{\varepsilon\varphi}] - \frac{1}{3}T_{\beta\varepsilon}T_{\varphi\gamma\delta}[\alpha^A_{\alpha\beta}\Theta^A_{\gamma\delta}\alpha^B_{\varepsilon\varphi} - \alpha^B_{\alpha\beta}\Theta^B_{\gamma\delta}\alpha^A_{\varepsilon\varphi}]\end{aligned} \tag{7.2}$$

and the dispersion dipole moment μ_α^{disp} (through the order R^{-7}):

$$\mu_\alpha^{disp} = \frac{1}{3\pi}\int_0^\infty d\omega[B^A_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)\alpha^B_{\varepsilon\varphi}(i\omega) - B^B_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)\alpha^A_{\varepsilon\varphi}(i\omega)]T_{\beta\varepsilon}T_{\varphi\gamma\delta}. \tag{7.3}$$

The dispersion contribution to the dipole moment of the ethylene complex at the moment could not be calculated using Eq. 7.3 because of the absence of the calculated imaginary frequency-dependent hyperpolarizability $B_{\alpha\beta,\gamma\delta}(0;i\omega,-i\omega)$ for the C_2H_4 molecule. Thus, we have used the constant ratio approximation CRA2 (Eq. 7.4), as described in the Second Chapter:

$$\mu_\alpha^{disp} = \frac{5C_6}{54\alpha^2}T_{\beta\varepsilon}T_{\varphi\gamma\delta}\Big[B^A_{\alpha\beta,\gamma\delta}\alpha^B_{\varepsilon\varphi} - B^B_{\alpha\beta,\gamma\delta}\alpha^A_{\varepsilon\varphi}\Big]. \tag{7.4}$$

As there is no literature data on the dipole-dipole-quadrupole polarizability of the ethylene molecule, we have calculated ourselves $B_{\alpha\beta,\gamma\delta}$ at the CCSD(T)/AVTZ level of theory using approach described in Ref. [185]. The values of the molecular parameters used for the analytical calculation of the dipole moment (Eq. 7.1) are listed in Table 8.3 in Appendix VIII. The coefficient $C_6 = 300.2\ E_h \cdot a_0^6$ was taken from Ref. [184].

The comparison of *ab initio* and analytically calculated dipole moment for six configurations of the ethylene complex is shown in Fig. 7.1. The figure shows that the analytical description (Eq. 7.1) of the dipole moment is in a good agreement with the *ab initio* calculated one at the CCSD(T)/AVTZ level of theory with the BSSE correction for $R > 11\ a_0$. In the same figure (and in the Table 8.8 in Appendix VIII) the dipole moment of the configuration 5 calculated at the CCSD(T)-F12/VTZ-F12 and MP2/AVTZ levels with the BSSE correction are shown. As expected, the MP2 level of theory does not account for the large part of the electrons correlation, that is why the difference between dipole moments calculated at the CCSD(T) and MP2 levels is about $\sim 5\%$. The results obtained at the CCSD(T)/AVTZ and CCSD(T)-F12/VTZ-F12 agree well for all R, thus CCSD(T)-F12/VTZ-F12 can be used for further calculations of the whole dipole moment surface as it is less demanding.

In fig. 7.2 different contributions to the dipole moment of the complex are presented. As expected the major contribution give the terms $A^A\Theta^B + A^B\Theta^A$, and the dispersion contribution $(B^A\alpha^B + B^B\alpha^A)$ is one of the smallest or of comparable value with the back induction contribution $(\alpha^A\Theta^A\alpha^B + \alpha^B\Theta^B\alpha^A)$. We suppose that the account for the dispersion terms is necessary for the dipole moment of this complex.

FIG. 7.1 - *Interaction-induced dipole moment μ_z of the $(C_2H_4)_2$ complex. Solid lines - calculations at the CCSD(T)/AVTZ level of theory with the BSSE correction; dash lines - analytical calculations. Olive color - configuration 5, black color - configuration 6, red color - configuration 7, blue color - configuration 9, orange color - configuration 10, magenta color - configuration 11. White circles - calculation at the CCSD(T)-F12/VTZ-F12 level of theory with the BSSE correction; black circles - calculation at the MP2/AVTZ level of theory with the BSSE correction.*

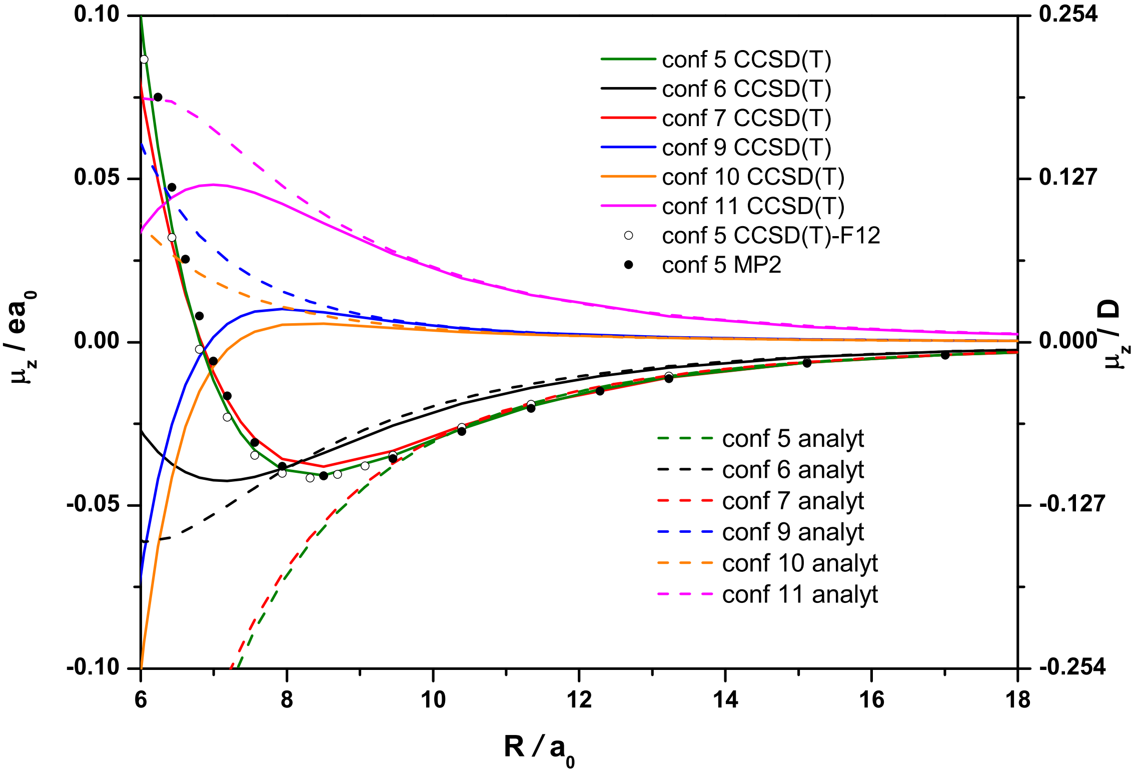
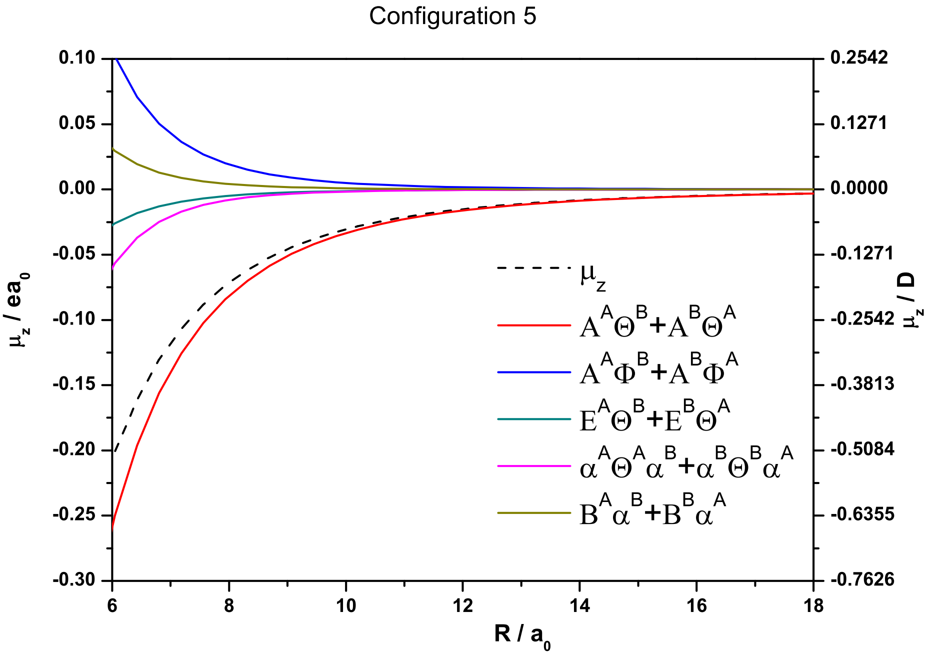


Fig. 7.2 - *Contributions to the dipole moment of the configurations 5 and 9 of the* $(C_2H_4)_2$ *complex. Red line -* $A^A\Theta^B + A^B\Theta^A$ *contributions, blue line -* $A^A\Phi^B + A^B\Phi^A$ *contributions, dark cyan line -* $E^A\Theta^B + E^B\Theta^A$ *contributions, magenta line -* $\alpha^A\Theta^A\alpha^B + \alpha^B\Theta^B\alpha^A$*, brawn line -* $B^A\alpha^B + B^B\alpha^A$ *contributions; dash line - total dipole moment in the framework of long-range approximation.*



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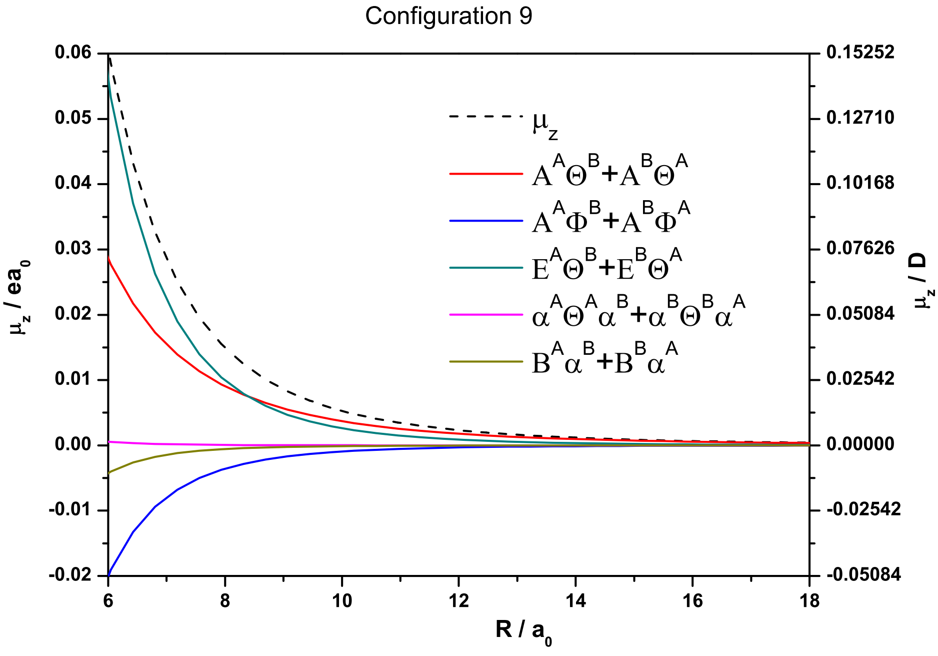

b

Fifth part

Conclusions

Chapter 8

Conclusions

During this thesis two main weakly-bound complexes were considered: the CH_4-N_2 and $(C_2H_4)_2$ van der Waals complexes.

CH_4-N_2 complex

We have carried out the calculations of the potential energy, dipole moment and polarizability of the CH_4-N_2 complex using both *ab initio* and analytical methods. *Ab initio* calculations were performed at the MP2 and CCSD(T) levels of theory with the BSSE correction using aug-cc-pVTZ basis set for a big number of mutual orientations and intermolecular separations (the chosen region covers both small repulsive and long-range attractive ranges). The analysis of the potential energy surface of the CH_4-N_2 complex calculated both at the MP2 and CCSD(T) level of theory employing aug-cc-pVTZ basis set showed that there is a family of the most stable geometries C_τ. These geometries are obtained by the rotation of the N_2 molecule around x-axis of an angle τ, where the initial geometry C_0 of the complex corresponds to the geometry 4. The recommended binding energy of the most stable configuration at $R_e = 6.8\ a_0$ almost doesn't depend on the method used for CBS limit calculations: ΔE = -820.536 μE_h when Martin's extrapolation scheme (the cardinal number X = 4, 5) for total energy is used and ΔE = -827.143 μE_h for Helgaker's scheme (X = (3), 4, 5) separately extrapolating Hartree-Fock and correlation energy.

The analytical calculations in the present work are based on the long-range classical approximation. In potential energy surface we have accounted for the electrostatic and dispersion contributions up to R^{-7}. In the dipole moment calculations the induction and dispersion terms were accounted completely through the order R^{-7}. For the polarizability calculations of the complex the induction (partially up to R^{-7}) and dispersion (up to R^{-6}) effects were taken into account.

The comparison of analytical and *ab initio* calculations have shown that the long-range approximation works well in the range $R > 10\ a_0$ for all properties under investigation (except for $\alpha_{yy}(R)$ and $\alpha_{zz}(R)$: there is a good agreement even for $R > 6\ a_0$). For smaller R, when electron shells of interacting molecules begin to overlap, this long-range multipolar approximation fails to describe correctly potential energy, dipole moment and polarizability (even including the higher order terms of perturbation theory).

For the description of the dipole moment a simple model based on asymptotic methods in atomic collisions was suggested. This model accounts for the exchange effects in the range of small overlap of the electron shells. The model is based on idea of additivity of the long-range and exchange terms. Suggested model was tested on a number of configurations of the CH_4-N_2 complex and proved to be good enough in spite of its simplicity. The model was applied for the analytical description of the dipole moment surface $\mu_\alpha(R,\tau)$ for the family of the most stable configurations. For these configurations the modulus of the dipole moment changes very weakly and with a good accuracy is equal to the value 0.01196 ea_0. Suggested model of taking into account the effects related to the overlap of shells of valence electrons is based on the point model of interacting molecules and can be applied only to small molecules. Such limitation is due to the fact, that the parameters of exchange interaction β_A and β_B are defined only by the ionization potentials of molecules and take into account neither the form nor the size of interacting molecules.

As far as the polarizability surface, the incorrect analytical description of the polarizability component $\alpha_{xx}(R)$ in comparison with the values obtained from *ab initio* (CCSD(T)/aug-cc-pVTZ) calculations for $R < 10$ a_0. results in the divergence of the mean ($\Delta\alpha$) and anisotropy ($\Delta\gamma$) of the interaction polarizability calculated by the two methods, and this divergence is more substantial for $\Delta\alpha$. The results of the calculations have shown also that the invariants of the interaction polarizability $\Delta\alpha$ and $\Delta\gamma$ for the CH_4-N_2 complex for the most stable configuration are negative. As a result, the invariants of polarizability tensor of the complex in this configuration are less than the sum of invariants for free molecules ($\alpha^{CH_4} + \alpha^{N_2}$ and γ^{N_2}). This leads to the fact, that the CH_4-N_2 complex formation in methane-nitrogen gas media decreases the index of refraction for such media and reduces the efficiency of light scattering, rotational Raman scattering. The reduction of the efficiency is also observed for the vibrational Raman scattering.

$(C_2H_4)_2$ complex

The calculations of the potential energy and, for the first time, dipole moment of the ethylene dimer were carried out using *ab initio* and analytical methods. *Ab initio* calculations were performed at the CCSD(T) (with the BSSE correction) and SAPT levels of theory using aug-cc-pVTZ basis set for 12 configurations of the complex for intermolecular separations 5.7 $a_0 < R < 20.0$ a_0. For the most and least profound configurations the calculations were carried out also at the MP2, MP2-F12, CCSD(T)-F12 and DFT-SAPT methods. The SAPT, MP2 and MP2-F12 methods proved to give not correct quantitive results for the interaction potential energy. However, these methods give the same qualitative result: the most profound configuration if the configuration 2. The binding energy of the complex being in different configurations was determined in CBS limit using extrapolation scheme of Helgaker et al. The recommended binding energy of the most stable configuration (configuration 2 - symmetry D_{2d}) calculated at the CCSD(T) level of theory in CBS limit (with the BSSE correction) at $R_e = 7.18$ a_0 (3.8 Å) is $\Delta E(R_e) =$ -2356.714 μE_h. The CCSD(T)-F12 level of theory with the BSSE correction gives values of energy close to the CBS limit $\Delta E(R_e)$ = -2323.555 μE_h, however, it takes 7-8 times more computer time for calculation. As for the analytical calculations of the potential energy surface, the electrostatic, induction and dispersion interactions were accounted up to R^{-8}, and for the dipole moment the induction and dispersion interactions were accounted completely through the order R^{-7}. In order to obtain the dispersion contribution to the total dipole moment of the complex the $B_{\alpha\beta,\gamma\delta}$ polarizability of the ethylene molecule was calculated. This dipole-dipole-quadrupole polarizability was obtained for the first time (the calculations were carried out at the CCSD(T) level of theory with aug-cc-pVTZ basis set).

The comparison of analytical and *ab initio* calculations have shown that the long-range approximation works well in the range $R > 11\ a_0$ both for the potential energy and dipole moment.

Perspectives

In perspective the full dimensional potential energy fitting can be carried out for the both CH_4-N_2 and $(C_2H_4)_2$ complexes. On the base of the results the IR spectra can be simulated. Obtained analytical representation of the dipole moment of the CH_4-N_2 complex can serve as a very good basis for further description of full dipole moment (dependence on all Euler angles) of the complex. As for the ethylene dimer, the polarizability calculations can be carried out for different configurations of the complex both analytically and *ab initio*. Also, the analytical description of the dipole moment of the ethylene dimer at short-range intermolecular separations (the ranges of potential wells) can be developed. Furthermore, the calculated *ab initio* potential energy surface for the CH_4-N_2 complex will be used for further calculations of line broadening coefficient for methane perturbed by nitrogen by Tony Gabard.

Sixth part

Appendixes

APPENDIX I (to the Part II)

$$\alpha^{(n)}_{\alpha\beta} = S(\alpha,\beta)\sum_{i\neq n}\frac{\langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \mu_\beta \mid n\rangle}{E^{(0)}_i - E^{(0)}_n}, \tag{8.1}$$

$$\begin{aligned}\beta^{(n)}_{\alpha\beta\gamma} = S(\alpha,\beta,\gamma)\sum_{i\neq n}\Big[\sum_{j\neq n}&\frac{\langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \mu_\beta \mid j\rangle\langle j \mid \mu_\gamma \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)(E^{(0)}_j - E^{(0)}_n)} \\ &-\frac{\langle n \mid \mu_\alpha \mid n\rangle\langle n \mid \mu_\beta \mid i\rangle\langle i \mid \mu_\gamma \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)^2}\Big],\end{aligned} \tag{8.2}$$

$$\begin{aligned}\gamma^{(n)}_{\alpha\beta\gamma\delta} = S(\alpha,\beta,\gamma,\delta)\times\sum_{i\neq n}\{\sum_{j\neq n}\Big[\sum_{k\neq n}&\frac{\langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \mu_\beta \mid j\rangle\langle j \mid \mu_\gamma \mid k\rangle\langle k \mid \mu_\delta \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)(E^{(0)}_j - E^{(0)}_n)(E^{(0)}_k - E^{(0)}_n)}\Big] \\ -\frac{\langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \mu_\beta \mid nj\rangle\langle n \mid \mu_\gamma \mid j\rangle\langle j \mid \mu_\delta \mid n\rangle + 2\langle n \mid \mu_\alpha \mid n\rangle\langle n \mid \mu_\beta \mid i\rangle\langle i \mid \mu_\gamma \mid j\rangle\langle j \mid \mu_\delta \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)^2(E^{(0)}_j - E^{(0)}_n)}&\Big] \\ +\frac{\langle n \mid \mu_\alpha \mid n\rangle\langle n \mid \mu_\beta \mid n\rangle\langle n \mid \mu_\gamma \mid i\rangle\langle i \mid \mu_\delta \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)^3}&\},\end{aligned} \tag{8.3}$$

$$A^{(n)}_{\alpha,\beta\gamma} = 2\sum_{i\neq n}\frac{\langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \Theta_{\beta,\gamma} \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)}, \tag{8.4}$$

$$\begin{aligned}B^{(n)}_{\alpha\beta,\gamma\delta} = S(\alpha,\beta)\sum_{i\neq n}\times\Big[\sum_{j\neq n}&\frac{2\langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \mu_\beta \mid j\rangle\langle j \mid \Theta_\gamma\delta \mid n\rangle + \langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \Theta_\gamma\beta \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)(E^{(0)}_j - E^{(0)}_n)} \\ &-\frac{2\langle n \mid \mu_\alpha \mid n\rangle\langle n \mid \mu_\beta \mid i\rangle\langle i \mid \Theta_\gamma\delta \mid n\rangle + \langle n \mid \Theta_\gamma\delta \mid n\rangle\langle n \mid \mu_\alpha \mid i\rangle\langle i \mid \mu_\beta \mid n\rangle}{(E^{(0)}_i - E^{(0)}_n)^2}\Big],\end{aligned} \tag{8.5}$$

$$C_{\alpha\beta,\gamma\delta} = \frac{2}{3}\sum_{i\neq n}\frac{\langle n|\Theta_{\alpha\beta}|i\rangle\langle i|\Theta_{\gamma\delta}|n}{E^0_i - E^0_n}, \tag{8.6}$$

where the symbol $S(\alpha,\beta,\gamma,\ldots)$ implies a summation of all the following tensor components in which $\alpha,\beta,\gamma,\ldots$ are permuted. Thus $S(\alpha,\beta,\gamma)X_{\alpha\beta\gamma} = X_{\alpha\beta\gamma} + X_{\alpha\gamma\beta} + X_{\beta\alpha\gamma} + X_{\beta\gamma\alpha} + X_{\gamma\alpha\beta} + X_{\gamma\beta\alpha}$; S is therefore a summetrizing operator. These formulas for polarizabilities are valid provided $E^0_i - E^0_n$ is large compared to $E_n - E^0_n$ for all states i that are mixed with n by the particular perturbation.

APPENDIX II (to the Part II)

TAB. 8.1 - *Number of Constants*[†]

Group	Multipole moments					(Hyper)polarizabilities						
	μ_α	$\Theta_{\alpha\beta}$	$\Omega_{\alpha\beta\gamma}$	$\Phi_{\alpha\beta\gamma\delta}$	$\Xi_{\alpha\beta\gamma\delta\varepsilon}$	$\alpha_{\alpha\beta}$	$\beta_{\alpha\beta\gamma}$	$\gamma_{\alpha\beta\gamma\delta}$	$A_{\alpha,\beta\gamma}$	$E_{\alpha,\beta\gamma\delta}$	$B_{\alpha\beta,\gamma\delta}$	$C_{\alpha\beta,\gamma\delta}$
C_1	3	5	7	9	11	6	10	15	15	21	30	15
C_i	0	5	0	9	0	6	0	15	0	21	30	15
C_s	2	3	4	5	6	4	6	9	8	11	16	9
C_2	1	3	3	5	5	4	4	9	7	11	16	9
C_{2h}	0	3	0	5	0	4	0	9	0	11	16	9
C_{2v}	1	2	2	3	3	3	3	6	4	6	9	6
D_2	0	2	1	3	2	3	1	6	3	6	9	6
D_{2h}	0	2	0	3	0	3	0	6	0	6	9	6
C_4	1	1	1	3	3	2	2	5	3	5	8	5
S_4	0	1	2	3	2	2	2	5	4	5	8	5
C_{4h}	0	1	0	3	0	2	0	5	0	5	8	5
C_{4v}	1	1	1	2	2	2	2	4	2	3	5	4
D_{2d}	0	1	1	2	1	2	1	4	2	3	5	4
D_4	0	1	0	2	1	2	0	4	1	3	5	4
D_{4h}	0	1	0	2	0	2	0	4	0	3	5	4
C_3	1	1	3	3	3	2	4	5	5	7	10	5
S_6	0	1	0	3	0	2	0	5	0	7	10	5
C_{3v}	1	1	2	2	2	2	3	4	3	4	6	4
D_3	0	1	1	2	1	2	1	4	2	4	6	4
D_{3d}	0	1	0	2	0	2	0	4	0	4	6	4
C_{3h}	0	1	2	1	2	2	2	3	2	3	6	3
C_6	1	1	1	1	1	2	2	3	3	3	6	3
C_{6h}	0	1	0	1	0	2	0	3	0	3	6	3
D_{3h}	0	1	1	1	1	2	1	3	1	2	4	3
C_{6v}	1	1	1	1	1	2	2	3	2	2	4	3
D_6	0	1	0	1	0	2	0	3	1	2	4	3
D_{6h}	0	1	0	1	0	2	0	3	0	2	4	3
T	0	0	1	1	0	1	1	2	1	2	3	2
T_h	0	0	0	1	0	1	0	2	0	2	3	2
T_d	0	0	1	1	0	1	1	2	1	1	2	2
O	0	0	0	1	0	1	0	2	0	1	2	2
O_h	0	0	0	1	0	1	0	2	0	1	2	2
$C_{\infty v}$	1	1	1	1	1	2	2	3	2	2	4	3
$D_{\infty h}$	0	1	0	1	0	2	0	3	0	2	4	3
K_h	0	0	0	0	0	1	0	1	0	0	1	1

[†] Taken from Ref. [32].

APPENDIX III

Rotation matrix used in the present work

$$M_{a,b} = \begin{pmatrix} cos(\varphi)cos(\theta)cos(\chi) - sin(\varphi)sin(\chi) & -cos(\varphi)cos(\theta)sin(\chi) - sin(\varphi)cos(\chi) & sin(\theta)cos(\varphi) \\ sin(\varphi)cos(\theta)cos(\chi) + cos(\varphi)sin(\chi) & -sin(\varphi)cos(\theta)sin(\chi) + cos(\varphi)cos(\chi) & sin(\theta)sin(\varphi) \\ -sin(\theta)cos(\varphi) & sin(\theta)sin(\chi) & cos(\theta) \end{pmatrix}$$

The relation between the tensor's components in coordinate system of the complex $T_{s,t}$ with the tensor's components in monomer coordinate system $T'_{k,l}$:

$$T_{s,t} = \sum_{k,l=1}^{3} M_{s,k} M_{t,l} T'_{k,l} \tag{8.7}$$

APPENDIX IV (to the Part III)

TAB. 8.2 - *Molecular properties for the CH_4 and N_2 molecules.*

Property	Definition	CH_4	N_2
U	first ionization potential, E_h	0.4770^a	0.5725^a
Θ_{zz}	quadrupole moment, ea_0^2	0	-1.1258^b
Ω_{xyz}	octopole moment, ea_0^3	2.4095^c	0
Φ_{zzzz}	hexadecapole moment, ea_0^4	-7.69^c	-6.75^b
α_{zz}	polarizability, $e^2a_0^2E_h^{-1}$	16.39^c	14.8425^b
α_{xx}	polarizability, $e^2a_0^2E_h^{-1}$	16.39^c	10.2351^b
β_{xyz}	first hyperpolarizability, $e^3a_0^3E_h^{-2}$	-8.31^c	0
$A_{x,yz}$	dipole-quadrupole polarizability, $e^2a_0^3E_h^{-1}$	9.01^d	0
$E_{z,zzz}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	-18.9^d	39.59^b
$E_{x,xxx}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	-18.9^d	-23.42^b
$D_{x,yzzz}$	dipole-hexadecapole polarizability, $e^2a_0^5E_h^{-3}$	$-66.58\sqrt{5/8}^e$	0
$D_{x,xxyz}$	dipole-hexadecapole polarizability, $e^2a_0^5E_h^{-3}$	$189.0\sqrt{5}/4^e$	0
$B_{zz,zz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-256^c	-216^b
$B_{xz,xz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-219^c	-124^b
$B_{xx,zz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	128^f	65^b
$B_{xx,xx}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-256^c	-126^b
γ_{zzzz}	second hyperpolarizability, $e^4a_0^4E_h^{-3}$	2254^c	1194^b
γ_{xxxx}	second hyperpolarizability, $e^4a_0^4E_h^{-3}$	2254^c	807^b
γ_{xxzz}	second hyperpolarizability, $e^4a_0^4E_h^{-3}$	800^c	322^b

[a] Reference [102].

[b] Reference [100].

[c] Reference [101].

[d] Reference [103].

[e] Reference [104].

[f] $B_{xx,zz} = -B_{zz,zz}/2$ for CH_4.

APPENDIX V (to the Part III)

Potential energy of the CH_4-N_2 complex

The calculations were carried out at the CCSD(T)/aug-cc-pVTZ level of theory.

$E_{N_2} = 40.440930179\ E_h$
$E_{CH_4} = 109.38084514\ E_h$

$$E^{tot} = E_{N_2} + E_{CH_4} + \Delta E$$

All angles are in Deg.

χ_A	θ_A	φ_A	θ_B	φ_B	R, Å	r_{NN}	E^{tot} CP-corrected (E_h)	$BSSE$ (E_h)
90	45	35.26438969	90	0	3.0	1.1040569	-149.749925670316	0.001940796035
					3.1		-149.770244268919	0.001645717693
					3.2		-149.785149306969	0.001408625123
					3.3		-149.796015198097	0.001225195513
					3.4		-149.803878920356	0.001086524656
					3.5		-149.809526043538	0.000976230494
					3.6		-149.813548202064	0.000881136543
					3.7		-149.816386980641	0.000796999938
					3.8		-149.818369412549	0.000723626617
					3.9		-149.819736222456	0.000659327853
					4.0		-149.820663724464	0.000600697739
					4.1		-149.821280436380	0.000545190092
					4.2		-149.821679522465	0.000492351374
					4.3		-149.821928047945	0.000443078661
					4.4		-149.822073902216	0.000398422035
					4.5		-149.822150967568	0.000358938426
					4.6		-149.822182979209	0.000324610645
					4.64		-149.822187043656	0.000312234902
					4.65		-149.822187448740	0.000309254592
					4.66		-149.822187632728	0.000306318362
					4.67		-149.822187606250	0.000303425515
					4.68		-149.822187379815	0.000300575309
					4.7		-149.822186367253	0.000294999407
					4.75		-149.822180992003	0.000281751668
					4.8		-149.822172308556	0.000269452191
					4.9		-149.822148417043	0.000247085518
					5.0		-149.822119605280	0.000227173002
					5.5		-149.821978170857	0.000148812907
					6.0		-149.821888752907	0.000089648161
					6.5		-149.821840411978	0.000047611182
					7.0		-149.821814305415	0.000026632869
					8.0		-149.821791171635	0.000013832085
					9.0		-149.821782663057	0.000008295111
					10.0		-149.821779066588	0.000004669805
					12.0		-149.821776521640	0.000000411174
					14.0		-149.821775796314	0.000000005847
					17.0		-149.821775465428	-0.000000000722
					20.0		-149.821775381642	-0.000000000802
					30.0		-149.821775348396	-0.000000000619
					40.0		-149.821775346567	-0.000000000803
					100.0		-149.821775346009	-0.000000000745
0	45	90	0	0	3.0	1.1040569	-149.817669856570	0.000753106426
					3.05		-149.818596914434	0.000706501923
					3.1		-149.819362479411	0.000662986961
					3.15		-149.819991856518	0.000622421341
					3.2		-149.820506657318	0.000584663839
					3.25		-149.820925304040	0.000549561567
					3.3		-149.821263471279	0.000516944484
					3.35		-149.821534469736	0.000486623088
					3.4		-149.821749581639	0.000458392762
					3.45		-149.821918347941	0.000432039685

					3.4		-149.821749581639	0.000458392762
					3.45		-149.821918347941	0.000432039685
					3.5		-149.822048822030	0.000407351004
					3.55		-149.822147785916	0.000384124648
					3.6		-149.822220937306	0.000362178970
					3.65		-149.822273007585	0.000341403770
					3.7		-149.822308077133	0.000321589420
					3.8		-149.822339832914	0.000284661683
					3.82		-149.822341455637	0.000277685204
					3.83		-149.822341789576	0.000274247198
					3.84		-149.822341825529	0.000270842838
					3.85		-149.822341578088	0.000267471912
					3.86		-149.822341061291	0.000264134586
					3.9		-149.822336559631	0.000251124310
					4.0		-149.822312185086	0.000221028301
					4.1		-149.822276075474	0.000194536834
					4.2		-149.822234410205	0.000171674117
					4.3		-149.822191166975	0.000152185458
					4.4		-149.822148808841	0.000135558898
					4.5		-149.822108777652	0.000121167139
					4.6		-149.822071833309	0.000108439640
					4.7		-149.822038292699	0.000096982248
					4.8		-149.822008192455	0.000086604834
					4.9		-149.821981401185	0.000077270733
					5.0		-149.821957693161	0.000069011827
					5.5		-149.821875758089	0.000042435477
					6.0		-149.821832960450	0.000028147874
					6.5		-149.821809932665	0.000018066568
					7.0		-149.821796980562	0.000011612120
					8.0		-149.821784713539	0.000004843573
					9.0		-149.821779855248	0.000001890234
					10.0		-149.821777700387	0.000000555149
					20.0		-149.821775380898	-0.000000001037
					30.0		-149.821775349372	-0.000000001066
					40.0		-149.821775346329	-0.000000000653
					100.0		-149.821775346111	-0.000000000833
0	45	35.26438969	90	0	3.0	1.1040569	-149.805443197667	0.000991612012
					3.2		-149.814400450754	0.000780358725
					3.3		-149.816999809776	0.000693218641
					3.4		-149.818798163830	0.000616476755
					3.5		-149.820024909939	0.000549991270
					3.6		-149.820847519402	0.000493236429
					3.7		-149.821387259199	0.000444990805
					3.8		-149.821731189082	0.000403662522
					3.9		-149.821941266100	0.000367754859
					4.0		-149.822061183403	0.000336130050
					4.1		-149.822121469729	0.000308031755
					4.15		-149.822136137191	0.000295148025
					4.2		-149.822143243916	0.000282981395
					4.22		-149.822144342321	0.000278307485
					4.23		-149.822144564566	0.000276010838
					4.24		-149.822144583212	0.000273740578
					4.25		-149.822144407962	0.000271496595
					4.26		-149.822144049400	0.000269278516
					4.3		-149.822140960338	0.000260661495
					4.4		-149.822124388809	0.000240815940
					4.5		-149.822100028159	0.000223166259
					5.0		-149.821964717704	0.000154492325
					5.5		-149.821877258879	0.000095416098
					6.0		-149.821831338092	0.000051201316
					6.5		-149.821807538024	0.000029376277
					7.0		-149.821794771045	0.000020063204
					8.0		-149.821783321977	0.000009937144
					9.0		-149.821779048607	0.000004028941
					10.0		-149.821777229418	0.000001207953
					12.0		-149.821775942363	0.000000061697
					14.0		-149.821775574683	0.000000000190

					16.0		-149.821775429618	-0.000000000747
					18.0		-149.821775378712	-0.000000000773
					20.0		-149.821775357519	-0.000000000906
					30.0		-149.821775346412	-0.000000000661
					40.0		-149.821775346273	-0.000000000787
					100.0		-149.821775345989	-0.000000000792
0	45	35.26438969	0	0	3.0	1.1040569	-149.820305665277	0.000680340890
					3.1		-149.821201909623	0.000606143048
					3.15		-149.821521069998	0.000572846726
					3.2		-149.821773366221	0.000541702340
					3.25		-149.821970366846	0.000512461823
					3.3		-149.822121812436	0.000484922665
					3.35		-149.822235886274	0.000458931003
					3.4		-149.822319445151	0.000434381132
					3.45		-149.822378221361	0.000411207106
					3.5		-149.822416993979	0.000389374738
					3.55		-149.822439735281	0.000368868903
					3.6		-149.822449695621	0.000349724529
					3.62		-149.822450757063	0.000342416309
					3.65		-149.822449682716	0.000331843211
					3.7		-149.822441894658	0.000315242543
					3.8		-149.822410014207	0.000285671089
					3.9		-149.822365057004	0.000260337527
					4.0		-149.822314223569	0.000238231228
					4.1		-149.822262091453	0.000218210207
					4.2		-149.822211448441	0.000199275098
					4.3		-149.822163880324	0.000180781622
					4.4		-149.822120185131	0.000162516046
					4.5		-149.822080656069	0.000144640153
					5.0		-149.821940226948	0.000074895457
					5.5		-149.821866890775	0.000045119120
					6.0		-149.821828590716	0.000030489311
					6.5		-149.821807733267	0.000020613269
					7.0		-149.821795836800	0.000013506879
					8.0		-149.821784380755	0.000004532596
					9.0		-149.821779754162	0.000001186168
					10.0		-149.821777671852	0.000000267556
					12.0		-149.821776118438	0.000000005089
					14.0		-149.821775651116	-0.000000000659
					17.0		-149.821775441030	-0.000000000882
					20.0		-149.821775381781	-0.000000000835
					30.0		-149.821775349131	-0.000000000869
					40.0		-149.821775346420	-0.000000000704
					50.0		-149.821775346103	-0.000000000682
					60.0		-149.821775345739	-0.000000000657
					80.0		-149.821775345934	-0.000000000724
					100.0		-149.821775345835	-0.000000000760
90	45	35.26438969	0	0	3.0	1.1040569	-149.807504575081	0.001170982264
					3.1		-149.811974803797	0.001074488041
					3.2		-149.815162628441	0.000985702284
					3.3		-149.817416122713	0.000899175290
					3.4		-149.818992719930	0.000812677247
					3.5		-149.820082184617	0.000726557276
					3.6		-149.820823624266	0.000643398777
					3.7		-149.821318625828	0.000566347677
					3.8		-149.821640896650	0.000497638410
					3.9		-149.821843521797	0.000437945902
					3.95		-149.821912288374	0.000411313695
					4.0		-149.821964414869	0.000386623085
					4.05		-149.822002939442	0.000363689624
					4.1		-149.822030403516	0.000342323806
					4.15		-149.822048927739	0.000322343238
					4.2		-149.822060274601	0.000303583781
					4.25		-149.822065905376	0.000285905944
					4.27		-149.822066834996	0.000279111605
					4.28		-149.822067051517	0.000275770704
					4.29		-149.822067113088	0.000272466447

					4.3		-149.822067027194	0.000269198241
					4.31		-149.822066801260	0.000265965437
					4.35		-149.822064633474	0.000253379870
					4.4		-149.822059537976	0.000238398911
					4.45		-149.822052405534	0.000224227960
					4.5		-149.822043776940	0.000210858455
					5.0		-149.821939047748	0.000118359073
					5.5		-149.821865546973	0.000067920277
					6.0		-149.821825638524	0.000042090126
					6.5		-149.821804598348	0.000029229873
					7.0		-149.821793162290	0.000019411776
					8.0		-149.821782786682	0.000009845567
					9.0		-149.821778852267	0.000004692724
					10.0		-149.821777150692	0.000001480299
					12.0		-149.821775925912	0.000000040399
					14.0		-149.821775570635	-0.000000000461
					17.0		-149.821775414530	-0.000000000620
					20.0		-149.821775371652	-0.000000000842
					30.0		-149.821775348241	-0.000000000848
					40.0		-149.821775346359	-0.000000000708
					100.0		-149.821775345872	-0.000000000730
0	45	90	90	0	3.0	1.1040569	-149.793074132710	0.001134738602
					3.1		-149.801621450166	0.000996114265
					3.2		-149.807800358956	0.000875320481
					3.3		-149.812231137477	0.000772211253
					3.4		-149.815380723148	0.000684376759
					3.5		-149.817597988501	0.000608914149
					3.6		-149.819141778848	0.000543636166
					3.7		-149.820202827662	0.000487204610
					3.8		-149.820920709176	0.000438684842
					3.9		-149.821396836119	0.000397137521
					4.0		-149.821704341652	0.000361484400
					4.1		-149.821895580335	0.000330576223
					4.2		-149.822007723306	0.000303319872
					4.3		-149.822066935882	0.000278778207
					4.4		-149.822091470705	0.000256227298
					4.44		-149.822094547595	0.000247646064
					4.45		-149.822094845418	0.000245535112
					4.46		-149.822094972481	0.000243437365
					4.47		-149.822094937107	0.000241352480
					4.48		-149.822094747150	0.000239280293
					4.5		-149.822093933954	0.000235172898
					4.55		-149.822089699719	0.000225111547
					5.0		-149.821994192887	0.000146808290
					5.5		-149.821898868503	0.000083896441
					6.0		-149.821844564679	0.000044829299
					6.5		-149.821815644545	0.000026684222
					7.0		-149.821799903594	0.000018826618
					8.0		-149.821785602958	0.000008811209
					9.0		-149.821780178848	0.000003941802
					10.0		-149.821777820271	0.000001777135
					12.0		-149.821776134466	0.000000142908
					14.0		-149.821775648811	0.000000001067
					16.0		-149.821775481364	-0.000000001081
					18.0		-149.821775413066	-0.000000001019
					20.0		-149.821775381866	-0.000000001050
					30.0		-149.821775349462	-0.000000001095
					40.0		-149.821775346955	-0.000000001074
					100.0		-149.821775346366	-0.000000001192
0	45	90	90	90	3.0	1.1040569	-149.817751598878	0.000767552004
					3.1		-149.819343564583	0.000680311577
					3.2		-149.820429175035	0.000604496355
					3.3		-149.821155070506	0.000538928663
					3.4		-149.821627991218	0.000481712149
					3.5		-149.821924998209	0.000430735919
					3.6		-149.822101425655	0.000384072752
					3.7		-149.822196467124	0.000340649792

					3.8		-149.822237732795	0.000300163626
					3.81		-149.822239700453	0.000296285206
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0	15		0	0	3.7	1.1040569	-149.822303866090	0.000338844139
0	15		0	0	3.8	1.1040569	-149.822322307921	0.000303783971
0	15		0	0	3.9	1.1040569	-149.822311582030	0.000272124920
0	15		0	0	4	1.1040569	-149.822283672428	0.000243322586
0	15		0	0	4.5	1.1040569	-149.822085838415	0.000134956913
0	15		0	0	5	1.1040569	-149.821944939700	0.000074833458
0	15		0	0	6	1.1040569	-149.821829226418	0.000030298320
0	15		0	0	7	1.1040569	-149.821795710842	0.000012803937
0	15		0	0	8	1.1040569	-149.821784213033	0.000005004310
0	15		0	0	9	1.1040569	-149.821779633759	0.000001738036
0	15		0	0	10	1.1040569	-149.821777593473	0.000000477604
0	15		0	0	20	1.1040569	-149.821775369135	0.000000000697
0	30		0	0	3	1.1040569	-149.819853659234	0.000693031789
0	30		0	0	3.3	1.1040569	-149.821966753297	0.000492136390
0	30		0	0	3.5	1.1040569	-149.822345991633	0.000395452594
0	30		0	0	3.6	1.1040569	-149.822403065407	0.000355284995
0	30		0	0	3.7	1.1040569	-149.822412143591	0.000319733829
0	30		0	0	3.8	1.1040569	-149.822391813119	0.000288362996
0	30		0	0	3.9	1.1040569	-149.822354634400	0.000260645592
0	30		0	0	4	1.1040569	-149.822308928586	0.000235992445
0	30		0	0	4.5	1.1040569	-149.822082766259	0.000138930699
0	30		0	0	5	1.1040569	-149.821941746745	0.000074045445
0	30		0	0	6	1.1040569	-149.821828844151	0.000030178134
0	30		0	0	7	1.1040569	-149.821795836714	0.000013163981
0	30		0	0	8	1.1040569	-149.821784350524	0.000004612966
0	30		0	0	9	1.1040569	-149.821779728989	0.000001315443
0	30		0	0	10	1.1040569	-149.821777654601	0.000000318191
0	30		0	0	20	1.1040569	-149.821775375392	0.000000000664

APPENDIX VI (to the Part III)

Dipole moment of the van der Waals complex CH_4-N_2

Angles χ_A, θ_A, φ_A, θ_B, φ_B are in Deg, intermolecular separation *R* is in Å, dipole moment μ_α is in ea_0.

Configurations with the dipole moment components that are of opposite sign but the same magnitude are not presented here.

μ_α - dipole moment without the BSSE correction

μ_α CP – dipole moment with the BSSE correction (Counterpoise correction scheme of Boys and Bernardi)

χ_A	θ_A	φ_A	θ_B	φ_B	*R*	μ_x CP	μ_x	μ_y CP	μ_y	μ_z CP	μ_z
90	45	t	90	0	3.2	.34798641	.34798809	0	0	0	0
					3.4	.22810884	.22811052				
					3.6	.15055088	.15055256				
					3.8	.10068426	.10068594				
					4.0	.06858796	.06858964				
					4.25	.04388745	.04388913				
					4.5	.02930131	.02930300				
					5.0	.01496538	.01496707				
					5.5	.00895493	.00895662				
					6.0	.00588320	.00588489				
					7.0	.00285285	.00285454				
					10.0	.00058356	.00058525				
					20.0	.00002705	.00002873				
0	45	90	0	0	3.2	-.00697742	-.00697720	0	0	0	0
					3.4	-.00770510	-.00770510				
					3.6	-.00770601	-.00770601				
					3.8	-.00720392	-.00720392				
					4.0	-.00648268	-.00648269				
					4.25	-.00546403	-.00546403				
					4.5	-.00448871	-.00448871				
					5.0	-.00299574	-.00299574				
					5.5	-.00202035	-.00202035				
					6.0	-.00141851	-.00141851				
					7.0	-.00079531	-.00079531				
					10.0	-.00020749	-.00020749				
					20.0	-.00001521	-.00001505				
0	45	t	90	0	3.2	.02411650	.02411482	0	0	0	0
					3.4	.02048846	.02048677				
					3.6	.01703583	.01703415				
					3.8	.01397994	.01397826				
					4.0	.01145725	.01145557				
					4.25	.00896137	.00895969				
					4.5	.00709872	.00709703				
					5.0	.00468911	.00468743				
					5.5	.00333109	.00332941				
					6.0	.00244104	.00243936				
					7.0	.00138048	.00137879				
					10.0	.00035038	.00034870				
					20.0	.00002737	.00002569				
0	45	t	0	0	3.2	-.01574719	-.01574888	-.00057984	-.00057866	0	0
					3.4	-.01379156	-.01379325	-.00043139	-.00043021		
					3.6	-.01194666	-.01194835	-.00035046	-.00034928		
					3.8	-.01017247	-.01017416	-.00030102	-.00029984		
					4.0	-.00858405	-.00858574	-.00026087	-.00025970		
					4.25	-.00687384	-.00687553	-.00021268	-.00021150		
					4.5	-.00550265	-.00550433	-.00017108	-.00016991		
					5.0	-.00357699	-.00357867	-.00011083	-.00010966		
					5.5	-.00237408	-.00237576	-.00007229	-.00007112		
					6.0	-.00164375	-.00164543	-.00004849	-.00004731		
					7.0	-.00088134	-.00088303	-.00002593	-.00002476		
					10.0	-.00023544	-.00023713	-.00000623	-.00000506		
					20.0	-.00001096	-.00001264	-.00000250	-.00000133		

90	45	t	0	0	3.2	.05478406	.05478574	.00023853	.00023736	0	0
					3.4	.02913663	.02913831	.00016656	.00016538		
					3.6	.01415217	.01415385	.00012617	.00012500		
					3.8	.00579015	.00579183	.00010232	.00010115		
					4.0	.00138856	.00139024	.00008769	.00008651		
					4.25	-.00105719	-.00105550	.00007454	.00007337		
					4.5	-.00184555	-.00184386	.00005817	.00005700		
					5.0	-.00174277	-.00174108	.00003935	.00003818		
					5.5	-.00124830	-.00124661	.00002837	.00002719		
					6.0	-.00084811	-.00084643	.00002096	.00001979		
					7.0	-.00051843	-.00051675	.00001274	.00001157		
					10.0	-.00016392	-.00016224	.00000466	.00000349		
					20.0	-.00001716	-.00001545	.00000095	-.00000019		
0	45	90	90	0	3.2	.04280164	.04280164	0	0	0	0
					3.4	.03558819	.03558818				
					3.6	.02875693	.02875693				
					3.8	.02292513	.02292513				
					4.0	.01826907	.01826907				
					4.25	.01380100	.01380100				
					4.5	.01067987	.01067987				
					5.0	.00689716	.00689716				
					5.5	.00473433	.00473433				
					6.0	.00336121	.00336121				
					7.0	.00179607	.00179607				
					10.0	.00042726	.00042726				
					20.0	.00002675	. 00002675				
0	45	t	15	0	3.2	-.01556548	-.01556716	-.00064694	-.00064577	-.00880737	-.00880737
					3.4	-.01318531	-.01318700	-.00047201	-.00047083	-.00667703	-.00667703
					3.6	-.01118396	-.01118565	-.00037012	-.00036895	-.00524229	-.00524229
					3.8	-.00941359	-.00941528	-.00030583	-.00030465	-.00420979	-.00420979
					4.0	-.00787745	-.00787913	-.00025815	-.00025698	-.00347081	-.00347081
					4.25	-.00625933	-.00626101	-.00020713	-.00020595	-.00279154	-.00279154
					4.5	-.00498567	-.00498736	-.00016540	-.00016423	-.00229057	-.00229057
					5.0	-.00321970	-.00322138	-.00010753	-.00010636	-.00159735	-.00159735
					5.5	-.00213806	-.00213974	-.00007104	-.00006987	-.00112118	-.00112118
					6.0	-.00146302	-.00146470	-.00004798	-.00004680	-.00081958	-.00081958
					7.0	-.00077021	-.00077189	-.00002511	-.00002394	-.00045579	-.00045579
					10.0	-.00020206	-.00020374	-.00000603	-.00000486	-.00010952	-.00010952
					20.0	-.00000866	-.00001035	-.00000250	-.00000132	-.00000691	-.00000691
0	45	t	30	0	3.2	-.01363738	-.01363906	-.00076519	-.00076401	-.01673668	-.01673668
					3.4	-.01053306	-.01053474	-.00054447	-.00054330	-.01278770	-.01278770
					3.6	-.00837126	-.00837294	-.00040465	-.00040347	-.01000490	-.01000490
					3.8	-.00676262	-.00676431	-.00031274	-.00031156	-.00800737	-.00800737
					4.0	-.00554029	-.00554197	-.00024965	-.00024848	-.00654473	-.00654473
					4.25	-.00432201	-.00432370	-.00019092	-.00018975	-.00521748	-.00521748
					4.5	-.00338749	-.00338918	-.00014914	-.00014797	-.00424062	-.00424062
					5.0	-.00211335	-.00211504	-.00009657	-.00009540	-.00290994	-.00290994
					5.5	-.00134527	-.00134695	-.00006483	-.00006365	-.00203915	-.00203915
					6.0	-.00088634	-.00088803	-.00004432	-.00004314	-.00148034	-.00148034
					7.0	-.00043005	-.00043173	-.00002226	-.00002108	-.00081600	-.00081600
					10.0	-.00009970	-.00010138	-.00000545	-.00000428	-.00019135	-.00019135
					20.0	-.00000209	-.00000377	-.00000248	-.00000130	-.00001268	-.00001268
0	45	t	45	0	3.2	-.00704247	-.00704415	-.00075674	-.00075557	-.02172706	-.02172706
					3.4	-.00419737	-.00419906	-.00053646	-.00053528	-.01678752	-.01678752
					3.6	-.00266710	-.00266879	-.00038821	-.00038704	-.01316976	-.01316976
					3.8	-.00183920	-.00184089	-.00028662	-.00028544	-.01050496	-.01050496
					4.0	-.00126927	-.00127096	-.00021741	-.00021624	-.00854907	-.00854907
					4.25	-.00087765	-.00087933	-.00015887	-.00015770	-.00670376	-.00670376
					4.5	-.00061072	-.00061240	-.00011938	-.00011821	-.00535540	-.00535540
					5.0	-.00024360	-.00024528	-.00007541	-.00007424	-.00359891	-.00359891
					5.5	-.00005229	-.00005397	-.00005059	-.00004941	-.00251531	-.00251531
					6.0	.00003057	.00002888	-.00003486	-.00003369	-.00180242	-.00180242
					7.0	.00008924	.00008755	-.00001700	-.00001583	-.00098263	-.00098263
					10.0	.00004573	.00004405	-.00000455	-.00000337	-.00023323	-.00023323
					20.0	.00000909	.00000741	-.00000245	-.00000127	-.00001283	-.00001283

0	45	t	60	0	3.2	.00513171	.00513002	-.00052204	-.00052087	-.02092986	-.02092986
					3.4	.00590252	.00590084	-.00037758	-.00037641	-.01639511	-.01639511
					3.6	.00565175	.00565006	-.00027336	-.00027218	-.01291510	-.01291510
					3.8	.00501502	.00501333	-.00019903	-.00019785	-.01028071	-.01028071
					4.0	.00430095	.00429927	-.00014754	-.00014636	-.00828255	-.00828255
					4.25	.00350156	.00349987	-.00010489	-.00010372	-.00643135	-.00643135
					4.5	.00287004	.00286836	-.00007500	-.00007383	-.00509222	-.00509222
					5.0	.00203245	.00203076	-.00004464	-.00004347	-.00335453	-.00335454
					5.5	.00150387	.00150218	-.00002962	-.00002845	-.00230243	-.00230243
					6.0	.00112740	.00112572	-.00002049	-.00001932	-.00162377	-.00162377
					7.0	.00068472	.00068304	-.00001023	-.00000906	-.00087015	-.00087015
					10.0	.00019435	.00019266	-.00000351	-.00000234	-.00020528	-.00020528
					20.0	.00001935	.00001766	-.00000242	-.00000124	-.00001115	-.00001115
0	45	t	75	0	3.2	.01829678	.01829509	-.00017735	-.00017617	-.01300437	-.01300436
					3.4	.01610492	.01610324	-.00013275	-.00013157	-.01030126	-.01030126
					3.6	.01366226	.01366058	-.00009746	-.00009628	-.00814540	-.00814540
					3.8	.01134301	.01134133	-.00007169	-.00007052	-.00647477	-.00647477
					4.0	.00937048	.00936880	-.00005354	-.00005237	-.00519270	-.00519270
					4.25	.00738003	.00737835	-.00003880	-.00003762	-.00400324	-.00400324
					4.5	.00588202	.00588033	-.00002754	-.00002637	-.00314786	-.00314786
					5.0	.00393395	.00393227	-.00001529	-.00001412	-.00204561	-.00204561
					5.5	.00281282	.00281114	-.00001017	-.00000899	-.00138398	-.00138398
					6.0	.00206499	.00206331	-.00000741	-.00000624	-.00096231	-.00096231
					7.0	.00118269	.00118100	-.00000442	-.00000325	-.00050795	-.00050795
					10.0	.00030782	.00030614	-.00000262	-.00000145	-.00012027	-.00012027
					20.0	.00002717	.00002549	-.00000240	-.00000122	-.00000638	-.00000638
0	45	t	90	0	3.2	.02411650	.02411482	0	0	0	0
					3.4	.02048846	.02048677				
					3.6	.01703583	.01703415				
					3.8	.01397994	.01397826				
					4.0	.01145725	.01145557				
					4.25	.00896137	.00895969				
					4.5	.00709872	.00709703				
					5.0	.00468911	.00468743				
					5.5	.00333109	.00332941				
					6.0	.00244104	.00243936				
					7.0	.00138048	.00137879				
					10.0	.00035038	.00034870				
					20.0	.00003012	.00002844				
0	45	t	15	90	3.2	-.01574436	-.01574604	-.00054491	-.00054374	-.00044753	-.00044753
					3.4	-.01379174	-.01379342	-.00039519	-.00039401	-.00029281	-.00029281
					3.6	-.01194770	-.01194939	-.00031293	-.00031175	-.00020522	-.00020521
					3.8	-.01017465	-.01017633	-.00026385	-.00026267	-.00015600	-.00015600
					4.0	-.00858384	-.00858552	-.00022628	-.00022510	-.00012924	-.00012924
					4.25	-.00687474	-.00687642	-.00018518	-.00018400	-.00010350	-.00010350
					4.5	-.00550279	-.00550447	-.00015042	-.00014925	-.00008433	-.00008433
					5.0	-.00357700	-.00357868	-.00009479	-.00009361	-.00005070	-.00005070
					5.5	-.00237392	-.00237561	-.00006200	-.00006083	-.00003188	-.00003188
					6.0	-.00164363	-.00164531	-.00004158	-.00004041	-.00002059	-.00002059
					7.0	-.00088122	-.00088291	-.00002256	-.00002139	-.00001042	-.00001043
					10.0	-.00023548	-.00023716	-.00000573	-.00000456	-.00000084	-.00000084
					20.0	-.00001095	-.00001264	-.00000249	-.00000131	-.00000028	-.00000028
0	45	t	30	90	3.2	-.01574128	-.01574297	-.00040702	-.00040584	-.00070065	-.00070065
					3.4	-.01379124	-.01379293	-.00027512	-.00027394	-.00047120	-.00047120
					3.6	-.01194874	-.01195042	-.00020103	-.00019986	-.00034164	-.00034164
					3.8	-.01017799	-.01017967	-.00016014	-.00015896	-.00026778	-.00026778
					4.0	-.00858410	-.00858578	-.00013356	-.00013239	-.00022437	-.00022437
					4.25	-.00687494	-.00687662	-.00010703	-.00010586	-.00017944	-.00017944
					4.5	-.00550255	-.00550423	-.00008869	-.00008752	-.00014612	-.00014612
					5.0	-.00357678	-.00357847	-.00005346	-.00005229	-.00008928	-.00008928
					5.5	-.00237378	-.00237547	-.00003510	-.00003392	-.00005661	-.00005661
					6.0	-.00164343	-.00164511	-.00002375	-.00002257	-.00003681	-.00003681
					7.0	-.00088129	-.00088297	-.00001362	-.00001245	-.00001879	-.00001879
					10.0	-.00023539	-.00023708	-.00000432	-.00000314	-.00000228	-.00000228
					20.0	-.00001095	-.00001264	-.00000248	-.00000131	-.00000033	-.00000033

0	45	t	45	90	3.2	-.01574436	-.01574604	-.00011889	-.00011772	-.00069347	-.00069347
					3.4	-.01379174	-.01379342	-.00006047	-.00005929	-.00048611	-.00048611
					3.6	-.01194770	-.01194939	-.00002713	-.00002596	-.00037016	-.00037016
					3.8	-.01017465	-.01017633	-.00001151	-.00001034	-.00030138	-.00030138
					4.0	-.00858384	-.00858552	-.00000552	-.00000435	-.00025552	-.00025552
					4.25	-.00687474	-.00687642	-.00000302	-.00000185	-.00020814	-.00020814
					4.5	-.00550278	-.00550447	-.00000390	-.00000273	-.00016909	-.00016909
					5.0	-.00357699	-.00357868	.00000039	.00000156	-.00010539	-.00010539
					5.5	-.00237392	-.00237561	-.00000025	.00000092	-.00006759	-.00006759
					6.0	-.00164363	-.00164531	-.00000085	.00000032	-.00004437	-.00004437
					7.0	-.00088123	-.00088291	-.00000179	-.00000062	-.00002283	-.00002283
					10.0	-.00023548	-.00023716	-.00000208	-.00000091	-.00000348	-.00000348
					20.0	-.00001095	-.00001264	-.00000255	-.00000138	-.00000028	-.00000028
0	45	t	60	90	3.2	-.01574719	-.01574887	.00028610	.00028728	-.00049994	-.00049994
					3.4	-.01379156	-.01379325	.00021119	.00021237	-.00037103	-.00037103
					3.6	-.01194666	-.01194834	.00016942	.00017059	-.00030021	-.00030021
					3.8	-.01017248	-.01017416	.00014184	.00014302	-.00025567	-.00025567
					4.0	-.00858406	-.00858574	.00012200	.00012317	-.00022096	-.00022096
					4.25	-.00687385	-.00687553	.00010062	.00010179	-.00018086	-.00018086
					4.5	-.00550265	-.00550433	.00008119	.00008237	-.00014555	-.00014555
					5.0	-.00357699	-.00357867	.00005169	.00005286	-.00009376	-.00009376
					5.5	-.00237407	-.00237576	.00003248	.00003366	-.00006044	-.00006044
					6.0	-.00164375	-.00164543	.00002056	.00002173	-.00003982	-.00003982
					7.0	-.00088134	-.00088303	.00000929	.00001046	-.00002038	-.00002038
					10.0	-.00023545	-.00023713	-.00000051	.00000066	-.00000329	-.00000329
					20.0	-.00001096	-.00001264	-.00000233	-.00000116	-.00000010	-.00000010
0	45	t	75	90	3.2	-.01574436	-.01574604	.00065617	.00065735	-.00024595	-.00024595
					3.4	-.01379174	-.01379342	.00044654	.00044771	-.00019312	-.00019312
					3.6	-.01194770	-.01194939	.00032814	.00032931	-.00016483	-.00016483
					3.8	-.01017465	-.01017633	.00025823	.00025940	-.00014533	-.00014533
					4.0	-.00858384	-.00858552	.00021665	.00021782	-.00012794	-.00012794
					4.25	-.00687474	-.00687642	.00017612	.00017730	-.00010395	-.00010395
					4.5	-.00550279	-.00550447	.00014302	.00014420	-.00008215	-.00008215
					5.0	-.00357699	-.00357868	.00008793	.00008910	-.00005563	-.00005563
					5.5	-.00237393	-.00237561	.00005503	.00005621	-.00003582	-.00003582
					6.0	-.00164363	-.00164531	.00003500	.00003617	-.00002367	-.00002368
					7.0	-.00088123	-.00088291	.00001657	.00001774	-.00001194	-.00001194
					10.0	-.00023548	-.00023716	-.00000017	.00000100	-.00000191	-.00000191
					20.0	-.00001095	-.00001264	-.00000207	-.00000090	-.00000006	-.00000006
0	45	t	90	90	3.2	-.01574129	-.01574297	.00080643	.00080760	0	0
					3.4	-.01379125	-.01379293	.00054095	.00054212		
					3.6	-.01194874	-.01195042	.00040825	.00040942		
					3.8	-.01017799	-.01017967	.00030372	.00030490		
					4.0	-.00858410	-.00858578	.00025366	.00025483		
					4.25	-.00687494	-.00687662	.00020360	.00020477		
					4.5	-.00550254	-.00550423	.00016521	.00016639		
					5.0	-.00357678	-.00357847	.00010092	.00010209		
					5.5	-.00237378	-.00237546	.00006295	.00006413		
					6.0	-.00164343	-.00164511	.00003994	.00004111		
					7.0	-.00088129	-.00088297	.00001898	.00002015		
					10.0	-.00023540	-.00023708	.00000001	.00000119		
					20.0	-.00001095	-.00001264	-.00000204	-.00000086		
0	45	0	0	0	3.2	.00415353	.00415353	-.00438506	-.00438506	0	0
					3.4	-.00184081	-.00184081	-.00442493	-.00442493		
					3.6	-.00471994	-.00471994	-.00418500	-.00418500		
					3.8	-.00570993	-.00570993	-.00378428	-.00378428		
					4.0	-.00579406	-.00579406	-.00331271	-.00331271		
					4.25	-.00521465	-.00521465	-.00270484	-.00270484		
					4.5	-.00441889	-.00441889	-.00215730	-.00215730		
					5.0	-.00294528	-.00294528	-.00136430	-.00136430		
					5.5	-.00194676	-.00194676	-.00089607	-.00089607		
					6.0	-.00133867	-.00133867	-.00060026	-.00060026		
					7.0	-.00075823	-.00075823	-.00027239	-.00027239		
					10.0	-.00020479	-.00020479	-.00004727	-.00004727		
					20.0	-.00001339	-.00001339	-.00000145	-.00000145		

0	45	15	0	0	3.2	-.01145180	-.01145287	-.00297702	-.00297674	0	0
					3.4	-.01142354	-.01142461	-.00292864	-.00292836		
					3.6	-.01055328	-.01055434	-.00275490	-.00275463		
					3.8	-.00938073	-.00938180	-.00248761	-.00248733		
					4.0	-.00811043	-.00811150	-.00217556	-.00217528		
					4.25	-.00661857	-.00661964	-.00178725	-.00178697		
					4.5	-.00533186	-.00533292	-.00145319	-.00145291		
					5.0	-.00343662	-.00343769	-.00096066	-.00096038		
					5.5	-.00226107	-.00226213	-.00063920	-.00063892		
					6.0	-.00156653	-.00156759	-.00042040	-.00042012		
					7.0	-.00085390	-.00085497	-.00019151	-.00019124		
					10.0	-.00022601	-.00022707	-.00003585	-.00003557		
					20.0	-.00001187	-.00001294	-.00000167	-.00000139		
0	45	30	0	0	3.2	-.01583172	-.01583337	-.00115022	-.00114929	0	0
					3.4	-.01391699	-.01391864	-.00101899	-.00101806		
					3.6	-.01206958	-.01207122	-.00091079	-.00090985		
					3.8	-.01028077	-.01028241	-.00080246	-.00080153		
					4.0	-.00866899	-.00867064	-.00069484	-.00069391		
					4.25	-.00693839	-.00694004	-.00057389	-.00057296		
					4.5	-.00554761	-.00554926	-.00047558	-.00047465		
					5.0	-.00359340	-.00359505	-.00032604	-.00032511		
					5.5	-.00237872	-.00238037	-.00021611	-.00021518		
					6.0	-.00164637	-.00164802	-.00013926	-.00013833		
					7.0	-.00088276	-.00088441	-.00006653	-.00006560		
					10.0	-.00023531	-.00023696	-.00001403	-.00001309		
					20.0	-.00001101	-.00001266	-.00000228	-.00000134		
0	45	t	0	0	3.2	-.01574719	-.01574888	-.00057984	-.00057866	0	0
					3.4	-.01379156	-.01379325	-.00043139	-.00043021		
					3.6	-.01194666	-.01194835	-.00035046	-.00034928		
					3.8	-.01017247	-.01017416	-.00030102	-.00029984		
					4.0	-.00858405	-.00858574	-.00026087	-.00025970		
					4.25	-.00687384	-.00687553	-.00021268	-.00021150		
					4.5	-.00550265	-.00550433	-.00017108	-.00016991		
					5.0	-.00357699	-.00357867	-.00011083	-.00010966		
					5.5	-.00237408	-.00237576	-.00007229	-.00007112		
					6.0	-.00164375	-.00164543	-.00004849	-.00004731		
					7.0	-.00088134	-.00088303	-.00002593	-.00002476		
					10.0	-.00023544	-.00023713	-.00000623	-.00000506		
					20.0	-.00001096	-.00001264	-.00000250	-.00000133		
0	45	45	0	0	3.2	-.01456132	-.01456286	.00025525	.00025679	0	0
					3.4	-.01286216	-.01286370	.00040162	.00040316		
					3.6	-.01121196	-.01121350	.00043680	.00043834		
					3.8	-.00966516	-.00966670	.00040744	.00040897		
					4.0	-.00821349	-.00821503	.00035915	.00036069		
					4.25	-.00662013	-.00662167	.00031012	.00031165		
					4.5	-.00532172	-.00532326	.00027581	.00027735		
					5.0	-.00347557	-.00347711	.00021152	.00021306		
					5.5	-.00231780	-.00231934	.00014240	.00014394		
					6.0	-.00161339	-.00161493	.00008538	.00008691		
					7.0	-.00086955	-.00087109	.00003449	.00003602		
					10.0	-.00023214	-.00023368	.00000594	.00000747		
					20.0	-.00001114	-.00001268	-.00000280	-.00000127		
0	45	60	0	0	3.2	-.01127479	-.01127573	.00087038	.00087203	0	0
					3.4	-.01062863	-.01062956	.00096595	.00096759		
					3.6	-.00966886	-.00966979	.00096499	.00096664		
					3.8	-.00856206	-.00856299	.00090012	.00090177		
					4.0	-.00743083	-.00743176	.00080993	.00081157		
					4.25	-.00609784	-.00609877	.00068764	.00068929		
					4.5	-.00494232	-.00494325	.00058174	.00058339		
					5.0	-.00324313	-.00324406	.00041511	.00041676		
					5.5	-.00217676	-.00217769	.00028576	.00028741		
					6.0	-.00153438	-.00153531	.00018300	.00018464		
					7.0	-.00083956	-.00084049	.00007876	.00008041		
					10.0	-.00022180	-.00022273	.00001526	.00001691		
					20.0	-.00001201	-.00001294	-.00000268	-.00000103		

0	45	75	0	0	3.2	-.00822972	-.00823000	.00071273	.00071379	0	0
					3.4	-.00855509	-.00855537	.00075671	.00075778		
					3.6	-.00828115	-.00828143	.00072378	.00072485		
					3.8	-.00759698	-.00759726	.00068865	.00068971		
					4.0	-.00675535	-.00675563	.00061465	.00061571		
					4.25	-.00564488	-.00564515	.00051350	.00051457		
					4.5	-.00461789	-.00461816	.00042190	.00042297		
					5.0	-.00306022	-.00306050	.00029056	.00029162		
					5.5	-.00206160	-.00206187	.00020901	.00021007		
					6.0	-.00145373	-.00145401	.00014139	.00014245		
					7.0	-.00080871	-.00080899	.00006073	.00006180		
					10.0	-.00021161	-.00021189	.00001181	.00001287		
					20.0	-.00001295	-.00001323	-.00000166	-.00000059		
0	45	90	0	0	3.2	-.00697833	-.00697833	0	0	0	0
					3.4	-.00770509	-.00770509				
					3.6	-.00770600	-.00770600				
					3.8	-.00720391	-.00720391				
					4.0	-.00648268	-.00648268				
					4.25	-.00546402	-.00546402				
					4.5	-.00448870	-.00448870				
					5.0	-.00299574	-.00299574				
					5.5	-.00202034	-.00202034				
					6.0	-.00141850	-.00141850				
					7.0	-.00079530	-.00079530				
					10.0	-.00020748	-.00020748				
					20.0	-.00001334	-.00001334				
0	45	105	0	0	3.2	-.00822972	-.00823000	-.00071273	-.00071379	0	0
					3.4	-.00855509	-.00855537	-.00075671	-.00075778		
					3.6	-.00828115	-.00828143	-.00072378	-.00072485		
					3.8	-.00759698	-.00759726	-.00068865	-.00068971		
					4.0	-.00675535	-.00675563	-.00061465	-.00061571		
					4.25	-.00564487	-.00564515	-.00051350	-.00051457		
					4.5	-.00461789	-.00461816	-.00042190	-.00042297		
					5.0	-.00306022	-.00306050	-.00029056	-.00029163		
					5.5	-.00206160	-.00206187	-.00020901	-.00021008		
					6.0	-.00145373	-.00145401	-.00014139	-.00014245		
					7.0	-.00080872	-.00080899	-.00006073	-.00006180		
					10.0	-.00021161	-.00021189	-.00001181	-.00001287		
					20.0	-.00001295	-.00001323	.00000166	.00000059		
0	45	120	0	0	3.2	-.01127479	-.01127572	-.00087038	-.00087203	0	0
					3.4	-.01062863	-.01062956	-.00096595	-.00096759		
					3.6	-.00966886	-.00966979	-.00096499	-.00096664		
					3.8	-.00856206	-.00856299	-.00090012	-.00090177		
					4.0	-.00743083	-.00743176	-.00080993	-.00081157		
					4.25	-.00609784	-.00609877	-.00068764	-.00068929		
					4.5	-.00494232	-.00494325	-.00058174	-.00058339		
					5.0	-.00324313	-.00324406	-.00041511	-.00041676		
					5.5	-.00217676	-.00217769	-.00028576	-.00028741		
					6.0	-.00153437	-.00153531	-.00018300	-.00018464		
					7.0	-.00083956	-.00084049	-.00007876	-.00008041		
					10.0	-.00022180	-.00022273	-.00001526	-.00001690		
					20.0	-.00001201	-.00001294	.00000268	.00000103		
0	45	135	0	0	3.2	-.01456132	-.01456286	-.00025525	-.00025679	0	0
					3.4	-.01286216	-.01286370	-.00040162	-.00040316		
					3.6	-.01121196	-.01121350	-.00043680	-.00043834		
					3.8	-.00966516	-.00966670	-.00040743	-.00040897		
					4.0	-.00821349	-.00821503	-.00035915	-.00036069		
					4.25	-.00662013	-.00662167	-.00031012	-.00031165		
					4.5	-.00532172	-.00532326	-.00027581	-.00027735		
					5.0	-.00347557	-.00347711	-.00021153	-.00021306		
					5.5	-.00231780	-.00231934	-.00014240	-.00014394		
					6.0	-.00161339	-.00161493	-.00008538	-.00008691		
					7.0	-.00086955	-.00087109	-.00003449	-.00003602		
					10.0	-.00023214	-.00023368	-.00000593	-.00000747		
					20.0	-.00001114	-.00001268	.00000280	.00000127		

0	45	150	0	0	3.2	-.01583172	-.01583337	.00115023	.00114929	0	0
					3.4	-.01391699	-.01391864	.00101899	.00101806		
					3.6	-.01206958	-.01207122	.00091078	.00090985		
					3.8	-.01028077	-.01028241	.00080246	.00080153		
					4.0	-.00866899	-.00867064	.00069484	.00069391		
					4.25	-.00693839	-.00694004	.00057389	.00057296		
					4.5	-.00554761	-.00554926	.00047558	.00047465		
					5.0	-.00359340	-.00359505	.00032604	.00032511		
					5.5	-.00237872	-.00238037	.00021611	.00021518		
					6.0	-.00164637	-.00164802	.00013926	.00013833		
					7.0	-.00088276	-.00088441	.00006653	.00006560		
					10.0	-.00023531	-.00023696	.00001403	.00001309		
					20.0	-.00001101	-.00001266	.00000228	.00000134		
0	45	165	0	0	3.2	-.01145180	-.01145287	.00297702	.00297674	0	0
					3.4	-.01142354	-.01142461	.00292864	.00292836		
					3.6	-.01055328	-.01055434	.00275490	.00275463		
					3.8	-.00938073	-.00938180	.00248761	.00248733		
					4.0	-.00811043	-.00811150	.00217556	.00217528		
					4.25	-.00661857	-.00661964	.00178725	.00178697		
					4.5	-.00533186	-.00533292	.00145319	.00145291		
					5.0	-.00343662	-.00343769	.00096066	.00096038		
					5.5	-.00226107	-.00226213	.00063920	.00063892		
					6.0	-.00156653	-.00156760	.00042040	.00042012		
					7.0	-.00085390	-.00085497	.00019151	.00019124		
					10.0	-.00022601	-.00022707	.00003585	.00003557		
					20.0	-.00001187	-.00001294	.00000167	.00000139		
0	45	180	0	0	3.2	.00415353	.00415353	.00438506	.00438506	0	0
					3.4	-.00184081	-.00184081	.00442493	.00442493		
					3.6	-.00471994	-.00471994	.00418500	.00418500		
					3.8	-.00570993	-.00570993	.00378428	.00378428		
					4.0	-.00579406	-.00579406	.00331271	.00331271		
					4.25	-.00521465	-.00521465	.00270484	.00270484		
					4.5	-.00441889	-.00441889	.00215730	.00215730		
					5.0	-.00294528	-.00294528	.00136430	.00136430		
					5.5	-.00194676	-.00194676	.00089607	.00089607		
					6.0	-.00133867	-.00133867	.00060026	.00060026		
					7.0	-.00075823	-.00075823	.00027239	.00027239		
					10.0	-.00020479	-.00020479	.00004727	.00004727		
					20.0	-.00001339	-.00001339	.00000145	.00000145		
0	45	195	0	0	3.2	.03104063	.03104170	.00407899	.00407871	0	0
					3.4	.01474626	.01474732	.00414134	.00414106		
					3.6	.00539018	.00539125	.00389276	.00389248		
					3.8	.00044591	.00044697	.00348527	.00348499		
					4.0	-.00189561	-.00189454	.00302502	.00302474		
					4.25	-.00292966	-.00292860	.00245659	.00245631		
					4.5	-.00298314	-.00298207	.00194411	.00194384		
					5.0	-.00225502	-.00225396	.00120388	.00120361		
					5.5	-.00153685	-.00153579	.00078033	.00078005		
					6.0	-.00104647	-.00104540	.00052446	.00052419		
					7.0	-.00062054	-.00061948	.00023890	.00023862		
					10.0	-.00018007	-.00017900	.00003966	.00003938		
					20.0	-.00001487	-.00001381	.00000173	.00000145		
0	45	210	0	0	3.2	.05280945	.05281110	.00146476	.00146383	0	0
					3.4	.02795199	.02795364	.00143730	.00143637		
					3.6	.01345012	.01345177	.00132928	.00132835		
					3.8	.00537354	.00537519	.00118130	.00118037		
					4.0	.00113819	.00113983	.00102185	.00102092		
					4.25	-.00119713	-.00119548	.00082979	.00082886		
					4.5	-.00192750	-.00192585	.00065423	.00065330		
					5.0	-.00177636	-.00177471	.00040415	.00040322		
					5.5	-.00126651	-.00126486	.00026239	.00026146		
					6.0	-.00086053	-.00085889	.00017744	.00017651		
					7.0	-.00052538	-.00052374	.00008286	.00008193		
					10.0	-.00016495	-.00016330	.00001508	.00001415		
					20.0	-.00001567	-.00001403	.00000230	.00000137		

0	45	180+t	0	0	3.2	.05478406	.05478574	.00023853	.00023736	0	0
					3.4	.02913663	.02913831	.00016656	.00016538		
					3.6	.01415217	.01415385	.00012617	.00012500		
					3.8	.00579015	.00579183	.00010232	.00010115		
					4.0	.00138856	.00139024	.00008769	.00008651		
					4.25	-.00105719	-.00105550	.00007454	.00007337		
					4.5	-.00184555	-.00184387	.00005817	.00005700		
					5.0	-.00174277	-.00174108	.00003935	.00003818		
					5.5	-.00124830	-.00124661	.00002837	.00002719		
					6.0	-.00084811	-.00084643	.00002096	.00001979		
					7.0	-.00051843	-.00051675	.00001274	.00001157		
					10.0	-.00016392	-.00016224	.00000466	.00000348		
					20.0	-.00001573	-.00001404	.00000248	.00000131		
0	45	225	0	0	3.2	.04852131	.04852285	-.00191129	-.00191283	0	0
					3.4	.02529441	.02529595	-.00206485	-.00206639		
					3.6	.01180657	.01180811	-.00198744	-.00198898		
					3.8	.00434949	.00435102	-.00179384	-.00179537		
					4.0	.00053203	.00053357	-.00155473	-.00155626		
					4.25	-.00158261	-.00158107	-.00125409	-.00125562		
					4.5	-.00217440	-.00217286	-.00098929	-.00099083		
					5.0	-.00189986	-.00189833	-.00060201	-.00060355		
					5.5	-.00133868	-.00133713	-.00038150	-.00038304		
					6.0	-.00090792	-.00090639	-.00025130	-.00025284		
					7.0	-.00054840	-.00054686	-.00010856	-.00011009		
					10.0	-.00016851	-.00016698	-.00001327	-.00001481		
					20.0	-.00001554	-.00001401	.00000270	.00000117		
0	45	240	0	0	3.2	0.02241048	0.0224115	-0.00359266	-0.00359441	0	0
					3.4	0.00924726	0.0092483	-0.00386524	-0.00386699		
					3.6	0.00198722	0.0019882	-0.00372267	-0.00372442		
					3.8	-0.00168597	-0.0016850	-0.00336047	-0.00336222		
					4.0	-0.00328301	-0.0032820	-0.00291413	-0.00291588		
					4.25	-0.00377746	-0.0037765	-0.00235123	-0.00235298		
					4.5	-0.00354452	-0.0035435	-0.00185132	-0.00185306		
					5.0	-0.00255189	-0.0025509	-0.00113847	-0.00114022		
					5.5	-0.00171972	-0.0017187	-0.00072453	-0.00072628		
					6.0	-0.00116469	-0.0011637	-0.00047567	-0.00047742		
					7.0	-0.00067393	-0.0006729	-0.00020626	-0.00020800		
					10.0	-0.00018834	-0.0001873	-0.00002833	-0.00003008		
					20.0	-0.00001479	-0.0000138	0.00000260	0.00000085		
0	45	255	0	0	3.2	-.00216677	-.00216649	-.00257945	-.00258051	0	0
					3.4	-.00597800	-.00597772	-.00281971	-.00282077		
					3.6	-.00741506	-.00741478	-.00276545	-.00276652		
					3.8	-.00751348	-.00751320	-.00253175	-.00253282		
					4.0	-.00697763	-.00697735	-.00220811	-.00220918		
					4.25	-.00597224	-.00597197	-.00177694	-.00177801		
					4.5	-.00493355	-.00493327	-.00139455	-.00139561		
					5.0	-.00323875	-.00323847	-.00086136	-.00086243		
					5.5	-.00213067	-.00213040	-.00055137	-.00055244		
					6.0	-.00145481	-.00145453	-.00036199	-.00036305		
					7.0	-.00080614	-.00080586	-.00015523	-.00015629		
					10.0	-.00020975	-.00020948	-.00002235	-.00002342		
					20.0	-.00001396	-.00001368	.00000150	.00000044		
0	45	270	0	0	3.2	-.01137322	-.01137322	0	0	0	0
					3.4	-.01162333	-.01162333				
					3.6	-.01085025	-.01085025				
					3.8	-.00968799	-.00968799				
					4.0	-.00839184	-.00839184				
					4.25	-.00683221	-.00683221				
					4.5	-.00547576	-.00547576				
					5.0	-.00351552	-.00351552				
					5.5	-.00229745	-.00229745				
					6.0	-.00157937	-.00157937				
					7.0	-.00086032	-.00086032				
					10.0	-.00021906	-.00021906				
					20.0	-.00001363	-.00001363				

APPENDIX VII (to the Part III)

Ab initio calculated polarizability components $\alpha_{\alpha\alpha}$ of the CH_4-N_2 van der Waals complex at the CCSD(T)/aug-cc-pVTZ level of theory without the BSSE correction. Intermolecular separation R is in Å. Values of polarizability components are in $e^2 a_0^2 E_h^{-1}$.

Component	*R*, Å	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6
α_{xx}	3.2	35.652489	28.828398	34.303261	28.617619	29.075051	34.428017
	3.4	34.925290	28.657396	34.012546	28.487924	28.938385	34.098452
	3.6	34.494535	28.501196	33.794796	28.351192	28.796477	33.880630
	3.8	34.197634	28.349127	33.601136	28.209954	28.640760	33.708071
	4.0	33.956892	28.201096	33.417184	28.069938	28.475359	33.527612
	4.5	33.424309	27.857171	32.982216	27.756838	28.071359	33.096930
	5.0	32.947713	27.584352	32.613813	27.516180	27.738721	32.709674
	5.5	32.573489	27.383698	32.339726	27.336617	27.491023	32.407800
	6.0	32.301284	27.240509	32.135841	27.206461	27.313635	32.186918
	7.0	31.962258	27.063456	31.882006	27.044798	27.096878	31.910010
	10.0	31.622348	26.870885	31.604942	26.866560	26.878136	31.645944
α_{yy}	3.2	25.469002	25.568492	25.293774	25.474291	25.468271	25.409092
	3.4	25.563646	25.754138	25.516374	25.666424	25.656853	25.607051
	3.6	25.698809	25.905521	25.700803	25.823711	25.820587	25.780052
	3.8	25.838295	26.029195	25.852312	25.952790	25.959405	25.926896
	4.0	25.968826	26.131362	25.979451	26.059808	26.075034	26.048962
	4.5	26.225381	26.312755	26.210620	26.258202	26.282188	26.268030
	5.0	26.381376	26.431166	26.356106	26.389990	26.412498	26.402646
	5.5	26.481470	26.511095	26.457222	26.481692	26.499124	26.492930
	6.0	26.550279	26.567602	26.527498	26.546112	26.559193	26.556377
	7.0	26.629888	26.639158	26.618240	26.626365	26.634921	26.634323
	10.0	26.722421	26.724199	26.719458	26.720591	26.723083	26.723572
α_{zz}	3.2	25.469063	29.387091	25.293701	29.642818	29.639627	25.094734
	3.4	25.563623	29.694208	25.516364	29.901571	29.897637	25.343334
	3.6	25.698750	29.949133	25.700828	30.117494	30.122266	25.553941
	3.8	25.838275	30.160994	25.852188	30.297610	30.313710	25.731236
	4.0	25.968825	30.338605	25.979447	30.448516	30.474278	25.878829
	4.5	26.225256	30.660953	26.210558	30.727706	30.767416	26.148492
	5.0	26.381528	30.870805	26.356088	30.911826	30.951734	26.318243
	5.5	26.481545	31.013265	26.456834	31.040878	31.073018	26.432358
	6.0	26.550144	31.114273	26.527255	31.133492	31.157997	26.511791
	7.0	26.629473	31.242064	26.618084	31.252056	31.267497	26.609721
	10.0	26.722575	31.387940	26.719254	31.390471	31.394540	26.717377

Ab initio calculated polarizability components $\alpha_{\alpha\alpha}$ of the CH_4-N_2 van der Waals complex at the CCSD(T)/aug-cc-pVTZ level of theory with the BSSE correction. Intermolecular separation *R* is in Å. Values of polarizability components are in $e^2 a_0^2 E_h^{-1}$.

Component	*R*, Å	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6
α_{xx}	3.2	35.622180	28.813355	34.266868	28.600682	29.005971	34.393075
	3.4	34.895957	28.642704	33.977557	28.471266	28.962726	34.064200
	3.6	34.465772	28.440076	33.761108	28.374892	28.780234	33.847027
	3.8	34.169528	28.330768	33.568133	28.190569	28.627068	33.674979
	4.0	33.929056	28.179990	33.385073	28.049236	28.463057	33.495596
	4.5	33.395815	27.832701	32.950289	27.732840	28.055585	33.066032
	5.0	33.004354	27.562247	32.624338	27.492288	27.719449	32.763591
	5.5	32.545966	27.367284	32.311854	27.318874	27.473448	32.368135
	6.0	32.279387	27.229569	32.112735	27.195474	27.301050	32.154160
	7.0	31.942083	27.058160	31.863444	27.039554	27.093122	31.894780
	10.0	31.618318	26.868592	31.602961	26.865163	26.876536	31.643222
α_{yy}	3.2	25.463098	25.532803	25.277256	25.444685	25.443389	25.389096
	3.4	25.557354	25.720606	25.500651	25.638939	25.633620	25.586506
	3.6	25.692286	25.786402	25.685576	25.798383	25.798499	25.759862
	3.8	25.832443	26.001485	25.837880	25.930756	25.938156	25.907473
	4.0	25.963170	26.107223	25.966433	26.040425	26.054700	26.031088
	4.5	26.217970	26.295613	26.201663	26.243851	26.266277	26.256043
	5.0	26.375435	26.418649	26.351891	26.379667	26.401860	26.395752
	5.5	26.478725	26.502214	26.456251	26.473423	26.491712	26.489580
	6.0	26.548889	26.560995	26.527323	26.539675	26.554270	26.553536
	7.0	26.629969	26.635759	26.618436	26.622415	26.632086	26.631149
	10.0	26.721140	26.722015	26.717940	26.719331	26.721828	26.721694
α_{zz}	3.2	25.463090	29.361670	25.277245	29.619610	29.611426	25.072181
	3.4	25.557346	29.670452	25.500578	29.880372	29.961231	25.321789
	3.6	25.692192	29.927278	25.685644	30.183396	30.188279	25.534385
	3.8	25.832493	30.229430	25.837785	30.365555	30.382075	25.713615
	4.0	25.963153	30.409559	25.966594	30.518913	30.449941	25.863639
	4.5	26.217844	30.642892	26.201629	30.711548	30.746552	26.138718
	5.0	26.375650	30.855796	26.351932	30.901469	30.935252	26.312353
	5.5	26.478828	31.002623	26.455831	31.034150	31.061809	26.429686
	6.0	26.548657	31.106246	26.526968	31.129134	31.150907	26.509192
	7.0	26.629610	31.236697	26.618233	31.249215	31.262893	26.606695
	10.0	26.721246	31.385621	26.717833	31.389243	31.393040	26.715219

Ab initio calculated polarizability components $\alpha_{\alpha\alpha}$ of the CH_4-N_2 van der Waals complex at the MP2/aug-cc-pVTZ level of theory without the BSSE correction. Intermolecular separation R is in Å. Values of polarizability components are in $e^2a_0^2E_h^{-1}$.

Component	R, Å	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6
α_{xx}	3.1	35.558	28.907	33.913	28.654	29.112	34.071
	3.2	34.992	28.803	33.717	28.590	29.035	33.826
	3.3	34.581	28.712	33.563	28.526	28.965	33.645
	3.4	34.279	28.630	33.438	28.461	28.897	33.508
	3.5	34.047	28.550	33.331	28.394	28.829	33.398
	3.6	33.866	28.474	33.234	28.326	28.758	33.303
	3.7	33.717	28.399	33.142	28.257	28.683	33.219
	3.8	33.589	28.324	33.054	28.188	28.605	33.146
	3.9	33.477	28.251	32.968	28.119	28.526	33.061
	4.0	33.370	28.179	32.884	28.051	28.445	32.980
	4.1	33.270	28.108	32.800	27.985	28.363	32.902
	4.2	33.172	28.040	32.716	27.921	28.283	32.821
	4.3	33.074	27.971	32.634	27.860	28.204	32.741
	4.4	32.977	27.906	32.554	27.801	28.126	32.661
	4.5	32.883	27.843	32.478	27.745	28.052	32.583
	5.0	32.443	27.575	32.133	27.508	27.727	32.222
	5.5	32.092	27.377	31.874	27.330	27.483	31.938
	6.0	31.834	27.235	31.680	27.201	27.308	31.729
	6.5	31.647	27.134	31.540	27.110	27.182	31.576
	7.0	31.513	27.060	31.437	27.042	27.093	31.464
	7.5	31.415	27.005	31.359	26.991	27.029	31.380
	8.0	31.343	26.963	31.300	26.952	26.982	31.316
	8.5	31.288	26.931	31.254	26.922	26.946	31.267
	9.0	31.246	26.905	31.219	26.898	26.917	31.229
	9.5	31.212	26.885	31.190	26.879	26.894	31.198
	10.0	31.184	26.868	31.168	26.864	26.875	31.218
	15.0	31.074	26.800	31.072	26.799	26.801	31.090
	20.0	31.088	26.783	31.087	26.783	26.783	31.052
α_{yy}	3.1	25.448	25.454	25.164	25.364	25.360	25.290
	3.2	25.456	25.561	25.291	25.475	25.462	25.396
	3.3	25.493	25.658	25.407	25.576	25.560	25.499
	3.4	25.550	25.747	25.514	25.667	25.651	25.596
	3.5	25.616	25.827	25.610	25.749	25.737	25.688
	3.6	25.687	25.900	25.698	25.823	25.816	25.771
	3.7	25.759	25.965	25.777	25.891	25.888	25.850
	3.8	25.829	26.024	25.850	25.952	25.955	25.920
	3.9	25.899	26.078	25.917	26.008	26.016	25.986
	4.0	25.962	26.127	25.978	26.059	26.071	26.044
	4.1	26.024	26.170	26.032	26.106	26.121	26.099
	4.2	26.081	26.211	26.082	26.148	26.167	26.147
	4.3	26.132	26.247	26.128	26.188	26.208	26.190
	4.4	26.177	26.280	26.169	26.224	26.245	26.230
	4.5	26.221	26.310	26.209	26.257	26.279	26.266
	5.0	26.379	26.429	26.356	26.389	26.410	26.401
	5.5	26.480	26.509	26.456	26.480	26.497	26.492
	6.0	26.548	26.566	26.527	26.545	26.557	26.555
	6.5	26.593	26.607	26.579	26.591	26.601	26.600
	7.0	26.628	26.637	26.617	26.625	26.633	26.633
	7.5	26.654	26.661	26.646	26.651	26.658	26.658
	8.0	26.674	26.679	26.668	26.671	26.677	26.677
	8.5	26.690	26.694	26.685	26.687	26.692	26.692
	9.0	26.702	26.705	26.698	26.700	26.704	26.704
	9.5	26.712	26.715	26.709	26.710	26.713	26.714
	10.0	26.720	26.722	26.717	26.718	26.721	26.722
	15.0	26.755	26.756	26.755	26.755	26.756	26.756
	20.0	26.764	26.764	26.764	26.764	26.764	26.764

Component	R, Å	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6
α_{zz}	3.1	25.448	28.831	25.164	29.102	29.091	24.958
	3.2	25.456	29.001	25.291	29.246	29.228	25.096
	3.3	25.493	29.156	25.407	29.378	29.359	25.224
	3.4	25.550	29.299	25.514	29.498	29.482	25.343
	3.5	25.616	29.428	25.610	29.607	29.596	25.453
	3.6	25.687	29.546	25.698	29.708	29.702	25.552
	3.7	25.759	29.654	25.777	29.799	29.801	25.645
	3.8	25.829	29.752	25.850	29.883	29.891	25.729
	3.9	25.899	29.842	25.917	29.960	29.973	25.808
	4.0	25.962	29.924	25.978	30.030	30.049	25.877
	4.1	26.024	29.998	26.032	30.094	30.118	25.943
	4.2	26.081	30.067	26.082	30.153	30.180	26.001
	4.3	26.132	30.129	26.128	30.208	30.238	26.054
	4.4	26.177	30.186	26.169	30.258	30.290	26.102
	4.5	26.221	30.239	26.209	30.304	30.337	26.147
	5.0	26.379	30.447	26.356	30.488	30.522	26.317
	5.5	26.480	30.590	26.456	30.616	30.645	26.431
	6.0	26.548	30.690	26.527	30.708	30.731	26.511
	6.5	26.593	30.762	26.579	30.776	30.793	26.567
	7.0	26.628	30.816	26.617	30.825	30.840	26.608
	7.5	26.654	30.856	26.646	30.863	30.875	26.639
	8.0	26.674	30.887	26.668	30.893	30.902	26.662
	8.5	26.690	30.911	26.685	30.916	30.923	26.681
	9.0	26.702	30.930	26.698	30.934	30.940	26.695
	9.5	26.712	30.946	26.709	30.948	30.953	26.707
	10.0	26.720	30.958	26.717	30.960	30.964	26.716
	15.0	26.755	31.012	26.755	31.012	31.013	26.755
	20.0	26.764	31.025	26.764	31.025	31.025	26.764

Ab initio calculated polarizability components $\alpha_{\alpha\alpha}$ of the CH_4-N_2 van der Waals complex at the MP2/aug-cc-pVTZ level of theory with the BSSE correction. Intermolecular separation R is in Å. Values of polarizability components are in $e^2 a_0^2 E_h^{-1}$.

Component	R, Å	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6
α_{xx}	3.0	36.321	29.009	34.142	28.696	29.174	34.375
	3.1	35.527	28.885	33.878	28.631	29.082	34.038
	3.2	34.962	28.782	33.684	28.568	29.006	33.793
	3.3	34.552	28.693	33.531	28.505	28.938	33.614
	3.4	34.251	28.611	33.408	28.440	28.873	33.477
	3.5	34.021	28.532	33.301	28.373	28.806	33.368
	3.6	33.841	28.455	33.205	28.305	28.737	33.274
	3.7	33.692	28.379	33.113	28.236	28.664	33.191
	3.8	33.565	28.304	33.027	28.166	28.588	33.118
	3.9	33.453	28.230	32.941	28.097	28.509	33.033
	4.0	33.346	28.157	32.857	28.028	28.429	32.953
	4.1	33.247	28.084	32.773	27.962	28.348	32.876
	4.2	33.149	28.015	32.690	27.898	28.267	32.796
	4.3	33.051	27.946	32.609	27.836	28.188	32.716
	4.4	32.954	27.881	32.529	27.776	28.110	32.637
	4.5	32.861	27.818	32.454	27.720	28.035	32.559
	4.6	32.768	27.759	32.380	27.667	27.962	32.483
	4.7	32.677	27.703	32.307	27.617	27.893	32.408
	4.8	32.589	27.650	32.237	27.570	27.827	32.336
	4.9	32.505	27.600	32.173	27.525	27.765	32.267
	5.0	32.422	27.554	32.111	27.484	27.707	32.200
	5.5	32.075	27.361	31.855	27.312	27.466	31.905
	6.0	31.820	27.225	31.662	27.191	27.296	31.699
	6.5	31.626	27.127	31.517	27.103	27.176	31.550
	7.0	31.493	27.055	31.417	27.037	27.090	31.449
	7.5	31.399	27.002	31.345	26.988	27.027	31.371
	8.0	31.333	26.961	31.296	26.950	26.980	31.310
	8.5	31.279	26.929	31.250	26.921	26.943	31.263
	9.0	31.240	26.903	31.215	26.897	26.915	31.226
	9.5	31.209	26.883	31.188	26.878	26.892	31.196
	10.0	31.181	26.867	31.166	26.863	26.874	31.216
	15.0	31.073	26.797	31.070	26.797	26.799	31.088
	20.0	31.086	26.780	31.085	26.781	26.781	31.050

Component	R, Å	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6
α_{yy}	3.0	25.475	25.298	25.005	25.210	25.224	25.159
	3.1	25.437	25.416	25.143	25.333	25.332	25.267
	3.2	25.445	25.524	25.271	25.445	25.435	25.372
	3.3	25.482	25.623	25.388	25.546	25.534	25.475
	3.4	25.540	25.714	25.494	25.639	25.626	25.572
	3.5	25.605	25.799	25.591	25.722	25.713	25.664
	3.6	25.677	25.869	25.680	25.798	25.793	25.748
	3.7	25.749	25.936	25.759	25.867	25.866	25.827
	3.8	25.820	25.997	25.833	25.930	25.933	25.898
	3.9	25.890	26.053	25.900	25.987	25.994	25.965
	4.0	25.953	26.103	25.962	26.040	26.050	26.023
	4.1	26.015	26.148	26.017	26.088	26.101	26.079
	4.2	26.072	26.191	26.068	26.132	26.148	26.128
	4.3	26.122	26.228	26.115	26.172	26.190	26.172
	4.4	26.168	26.262	26.157	26.209	26.228	26.213
	4.5	26.211	26.293	26.198	26.244	26.263	26.251
	4.6	26.250	26.323	26.234	26.275	26.296	26.285
	4.7	26.284	26.349	26.267	26.304	26.325	26.315
	4.8	26.316	26.374	26.295	26.331	26.352	26.344
	4.9	26.346	26.396	26.324	26.356	26.377	26.369
	5.0	26.372	26.417	26.350	26.379	26.399	26.393
	5.5	26.476	26.501	26.454	26.472	26.490	26.488
	6.0	26.546	26.560	26.526	26.538	26.553	26.552
	6.5	26.593	26.603	26.580	26.586	26.598	26.598
	7.0	26.628	26.635	26.617	26.622	26.631	26.630
	7.5	26.653	26.659	26.645	26.649	26.656	26.655
	8.0	26.673	26.677	26.666	26.670	26.676	26.675
	8.5	26.689	26.692	26.683	26.686	26.691	26.691
	9.0	26.701	26.704	26.697	26.699	26.703	26.703
	9.5	26.712	26.713	26.708	26.709	26.713	26.712
	10.0	26.720	26.721	26.716	26.718	26.720	26.720
	15.0	26.754	26.754	26.753	26.753	26.754	26.754
	20.0	26.762	26.762	26.762	26.762	26.762	26.762

Component	R, Å	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6
α_{zz}	3.0	25.475	28.626	25.005	28.927	28.929	24.782
	3.1	25.437	28.813	25.143	29.086	29.070	24.931
	3.2	25.445	28.984	25.271	29.231	29.209	25.068
	3.3	25.482	29.141	25.388	29.364	29.340	25.197
	3.4	25.540	29.284	25.494	29.485	29.464	25.317
	3.5	25.605	29.414	25.591	29.596	29.579	25.428
	3.6	25.677	29.534	25.680	29.697	29.686	25.529
	3.7	25.749	29.642	25.759	29.789	29.785	25.623
	3.8	25.820	29.741	25.833	29.873	29.876	25.708
	3.9	25.890	29.832	25.900	29.951	29.959	25.788
	4.0	25.953	29.915	25.962	30.021	30.035	25.859
	4.1	26.015	29.989	26.017	30.086	30.104	25.926
	4.2	26.072	30.059	26.068	30.146	30.168	25.985
	4.3	26.122	30.121	26.115	30.201	30.225	26.039
	4.4	26.168	30.179	26.157	30.252	30.278	26.089
	4.5	26.211	30.232	26.198	30.298	30.326	26.135
	4.6	26.250	30.281	26.234	30.341	30.370	26.177
	4.7	26.284	30.326	26.267	30.382	30.411	26.214
	4.8	26.316	30.367	26.295	30.418	30.448	26.249
	4.9	26.346	30.406	26.324	30.453	30.482	26.281
	5.0	26.372	30.441	26.350	30.485	30.513	26.310
	5.5	26.476	30.585	26.454	30.614	30.639	26.428
	6.0	26.546	30.685	26.526	30.707	30.727	26.509
	6.5	26.593	30.759	26.580	30.774	30.790	26.565
	7.0	26.628	30.812	26.617	30.824	30.837	26.605
	7.5	26.653	30.854	26.645	30.862	30.873	26.636
	8.0	26.673	30.885	26.666	30.892	30.900	26.660
	8.5	26.689	30.909	26.683	30.915	30.921	26.679
	9.0	26.701	30.929	26.697	30.933	30.939	26.693
	9.5	26.712	30.944	26.708	30.948	30.952	26.705
	10.0	26.720	30.957	26.716	30.960	30.963	26.714
	15.0	26.754	31.009	26.753	31.010	31.011	26.753
	20.0	26.762	31.022	26.762	31.023	31.023	26.761

APPENDIX VIII (to the Part IV)

TAB. 8.3: Molecular properties for the C_2H_4 molecule.

Property	Definition	Present work[a]	Literature
U	first ionization potential, E_h		0.3862425[b]
Θ_{xx}	quadrupole moment, ea_0^2	-2.47	-2.42[c]
Θ_{yy}	quadrupole moment, ea_0^2	1.25	1.23[c]
Θ_{zz}	quadrupole moment, ea_0^2	1.22	1.19[c]
Φ_{xxxx}	hexadecapole moment, ea_0^4	18.90	18.42[c]
Φ_{yyyy}	hexadecapole moment, ea_0^4	-17.02	-16.27[c]
Φ_{zzzz}	hexadecapole moment, ea_0^4	-15.89	-15.51[c]
α_{xx}	polarizability, $e^2a_0^2E_h^{-1}$	22.05	22.41[d]
α_{yy}	polarizability, $e^2a_0^2E_h^{-1}$	24.96	25.21[d]
α_{zz}	polarizability, $e^2a_0^2E_h^{-1}$	34.24	34.24[d]
$E_{x,xxx}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	-65.27	-80.67[e]
$E_{y,yyy}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	-92.39	-81.01[e]
$E_{z,zzz}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	71.29	88.90[e]
$E_{x,xyy}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	-8.81	-8.11[e]
$E_{x,xzz}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	74.08	88.78[e]
$E_{z,zxx}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	-78.43	-62.24[e]
$E_{z,zyy}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	7.14	-26.63[e]
$E_{y,yxx}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	-75.09	-88.80[e]
$E_{y,yzz}$	dipole-octopole polarizability, $e^2a_0^4E_h^{-1}$	167.48	169.82[e]
$C_{xx,xx}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	72.19	51.93[e]
$C_{xx,yy}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	-19.88	-10.65[e]
$C_{xx,zz}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	-52.31	-41.27[e]
$C_{xy,xy}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	45.35	29.24[e]
$C_{xz,xz}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	75.40	58.71[e]
$C_{yy,yy}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	75.82	51.47[e]
$C_{yy,zz}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	-55.95	-40.82[e]

Property	Definition	Present work[a]	Literature
$C_{yz,yz}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	118.68	101.00[e]
$C_{zz,zz}$	quadrupole polarizability, $e^2a_0^4E_h^{-1}$	108.26	82.09[e]
$B_{xx,xx}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-733.70	
$B_{xx,yy}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	314.70	
$B_{xx,zz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	419.00	
$B_{xy,xy}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-399.39	
$B_{xz,xz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-574.40	
$B_{yy,yy}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-394.06	
$B_{yy,zz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	188.14	
$B_{yz,yz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-591.64	
$B_{zz,zz}$	dipole-dipole-quadrupole polarizability, $e^3a_0^4E_h^{-2}$	-579.30	

[a] Calculated at the CCSD(T)/AVTZ level of theory using approach described in Ref. [185].

[b] Reference [102].

[c] Reference [186].

[d] Reference [187].

[e] Recalculated using $\alpha_{lm;l'm'}$ from Table 6 (basis D, third column) taken from Ref. [173].

APPENDIX IX (to the Part IV)

$$E^{tot} = 2E^{C_2H_4} + \Delta E$$

$$E^{C_2H_4} = -78.443733971266\ E_h\ (CCSD(T)/AVTZ\ BSSE)$$

TAB. 8.4: Interaction potential energy ΔE (in μE_h) for the $(C_2H_4)_2$ dimer calculated at the CCSD(T)/aug-cc-pVTZ basis set with the BSSE correction.

R, Å	conf.1	conf. 2	conf. 3	conf. 4	conf. 5	conf. 6
3.2		1441.6167				1522.403636
3.3		-118.24990				306.2568996
3.4		-1122.4302				-509.528150
3.5	164224.1684	-1728.2397	1680.0	1528.09884	10860.07706	-1033.24391
3.6	116985.2750	-2053.7784	1110.0	1015.98582	7180.909182	-1346.75668
3.7	82794.72581	-2186.6890	707.744	647.874269	4535.565094	-1511.44381
3.8	58126.93757	-2191.1681	420.928	387.211135	2657.439565	-1572.79837
3.9	40408.58992	-2113.5828	222.31	206.129377	1344.394048	-1564.62594
4.0	27752.26542	-1986.8831	88.1902	83.5126857	444.6031285	-1511.23069
4.1	18772.26793	-1834.0320	0.792884	3.41943535	-155.691226	-1430.15293
4.2	12451.50886	-1670.6429	-53.1662	-46.131399	-541.119045	-1333.78411
4.3	8044.534479	-1506.9910	-83.5649	-74.092230	-774.246019	-1230.69870
4.4	5006.458575	-1349.5436	-97.6979	-87.100506	-900.995700	-1126.67377
4.5	2940.055641	-1202.0956	-100.906	-90.036986	-954.809293	-1025.46419
4.6	1558.127518		-97.4472	-86.452456	-959.821462	
4.7	653.8609506		-89.3163	-78.897673	-933.272292	
4.8	79.41859536		-78.8489	-69.175508	-887.334060	
4.9	-270.114510		-67.3887	-67.388706	-830.484899	
5.0	-468.590689	-649.23685	-55.8354	-47.811110	-768.533995	-613.521411
5.1	-567.521348					
5.2	-602.465315		-34.5197	-28.444479		

5.3	-597.681903					
5.4	-569.495932					
5.5	-528.708374	-349.42683	-10.0046	-5.4039003	-478.721663	-363.382039
5.6	-482.313347		-3.90681	-0.1933723		
5.7			1.26338	4.54439680		
5.8			5.59733	8.89403308		
5.9			9.18979	9.18978869		
6.0	-305.717292	-193.89664	12.1316	14.4118154	-287.139656	-221.094379
6.5	-163.419492	-112.24952	19.7625	21.4468741	-175.666142	-139.607162
7.0	-88.9324591	-67.661316	20.6128	21.7747967	-111.432775	-91.5135921
8.0	-29.5738233	-27.071538	16.5075	16.8211371	-50.1366947	-43.3332541
9.0	-11.2418879	-12.054207	11.4918	11.6344489	-25.3647529	-22.6818415
10.0	-4.66708040	-5.7808858	7.82417	7.89529515	-13.9778292	-12.7916789
12.0			3.72255	3.74633528		
14.0			1.89279	1.90330023		
16.0			1.02665	1.02665488		
18.0			0.589179	0.59192041		
20.0	-0.35791337	0.0000001	0.353037	0.35422398	-0.32727462	-0.32125770

R, Å	conf. 7	conf. 8	conf. 9	conf. 10	conf. 11	conf. 12
3.2					2276.63950	
3.3					733.29207	
3.4					-294.84469	
3.5	10418.59026	91904.96514	9489.16978	32258.83712	-953.08207	7866.03197
3.6	6931.84768	66581.79697	5717.20155	22010.86610	-1348.72101	4846.82334
3.7	4411.50532	47580.31970	3072.40619	14739.42092	-1560.80568	2801.06090
3.8	2612.22348	33478.77195	1259.72443	9626.08943	-1647.07069	1439.28089
3.9	1347.17109	23127.86909	53.40737	6069.82898	-1649.32798	553.64211
4.0	474.99461	15615.36993	-716.82974	3629.15813	-1597.55270	-4.20024
4.1	-111.08888	10228.53749	-1178.41764	1981.66499	-1512.96759	-339.30233
4.2	-490.68687		-1425.60251	892.71774	-1410.36445	-526.07404
4.3	-723.07958	3762.77557	-1527.28998	192.83908	-1299.84538	-613.83245
4.4	-852.03175	1947.62722	-1533.23146	-239.39541	-1188.12517	-639.83426
4.5	-909.59188	735.47577	-1478.85014	-490.21976	-1079.50165	-627.47719
4.6	-919.01589	-48.89209		-620.30293		
4.7	-897.01042	-533.94604		-671.89428		
4.8	-855.44199	-812.94219		-674.07945		
4.9	-802.63207	-952.85854		-646.61658		
5.0	-744.32448	-1001.24952	-939.68325	-602.71251	-640.18847	-394.82740
5.1		-991.45462				

5.2		-946.51548				
5.3		-882.08604				
5.4		-808.57702				
5.5	-467.04799	-732.70799	-514.13367	-348.45782	-376.59984	-207.40964
6.0	-281.40247	-413.55071	-279.63761	-183.39499	-227.99248	-108.19430
6.5	-172.70039	-228.34750	-157.43776	-97.70358	-143.35835	-58.15520
7.0	-109.80221	-130.26246	-92.55272	-53.92672	-93.65559	-32.34640
8.0	-49.53971	-48.25308	-36.00168	-18.21419	-44.15627	-10.80965
9.0	-25.10566	-20.68305	-15.88454	-6.78879	-23.05382	-3.79104
10.0	-13.85058	-9.86105	-7.69304	-2.65066	-12.97889	-1.28275
20.0	-0.32537	-0.09117	-0.06214	0.06468	-0.32414	0.06357

Tab. 8.5 - *Interaction potential energy ΔE (in μE_h) for the configuration 2 of the $(C_2H_4)_2$ dimer calculated at different level of theory using aug-cc-pVTZ basis set with the BSSE correction.*

R, Å	CCSD(T)	CCSD(T) -F12	MP2	MP2-F12	SAPT	DFT-SAPT PBE0	DFT-SAPT B3LYP
3.0		6393.4237		5539.5582		5826.1890	6707.7413
3.1						2828.1542	3502.1491
3.2	1441.6167	964.0644		413.5668		758.9525	1270.7368
3.3	-118.2499				-356.5500	-619.8755	-233.3338
3.4	-1122.4302	-1435.8410	-489.4169	-1788.2642	-1361.4400	-1497.2457	-1206.0312
3.5	-1728.2397	-1981.5277	-1418.2632	-2263.9293	-1961.4760	-2013.3784	-1793.6862
3.6	-2053.7784	-2258.0438	-1964.5342	-2485.1120	-2275.5327	-2273.4365	-2107.9928
3.7	-2186.6890	-2351.1795	-2243.3298	-2534.7127	-2392.8630	-2358.9150	-2234.8967
3.8	-2191.1681	-2323.5546	-2340.7533	-2472.9283	-2379.3807	-2328.8741	-2236.5670
3.9	-2113.5828	-2220.1000	-2316.7884	-2342.7029	-2282.9210	-2224.9769	-2156.3395
4.0	-1986.8831	-2072.5195	-2217.0651	-2174.1256	-2137.5424	-2078.2518	-2026.9947
4.1	-1834.0320	-1902.7587	-2073.1195	-1987.8540	-1966.9532		-1872.4663
4.2	-1670.6429	-1725.6417	-1906.7846	-1797.6952	-1787.2081	-1735.9959	-1707.3150
4.3	-1506.9910	-1550.8735	-1732.8051	-1612.5597	-1608.7960		-1540.5837
4.4	-1349.5436	-1384.4718	-1560.7423	-1437.8464	-1438.2400		-1379.4321
4.5	-1202.0956	-1229.8644		-1276.5100	-1279.2700	-1240.9660	-1228.6258
5.0	-649.2369	-658.0719		-684.7221	-687.7500	-670.1661	-667.1602
5.5	-349.4268	-352.8082		-369.7015	-369.7200	-359.6912	-358.5858
6.0	-193.8966	-195.7663		-206.8888	-205.6300	-197.4286	-196.6879
6.5	-112.2495				-119.2800		
7.0	-67.6613	-68.3334		-73.3949	-72.0600	-68.1686	-58.1686
8.0	-27.0715	-27.5881		-30.0301	-29.1900	-27.4690	-17.4690
9.0	-12.0542	-12.4210		-13.6795	-13.1800	-12.2837	10.9220
10.0	-5.7809	-6.0767		-6.7628	-6.4700	-5.9490	7.5012

Tab. 8.6 - *Interaction potential energy ΔE (in μE_h) for the configuration 3 of the $(C_2H_4)_2$ dimer calculated at different level of theory using aug-cc-pVTZ basis set with the BSSE correction.*

R, Å	CCSD(T)	CCSD(T) -F12	MP2	MP2-F12	SAPT	DFT-SAPT PBE0	DFT-SAPT B3LYP
3.7	707.7442				1150.9412	382.3414	331.8103
3.8	420.9282	325.6588	26.2065	81.0806	791.9975	20.8042	107.4413
3.9	222.3105	144.3336	-118.0612	-65.2164	534.3539	-69.0388	-38.4985
4.0	88.1902	23.8674	-206.1905	-155.4229	352.3715	-120.9499	-128.3658
4.1	0.7929	-52.8025	-254.5873	-206.0154	226.3602	-147.0270	-178.9382
4.2	-53.1662	-98.3215	-275.3587	-229.1575	141.3030	-155.5514	-202.6613
4.3	-83.5649	-122.0074	-277.3597	-233.7587	85.8294	-152.4418	-208.3978
4.4	-97.6979	-130.7021	-267.0421	-226.2796	51.3998	-141.9159	-202.2375
4.5	-100.9063	-129.4053	-249.0735	-212.4082	31.6573	-127.2544	-188.4001
4.6	-97.4472	-121.7564	-226.7990	-192.2369	21.9167	-110.5908	-170.4051
4.7	-89.3163	-110.3739	-202.5928	-171.2000	18.7619	-93.4398	-150.5076
4.8	-78.8489	-97.1168	-178.0975	-149.7627	19.7351	-76.7573	-130.2403
4.9	-67.3887	-83.2622	-154.3968	-128.9190	23.0968	-61.1800	-110.5476
5.0	-55.8354	-69.6534	-132.1671	-109.2810	27.6425	-47.0865	-92.1367
5.1					32.5637	-34.5583	-75.4468
5.2		-45.0522	-93.4202	-74.8452	37.3417	-23.6256	-60.5344
5.3					41.6660	-14.2004	-47.4558
5.4					45.3725	-6.1460	-36.1020
5.5	-34.5197	-17.0914	-50.2219	-36.2146	48.3974	0.5934	-26.2062
5.6							-17.8040
5.7							-10.7334
5.8							-4.8138
5.9							0.0829
6.0	12.1316	8.2950	-9.7604	-0.4178	54.3391	17.3030	4.1180
6.5	19.7625	17.5484	7.3673	13.6327	50.6866	24.2820	15.3512
7.0	20.6128	19.3644	13.4369	17.5567	43.5203	24.5576	18.3800
8.0	16.5075	15.8164	13.6414	15.4726	29.1373	18.6599	15.4536
9.0	11.4918	11.1911	10.3347	11.2085	18.9036	12.7269	10.9220
10.0	7.8242	7.6698	7.3213	7.7961	12.3703	8.0110	7.5012

APPENDIX X (to the Part IV)

TAB. 8.7 - *Dipole moment* μ_z *(in* ea_0*) for the* $(C_2H_4)_2$ *dimer calculated at the CCSD(T)/aug-cc-pVTZ basis set with the BSSE correction.*

R, Å	Conf. 5	Conf. 6	Conf. 7	Conf. 9	Conf. 10	Conf. 11
3.0	0.17693625	-0.01397554	0.13138746	-0.13194765	-0.18177764	0.01855188
3.1	0.12890910	-0.02213494	0.09902935	-0.09402283	-0.13084347	0.02825979
3.2	0.09050533	-0.02856320	0.07200146	-0.06448805	-0.09192664	0.03548611
3.3	0.05982511	-0.03359033	0.04938602	-0.04198691	-0.06264934	0.04073006
3.4	0.03534663	-0.03728276	0.03041882	-0.02522697	-0.04133934	0.04428860
3.5	0.01587515	-0.03985741	0.01458794	-0.01303487	-0.02593817	0.04664661
3.6	0.00047848	-0.04147798	0.00148060	-0.00438781	-0.01506027	0.04786453
3.7	-0.01157749	-0.04229770	-0.00918990	0.00156278	-0.00745393	0.04821808
3.8	-0.02088009	-0.04245696	-0.01773472	0.00556857	-0.00233161	0.04788690
3.9	-0.02790882	-0.04208307	-0.02441889	0.00796839	0.00099103	0.04702339
4.0	-0.03306256	-0.04128777	-0.02942783	0.00937833	0.00324077	0.04575599
4.2	-0.03903327	-0.03880869	-0.03571059	0.01020160	0.00530605	0.04241794
4.5	-0.04078001	-0.03392166	-0.03816214	0.00912314	0.00564111	0.03649545
5.0	-0.03480793	-0.02551958	-0.03325449	0.00633727	0.00436040	0.02696509
5.5	-0.02651619	-0.01878073	-0.02570204	0.00425046	0.00314017	0.01960198
6.0	-0.01960726	-0.01393212	-0.01915601	0.00291301	0.00228030	0.01441697
7.0	-0.01076445	-0.00778240	-0.01079427	0.00154911	0.00126707	0.00793803
8.0	-0.00628237	-0.00458995	-0.00622233	0.00087949	0.00073953	0.00463489
9.0	-0.00386230	-0.00290838	-0.00383102	0.00052885	0.00045869	0.00293207
10.0	-0.00252431	-0.00193040	-0.00250733	0.00033661	0.00029919	0.00194440
20.0	-0.00016299	-0.00012893	-0.00016280	0.00001843	0.00001801	0.00013048

Tab. 8.8 - *Dipole moment μ_z (in ea_0) for the $(C_2H_4)_2$ dimer being in configuration 5 calculated at the CCSD(T)/aug-cc-pVTZ, CCSD(T)-F12/VTZ-F12 and MP2/aug-cc-pVTZ levels of theory with the BSSE correction.*

R,Å	CCSD(T)	CCSD(T)-F12	MP2
3.0	0.17693625	0.17200023	0.20649
3.2	0.09050533	0.08661011	0.10959
3.4	0.03534663	0.03209277	0.04748
3.6	0.00047848	-0.00213772	0.00798
3.8	-0.02088009	-0.02295398	-0.01647
4.0	-0.03306256	-0.03464703	-0.03071
4.2	-0.03903327	-0.04015046	-0.03804
4.5	-0.04078001	-0.04099889	-0.04094
5.0	-0.03480793	-0.03464038	-0.03564
5.5	-0.02651619	-0.02609609	-0.02737
6.0	-0.01960726	-0.01908033	-0.02031
7.0	-0.01076445	-0.01042497	-0.01114
8.0	-0.00628237	-0.00612161	-0.00649
9.0	-0.00386230	-0.00383899	-0.00399
10.0	-0.00252431	-0.00253408	-0.00261
20.0	-0.00016299	-0.00016233	-0.00017

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Curriculum Vitae

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2001-2005	Bachelor of Science in Physics at Tomsk State University (Department of Optics and spectroscopy), Tomsk, Russia
1998-2001	Tomsk Humanitarian Lyceum, Tomsk, Russia

Field of interest:

Molecular physics, theoretical atomic and molecular spectroscopy, quantum chemistry calculations: electric properties (dipole moment, polarizability, hyperpolarizability) of atoms, molecules and their complexes.

Scientific software: Gaussian, Molpro, ADF, Gamess, Atomic calculations (HF), ChemOffice, Fortran, Mathematica, Mathlab

Presentation and Graphics Software: MS Office, OpenOffice.Org, Adobe Photoshop, Origin, Corel Draw, LaTex

Honors and Awards:

2006	Medal of the Russian Academy of Sciences for students of Higher Educational Institutions of Russia
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2007	2nd place in All-Russian Student Competition in Mathematica (scientific software), Wolfram Research Incorporation
2007	State Award of Tomsk Region in the field of education and science
2007-2008	Scholarship of the French Embassy in Moscow (Russia) for PhD students (thesis under the joint French-Russian supervision)
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List of Major Publications:

1. Buldakov M. A., Cherepanov V. N., Kalugina Yu. N. Semi-empirical function of the dipole moment of LiH molecule // *Atmos. Ocean Opt.*, Vol. 17, No. 12, pp. 920 - 923 (2004).
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1. Buldakov M. A., Cherepanov V. N., Kalugina Yu. N. Dipole moment function of LiH molecule // Proceedings of SPIE, V. 5743, p. 16 - 19 (2004).
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