

PERTURBATION CALCULATIONS ON THE VARIATION OF HYDROGEN-BOND ENERGIES WITH INTERMOLECULAR DISTANCE

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In previous perturbation calculations on the hydrogen bond [6] the short-range repulsion was seriously underestimated. It is shown that this can be remedied by choosing a more realistic model system and using exact 3-centre integrals.

1. INTRODUCTION

The problem of calculating the stability of hydrogen bonds has recently been attacked at several levels of sophistication. Most authors have adopted the "supersystem approach" [1] in which the H-bond energy is obtained as the difference between the energy of the complex and the energy of its components at infinite separation. The most accurate calculations of this kind have been performed by Clementi [2] and Morokuma and Pederesen [3] who employed the SCF-LCAO-MO method. It seems likely that the energy of a H-bonding system can be estimated fairly accurately in this way, providing the basis set of AO's is sufficiently large [3]. However, this approach does not yield simple concepts which could be used to rationalize qualitative differences between different systems. There are indications that such concepts may be obtained more readily using the "separated systems approach" [1] where the H-bond energy is calculated directly, e.g. by means of an extended version of London's perturbation theory of intermolecular forces [4,5]. Such calculations have recently been performed for a linear model system A-H...B [6,7]. An unsatisfactory feature of these calculations was that they predict a collapse at short H...B distances. We now wish to show that this erroneous behaviour can be remedied by improving the calculation of the first order energy.

2. METHOD AND RESULTS

The first order interaction energy (E^1) of two closed-shell molecules R and T may be written as the sum of a Coulomb or electrostatic term (E_{Coul}) and an exchange term (E_{exch}). E_{Coul} accounts for the long-range multipole interaction and E_{exch} is responsible for the short-range repulsion.

If the MO's of R and T are labelled a_i and b_j , respectively and if the respective nuclei are labelled μ and ν then we may write, using the notation of ref. [8]:

$$E_{\text{Coul}} = 2 \sum_i (a_i^2 | V^T) + 2 \sum_j (b_j^2 | V^R) - 4 \sum_i \sum_j (a_i^2 | b_j^2) + \sum_{\mu} \sum_{\nu} Z_{\mu} Z_{\nu} r_{\mu\nu}^{-1} \quad (1)$$

$$E_{\text{exch}} = -2 \sum_i \sum_j \{ (\rho_{ij}^R | \rho_{ij}^T) + (\rho_{ij}^R | V^T) (a_i | b_j) + (V^R | \rho_{ij}^T) (a_i | b_j) \} \quad (2)$$

where the potentials V^R , V^T and the densities ρ are defined as follows:

$$V^R(1) = 2 \sum_i \int a_i^2(2) r_{12}^{-1} d\tau_2 - \sum_{\mu} Z_{\mu} r_{1\mu}^{-1} \quad (3)$$

$$V^T(1) = 2 \sum_j \int b_j^2(2) r_{12}^{-1} d\tau_2 - \sum_{\nu} Z_{\nu} r_{1\nu}^{-1} \quad (4)$$

$$\rho_{ij}^R = a_i b_j - \sum_i (a_i | b_j) a_i a_i \quad (5)$$

$$\rho_{ij}^T = a_i b_j - \sum_j (a_i | b_j) b_j b_j \quad (6)$$

3. CALCULATIONS ON A SIMPLE MODEL SYSTEM

In ref. [6] only the bonding orbital a_1 of the A-H bond (system R) and the lone pair orbital b_1 at atom B (system T) have been considered explicitly. E_{Coul} and E_{exch} were calculated from the simplified expressions

$$E_{\text{Coul}} = (b_1^2 | v^{\text{AH}}) + (2a_1^2 - \sigma_A^2 | v^{\text{B}}) - (2a_1^2 - \sigma_A^2 | b_1^2) + r_{\text{HB}}^{-1} \quad (7)$$

$$E_{\text{exch}} = -2\{(a_1 | b_1)(\rho_{11}^{\text{AH}} | v^{\text{B}}) + (a_1 | b_1)(\rho_{11}^{\text{B}} | v^{\text{AH}}) + (\rho_{11}^{\text{AH}} | \rho_{11}^{\text{B}})\} \quad (8)$$

with

$$v^{\text{AH}}(1) = -r_{\text{H1}}^{-1} + \int \{2a_1^2(2) - \sigma_A^2(2)\} r_{12}^{-1} d\tau_2$$

$$v^{\text{B}}(1) = -r_{\text{B1}}^{-1} + \int b_1^2(2) r_{12}^{-1} d\tau_2 \quad (9)$$

$$\rho_{11}^{\text{AH}} = a_1 a_1 - (a_1 | b_1) a_1^2$$

$$\rho_{11}^{\text{B}} = a_1 b_1 - (a_1 | b_1) b_1^2 \quad (10)$$

In evaluating these expressions the orbital a_1 was written in the form

$$a_1 = N(\sigma_A + kh) \quad (11)$$

where σ_A and h are $2p\sigma$ and $1s$ Slater AO's on the atoms A and H respectively*, N is a normalization constant and k is an ionicity parameter. The orbital b_1 was taken to be an sp^2 hybrid directed along the B-A axis. The 3-centre integrals which arise in the calculations were approximated by a sum of 2-centre integrals. All 2-centre integrals were evaluated exactly.

The total interaction energy (E_{total}) was obtained by adding a second order energy (E^2), consisting of an induction, a dispersion and a charge-transfer term to the E_{Coul} and E_{exch} of

(7) and (8). Some typical results for E^1 and E^2 have been summarized in table 1, column I. The total energies are shown in fig. 1. The most striking feature of these results is that the energy becomes very attractive at short distances, and there is no energy-minimum in the usual range of H-bonding distances ($r_{\text{HB}} = 3 - 4$ a.u. = $1.59 - 2.12$ Å). We have recently repeated these calculations without any approximations** in the integrals. This led to some changes in the individual terms of E^1 and E^2 , but the r_{HB} -dependence of E_{total} was still anomalous.

4. CALCULATIONS USING AN IMPROVED v^{B}

In ref. [6] it was attempted to improve this anomalous behaviour by including the potential due to the remaining electrons at atom B in the v^{B} of (9) to give

$$v^{\text{B}}(1) = -5/r_{\text{B1}} + \int \{b_1^2(2) + 4s_{\text{B}}^2(2)\} r_{12}^{-1} d\tau_2 \quad (12)$$

and the expression for E_{Coul} was modified accordingly:

$$E_{\text{Coul}} = (b_1^2 + 4s_{\text{B}}^2 | v^{\text{AH}}) + (2a_1^2 - \sigma_A^2 | v^{\text{B}}) - (2a_1^2 - \sigma_A^2 | b_1^2 + 4s_{\text{B}}^2) + 5/r_{\text{HB}} \quad (13)$$

(There is no formal change in the expressions for the remaining contributions to E^1 and E^2 .) This was found to make E_{Coul} more attractive while E_{exch} becomes more repulsive. However these changes largely cancel one another, hence the effect on E_{total} is slight. In particular there is no improvement in the r_{HB} -dependence of E_{total} [6].

These calculations have now been repeated using the accurate 3-centre integrals. The results are shown in fig. 2 and table 1, column II. Here E^2 includes a second-order exchange term, in addition to the terms mentioned above. This term is negligible for $r_{\text{HB}} > 4.0$ a.u. and comparable to the induction energy for $r_{\text{HB}} < 3.0$ a.u.

These results confirm that if we use (12) and (13) then E_{Coul} becomes more attractive and E_{exch} becomes more repulsive. However these changes no longer cancel and E^1 as well as E_{total} become repulsive at short distances.

* In all calculations presented here the orbital exponents have been chosen as follows: $\zeta_{2s} = \zeta_{2p} = 2.0$ and $\zeta_{\text{H}} = 1.0$.

** We are indebted to Dr. G. Shaw for making the accurate 3-centre integrals available to us.

Table 1
Contributions to the H-bond energies for various model systems

k	r_{HB}	I. Simple model system *			II. As I. with modified V^B			III. Extended model system		
		$E_{Coul}^{a)}$	$E_{exch}^{b)}$	E^2	$E_{Coul}^{c)}$	$E_{exch}^{b)}$	E^2	$E_{Coul}^{d)}$	$E_{exch}^{e)}$	E^2
1.0	2.0	-0.09897	+0.09659	-0.07588	-0.15807	+0.23132	-0.02730	-0.19448	-0.31070	-0.02730
	2.5	-0.03628	-0.05336	-0.03941	-0.06971	-0.11568	-0.02813	-0.09210	+0.15064	-0.02813
	3.0	-0.00956	+0.02416	-0.01691	-0.02661	-0.05038	-0.01594	-0.04169	+0.06493	-0.01594
	3.5	+0.00011	+0.00990	-0.00739	-0.00881	+0.02032	-0.00760	-0.01958	+0.02608	-0.00760
	4.0	+0.00295	+0.00388	-0.00362	-0.00206	+0.00786	-0.00372	-0.01021	-0.01011	-0.00372
0.8	2.0	-0.10508	+0.07918	-0.08586	-0.14652	-0.19726	-0.03072	-0.18052	-0.26587	-0.03072
	2.5	-0.04367	+0.04357	-0.04296	-0.06965	-0.09701	-0.03127	-0.09025	-0.12626	-0.03127
	3.0	-0.01614	+0.01959	-0.01834	-0.03013	-0.04180	-0.01747	-0.04388	-0.05369	-0.01747
	3.5	-0.00516	+0.00795	-0.00774	-0.01284	+0.01672	-0.00821	-0.02262	+0.02134	-0.00821
	4.0	-0.00112	+0.00308	-0.00370	-0.00563	-0.00643	-0.00395	-0.01301	-0.00821	-0.00395
0.6	2.0	-0.11284	+0.05843	-0.09658	-0.13437	+0.15567	-0.03753	-0.16523	-0.21319	-0.03753
	2.5	-0.05304	+0.03216	-0.04874	-0.07053	+0.07487	-0.03574	-0.08880	-0.09814	-0.03574
	3.0	-0.02448	+0.01436	-0.01967	-0.03489	+0.03174	-0.01939	-0.04690	-0.04082	-0.01939
	3.5	-0.01185	-0.00576	-0.00793	-0.01798	+0.01254	-0.00892	-0.02646	-0.01594	-0.00892
	4.0	-0.00630	+0.00219	-0.00368	-0.01010	-0.00476	-0.00416	-0.01649	-0.00605	-0.00416

* Results in part from ref. [6].

a) E_{Coul} from eq. (7).

b) E_{exch} from eq. (8).

c) E_{Coul} from eq. (13).

d) E_{Coul} from eq. (1).

e) E_{exch} from eq. (2).

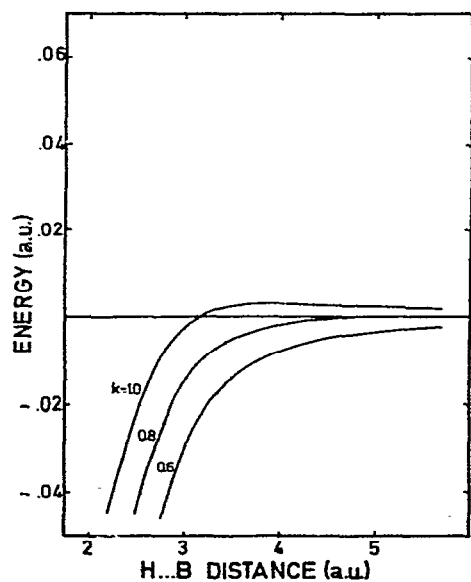


Fig. 1. The H-bond energy for the simple model system [6].

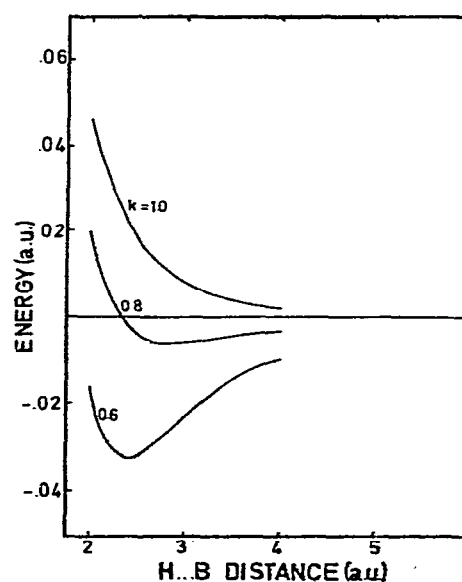


Fig. 2. Same as fig. 1. with improved V^B and exact 3-centre integrals.

5. CALCULATIONS ON AN EXTENDED MODEL SYSTEM

The above results suggest that E_{total} is rather sensitive to the form of the potentials V^B and V^A . That is, in order to obtain a reliable interaction energy one should employ a more detailed description of the electron distribution of the A-H and B groups. In particular, the presence of additional lone pairs on A or B should be taken into account explicitly. This may be achieved in the following way.

In the case that A-H represents the HF molecule we assume that in addition to the two electrons which occupy the A-H orbital (cf. ref. [11]) there are six electrons in 3 equivalent s-p hybrids a_2 , a_3 and a_4 whose hybridization is determined by the condition that the orbitals $a_1 - a_4$ be orthonormal. Likewise, if NH_3 is the proton-accepting molecule then in addition to the lone pair orbital b_1 (which we take to be sp^2 hybridized, as before) there will be three equivalent N-H orbitals. If we neglect the presence of the H atoms these orbitals may be replaced by three equivalent s-p hybrids b_2 , b_3 and b_4 which are orthogonal to b_1 and which are taken to be singly occupied. (In this approximation V^B reduces to eq. (12).)

We have calculated the first order energy corresponding to this extended model system using

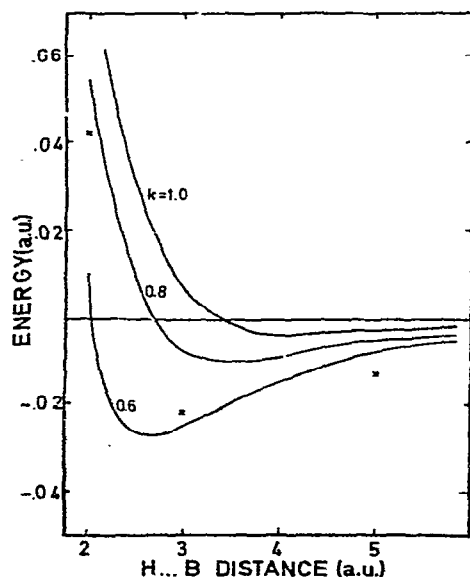


Fig. 3. The H-bond energy for the extended model system. The crosses refer to energies for $\text{NH}_3 \dots \text{HCl}$ as calculated by Clementi [2].

the E_{Coul} and E_{exch} of (1) and (2) and without any approximations in the 2 and 3-centre integrals. E^2 was taken to be the same as in table 1, column II. The results are shown in fig. 3 and table 1, column III. Again, E^1 as well as E_{total} become repulsive at short distances. For $r_{\text{HB}} < 2.5$ E_{total} is more repulsive than in fig. 2 and for $r_{\text{HB}} > 3.0$ it is more attractive. As a result the position of the energy-minimum has shifted to longer HB-distances. In addition there is a stronger tendency for weak bonds to have a long equilibrium distance. Since these results appear to be in agreement with experiment it may be possible to use this model for predicting equilibrium distances and energies of such H bonds as $\text{CH}_4 \dots \text{NH}_3$, $\text{HF} \dots \text{NH}_3$, $\text{H}_2\text{O} \dots \text{H}_2\text{O}$, etc. This would necessitate a change in the population numbers in the hybrid AO's not involved in the H bond and we would have to devise some method for choosing the parameters for the model. In this context it is of interest that in fig. 3 (which is supposed to be valid for $\text{HF} \dots \text{NH}_3$) the curve $k = 0.6$ agrees fairly closely with the curve computed by Clementi [2] for the $\text{NH}_3 \dots \text{HCl}$ interaction*.

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* In making this comparison we have used Clementi's results for $r_{\text{HCl}} = 2.408673$ a.u., and we have assumed that his $E_{\text{NH}_3} - E_{\text{HCl}}$ at infinite separation equals -515.7995 a.u.