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Commentationes

Application of SCF-Perturbation Theory to Hydrogen Bonding in Water Dimers

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The usefulness of Self-consistent perturbation theory and of a variation perturbation treatment both in semiempirical form (CNDO/2) is tested by application to hydrogen bonding in water dimers. The results are comparable to variational calculations. A splitting of the total energy in various components provides insight into the nature of hydrogen bonding.

Die Anwendbarkeit von SCF-Störungstheorie und eines Variationsstörverfahrens, beide in semiempirischer Form (CNDO/2), wird an der Wasserstoffbrückenbindung im dimeren Wasser geprüft. Die Ergebnisse sind vergleichbar mit Variationsrechnungen. Eine Aufspaltung der Gesamtenergie in verschiedene Komponenten vermittelt einen Einblick in die Natur der Wasserstoffbrückenbindung.

Introduction and Methods of Calculation

A self-consistent perturbation theory for interacting electron systems, based on a perturbation of the Fock-Dirac density matrix [1], has recently been developed [2]. The semiempirical MINDO version [3] of this theory was applied successfully to problems in chemical reactivity [4]. It has now been rewritten for the CNDO/2 [5] approximation [6]. The usefulness of such a theory for intermolecular forces is compared to a variation perturbation treatment which makes use of zero order SCF-wave functions but is not self consistent. This latter theory had been developed by Pople [7] and was applied by Pople and Schofield [8] to π-electron systems. It has been extended to two electron perturbations in order to treat interacting electron systems [9] and was programmed for the CNDO/2 approximation [10].

Both formalisms are based on the same zero order wave function and therefore give identical results for the first order energy [2, 4]. Incorporation of the change in nuclear repulsion gives a first order change of total energy:

$$\delta E^{(1)} = \sum_{kl} [q_k q_l \gamma_{kl} + (14.399/R_{kl} - \gamma_{kl}) C_k C_l] \tag{1}$$

$q_{k(l)}$ are the excess charges of atoms k and l of the two subsystems K and L. γ_{kl} represents the repulsion of two electrons on atom k and l at the distance R_{kl} and $14.399/R_{kl}$ is the repulsion of two point charges in eV. $C_{k(l)}$ are core charges. The first term in Eq. (1) depends on excess charges and will be called charge interaction, the second term also coulombic in nature includes most of what commonly is considered to be steric hindrance and will be called steric interaction.

The second order energy in the semiempirical SCF-perturbation theory is obtained as the sum of a covalent term (2) and an electrostatic contribution (3) [4]. This is independent of the MINDO or CNDO approximation.

$$\delta E^{(2)}_{\mathrm{COV.}} = \tfrac{1}{2}\sum_{\mu\lambda} P'^{KL}_{\mu\lambda} H'^{KL}_{\lambda\mu} + \tfrac{1}{2}\sum_{\kappa\nu} P'^{LK}_{\kappa\nu} H'^{LK}_{\nu\kappa}\,, \tag{2}$$

$$\delta E^{(2)}_{\mathrm{elec.}} = \tfrac{1}{2}\sum_{kl} (Q'_k q_l + Q'_l q_k)\,\gamma_{kl}\,. \tag{3}$$

Both (2) and (3) [11] depend on the change in the first order density matrix. The change in electron distribution in the subsystems ($Q'_{k(l)}$) should be negligible for the interaction of neutral molecules. Therefore (3) should have no significance in these cases.

The second order energy in the variation perturbation treatment differs from (2) and (3). According to Pople the perturbed wave function ψ is expanded as linear combination of the ground state ψ_0 and singly excited singlet states.

$$\psi = a\psi_0 + \sum_{s>0} b_s \psi_s\,. \tag{4}$$

The second order energy is given by Eq. (5) where $\boldsymbol{H}'$ is defined as in Ref. [2].[1]

$$\delta E^{(2)} = -\sum_{s>0} \frac{\langle\psi_0|\boldsymbol{H}'|\psi_s\rangle\,\langle\psi_s|\boldsymbol{H}'|\psi_0\rangle}{E_s - E_0}\,. \tag{5}$$

Carrying this through one obtains in the CNDO/2 approximation:

$$\delta E^{(2)} = -2\sum_{u}^{\mathrm{occ}}\sum_{p}^{\mathrm{unoc}}\Big[\sum_{\mu}\sum_{\lambda} c_{u\mu}c_{p\lambda}\beta_{\mu\lambda}\Big]^2 E_u^{p^{-1}} \tag{6a}$$

$$-2\sum_{p}^{\mathrm{occ}}\sum_{u}^{\mathrm{unoc}}\Big[\sum_{\lambda}\sum_{\mu} c_{p\lambda}c_{u\mu}\beta_{\lambda\mu}\Big]^2 E_p^{u^{-1}} \tag{6b}$$

$$-2\sum_{u}^{\mathrm{occ}}\sum_{v}^{\mathrm{unoc}}\Big[\sum_{\mu}\sum_{l} c_{u\mu}c_{v\mu}\gamma_{\mu l}q_l\Big]^2 E_u^{v^{-1}} \tag{6c}$$

$$-2\sum_{p}^{\mathrm{occ}}\sum_{q}^{\mathrm{unoc}}\Big[\sum_{\lambda}\sum_{k} c_{p\lambda}c_{q\lambda}\gamma_{\lambda k}q_k\Big]^2 E_p^{q^{-1}} \tag{6d}$$

The terms (6a) and (6b), being a function of resonance integrals $\beta_{\mu\lambda}$, express the covalent interaction of the systems K and L analogous to (2); (6c) and (6d) are, similar to (3), electrostatic in nature. All terms are devided by an excitation

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[1] A comment on the definition of $\boldsymbol{H}'$ may be useful at this point. As was pointed out in Ref. 2 ψ_0 is not an eigenfunction of $\boldsymbol{H}_0$. This difficulty has also been recognized by others and has been solved by using projection operator techniques [Yaris, R.: J. chem. Physics **44**, 3894 (1966); Murrell, J. N., Shaw, G.: J. chem. Physics **46**, 1768 (1967)]. Kreek and Meath [J. chem. Physics **50**, 2289 (1969)] point out, that a satisfactory intermolecular perturbation theory can be formulated by neglecting electron exchange. This assumption is also a consequence of the CNDO approximation which is used in the present treatment.

energy (7).[2] For (6a) and (6b) this is a charge transfer excitation energy, for (6c) and (6d) a local excitation energy. It is interesting to note that the significance of

$$E^i_j = \langle \psi_{i\to j} | \boldsymbol{H}_0 | \psi_{i\to j} \rangle - \langle \psi_0 | \boldsymbol{H}_0 | \psi_0 \rangle \,. \tag{7}$$

(6a) and (6b) should be the greater the lower the charge transfer excitation energies. This parallels results of independent electron models where the excitation energy (7) is replaced by the differences of orbital energies.

Application to Hydrogen Bonding in Water Dimers

The hydrogen bond of water dimers is by no means a new subject as the *ab initio* [11–14, 23] and semiempirical [15–18] calculations demonstrate. The energy and geometry of possible intermolecular complexes has been studied extensively. The aim of this communication is to show the usefulness of SCF-perturbation theory for hydrogen bonding. Perturbational approaches had been deviced by Bratoz [19], by van Duijneveldt and Murrell [20], and van Duijneveldt-van de Ridt and van Duijneveldt [24]. Bratoz evaluates the linear water hydrogen bond using as a basis the occupied and unoccupied hydroxy bond orbitals and a lone pair of the oxygen atom of the hydrogen acceptor in a colinear p-orbital. The problem is then solved analogous to our variation perturbation treatment. His final formula resembles the sum of our first and second order energy. It does not contain a second order electrostatic term and treats the short range repulsion (term 2 in Eq. (1)) by an exponential with empirical parameters. The difficulty in assessing the different quantities caused this theory to remain a qualitative one. Van Duijneveldt and Murrell [20] also restrict themselves to the linear O···H—O fragment. The free electron pair occupies a sp^2 – hybrid orbital. A long range perturbation theory for small intermolecular overlap [21] is applied to this model. However, this theory does not take proper account of short range interactions. For the hydrogen bond it does not lead to an energy minimum. Van Duijneveldt-van de Ridt and van Duijneveldt [24] have extended this latter theory in order to account for this failure. Recently Santry and Bacon [22] proposed an SCF-perturbational approach to treat hydrogen bonding similar to our theory [2, 4].

In our calculations we followed earlier investigations for the linear, bifurcated and cyclic water dimers [14]. The energy components are listed in Table 1 for the SCF-perturbation treatment and the variation perturbation calculations. The linear arrangement has been compared to a direct CNDO/2 calculation. The total SCF-perturbation energies agree within 1–2% (convergence limit for the maximum change of an element in the 1. order density matrix was ≤ 0.001). The value of the second order variation perturbation energy in the linear complex is smaller than the SCF-value. This becomes more pronounced the closer the separation of the two molecules, i.e. the higher the perturbation.

The superposition of the repulsive first order energy and the attractive second order energy yields potential curves which are almost identical to full variational calculations. Yet the perturbation calculations provide more insight. The first

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[2] We use the following index convention: u, v: MO's in K; p, q: MO's in L; μ, ν: AO's in K; κ, λ: AO's in L

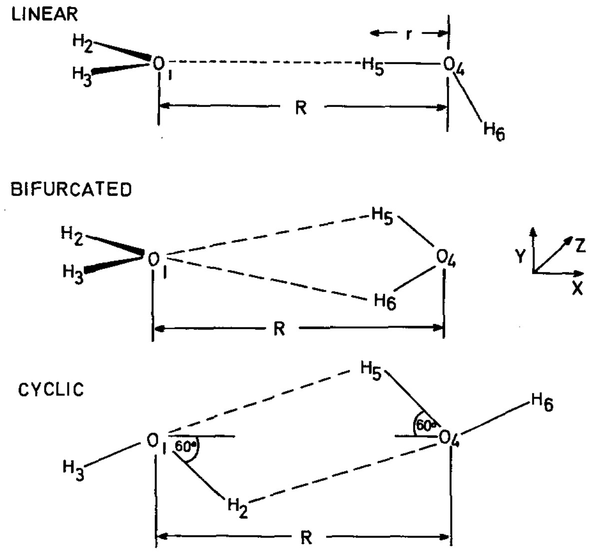

Fig. 1. Geometries of the linear, bifurcated and cyclic water dimers

order energy and the second order energy both can be split into two components. This has been done for the SCF-results in Fig. 2. The picture is dominated by the steric and the covalent contributions. The charge interactions are small (of the order of 1–2 kcal/mole) and do not show significant distance dependence. The second order electrostatic effects ((3), (6c) and (6d)) are negligible. They amount to 1–2% of the second order energy and are omitted from Fig. 2. The most stable structure is the linear. Even though the total energy for the other complexes is comparable the individual components differ appreciably.

Table 1. Perturbation energies for the linear (a), bifurcated (b) and cyclic (c) water dimers of Fig. 1 in kcal/mole. SCF = self consistent perturbation theory; VP = Variation perturbation theory; $E_{CNDO/2}$ = direct CNDO/2 calculation

	R(Å)	$\delta E^{(1)}$	$\delta E^{(2)}_{SCF}$	$\delta E^{(2)}_{VP}$	E^{total}_{SCF}	E^{total}_{VP}	$E_{CNDO/2}$
a	3.0	1.290	− 3.952	− 3.838	−2.662	−2.548	−2.811
	2.8	3.651	− 8.001	− 7.703	−4.350	−4.052	−4.468
	2.53	13.137	−19.306	−18.352	−6.168	−5.215	−6.255
	2.4	23.742	−28.425	−26.817	−4.683	−3.075	−4.844
b	3.0	0.034	− 1.041	− 1.045	−1.007	−1.011	
	2.8	0.497	− 2.059	− 2.064	−1.563	−1.568	
	2.44	3.703	− 6.303	− 6.315	−2.600	−2.612	
	2.4	4.470	− 7.063	− 7.077	−2.593	−2.608	
c	3.0	0.109	− 0.635	− 0.636	−0.525	−0.527	
	2.4	2.786	− 4.651	− 4.616	−1.866	−1.830	
	2.25	5.390	− 7.432	− 7.376	−2.042	−1.986	
	2.2	6.690	− 8.663	− 8.601	−1.973	−1.911	

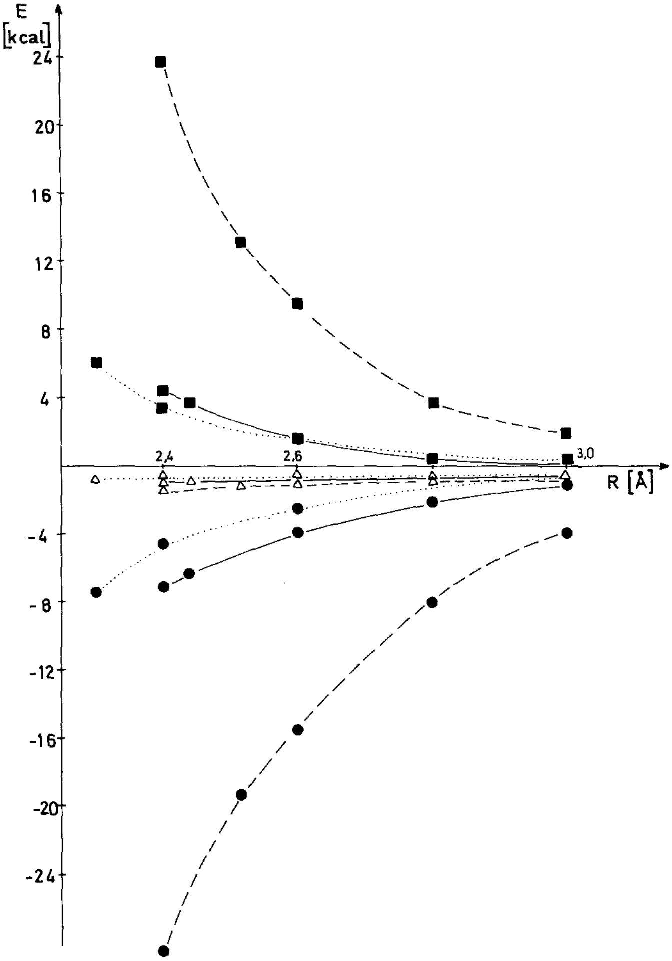

Fig. 2. Steric interactions (■), charge interactions (△) and covalent contributions (●) for the linear (- - - -), bifurcated (——) and cyclic (······) water dimers of Fig. 1

The SCF-perturbation theory allows a further splitting of the second order energy in contributions from the individual atomic orbitals of the subsystems [4]. This has been done for the $2s_1$ and $2p_{x1}$ atomic orbitals of the electron pair donor (for numbering see Fig. 1), the $1s_5$ atomic orbital of the bridged hydrogen atom and the $2p_{x4}$ atomic orbital of the second water molecule in Table 2. A comparison shows that these energy components amount to almost all of the second order energy. The variation perturbation theory elucidates that charge transfer interactions from the electron pair donor to unoccupied molecular orbitals of the hydrogen donor are responsible for more than 90% of the second order energy.

This detailed analysis justifies nicely the models of Bratoz [19] and of van Duijneveldt and Murrell [20]. Yet their approaches have limitations. Besides the restrictions mentioned earlier they are not capable to consider non linear struc-

Table 2. Second order contributions (kcal/mole) by atomic orbitals of the linear structure. For numbering and coordinate system see Fig. 1

R(Å)	$2s_1$	$2p_{x1}$	$1s_5$	$2p_{x4}$	Sum
3.0	−0.705	−1.204	− 2.139	0.126	− 3.922
2.8	−1.440	−2.426	− 4.407	0.309	− 7.964
2.53	−3.517	−5.779	−11.026	1.027	−19.295
2.4	−5.209	−8.429	−16.623	1.792	−28.469

tures. Therefore the influence of other atoms or groups in a molecule can not be assessed.

The cyclic and bifurcated structure are both less stable. The steric energies are more favourable because the intermolecular distances of the hydrogen and oxygen atom are greater. However, the covalent stabilization also decreases. The variation perturbation treatment traces this back to smaller charge transfer interactions from the oxygen lone pair to the unoccupied orbitals of the hydrogen donor.

Conclusions

The perturbational evaluation of water dimers not only provides comparable results to variation calculations but furthermore yields insight into the factors determining the most stable structure. The splitting of the total energy into four components reveals that coulombic forces (due to the polarity of the molecules) are not important in determining the most stable complexes. Rather the interplay of steric and covalent contributions gives rise to the observed minimum structure. The variation perturbation theory yields good results as long as the perturbation remains small. It has the advantage of shorter computation times and the possibility of interpretations similar to independent electron perturbation theory. The SCF-CNDO/2-perturbation program, the variation perturbation program will be available from QCPE. Further work on hydrogen bonding will be published in due time.

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