

Perturbation Calculations of the Interaction Energies between Non-Bonded Hydrogen Atoms

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This paper presents calculations of the interaction energies between non-bonded hydrogen atoms in the planar model systems A—H...H—B for R_{HH} distances from 1.0 to 15.0 a.u. using a perturbation formalism including exchange. Trends in the interaction energy have been examined as a function of the parameters of the model. The analysis in terms of electrostatic concepts was attempted and the extension of such concepts to small H...H separations appears questionable. Finally, a convenient functional representation of the interaction energy was obtained for both linear and non-linear cases.

The calculation of intermolecular forces using perturbation theories which include exchange has received considerable attention recently.* Van Duyneveldt and Murrell² applied such a perturbation formalism to calculations of the energy of the hydrogen "bond" in A—H...B. Although this interaction is important, the H...H interactions also play a significant role in many biologically important molecules. Consequently the model of Van Duyneveldt and Murrell was extended to cover the planar model system A—H...H—B. Since the calculations of J. G. C. M. Van Duyneveldt and F. B. Van Duyneveldt³ indicated a marked sensitivity to the accuracy of their basic integrals, approximations were avoided by the use of Huzinaga's method^{4, 5} for representing Slater orbitals by a gaussian expansion and subsequent evaluation of the pertinent gaussian integrals.†

The actual values of the interaction are certainly of interest. Further since this model contains the essential variables of the H...H interaction, a thorough investigation yields quantitative concepts which could be generalized to more complex systems.

Consequently, an analysis of the dependence of the interaction energy on the parameters of the model was undertaken. In an attempt to clarify this dependence the use of simple electrostatic arguments and the "overlap concept" were investigated. In addition, various functional representations for the interaction energies were investigated and it appeared that for linear cases $(A_1/R + A_2R) \exp(-BR)$ and for non-linear cases $C_0 + C_1 \cos \theta + C_2 \cos^2 \theta$ gave the best results. Finally, as an application of the model, sets of parameters were selected to represent the molecular fragments CH and NH and the calculated interaction energies for these fragments were compared to semi-empirical data.

MODEL

The description used for the bonds A—H and B—H in the model A—H...H—B was essentially the same as the one used by Van Duyneveldt and Murrell² for the A—H bond in their calculations. Therefore we repeat only the essentials. The

* for an extensive review of the literature see ref. (1).

† The necessary programme was supplied by Prof. S. Huzinaga.

AH and BH bond lengths were taken to be 2 a.u. and since only situations in which all four centres are in one plane were considered, the geometry of the system can be characterized by three parameters (see fig. 1).

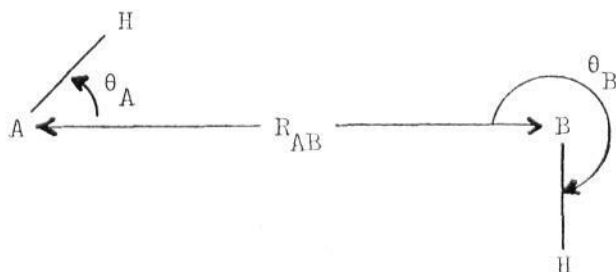


FIG. 1.—Geometry of the planar system A—H...H—B in terms of the distance R_{AB} and the angles θ_A and θ_B .

The bonding molecular orbital (MO) for AH, a , will be denoted as

$$a = N(\sigma_A + kh_A)$$

and the corresponding antibonding MO, a' , as

$$a' = N'(h_A - k'\sigma_A).$$

In these expressions h_A and σ_A represent, respectively, a Slater $1s$ orbital on H with exponent ζ_H and a Slater $2p_\sigma$ orbital on A with exponent ζ_A , and k is the polarity parameter. Similar to a and a' , the bonding and antibonding MO on BH, b and b' , respectively are linear combinations of h_B and σ_B where the polarity parameter is denoted by l .

The explicit expressions for the various contributions to the interaction energy were obtained from the prescriptions given by Williams, Schaad and Murrell⁶ for the first-order energies, and by Van Duyneveldt⁷ for the second-order energies. Since the actual expressions for the coulomb energy E_{coul} , the first-order exchange energy $E_{\text{exch}}^{(1)}$, the induction energy E_{ind} and the dispersion energy E_{disp} are used in the discussion we present them here. Although the second-order exchange energy $E_{\text{exch}}^{(2)}$ was evaluated, the expression for this contribution does not enter the discussion and is therefore omitted:

$$E_{\text{coul}} = 2(a^2 | V^{\text{BH}}) + 2(b^2 | V^{\text{AH}}) - 4(a^2 | b^2) + 1/R_{\text{HH}} + (\sigma_A^2 | \sigma_B^2) + (\sigma_A^2 | H_B^{-1}) + (\sigma_B^2 | H_A^{-1}), \quad (1)$$

where

$$V^{\text{AH}}(1) = -\frac{1}{r_{\text{HA}1}} + \int \{2a^2(2) - \sigma_A^2(2)\} r_{12}^{-1} d\tau_2$$

is the potential field of the AH bond. The potential field V^{BH} of the BH bond is given by an analogous expression. The integrals involved are denoted by

$$\begin{aligned} (a^2 | V^{\text{BH}}) &= \int a^2(1) V^{\text{BH}}(1) d\tau_1 \\ (a^2 | b^2) &= \int a^2(1) r_{12}^{-1} b^2(2) d\tau_1 d\tau_2 \\ (\sigma_A^2 | H_B^{-1}) &= \int \sigma_A^2(1) r_{\text{HA}1}^{-1} d\tau_1 \end{aligned}$$

Further,

$$E_{exch}^{(1)} = -2\{(S_{ab}V^{BH} | \rho_{ab}^{AH}) + (S_{ab}V^{AH} | \rho_{ab}^{BH}) + (\rho_{ab}^{BH} | \rho_{ab}^{AH})\}, \quad (2)$$

where $S_{ab} = \int ab \, d\tau$ is the intermolecular overlap and $\rho_{ab}^{AH} = ab - S_{ab}a^2$ and $\rho_{ab}^{BH} = ab - S_{ab}b^2$. Finally,

$$E_{ind} = \frac{-2(aa' | V^{BH})^2}{\Delta E_{a \rightarrow a'}} + \frac{-2(bb' | V^{AH})^2}{\Delta E_{b \rightarrow b'}}, \quad (3)$$

and

$$E_{disp} = \frac{-4(aa' | bb')^2}{\{\Delta E_{a \rightarrow a'} + \Delta E_{b \rightarrow b'}\}}. \quad (4)$$

In eqn (3) and (4), $\Delta E_{a \rightarrow a'}$ and $\Delta E_{b \rightarrow b'}$ are the energy differences between the first excited singlet state and the ground state of the fragments AH and BH respectively for which, following Van Duyneveldt and Murrell,² the value 0.25 a.u. was used in all our calculations.

In order to facilitate discussions pertaining to electrostatic concepts and the meaning of parameters such as k , ζ_A and ζ_H , we present in table 1 some bond properties, such as the position of the centre of the charge distribution a^2 (d_A), the dipole moment and the polarizability as functions of the above-mentioned parameters. Choosing the z-axis along the bond axis one obtains $d_A = \int aza \, d\tau$. Because of the symmetry of the system the dipole moment as well as the polarizability have only one non-zero component, i.e., the component along the bond axis which is denoted by μ (dipole moment) and α (polarizability). The two-centre integral required in the calculation of d_A , μ and α , $\int \sigma_A z h_A \, d\tau$ was evaluated using formulas given by Sahni.⁸ The value of d_A in table 1 refers to H as origin, whereas α was calculated using A as origin. Atomic units have been used in table 1 as they are throughout the paper.

TABLE 1.—SELECTED BOND PROPERTIES (IN ATOMIC UNITS) AS A FUNCTION OF THE ORBITAL PARAMETERS k , ζ_A , AND ζ_H

ζ_A	ζ_H	k	d_A	μ^*	α
1.5	1.0	0.5	1.12458	-0.25	28.65
1.5	1.2	0.5	1.15309	-0.31	28.52
2.0	1.0	0.5	1.26458	-0.53	20.72
2.0	1.2	0.5	1.27879	-0.56	20.81
2.5	1.0	0.5	1.36718	-0.73	16.50
2.5	1.2	0.5	1.37590	-0.75	16.52
2.0	1.0	1.0	0.76977	+0.46	18.73
2.0	1.2	1.0	0.79582	+0.41	19.21

* A negative dipole moment indicates a polarity in the sense A^-H^+

RESULTS AND DISCUSSION

Calculations using the model described in the previous section were performed over the following ranges of parameters:

- (i) $\zeta_A, \zeta_B = 1.5-2.5$;
- (ii) $\zeta_H = 1.0-1.2$ (in all calculations $\zeta_{HA} = \zeta_{HB} = \zeta_H$);
- (iii) $k, l = 0.5-1.0$;

(iv) $R_{\text{HH}} = 1.0\text{--}15.0$ a.u.

(v) $\theta_{\text{A}} = \theta_{\text{B}} = 0\text{--}45^\circ$,

and $\theta_{\text{A}} = (360^\circ - \theta_{\text{B}}) = 0\text{--}45^\circ$.

An exhaustive investigation of these cases was not undertaken; however, a number of representative cases were selected and investigated in depth for the purpose of developing concepts which could be applied more generally.

LINEAR SYSTEMS

The results given in table 2 will be discussed first.

TABLE 2.—CONTRIBUTIONS TO THE INTERACTION ENERGY (IN ATOMIC UNITS) BETWEEN TWO NON-BONDED HYDROGEN ATOMS IN THE LINEAR MODEL SYSTEM A—H...H—B

parameter values $k = l = 0.5, \zeta_{\text{A}} = \zeta_{\text{B}} = 1.5, \zeta_{\text{H}} = 1.0$ (case I)					
$R_{\text{HH}}(\text{a.u.})$	E_{coul}	E_{ind}	E_{disp}	E_{exch}	E_{total}
1.0	0.195 64	-0.127 89	-0.011 85	0.140 57	0.196 46
2.0	0.016 30	-0.016 28	-0.007 80	0.041 80	0.034 02
4.0	0.001 80	-0.000 47	-0.001 33	0.001 78	0.001 77
6.0	0.000 62	-0.000 05	-0.000 26	0.000 06	0.000 36
10.0	0.000 13	—	-0.000 02	—	0.000 11
15.0	0.000 04	—	—	—	0.000 04
parameter values $k = l = 0.5, \zeta_{\text{A}} = \zeta_{\text{B}} = 2.0, \zeta_{\text{H}} = 1.0$ (case II)					
1.0	0.232 77	-0.119 38	-0.007 35	0.099 78	0.205 82
2.0	0.003 47	-0.018 90	-0.004 94	0.024 39	0.034 02
4.0	0.005 12	-0.000 90	-0.000 81	0.001 01	0.004 41
6.0	0.001 79	-0.000 12	-0.000 16	0.000 03	0.001 54
10.0	0.000 44	-0.000 01	-0.000 01	—	0.000 42
15.0	0.000 14	—	—	—	0.000 14
parameter values $k = l = 0.5, \zeta_{\text{A}} = \zeta_{\text{B}} = 2.5, \zeta_{\text{H}} = 1.0$ (case III)					
1.0	0.266 47	-0.117 09	-0.005 06	0.079 64	0.223 96
2.0	0.046 11	-0.020 85	-0.003 48	0.019 45	0.041 22
4.0	0.007 99	-0.001 17	-0.000 57	0.000 87	0.007 12
6.0	0.002 93	-0.000 17	-0.000 11	0.000 03	0.002 68
10.0	0.000 76	-0.000 01	-0.000 01	—	0.000 74
15.0	0.000 25	—	—	—	0.000 25
parameter values $k = l = 1.0, \zeta_{\text{A}} = \zeta_{\text{B}} = 2.0, \zeta_{\text{H}} = 1.0$ (case IV)					
1.0	0.096 75	-0.073 73	-0.004 11	0.189 87	0.208 77
2.0	-0.010 69	-0.003 81	-0.004 50	0.058 99	0.039 99
4.0	-0.000 38	-0.000 03	-0.000 85	0.002 97	0.001 71
6.0	0.000 31	-0.000 02	-0.000 16	0.000 11	0.000 24
10.0	0.000 14	—	-0.000 02	—	0.000 12
15.0	0.000 06	—	—	—	0.000 06

COULOMB ENERGY

At long distances the coulomb energy reduces to the multipole-multipole interaction between the two systems. However, when the charge densities of the two systems overlap, this simple picture is no longer valid and following Van Duyneveldt

and Murrell² we divide E_{coul} into a multipole energy E_{mult} and a "penetration energy" E_{pen} . The multipole energy

$$E_{\text{mult}} = \frac{1}{R_{\text{HH}}} + \frac{1}{R_{\text{AB}}} + \frac{2}{R_{\text{HH}}+2} + \frac{4}{R_{\text{HH}}+d_{\text{A}}+d_{\text{B}}} - \frac{2}{R_{\text{HH}}+d_{\text{A}}} - \frac{2}{R_{\text{HH}}+d_{\text{B}}} - \frac{2}{R_{\text{HH}}+2+d_{\text{A}}} - \frac{2}{R_{\text{HH}}+2+d_{\text{B}}},$$

where d_{B} , analogous to d_{A} , is the centre of the charge distribution b^2 , calculated using H_{B} as origin. This expression for E_{mult} results from replacing all contributions to E_{coul} (see eqn (1)) by their monopole-monopole analogues. The penetration energy is simply defined as the difference between E_{coul} and E_{mult} .

For the range $R_{\text{HH}} \leq 2.0$ a.u., it appears that, although there may be components of E_{coul} which are not well represented by a monopole-monopole term, they largely cancel with the result that E_{mult} provides not less than 85% of E_{coul} . Consequently, the increase in E_{coul} can be attributed to the increase in the terms d_{A} and d_{B} occurring in E_{coul} , which explains the dependence of E_{coul} on k and ζ in this range.*

For $2.0 \leq R_{\text{HH}} \leq 6.0$ a.u., E_{mult} is still an adequate guide if k is small. However, if k is large the expected inadequacy is significant (up to 70%); for example, E_{coul} , which one expects to be repulsive on the basis of a simple multipole representation, actually is slightly attractive for $k = 1.0$ and $R_{\text{HH}} = 2.0$ - 4.0 a.u. which can be explained on basis of the relatively large proton attraction terms.

INDUCTION ENERGY

Since the terms

$$-\frac{(aa' | V^{\text{BH}})^2}{\Delta E_{a \rightarrow a'}} \quad \text{and} \quad -\frac{(bb' | V^{\text{BH}})^2}{\Delta E_{b \rightarrow b'}}$$

appearing in E_{ind} are essentially quantum-mechanical analogues of dipole induced-dipole interactions the corresponding electrostatic representation

$$E_{\text{ind}}^{\text{electr}} = -\frac{2}{R^6} \{ \alpha_{\text{AH}} \mu_{\text{BH}}^2 + \alpha_{\text{BH}} \mu_{\text{AH}}^2 \}$$

was attempted with $R = \frac{1}{2}(R_{\text{AB}} + R_{\text{HH}})$. For distances $R_{\text{HH}} \geq 6.0$ a.u., $E_{\text{ind}}^{\text{electr}}$ reproduced the essential features of our quantum-mechanical calculation. Unfortunately, for distances $R_{\text{HH}} < 6.0$ a.u., this simple representation departs from the $1/R^6$ dependence and is unable to account for the dependence of E_{ind} on ζ and k . For these distances one should examine the quantum-mechanical expression. For small k , the value obtained from $E_{\text{ind}}^{\text{electr}}$ becomes less attractive as ζ decreases, whereas our calculations show the opposite behaviour for E_{ind} . This, and the fact that $E_{\text{ind}}^{\text{electr}}$ is less attractive than E_{ind} for small k , can be understood from the ζ dependence of the relatively important proton attraction terms in $(aa' | V^{\text{BH}})$ and $(bb' | V^{\text{AH}})$.

On varying k from 0.5 to 1.0, the dipole moment of AH changes sign and consequently $E_{\text{ind}}^{\text{electr}}$ goes through a minimum. However, for $R_{\text{HH}} \leq 2.0$ a.u. and the same variation in k , E_{ind} decreases monotonically since the term $(aa' | V^{\text{BH}})$ does not change sign. (It appears that for this range of R_{HH} the proton attraction term $(aa' | H_{\text{B}}^{-1})$ is important enough to outweigh the increase in the electron repulsion term $(aa' | b^2)$ as k increases so that $(aa' | V^{\text{BH}})$ remains attractive.) Thus, even though the dipole moment may be zero, the value of E_{ind} need not be zero. As R_{HH} is increased

* Where $\zeta_{\text{A}} = \zeta_{\text{B}}$ we denote them by ζ .

beyond 2.0 a.u. a separation is reached that permits a changing k to bring about a change in sign of $(aa' | V^{BH})$; the specific value of k for which this sign change occurs depends on R_{HH} and decreases as R_{HH} increases.

DISPERSION ENERGY

London⁹ has given the following form for the dispersion energy between two cylindrically symmetric systems:

$$E_{disp} = -R^{-6} \alpha_{AH} \alpha_{BH} \overline{\Delta E_{AH}} \overline{\Delta E_{BH}} / (\overline{\Delta E_{AH}} + \overline{\Delta E_{BH}})$$

Using this equation, setting R equal to $\frac{1}{2}(R_{AB} + R_{HH})$ and $\overline{\Delta E_{AH}}$ and $\overline{\Delta E_{BH}}$ equal to $\Delta E_{a \rightarrow a'}$ and $\Delta E_{b \rightarrow b'}$ respectively, the essential features of our calculations of E_{disp} were reproduced.* Thus the dependence of E_{disp} on k and ζ follow from the dependence of α_{AH} on k and ζ (see table 1).

EXCHANGE ENERGY

In order to check the validity of arguments that $E_{exch}^{(2)}$ would be small compared to $E_{exch}^{(1)}$ (see, e.g., ref. (10)) this quantity was evaluated explicitly and was 10-100 times as small as $E_{exch}^{(1)}$. Since both the first- and second-order exchange energy are due to the inclusion of exchange terms in the perturbation expansion these two contributions were taken together in the discussion and their sum will be denoted by E_{exch} . The calculations show that the repulsive character of E_{exch} increases strongly for decreasing ζ and $1/k$ and that it is important only at short distances. These trends suggest that E_{exch} is a sensitive function of the intermolecular overlap and distance. It has been argued (see, e.g., ref. (11)) that E_{exch} could be represented by $\beta S_{ab}^2/R_{HH}$. However, from our calculations it follows that β is not a constant but increases for increasing intermolecular distance (see table 3). Detailed analysis of the various terms in $E_{exch}^{(1)}$ shows that $E_{exch}^{(1)}$ (and therefore in fact also E_{exch}) varies like S_{ab}^n/R_{HH} , where n lies between 1 and 2 and decreases with increasing R_{HH} ; this explains why β increases with increasing R .

TABLE 3.—VALUES OF β (IN ATOMIC UNITS) IN THE REPRESENTATION OF E_{exch} BY $\beta S_{ab}^2/R_{HH}$

R_{HH} (a.u.)	S_{ab} (case II)	S_{ab} (case IV)	β (case II)	β (case IV)
1.0	0.293 70	0.489 45	1.2	0.8
2.0	0.165 04	0.297 44	1.8	1.3
4.0	0.042 01	0.083 66	2.3	1.7
6.0	0.009 20	0.019 38	2.5	1.8

In order to facilitate comparison between our results and those of others we fitted our results for E_{exch} for $1.0 \leq R_{HH} \leq 6.0$ a.u. to a curve of the type $A \exp(-BR)$. Using a least-squares technique † a reasonable fit was obtained and the values obtained for A and B (see table 4) may be compared to those reported by Craig *et al.*¹²

TOTAL ENERGY

For small k values the total energy increases for increasing ζ . This behaviour is caused by E_{coul} , which increases with increasing ζ values and which is for all distances, the dominant term for systems with small k values. For large k , at small

* The only exception occurred for $R_{HH} = 1.0$ a.u. and large k , where E_{disp} is smaller than predicted from electrostatic formulas. The reason is that in this situation, the repulsive character of $(aa' | bb')$ is strongly reduced by the attractive terms $-(\sigma_A^2 | h_B^2)$ and $-(h_A^2 | \sigma_B^2)$.

† In the least-squares procedure the values of the pertinent energies at $R_{HH} = 1.0, 2.0, 3.0, 4.0, 5.0$ and 6.0 a.u. were used. The total square deviation was in all cases less than 10^{-3} a.u.

distances E_{exch} is the dominant repulsive term. Since E_{exch} decreases rapidly with increasing distance and also because for large k E_{coul} is small (or even attractive) for intermediate distances, the total energy diminishes very rapidly for these distances. In all cases for distances $R_{\text{HH}} > 6.0$ a.u. E_{coul} is the most important term and thus at these distances the total interaction energy can be represented roughly by the dipole-dipole interaction energy.

TABLE 4.—VALUES OF A AND B (IN ATOMIC UNITS) IN THE REPRESENTATION OF E_{exch} BY $A \exp(-BR)$

case	A	B
I	0.86	1.57
II	0.59	1.62
III	0.44	1.58
IV	1.08	1.50

The results for E_{tot} in the range $1.0 \leq R_{\text{HH}} \leq 6.0$ a.u. were fitted * to a number of curves and it appeared that the curve $(A_1/R + A_2R) \exp(-BR)$ gave the most satisfactory results (see table 5). The differences between the coefficients for the various cases can be readily understood from the discussion given above.

TABLE 5.—VALUES OF A_1 , A_2 AND B (IN ATOMIC UNITS) IN THE REPRESENTATION OF E_{total} BY $(A_1/R + A_2R) \exp(-BR)$

case	A_1	A_2	B
I	0.56	0.0097	1.08
II	0.41	0.0044	0.78
III	0.41	0.0064	0.69
IV	0.54	-0.0102	0.93

CALCULATIONS WITH $\zeta_{\text{H}} = 1.2$

Since in molecular orbital calculations for molecules which contain hydrogen the optimum orbital coefficient for the hydrogen $1s$ orbital appears to be about 1.2, it was considered worthwhile to investigate the changes in the various contributions to the interaction energy under a change of ζ_{H} from 1.0 to 1.2 † (see fig. 2(i)-(iv) for the pertinent results). Before discussing the various contributions we note that the centre of the charge distribution a^2 shifts towards centre A and that the polarizability increases if one increases ζ_{H} from 1.0 to 1.2 (see table 1).

$$k = l = 0.5, \zeta_{\text{A}} = \zeta_{\text{B}} = 1.5, \zeta_{\text{H}} = 1.2 \quad (\text{case I}');$$

$$k = l = 0.5, \zeta_{\text{A}} = \zeta_{\text{B}} = 2.5, \zeta_{\text{H}} = 1.2 \quad (\text{case III}');$$

$$k = l = 1.0, \zeta_{\text{A}} = \zeta_{\text{B}} = 2.0, \zeta_{\text{H}} = 1.2 \quad (\text{case IV}').$$

(i) E_{coul} ; (ii) E_{London} ; (iii) E_{exch} ; (iv) E_{tot} .

These two features explain the differences in E_{coul} and E_{London} ‡ between $\zeta_{\text{H}} = 1.0$ and $\zeta_{\text{H}} = 1.2$ for $R_{\text{HH}} \geq 6.0$ a.u. where these contributions can be obtained from their electrostatic representations. For short and intermediate distances ($R_{\text{HH}} < 6.0$ a.u.) differences of the above-mentioned contributions for $\zeta_{\text{H}} = 1.0$ and $\zeta_{\text{H}} = 1.2$ can be understood from the behaviour of the proton attraction and electron repulsion terms in the pertinent matrix elements. For E_{London} , the increase in proton

* see footnote on p. 1835.

† For an examination of the change in dispersion energy under this orbital contraction see ref. (13).

‡ $E_{\text{London}} \equiv E_{\text{ind}} + E_{\text{disp}}$.

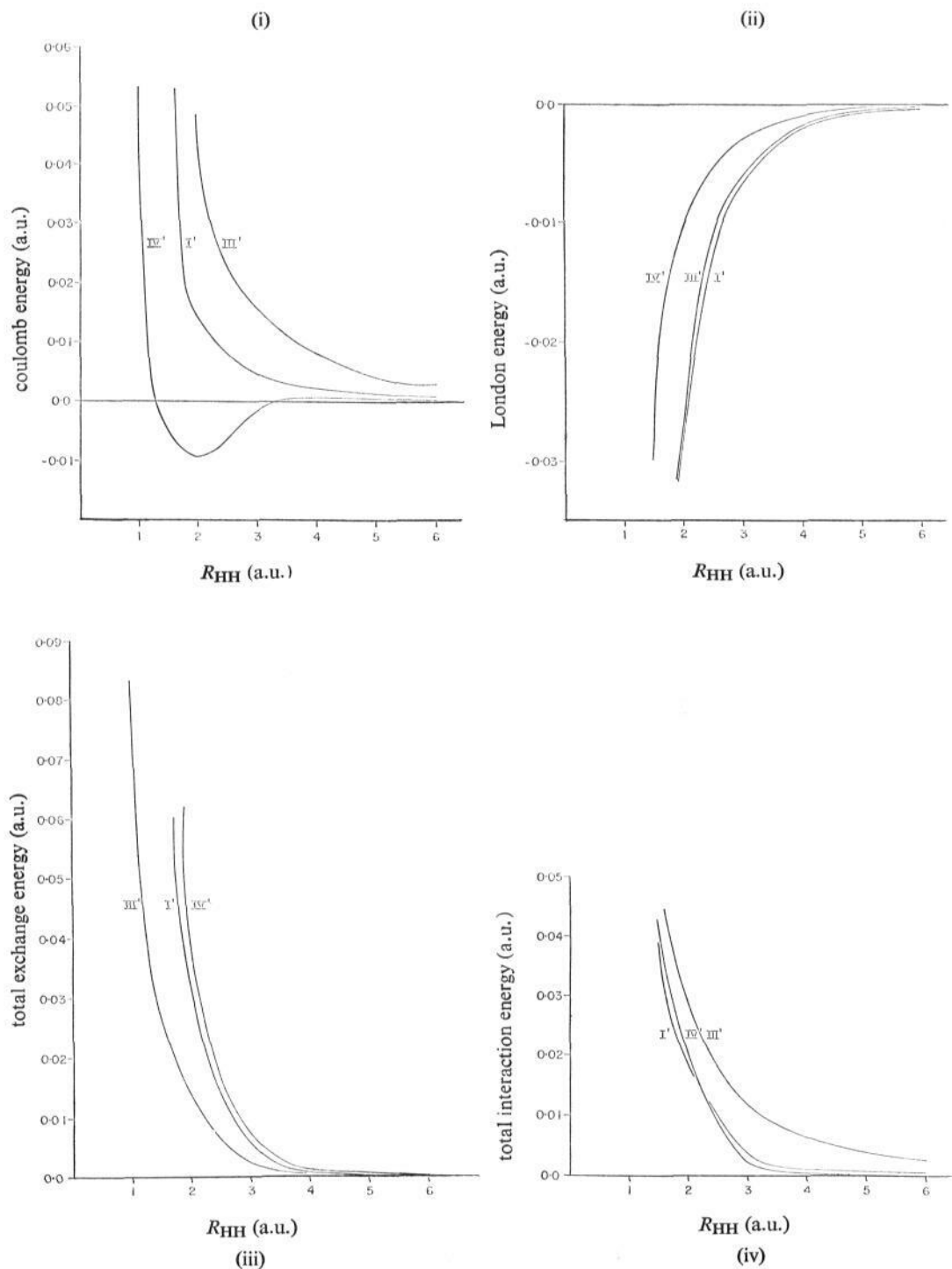


FIG. 2.—Contributions to the interaction energy between two non-bonded hydrogen atoms in the linear model system $A-H\dots H-B$ for the parameter values:

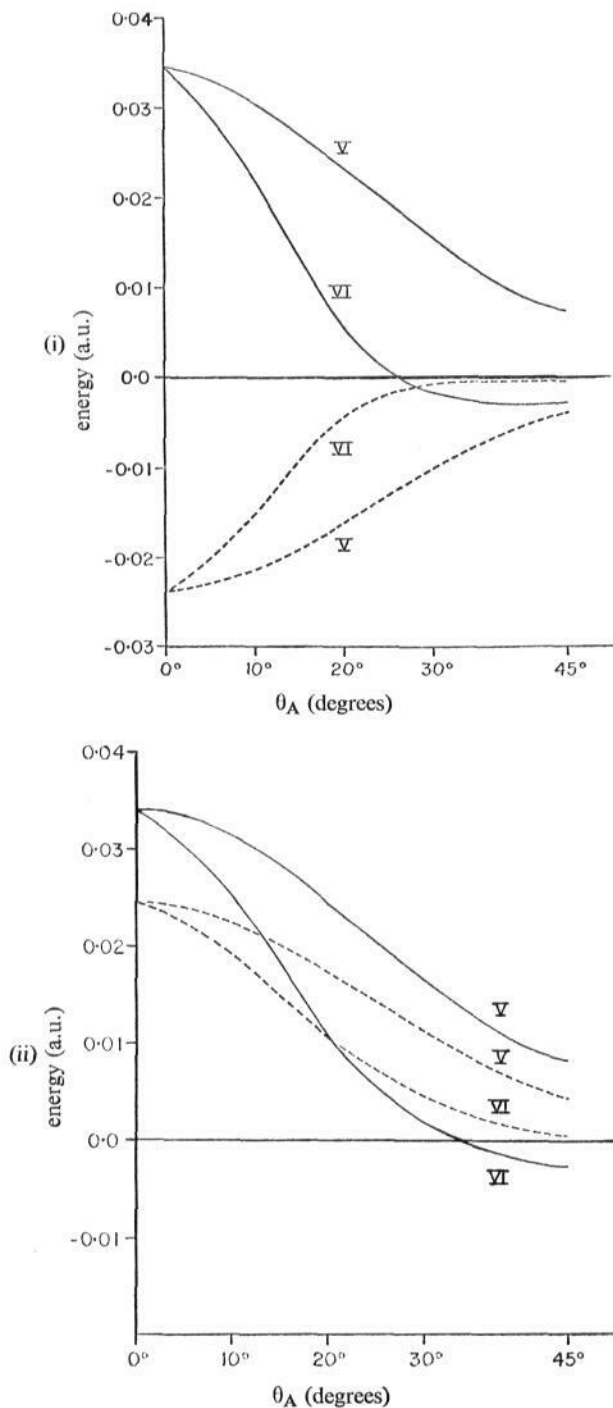


FIG. 3.—Contributions to the interaction energy between two non-bonded hydrogen atoms in the model system $A-H \cdots H-B$ for the parameter values $k = l = 0.5$, $\zeta_A = \zeta_B = 2.0$, $\zeta_H = 1.0$, $R_{AB} = 6.0$ a.u., $\theta_B = \theta_A$ (case V) and $\theta_B = (360^\circ - \theta_A)$ (case VI). (i) The solid curves give E_{coul} and the dashed curves give E_{London} . (ii) The solid curves give E_{tot} and the dashed curves give E_{exch} .

attraction terms dominates the increase in electron repulsion terms for all $R_{\text{HH}} < 6.0$ a.u. Although this explanation also holds for the change in E_{coul} in the range $R_{\text{HH}} \leq 2.0$ a.u. the trend for $2.0 \leq R_{\text{HH}} < 6.0$ a.u. is due to the fact that the proton attraction terms decrease less than do the electron repulsion terms. The result is that for $R_{\text{HH}} < 6.0$ a.u., E_{coul} is less repulsive and E_{ind} is more attractive for $\zeta_{\text{H}} = 1.2$ than for $\zeta_{\text{H}} = 1.0$.

The intermolecular overlap decreases upon increase of ζ_{H} from 1.0 to 1.2 which makes it plausible that E_{exch} decreases. From the discussion on E_{coul} , E_{London} and E_{exch} , for $R_{\text{HH}} < 6.0$ a.u., E_{tot} always decreases quite substantially upon changing ζ_{H} from 1.0 to 1.2. For $R_{\text{HH}} \geq 6.0$ a.u. where E_{coul} is the dominant term, E_{tot} increases for small k and decreases for large k .

NON-LINEAR SYSTEMS

In linear systems the two protons are the main interacting centres and although important, the potentials on A and B are less essential than for non-linear situations where the A...H_B and B...H_A interactions become relatively more important. Due to the fact that the potentials on A and B are simple, it appears that only calculations up to $\theta_{\text{A}}, \theta_{\text{B}} = \pm 45^\circ$ would be appropriate.

In the previous paragraphs we investigated the correctness of electrostatic formulas to calculate interaction energies in linear systems for short intermolecular distances. This investigation is now extended to an examination of the correctness of the angular dependence of the interaction energies predicted by electrostatic theory. The angular dependence of the electrostatic dipole-dipole interaction is given by (see, e.g., ref. (14))

$$f(\theta_{\text{A}}, \theta_{\text{B}}) = 2 \cos \theta_{\text{A}} \cos \theta_{\text{B}} + \sin \theta_{\text{A}} \sin \theta_{\text{B}}$$

The results of our calculations for E_{coul} (see fig. 3(i)) decrease more rapidly with increasing θ than predicted from the formula given above. For $\theta_{\text{A}} = (360 - \theta_{\text{B}}) = 30^\circ$, E_{coul} even becomes attractive. The rapid decrease of E_{coul} is due to the fact that the proton attraction terms decrease less rapidly than the electron repulsion terms, because for non-linear situations the matrix elements can be split up into " $\sigma-\sigma$ " and " $\pi-\pi$ " type* interactions which will affect the electron repulsion terms more than the proton attraction terms. The angular dependence of E_{ind} (see, e.g., ref. (14)) and E_{disp} ⁹ is given by $f^2(\theta_{\text{A}}, \theta_{\text{B}})$ and in this case also the results of our calculations (see fig. 3(i)) decrease more rapidly than predicted on basis of electrostatic theory. The same explanation as for E_{coul} may be put forward for this feature. Although the arguments on which the representation of E_{exch} by $\beta S_{\text{ab}}^2/R_{\text{HH}}$ is based refer essentially to the variation of E_{exch} with R_{HH} in linear systems, this representation was nevertheless attempted and appeared to be reasonable.

TABLE 6.—VALUES OF C_0 , C_1 AND C_2 (IN ATOMIC UNITS) IN THE REPRESENTATION OF E_{total} BY $C_0 + C_1 \cos \theta_{\text{A}} + C_2 \cos^2 \theta_{\text{A}}$

case	C_0	C_1	C_2
V	0.128	-0.351	0.257
VI	0.451	-1.176	0.757

The results for E_{tot} given in fig. 3(ii) were fitted to an equation of the type $C_0 + C_1 \cos \theta_{\text{A}} + C_2 \cos^2 \theta_{\text{A}}$ using a least-squares technique † (see table 6). A satisfactory

* The symbols σ and π refer to symmetry with respect to the line between the respective interacting centres.

† In the least-squares procedure the values of the total interaction energy at $\theta_{\text{A}} = 0, 10, 20, 30$ and 45° were used. The total square deviation was in all cases less than 10^{-4} a.u..

fit was obtained and the negative coefficient C_1 reflects the rapid decrease of E_{tot} as a function of θ .

CONTACT WITH REAL FRAGMENTS

The most important non-bonded hydrogen-hydrogen interactions are CH...HC and NH...HN and therefore it seems worthwhile to try to select combinations of parameters to represent these fragments. In doing so we are basically guided by the dipole moment, the polarizability, the Slater exponent on A and calculated molecular wave functions.* According to the rules given by Slater one obtains $\zeta_{C_{2p}} = 1.625$ and $\zeta_{N_{2p}} = 1.95$, therefore it was decided to relate CH and NH to a set of parameters with $\zeta_A = 1.5$ and $\zeta_A = 2.0$ respectively. The dipole moments should be treated with care, since in our calculations not all electrons were taken into account. Although we may still be able to account for trends in polarity, it is questionable whether one should choose k in such a way as to obtain the right magnitude of the dipole moment.† Also, the polarizability is a questionable guide. The

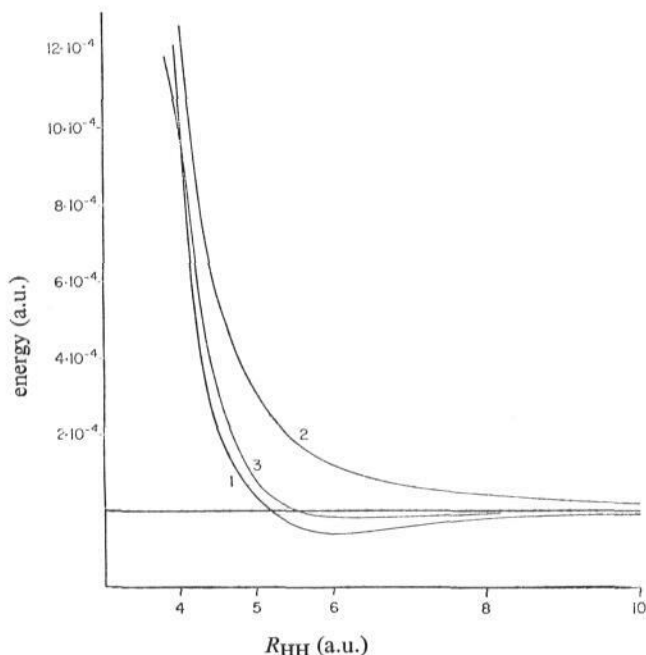


FIG. 4.—Interaction energies between molecular fragments 1, CH...HC ($k = 0.6, \zeta_A = 1.5, \zeta_H = 1.0$); 2, NH...NH ($k = 0.7, \zeta_A = 2.0, \zeta_H = 1.0$). 3, Williams' curve for the interaction between non-bonded hydrogen atoms in crystals of aromatic hydrocarbons.

polarizability obtained from this model deviates in two ways from the experimentally obtained bond polarizabilities for CH and NH (see e.g., ref. (14), chap. 13), i.e., in our model $\alpha_{\perp} = 0$ and α_{\parallel} is about four times too large. These defects are due to the fact that in our model the electron density is cylindrically symmetric and that not

* For a related discussion see ref. (7), chap. 5.

† In order to reproduce the dipole moments calculated by Cade and Huo¹⁵ ($\mu_{\text{CH}} = 0.6179$ a.u. and $\mu_{\text{NH}} = 0.6401$ a.u., polarity in the sense $A-H^+$), one would obtain for CH a k value of 0.3 to 0.4 and for NH a k value of 0.4 to 0.5.

all electrons are taken into account. Because of these difficulties it was decided to compare the MO a to the localized molecular orbitals given by Edmiston and Ruedenberg.¹⁶ They find *

$$\phi_{\text{bonding CH}} = N (0.34 C_{2s} + 0.51 C_{2p\sigma} + 0.52 H_{1s})$$

$$\phi_{\text{bonding NH}} = N' (0.28 N_{2s} + 0.23 N_{2p\sigma} + 0.52 N_{2p\pi} + 0.52 H_{1s})$$

In order to make contact with our simple MO a , we define the amount of H_{1s} -character as follows

$$\chi_{H_{1s}} = (\text{square of coefficient of } H_{1s}) / \text{sum of the squares of all coefficients.}$$

This yields

$$\chi_{H_{1s}}(a) = k^2 / (1 + k^2); \quad \chi_{H_{1s}}(\phi_{\text{bond.CH}}) = 0.40; \quad \chi_{H_{1s}}(\phi_{\text{bond.NH}}) = 0.41.$$

In order to simulate a $\chi_{H_{1s}} \approx 0.4$, k must be roughly equal to 0.8. However, then we would get for CH and NH polarities in the sense A^+H^- . Since this is not satisfactory, it was decided to use those k values close to $k = 0.8$ but which still yield a polarity in the sense A^-H^+ . Then we get $k = 0.6$ for CH and $k = 0.7$ for NH. Further, for the orbital exponent on H_{1s} the value 1.0 was used.

The total interaction energy for C—H...H—C and N—H...H—N is presented in fig. 4 and also included is the curve obtained by Williams¹⁷ for the interaction between non-bonded hydrogen atoms in crystals of aromatic hydrocarbons. The correspondence between the results given by Williams and the results of our calculations is reasonably good. However, this whole scheme of relating sets of parameters to molecular fragments although useful is far from rigorous.

CONCLUSIONS

At short intermolecular distances electrostatic concepts should be handled with care. Not only do they fail to give the right magnitude of the interaction energies but they may also give the wrong trends. In addition, the usual representation of the exchange energy by $\beta S_{ab}^2 / R_{HH}$ does not satisfactorily represent the exchange energy over an extended range of intermolecular distances.

Further, a change of the Slater exponent of the hydrogen $1s$ -orbital from 1.0 to 1.2 is not only important in molecular orbital calculations of bonded hydrogen but for the calculations presented here has also a significant effect on the non-bonded hydrogen interaction energies for $R_{HH} < 6.0$ a.u. Finally, although the model is simple, it is possible with only the two parameters ζ_A and k to obtain interaction energies with different characteristics. Indeed, by an appropriate selection of these two parameters, a reasonable result for the CH...HC interaction could be obtained.

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