

Perturbation study of hydrogen-bonded systems

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A diagrammatic many-body Rayleigh—Schrödinger perturbation theory combined with the CNDO/2 Hamiltonian is applied to the study of intermolecular hydrogen bonds in the MeOH...O₂NMe, MeOH...NMe₃, MeOH...OMe₂, and HCOOH...HCOOH systems. The results are discussed in relation to other theoretical approaches and experimentally obtained values.

Диаграмматическая многочастичная теория возмущений Рэля—Шредингера комбинированная с Гамильтонианом CNDO/2 была использована для изучения межмолекулярных водородных связей в системах MeOH...O₂NMe, MeOH...NMe₃, MeOH...OMe₂ и HCOOH...HCOOH. Результаты обсуждаются с учетом других теоретических подходов и экспериментальных значений.

Many theoretical approaches have been used to investigate the nature of the hydrogen bond (H bond) [1—6]. Different semiempirical MO methods, mainly EHT and CNDO/2 methods, as well as different *ab initio* approaches have been used to study the H bond. Only a few attempts are known to study the H bond using perturbation approach. Among the perturbation approaches we want to mention the approach of *Duijneveldt et al.* [7—11] who used the intermediate overlap perturbation formalism developed by *Murrell et al.* [12] for calculation of some of the contributions to the H-bond energy. We are not going to give here the details of various perturbation approaches to the study of hydrogen bond, but we refer the reader to the paper by *Schuster* [6].

A diagrammatic many-body Rayleigh—Schrödinger perturbation theory is now widely used as a suitable tool for studying the correlation energy of molecules [13—15]. In this paper applications of this theory with CNDO/2 Hamiltonian to the H-bond interaction in the MeOH...O₂NMe, MeOH...NMe₃, MeOH...OMe₂, and HCOOH...HCOOH systems are presented.

Method of calculation

The derivation of interaction energies is presented in [16—19]. Calculations have been performed using the minimal basis set and using the original version of CNINDO programs [20] combined with the program written for the perturbation theory [17].

The experimental molecular geometries and structural parameters reported before [21] were used. The H-bond energy is taken as a calculated interaction energy at the equilibrium intermolecular distance.

Results and discussion

The H-bond interaction in the MeOH...O₂NMe, MeOH...NMe₃, and MeOH...OMe₂ systems was studied by us in details earlier [18, 22]. The H bond is assumed to form the linear X—H...Y conformation. The approaching of methanol and nitromethane molecules toward each other has been studied in two ways. Firstly, the nitromethane molecule is approached in such a way that a symmetrical three-centre H bond is formed including the oxygen atom of methanol and the two oxygens of nitromethane. The hydrogen and oxygen atoms of the O—H group in methanol and the nitrogen atom in nitromethane are taken to be collinear with the planes of COH and NO₂ parts perpendicular to each other. Secondly, a linear O—H...O approach is studied [22].

In our perturbation method presented here we used the same CNDO/2 Hamiltonian as in [22]. We do not reproduce the potential energy curves again, but we rather use the equilibrium distances [22]. The perturbation theory used gives us within CNDO/2 type of Hamiltonian the interaction energy splitted into different contributions, namely: Coulomb, polarization, charge-transfer, and dispersion interaction energies. Table 1 shows the calculated interaction energy in each system. In case of the MeOH...O₂NMe H-bonded complex there does exist a fairly good agreement between the experimental H-bond energy 8.95 ± 5.71 kJ mol⁻¹ and the calculated values 17.72 kJ mol⁻¹ (in case of linear O—H...O H-bond interaction) and 11.30 kJ mol⁻¹ (for a three-centre symmetrical H-bond interaction). The calculated interaction energy for the MeOH...NMe₃ system, 16.93 kJ mol⁻¹, is lower than the experimental value 31.50 ± 2.1 kJ mol⁻¹ [23]. For the systems MeOH...OMe₂ the calculated interaction energy is found to be 15.54 kJ mol⁻¹.

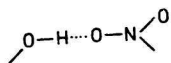
The interaction energy of two formic acid molecules approaching each other in a linear O—H...O configuration is calculated as a function of H...O distance by the perturbation theory. The interaction energy together with all the individual contributions is shown in Fig. 1. The interaction energy shows a minimum value of 141.96 kJ at O...H distance of 1.5×10^{-10} m. This amounts to the H-bond energy of 70.98 kJ/1 H bond [24]. We want to mention here that the H bond in formic acid

Table 1

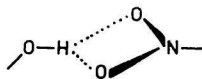
Calculated and experimental H-bond interaction energies

System	Calc. H-bond perturbation kJ mol ⁻¹	Energy CNDO/2	Exp kJ mol ⁻¹	H...Y 10 ⁻¹⁰ m
MeOH...O ₂ NMe*	17.72	32.17 ^a	8.95 ± 5.71 ^b	1.62
MeOH...O ₂ NMe**	11.30	24.74 ^a		2.05***
MeOH...NMe ₃	16.93	36.58 ^a	31.5 ± 2.1 ^c	1.63
MeOH...OMe ₂	15.54	30.24 ^a		1.64
HCOOH...HCOOH	70.98	71.40 ^d	37.38 ^e	1.55

*Linear O—H...O H-bond interaction



**Three-centre symmetrical H-bond interaction



***Y is the N atom.

a) Ref. [18] and [22]; b) [27]; c) [23]; d) [26]; e) [24].

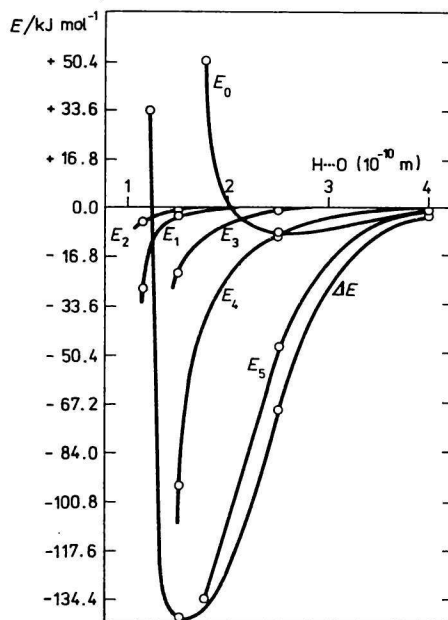


Fig. 1. Different contributions to the H-bond energy in (HCOOH) dimer.

dimer was studied by different authors [25, 26]. The cyclic dimer has been found to be more stable than the open one [25], and a too high calculated H-bond energy 71.40 mol^{-1} is also obtained [26]. The overestimation of the H-bond energy in case of formic acid dimer may be attributed to an underestimation of the Coulomb interaction energy and an overestimation of the charge-transfer interaction energy in such a geometrical arrangement. This may be attributed to the use of CNDO/2 Hamiltonian in the methods where three- and four-centre electron repulsion integrals are neglected and the Coulomb energy is calculated for point charges. The H-bond energies calculated are presented in Table 2, each partitioned into its different contributions.

Table 2

Different contributions* to the X—H...Y H bonds studied
(in kJ mol^{-1})

System	$\frac{X...Y}{10^{-10} \text{ m}}$	E_0	E_1	E_2	E_3	E_4	E_5
MeOH...O ₂ NMe**	2.57	+42.088	-0.529	-0.181	-3.982	-9.446	-45.688
MeOH...O ₂ NMe***	3.03	+37.208	-0.252	-0.038	-1.491	-0.231	-46.511
MeOH...NMe ₃	2.59	+59.018	-0.063	-0.206	-5.590	-4.586	-65.520
MeOH...OMe ₂	2.59	+42.622	-0.227	-0.147	-3.709	-5.930	-48.170
HCOOH...HCOOH	2.57	+73.122	-1.722	-0.000	-14.280	-50.400	-148.680

* E_0 — the Coulomb energy contribution; E_1 — the contribution due to the polarization of the proton donor molecule by the proton acceptor molecule; E_2 — the contribution due to the reverse polarization; E_3 — the contribution due to the dispersion energy; E_4 — the contribution due to charge transfer from the proton donor molecule to the proton acceptor molecule; E_5 — the contribution due to the reverse charge transfer.

**Linear O—H...O H-bond.

***Three-centre symmetrical H-bond interaction (Y is the N atom and the O...O distance is $2.73 \times 10^{-10} \text{ m}$).

From Fig. 1 it is clear that as the H...Y distance becomes shorter than $3 \times 10^{-10} \text{ m}$ the Coulomb energy contribution becomes repulsive and the stabilizing effects due to the dispersion and charge-transfer contributions increase markedly. The charge transfer from the proton acceptor molecule to the proton donor molecule comprises the most stabilizing contribution. From the results presented it is clear that also the polarization contributions are taking part in the long range region and their role increases in the short range.

To conclude this article we note that in comparing the calculated H-bond properties with those obtained experimentally, molecular geometries are to be taken into consideration as one of the important factors which affect the calculated

enthalpy of the H-bond formation [18, 19]. The aim was not to get the best possible comparison with the experimental values. In this respect one has to have in mind the fact that we work with CNDO/2 Hamiltonian which suffers from several limitations combined with the limitations which originate from convergency of the perturbation theory when applied to such a problem as H-bond interaction. We believe that this work will serve as a challenge to apply the *ab initio* Hamiltonian with many-body perturbation approach to the study of the H-bond interaction energy.

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