

Application of the many-body perturbation theory to the molecular complexes formation

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The many-body perturbation theory up to the second order with the Hamiltonian of CNDO/2 method was applied to the study of benzene—Cl₂, ammonia—Cl₂, ammonia—F₂, ammonia—FCl, and ammonia—ClF complexes formation. Calculated total interaction energy and equilibrium geometry of the benzene—Cl₂ system are in good agreement with the experiment. Results obtained for ammonia—halogen complexes are in quantitative agreement with the *ab initio* SCF MBS ones. In spite of the good values of the calculated total interaction energy for the studied systems individual interaction terms calculated in this manner seem to be incorrect.

Для изучения возникновения комплексов бензол—Cl₂, аммиак—Cl₂, аммиак—F₂, аммиак—FCl и аммиак—ClF применялась теория возмущений многих частиц в приближении до второго порядка с Гамильтонианом метода CNDO/2. Рассчитанная полная энергия взаимодействия и равновесная геометрия системы бензол—Cl₂ в хорошем согласии с экспериментом. Результаты полученные для комплексов аммиак—галоген количественно согласуются с результатами *ab initio* SCF MBS метода. Несмотря на хорошие значения полученной полной энергии взаимодействия отдельные слагаемые вычисленные этим методом кажутся неправильными.

The extent to which “charge-transfer” forces in comparison with “classical” forces contribute to the energy of formation of weak molecular complexes is the subject of a number of papers [1—10]. Theoretically calculated values of the formation energies for the studied systems [2—9] were in good agreement with the experimental ones. The conclusion made from these studies after division of the total interaction energy into individual types of interaction was that most of the binding arises from Coulomb and polarization type of interaction, or from dispersion forces [5, 6].

In this connection, it is necessary to make a remark that the calculation of contributions to the total interaction energy was performed in a nonconsistent manner. In [2—4, 8, 9] which are devoted to the study of benzene—halogen

complex formation by the methods based on the perturbation theory of bimolecular interaction elaborated by *Murrell et al.* [11] some interaction terms were evaluated using theoretically calculated values and other ones using experimental or semiempirical parameters.

The perturbation theory elaborated by *Kvasnička et al.* [12] enables practical calculation of individual energy contributions to the total interaction energy at the same level of approximations. The possibility of application of the above-mentioned theory to the molecular complexes formation is studied in the present paper.

Method used

The problems arising from the requirement of antisymmetry of wave functions of bimolecular system were suitably resolved in [12]. In the framework of the second quantization formalism, the antisymmetry requirement was fulfilled "automatically" by means of anticommutation relations between creation and annihilation operators. Using this formalism and the diagrammatic technique, the perturbation method for molecular interaction in intermediate overlap region was derived. The exact Hamiltonian operator was used in this treatment. The states Ψ_A and Ψ_B were orthogonalized by the Löwdin orthogonalization procedure (convenient for the *ab initio* types of calculations). The use of ZDO (zero-differential overlap) approximation in this connection is advantageous for subsequent application of semiempirical methods (CNDO/2, INDO). The resultant relation [14] for a total interaction energy of two closed-shell molecules in their ground electronic states in the framework of the approximations of CNDO/2 method is as follows

$$\begin{aligned}
 E_{AB}^{\text{int}} = & \sum_{C_1}^A \sum_{C_2}^B \{ \{ Q_{C_1} Q_{C_2} - Q_{C_1} Z_{C_2} - Q_{C_2} Z_{C_1} \} \Gamma_{C_1 C_2} + Z_{C_1} Z_{C_2} R_{C_1 C_2}^{-1} \} + \\
 & + \sum_{i \in A}^{\text{un}} \sum_{j \in A}^{\text{occ}} 2 / (\varepsilon_j - \varepsilon_i) \left\{ \sum_{C_1}^A \sum_{C_2}^B \sum_{\mu}^{C_1} c_{\mu i} c_{\mu j} \Delta Q_{C_2} \Gamma_{C_1 C_2} \right\}^2 + \\
 & + \sum_{i \in B}^{\text{un}} \sum_{j \in B}^{\text{occ}} 2 / (\varepsilon_j - \varepsilon_i) \left\{ \sum_{C_1}^A \sum_{C_2}^B \sum_{\rho}^{C_2} c_{\rho i} c_{\rho j} \Delta Q_{C_1} \Gamma_{C_1 C_2} \right\}^2 + \\
 & + \sum_{i \in B}^{\text{un}} \sum_{j \in A}^{\text{occ}} 2 / (\varepsilon_j - \varepsilon_i) \left\{ \sum_{\mu}^A \sum_{\rho}^B c_{\rho i} c_{\rho j} h_{\mu \rho} \right\}^2 + \\
 & + \sum_{i \in A}^{\text{un}} \sum_{j \in B}^{\text{occ}} 2 / (\varepsilon_j - \varepsilon_i) \left\{ \sum_{\mu}^A \sum_{\rho}^B c_{\mu i} c_{\rho j} h_{\mu \rho} \right\}^2 + \\
 & + \sum_{i \in B}^{\text{occ}} \sum_{l \in A}^{\text{occ}} \sum_{j \in B}^{\text{un}} \sum_{k \in A}^{\text{un}} 4 / \{ (\varepsilon_i - \varepsilon_j) + (\varepsilon_l - \varepsilon_k) \} \cdot \\
 & \cdot \left\{ \sum_{C_1}^A \sum_{C_2}^B \sum_{\mu}^{C_1} \sum_{\rho}^{C_2} c_{\rho i} c_{\rho j} c_{\mu l} c_{\mu k} \Gamma_{C_1 C_2} \right\}^2
 \end{aligned} \tag{1}$$

In eqn (1) Q_{C_1} is electron density of the atom C_1 and its value is equal to $2 \sum_{\mu}^{occ} \sum_{\mu_1}^{C_1} c_{\mu_1}^2$, Z_{C_2} is "core" charge of this atom. The intersystem "core" matrix elements $h_{\mu\nu}$ are approximated by such a manner as used in the CNDO/2 method [15]. $\Gamma_{C_1C_2}$ — intersystem electron repulsion integrals are evaluated theoretically over s atomic orbitals of the atoms.

The physical meaning of individual terms in eqn (1) is as follows

$$E_{AB}^{int} = E_C - E_{POL}^{(1)} - E_{POL}^{(2)} - E_{CT}^{(1)} - E_{CT}^{(2)} - E_{DISP} \quad (2)$$

In this treatment the Coulomb energy is calculated as the sum of intersystem electron repulsions, intersystem nuclear repulsions, and attraction of electrons of the molecule A by nuclei of the molecule B and *vice versa*. Polarization energy $E_{POL}^{(1)}$ ($E_{POL}^{(2)}$) represents a stabilization contribution to the total interaction energy arisen in the consequence of polarization of molecule A (B) by the system of nuclei and electrons of molecule B (A). Importance of a polarization contribution is determined by polarizability of molecule A (B) and at the same time by polarity of interacting molecules (dependence on ΔQ_{C_1}). The charge-transfer terms arise as a result of electron transfer from the occupied MOs of molecule A (B) to unoccupied MOs of B (A). The last term, dispersion energy, is important in the case of interaction of molecules the energy levels of which lie close to each other. With an increase of size of interacting molecules the importance of this term will rise due to a larger number of interacting electron levels. The exchange-repulsion energy is not included in the expression of total interaction energy (eqn (1)) because of the application of ZDO approximation to orthogonalization of states Ψ_A , Ψ_B .

Results and discussion

The geometry of the benzene—Cl₂ complex in our study is the same as an unsymmetrical model which *Schug* and *Levinson* have predicted by the CNDO/2 method as one of the most stable [13]. In this model, planes of interacting molecules are perpendicular and the plane containing Cl₂ bisects the CC bond of the benzene ring. The bond of chlorine molecule and plane of benzene ring form an angle of 60°

Calculations of ammonia—X₂ (X₂ = Cl₂, F₂, FCl, ClF) complexes were performed for axial models.

The internal coordinates of interacting molecules in all studied systems were preserved during the calculation of interaction energy. There are variations only in the distances of the molecular midpoints. The bond lengths CC 0.1397 nm, CH 0.1084 nm, ClCl 0.1989 nm, FCl 0.1628 nm, FF 0.1417 nm, and NH 0.10124 nm were used. The angle HNH in the ammonia molecule: 106.67°. The calculations

were performed in double precision accuracy on the Siemens 4004/150 computer at the Calculating Centre, Komenský University, Bratislava.

Results obtained for benzene—Cl₂ complex by the CNDO/2 method are in Table 1 and those obtained by the perturbation method are in Table 2. As it is obvious from Table 2, the dispersion energy (the largest time-consuming term) was calculated only for the distance 0.42 nm of molecular midpoints. Its value at this distance was $-0.958 \text{ kJ mol}^{-1}$. The value of the total interaction energy of benzene—chlorine complex formation (unsymmetrical model) calculated by the perturbation method is then $-4.325 \text{ kJ mol}^{-1}$. This result is in good agreement with the experimental value $-4.605 \text{ kJ mol}^{-1}$ [2—4]. In addition, the equilibrium intermolecular distance calculated for this model $\sim 0.42 \text{ nm}$ agrees with the value of 0.424 nm measured for benzene—Cl₂ complex in the solid state [19, 20].

Application of the perturbation method (eqn (1)) to the ammonia—halogen complexes gives the results which are summarized in Table 3. In Table 4 there are results obtained by application of the *ab initio* SCF method to the systems under discussion [21].

As we have used the unsymmetrical model for benzene—Cl₂ complex, direct comparison of our results with the ones of authors [2—4, 8] is impossible (axial model). However, essential difference between these results is obvious at the first sight. It is the extent of charge-transfer interaction with respect to the total interaction energy of the system. The results of our study in contradiction to [2—4, 8] indicate the priority role of charge-transfer interactions for this system. The charge-transfer energy obtained in the works [2—4, 8] seems to be underestimated.

Table 1

Results of the interaction calculated by the CNDO/2 method^d
System benzene—Cl₂

Distance of interacting molecules ^a , nm	0.35	0.36	0.38	0.40	0.42	0.44
Dipole moment, <i>D</i>	1.023	0.817	0.498	0.293	0.162	0.092
Charge transfer ^b , e ⁻	0.028	0.023	0.014	0.008	0.005	0.003
Interaction energy ^c kJ mol ⁻¹	+ 8.395	- 2.499	- 11.409	- 9.073	- 6.272	- 4.279

a) Distance of molecular midpoints.

b) Electron transfer from benzene to chlorine.

c) $\Delta E_{AB}(R) = E_{AB}(R) - (E_A + E_B)$.

d) *sp* AOs base was used.

Table 2
Energy contributions to the total interaction energy calculated by the perturbation method^a
System benzene—Cl₂

Intermolecular distance mm	0.35	0.36	0.38	0.40	0.42	0.44
	Energy, kJ mol ⁻¹					
Coulomb	+ 121.861	+ 84.703	+ 39.913	+ 18.217	+ 8.089	+ 4.1868
Polarization ^b						
A by B	0.0	0.0	0.0	0.0	0.0	0.0
B by A	- 16.7 × 10 ⁻⁴	- 13.8 × 10 ⁻	- 9.6 × 10 ⁻⁴	- 6.6 × 10 ⁻⁴	- 4.6 × 10 ⁻⁴	- 3.3 × 10 ⁻⁴
Charge transfer						
occ MOsA un MOsB	- 51.882	- 42.111	- 26.305	- 15.407	- 8.533	- 5.158
un MOsA occ MOsB	- 26.863	- 20.285	- 11.131	- 5.828	- 2.922	- 1.339
Interaction energy without dispersion	+ 43.116	+ 22.307	+ 2.474	- 3.018	- 3.366	- 2.311
Dispersion	—	—	—	—	- 0.958	—
Total interaction energy	—	—	—	—	- 4.325	—

a) *sp* AOs base was used.

b) A — benzene molecule; B — Cl₂ molecule.

Table 3

Interaction energies and equilibrium distances calculated by the perturbation method for ammonia—halogen complexes^a

System	Equilibrium distance ^b nm	Energy, kJ mol ⁻¹						
		Coulomb	Polarization		Dispersion	Charge transfer		Total interaction energy
			NH ₃ /X ₂	X ₂ /NH ₃		H ₃ N→X ₂	X ₂ →NH ₃	
H ₃ N—Cl ₂	0.25	11.735	0.0	-0.067	-0.657	-13.561	-2.236	-4.785
H ₃ N—F ₂	0.25	0.821	0.0	-0.033	-0.435	-2.462	-0.565	-2.675
H ₃ N—ClF	0.34	0.113	0.0	-0.0	-0.025	-0.004	-0.121	-0.347
H ₃ N—FCI	—	Repulsive potential curve						

a) *sp* AOs base was used.b) Distance of nitrogen atom of NH₃ and neighbouring atom of halogen molecule.

Table 4

Ammonia—halogen complexes calculated by the *ab initio* single configuration SCF method [21]

System	Base used ^b	Equilibrium distance nm	Interaction energy ^a kJ mol ⁻¹
NH ₃ —Cl ₂	MBS	0.295	-4.564
	DZ	0.293	-9.965
NH ₃ —F ₂	MBS	0.281	-1.800
	DZ	0.308	-2.512
	extended	0.308	-2.596
	polarized	0.304	-3.307
NH ₃ —ClF	MBS	0.332	-0.712
	DZ	0.365	-32.071
	polarized	0.262	-31.066
NH ₃ —FCI	MBS	0.271	-3.894
	DZ	—	repulsive

a) $\Delta E_{AB} = E_{AB} - (E_A + E_B)$.b) MBS, tree-Gaussian expansion of a minimum basis set of Slater functions; DZ, Dunning's double- ξ basis for H, N, C, F, and Cl: (9*s*,5*p*/4*s*,2*p*); extended; (9*s*,5*p*/4*s*,3*p*); polarized: (9*s*,5*p*,1*d*/4*s*,2*p*,1*d*).It is probably due to an inaccuracy of the determination of the proportionality constant *k* in the term for charge-transfer energy

$$E_{\text{CT}} = - \sum_{\mu}^{\text{A}} \sum_{\nu}^{\text{B}} |kS_{\mu\nu}|^2 / h\nu_{\text{CT}} \quad (3)$$

This type of calculation cannot give a charge-transfer energy arising as a consequence of reverse intermolecular electron transfer (*i.e.* from chlorine to benzene). In spite of the small net amount of charge-transfer (see Table 1) which is due to back donation ($\text{Cl}_2 \rightarrow \text{benzene}$), total charge-transfer energy contribution is significant.

The results of our study show that the energy of reverse electron transfer for this system contributes to the total charge-transfer energy with about 25% at the equilibrium distance of interacting molecules. Similar results were obtained by application of the MINDO/2 method [22].

Although an interaction of HOMO with LUMO is very important, it does not cover the whole charge-transfer energy. For example, at equilibrium distance energy arising as a consequence of electron transfer from HOMO of benzene to LUMO of chlorine contributes to the total charge-transfer energy with about 30%, which is about 40% of charge-transfer energy arising by electron transfer from benzene to chlorine. Interaction of HOMO of chlorine with LUMO of benzene contributes to the total charge-transfer energy with about 4%.

The absence of exchange-repulsion term in the used calculation scheme (eqn (1)) seems to be well compensated by the parametrization of CNDO/2 method. But this compensation is apparent as it follows from the comparison of our results for ammonia—halogen complexes with those obtained by the *ab initio* SCF method (Tables 3 and 4). In spite of the fact that our results are comparable with the results of the *ab initio* SCF minimal basis set (MBS), a disagreement arises when a polarized or extended basis set is used [21]. Increase of the interaction energy for the systems under discussion in this case shows a leading role of the polarization phenomena with these complexes.

The many-body perturbation theory with the CNDO Hamiltonian when applied to formation of molecular complexes overestimates charge-transfer term and the short range repulsive forces are reproduced through erroneous Coulomb contributions. In the used calculation scheme (the second order of perturbation theory) Coulomb contributions are calculated using charge distribution of isolated molecules — Q_{C} in eqn (1). This may be one of the reasons for too large values of Coulomb term at short intermolecular distances.

When a molecular complex is calculated by the SCF procedure — method of supermolecule — the charge distribution is different from that of isolated molecules (effort for repulsion lowering). For this reason probably the SCF equilibrium intermolecular distance is shorter than that calculated by the perturbation method (eqn (1)) in the framework of the same parametrization scheme — CNDO/2 Hamiltonian (see Table 1 and 2). On the other hand, minimal basis set gives only a small part of the molecular polarizability and therefore the polarization

contributions in this calculation scheme may be underestimated.

Recently *Morokuma* and coworkers have published results of single configuration SCF *ab initio* calculations for weak [16, 17] and strong [18] molecular complexes. In case of weak molecular complexes, the electrostatic, charge-transfer, exchange repulsion, and dispersion energies are all of approximately equal importance. The lack of electrostatic interaction in case of strong molecular complexes would make the complex unstable to dissociation, however, the absence of polarization or charge-transfer interaction would still retain the strength of the complex (excluding OC—NH₃).

As it follows from our results the perturbation theory up to the second order with the CNDO/2 Hamiltonian cannot give a correct answer to interesting and difficult theoretical question concerning the origin of stabilization, *i.e.* the relative importance of electrostatic and charge-transfer forces in the ground state of the molecular complexes. Definitive answer about the role of individual types of interaction can be given only after direct calculation of individual interaction terms at the *ab initio* level. Possibility of such calculation offers the many-body perturbation theory [12] up to higher than the second order with the *ab initio* Hamiltonian.

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