Why Do Molecules Interact? The Origin of Electron Donor–Acceptor Complexes, Hydrogen Bonding, and Proton Affinity

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Atoms and molecules interact with one another. As one limit there are the weak attractions (generally less than 1 kcal/mol) of two closed-shell atoms attributable to dispersion or van der Waals interaction.[1] As a second extreme there is the strong interaction of a chemical bond with a stabilization of 50 kcal/mol or more. Between these two limits are various interactions of intermediate strength, including electron donor-acceptor (EDA) complexes and hydrogen bonds. The nature or "origin" of such interactions is often complicated because different terms of energy—electrostatic, charge transfer, etc.—can make comparable contributions to the stabilization.

Ab initio molecular orbital theories have been successful in predicting the most stable geometry of such intermediate-strength complexes.[2] For instance, the water dimer was predicted to be a "linear" dimer with a linear O—H···O bond.[3] Subsequent to this prediction, experiments have confirmed such a structure.[4] In addition to the "prediction" of geometries, however, a theory should be able to interpret the results, or give reasons why such results were obtained. Toward this goal, we have developed within the ab initio SCF theory a scheme in which the interaction energy, ΔE, of a complex is decomposed into five components—electrostatic (ES), polarization (PL), exchange repulsion (EX), charge transfer (CT), and coupling (MIX).[5] Employing this method, we have been able to gain insight on the "origin" of molecular interactions. In this review we will discuss mainly what energy components are essential at the equilibrium geometry of a molecular complex and what components determine the geometry.

Components of the Interaction Energy and Electron Density[5,6]

In the following discussion we assume for simplicity that the geometries of isolated molecules are retained in the complex. The SCF wave functions of two isolated molecules A and B will be called $\mathcal{Q}\Psi_A^0$ and $\mathcal{Q}\Psi_B^0$ and the sum of their energies E_0. Here $\mathcal{Q}$ indicates that the wave function is antisymmetrized in accordance with the Pauli principle. If one denotes the SCF wave function and the energy of the "supermolecule" AB, respectively, as

$$\Psi_4 = \mathcal{Q}\Psi_{AB}, E_4$$

the total interaction energy ΔE is given by

$$\Delta E = E_4 - E_0$$

In the following we show how energy components are traditionally defined and how they are calculated in our scheme.

ES is the electrostatic interaction, i.e., the interaction between the undistorted electron distribution of a monomer A and that of a monomer B. This contribution includes the interactions of all permanent charges and multipoles, such as dipole–dipole, dipole–quadrupole, etc. This interaction may be either attractive or repulsive. In our scheme ES is calculated

$$ES = E_1 - E_0$$

as the difference between E_1 and E_0, E_1 being the energy associated with the wave function Ψ_1, which is

$$\Psi_1 = \mathcal{Q}\Psi_A^0 \cdot \mathcal{Q}\Psi_B^0, E_1$$

a product of undistorted wave functions of A and B and allows no electron exchange between the monomers.

PL is the polarization interaction, i.e., the effect of the distortion (polarization) of the electron distribution of A by B, the distortion of B by A, and the higher order coupling resulting from such distortions. This component includes the interactions between all permanent charges or multipoles and induced multipoles, such as dipole–induced dipole, quadrupole–induced dipole, etc. This is always an attractive interaction. In our scheme PL is obtained as the difference between E_2 and E_1,

$$PL = E_2 - E_1$$

where E_2 is the energy of the wave function Ψ_2

$$\Psi_2 = \mathcal{Q}\Psi_A \cdot \mathcal{Q}\Psi_B, E_2$$

Keiji Morokuma was born and raised in Japan. After finishing his Ph.D. degree under Kenichi Fukui and teaching at Kyoto University, he came to the United States in 1964 and worked with Martin Karplus at Columbia and Harvard. In 1967 he jointed the faculty at the University of Rochester as Assistant Professor and became Professor in 1971. Recently he accepted the chair of Professor of Theory at the new Institute for Molecular Science at Okazaki, but remains in Rochester as Visiting Professor until the summer of 1977. He cordially invites you to visit this new national institute. His research interests, in addition to molecular interaction, include forces in chemical reactions, potential-energy surfaces, and collision dynamics.

(1) (a) H. Margenau, *Rev. Mod. Phys.*, 11, 1 (1939); (b) H. Margenau and N. R. Kestner, "Theory of Intermolecular Forces", 2nd ed, Pergamon Press, New York, N.Y., 1971; (c) J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, "Theory of Gases and Liquids", Wiley, New York, N.Y., 1964.

(2) Reviews: (a) P. A. Kollman and L. C. Allen, *Chem. Rev.*, 72, 283 (1972); (b) M. D. Joesten and L. J. Schaad, "Hydrogen Bonding", Marcel Dekker, New York, N.Y., 1974; (c) P. A. Kollman in "Modern Theoretical Chemistry", H. F. Schaefer, Ed., Plenum, New York, N.Y., in press.

(3) (a) K. Morokuma and L. Pedersen, *J. Chem. Phys.*, 48, 3275 (1968); (b) K. Morokuma and J. R. Winick, *ibid.*, 52, 1301 (1971); (c) P. A. Kollman and L. C. Allen, *ibid.*, 51, 3286 (1969); (d) J. Del Bene and J. A. Pople, *ibid.*, 52, 4858 (1970); (e) D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *ibid.*, 53, 4544 (1970); (f) G. H. F. Diercksen, *Theor. Chim. Acta*, 21, 335 (1971); (g) H. Popkie, H. Kistenmacher, and E. Clementi, *J. Chem. Phys.*, 59, 1325 (1973).

(4) T. R. Dyke and J. S. Muenter, *J. Chem. Phys.*, 60, 2929 (1974).

(5) (a) K. Morokuma, *J. Chem. Phys.*, 55, 1236 (1971); (b) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, 10, 325 (1976).

(6) K. Morokuma, S. Iwata, and W. A. Lathan in "The World of Quantum Chemistry", R. Daudel and B. Pullman, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1974, p 277.

This is a product of wave functions of monomers A and B each of which is permitted to distort by the presence of the other. The electron exchange between A and B is not allowed.

EX is the exchange repulsion, i.e., the interaction caused by exchange of electrons between A and B. More physically, this is the short-range repulsion due to overlap of electron distribution of A with that of B. EX is calculated as

$$EX = E_3 - E_1$$

where E_3 is the energy of Ψ_3

$$\Psi_3 = \mathcal{Q} \, (\Psi_A{}^0 \cdot \Psi_B{}^0), \, E_3$$

Here the undistorted wave functions of A and B are used and the exchange of electrons between A and B is allowed to satisfy the Pauli principle.

CT is the charge transfer or electron delocalization interaction, i.e., the interaction caused by charge transfer from occupied MO's of A to vacant MO's of B, and from occupied MO's of B to vacant MO's of A, and the higher order coupled interactions. In our scheme this is calculated as the difference between E_6, an energy obtained by including the $A_{occ} \leftrightarrow B_{vac}$ and $A_{vac} \leftrightarrow B_{occ}$ interactions, and E_5 without the interactions. Readers are referred to the original reference for details.[5]

MIX, the coupling term, is the difference between the total interaction energy ΔE and the sum of the above four components, and accounts for higher order interaction between various components.

In addition to the above components calculated within the SCF scheme, the total interaction energy has a contribution from the electron-correlation energy, CORR. The most significant portion of the intermolecular correlation energy is known as the dispersion energy, DISP.[1] This is the attraction resulting from the instantaneous and simultaneous polarization of A and B. Calculations for molecular complexes indicate that the effect of CORR is relatively unimportant for interactions of polar molecules.[7,8] In this review CORR effects are completely neglected, unless empirical estimates suggest their importance. In those cases a second-order perturbation calculation for DISP has been carried out and included in the discussion.[8]

From each wave function Ψ_i, $i = 1, 2, ..., 6$ discussed above, one can calculate the electron density $\rho_i(r)$, i.e., the probability of finding an electron at a positron r.[9] In the same fashion as for the energy, the total change in electron density, $\Delta\rho$, and its components can be defined:

$$\Delta\rho = \rho_4 - \rho_1$$

$$\rho_{PL} = \rho_2 - \rho_1$$

$$\rho_{EX} = \rho_3 - \rho_1$$

$$\rho_{CT} = \rho_6 - \rho_5$$

$$\rho_{MIX} = \Delta\rho - (\rho_{PL} + \rho_{EX} + \rho_{CT})$$

A word of warning is in order against overinterpreting the energy decomposition results. There is no unique

Table I
Energy Components in kcal/mol for the Complex OC-BH₃ as a Function of $R(C \cdots B)$, C_{3v} Approach

	R, Å			
	1.57	1.77	2.30	3.00
ΔE	−27.9	−24.5	−11.3	−4.1
ES	−70.0	−42.2	−10.4	−2.2
EX	118.8	63.3	10.6	0.8
PL	−82.2	−33.0	−3.1	−0.3
CT	−89.5	−40.3	−9.5	−2.5
MIX	95.0	27.4	1.2	0.1

choice for the intermediate wave function (Ψ_1, Ψ_2, and Ψ_3), and they do not correspond to the reality (e.g., Ψ_1 and Ψ_2 do not satisfy the Pauli principle!). The virtue of the decomposition is to give a reasonable interpretation to quantum mechanical calculations. We feel that the present scheme is rather close to the classical interpretation and provides a qualitatively correct picture of molecular interpretation.[1]

All the calculations in this Account have been carried out with the 4-31G basis set with standard parameters.[10] This basis set tends to overestimate the polarity of molecules, and consequently overemphasizes the contribution of ES. However, careful analyses[11] indicate that the results are quite appropriate for qualitative discussions.

An Example of Detailed Analysis. H₃B-CO.[12]

In this section, an exemplary, detailed energy and charge-density analysis is presented for the complex of borane and carbon monoxide. The most stable conformer is that in which the CO axis is coincident with the C_{3v} axis of BH₃, with the carbon atom adjacent to the nucleophilic boron center. At first we bring CO along the C_{3v} axis of BH₃ with C and B heading each other. Table I shows the calculated interaction energy and its components as functions of $R(C\text{-}B)$ for this configuration. It is noted that the relative importance of the components is strongly dependent on the intermolecular distance. This phenomenon is, in general, true. Near the equilibrium separation $R(C\text{-}B) = 1.57$ Å (experimental), the three attractive components are found to be almost equally important. Therefore we can call this complex a "CT–PL–ES" complex which, as we will find out, is rather unique.[13]

Component density maps in Figure 1 enable one to comprehend pictorially the motion of the electron density upon complex formation. EX depletes the electron density from the interaction region. On the other hand CT gives rise to a large accumulation of charge in the interaction region, suggesting a strong bond formation. Though these features are more or less generally observed, at larger intermolecular separations the building of CT density is not nearly as complete. This is of particular significance for weaker complexes

(7) O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, **64**, 1351 (1976); G. H. F. Diercksen, W. P. Kraemer, and B. O. Ross, *Theor. Chim. Acta*, **36**, 249 (1975); H. Lischka, *J. Am. Chem. Soc.*, **96**, 4761 (1974).
(8) W. A. Lathan, G. R. Pack, and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 6624 (1975).
(9) S. Yamabe and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 4458 (1975).

(10) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., 1973.
(11) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **99**, 1316 (1977).
(12) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 7208 (1976).
(13) The electron correlation energy contribution to the stabilization of this strong complex is substantial. W. C. Ermler, F. D. Glasser, and C. W. Kern (*J. Am. Chem. Soc.*, **98**, 3799 (1976)) estimated it to be about 18 kcal/mol. Since the SCF energy components are substantially larger than the correlation energy contribution, the classification used here is still qualitatively correct. One may of course more accurately call this a "CT–PL–ES>CORR" complex.
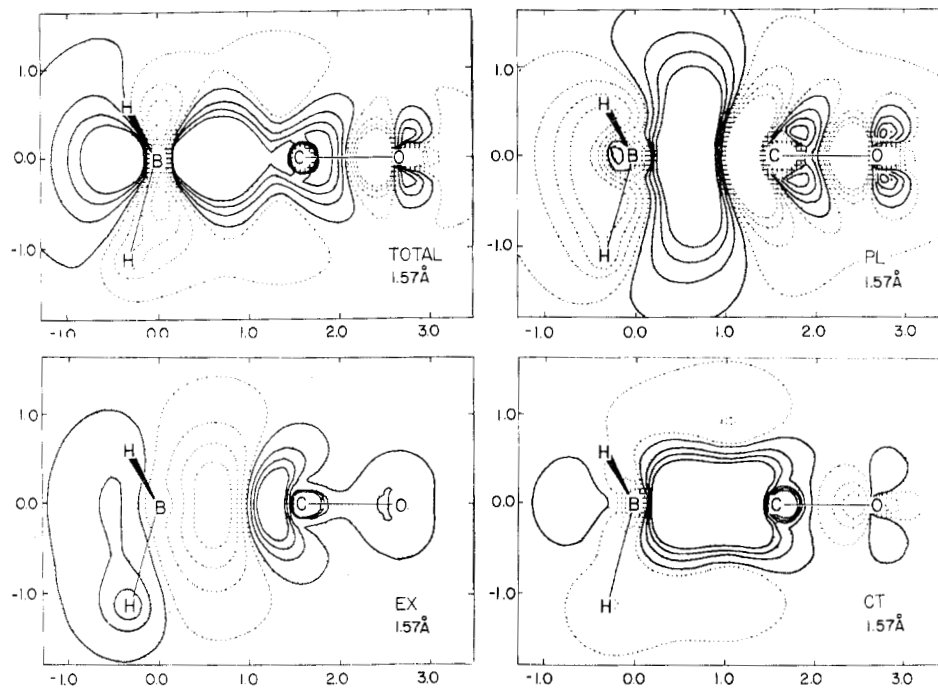
Figure 1. Component electron density maps for the complex OC–BH$_3$ at R(C$\cdots$B) = 1.57 Å in the C_{3v} approach. Full lines indicate density increases and dotted lines indicate decreases. Contours indicated are, successively, ±1, ±5, ±9, ±13 × 10^{-3} bohr^{-3}. The coordinates are in ångströms relative to the boron atom, and the plotting is made for an HBCO plane.
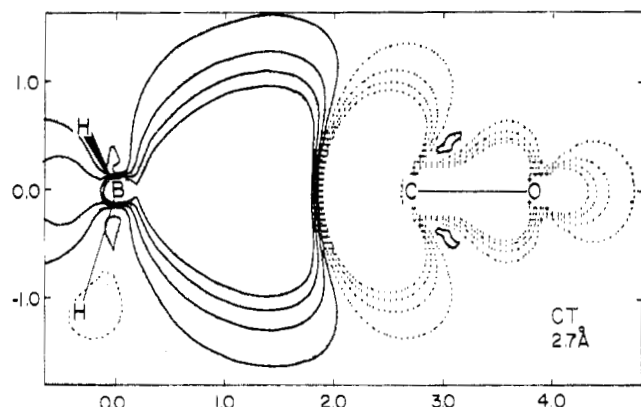

Figure 2. CT electron density maps for the complex OC–BH$_3$ at R(C$\cdots$B) = 2.70 Å in the C_{3v} approach. Contours indicated are, successively, ±1, ±0.3, ±0.5, ±0.7 × 10^{-3} bohr^{-3}.

which have large equilibrium separations. This effect is depicted for this complex in Figure 2, R(C--B) = 2.7 Å. PL is responsible for the largest overall change in the electron distribution and causes the propagation of an induced polarity, H$_3{}^{+\delta-\delta}$B$^{+\delta-\delta+\delta}$C$^{-\delta+\delta}$O$^{-\delta+\delta}$. This alternant polarization has been observed for all complexes which we have studied. As will be seen later, at larger distances and for weaker complexes the PL contribution to the stabilization energy is usually negligibly small. Even so, PL remains the dominant term in the electron redistribution. Figure 3 shows the example of (H$_2$O)$_2$, where the total density change, $\Delta\rho$, is almost indistinguishable from ρ_{PL}.[9]

CT can be further decomposed[5,12] into CT from CO to BH$_3$ and the back-donation from BH$_3$ to CO. The shape of electron density maps in Figure 4 indicates
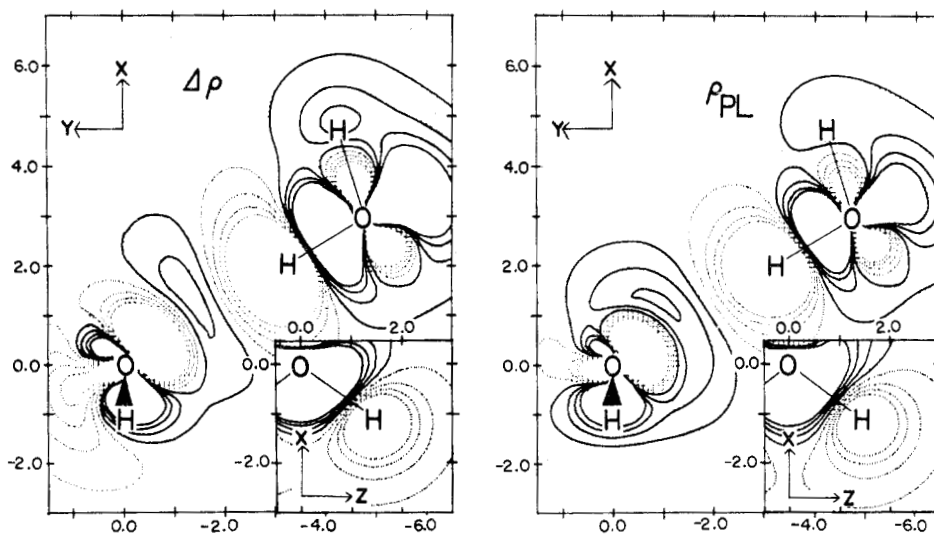

Figure 3. The total and PL density maps for the water dimer. Contours are successively ±0.2, ±0.6, ±1.0, ±1.4 × 10^{-3} bohr^{-3}. The coordinates are in bohr, relative to the oxygen atom of the proton acceptor.

Table II
Energy Components in kcal/mol at the Optimized Intermolecular Separation
R_e and Qualitative Classification of EDA Complexes

Donor-Acceptor	Type	Symmetry	R_e, Å	$\Delta E_{SCF}{}^a$	ES	EX	PL	CT	MIX	DISP[b]	Classification
H_3N-BF_3	n-σ*	C_{3v}	1.60	-71.5	-142.3	136.3	-42.7	-52.7	29.9		Strong ES
H_3N-BH_3	n-σ*	C_{3v}	1.70	-44.7	-92.9	86.9	-17.2	-27.1	5.6		Strong ES
OC-BH_3	σ-σ* π*-π	C_{3v}	1.63	-28.5	-60.9	98.9	-61.8	-68.3	63.6		Strong CT-PL-ES
H_3N-ClF	n-σ*	C_{3v}	2.72	-8.2	-11.2	7.4	-1.1	-3.6	0.2		Intermediate ES
H_2O-$OC(CN)_2$	n-π*	C_s	2.70	-8.0	-9.7	4.4	-1.0	-1.8^d		-1.2	Intermediate ES
C_6H_6-$OC(CN)_2$	π-π*	C_s	3.6^c	-4.2	-2.8	1.8	-1.7	-1.6	0.1	-2.6	Intermediate ES-DISP-PL-CT
HF-ClF	n-σ*	C_s	2.74	-3.4	-3.6	1.8	-0.2	-1.4	0.1		Weak ES
H_3N-Cl_2	n-σ*	C_{3v}	2.93^c	-2.9	-4.0	3.9	-0.8	-2.3	0.3		Weak ES-CT
C_6H_6-ClF	π-σ*	C_s	3.6	-1.8	-1.6	0.6	-0.1	-0.8	0.0	-0.5	Weak ES-CT
H_3N-F_2	n-σ*	C_{3v}	3.00	-1.1	-0.8	0.6	-0.3	-0.6	0.0		Weak ES-CT
H_2CO-F_2	n-σ*	C_s	2.91	-0.7	-0.4	0.3	-0.1	-0.5	0.0		Weak CT-ES-DISP
H_2CO-C_2H_4	π-π*	C_s	3.75	-0.7	-0.5	0.4	-0.1	-0.5^d		-0.4	Weak CT-ES-DISP
C_6H_6-Cl_2	π-σ*	C_s	3.6	-0.6	-0.5	0.7	-0.1	-0.8	0.0	-0.7	Weak CT-DISP-ES
C_6H_6-F_2	π-σ*	C_s	3.3	-0.3	-0.2	0.3	-0.0	-0.4	0.0	-0.4	Weak DISP-CT-ES
F_2-F_2	n-σ* π-σ*	C_s	2.7	-0.2	-0.1	0.3	0.0	-0.4	0.0	-0.2	Weak DISP-CT

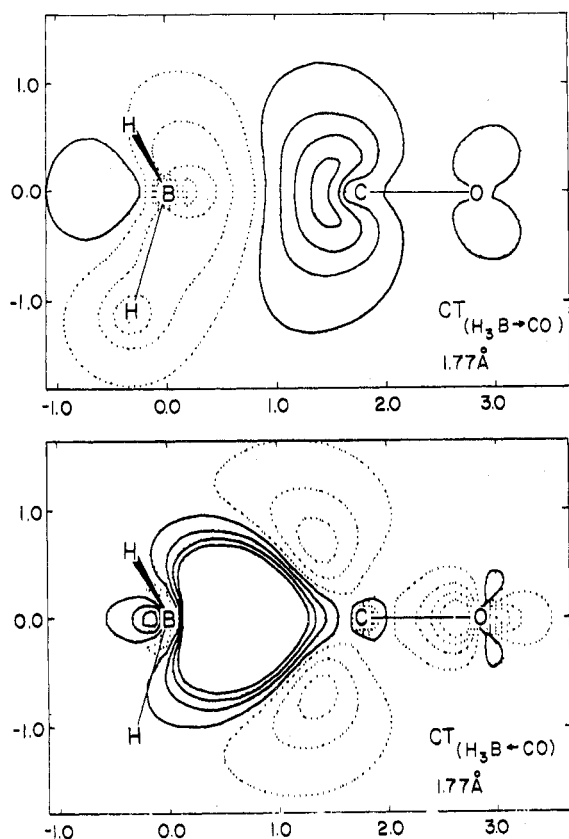^{a} Does not include DISP. ^{b} Estimated by a perturbation calculation. ^{c} Not optimized. ^{d} CT + MIX.

Figure 4. Density maps of forward and back charge-transfer components for the complex OC-BH_3 at R(C⋯B) = 1.77 Å in the C_{3v} approach. Contours indicated are, successively, ±0.5, ±2.0, ±3.5, ±5.0 × 10⁻³ bohr⁻³.

that $CT_{H_3B \leftarrow CO}$ is mainly from the σ lone pair of C to the vacant σ orbital of B. The back-donation $CT_{H_3B \rightarrow CO}$ is principally through π orbitals, i.e., hyperconjugation from the pseudo-π orbital of BH_3 to the π* orbital of CO. Near the equilibrium geometry the ratio of the energy contributions $CT_{H_3B \rightarrow CO} : CT_{H_3B \leftarrow CO}$ is found to be approximately 1:2, indicating a substantial back-donation which is indispensable to the large stability of the complex. In order to examine why the H_3B-CO complex is the most stable when it has a C_{3v} structure with C in contact with B, various other geometries have
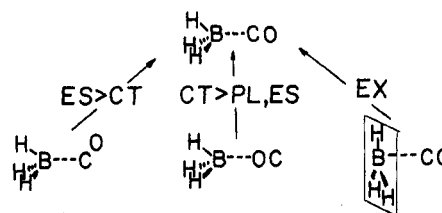

Figure 5. Energy components controlling geometry changes in the complex OC-BH_3.

been examined. Results are shown diagramatically in Figure 5. The structure in which the O is off the C_{3v} axis is less stable, principally due to a decrease in ES, supplemented in part by a decrease in CT. This can be understood in terms of the electron distribution in CO, i.e., the π electron distribution of type $C^{+\delta-\delta}O$ and the σ electron distribution with an opposite polarity $^{-\delta}C$-$O^{+\delta}$. ES is most favorable when the electron-deficient B approaches C along the extension of the CO axis. A C_{3v} complex with O in contact with B is less stable because of a loss in CT, supplemented by a loss in PL and ES. The complex between the planar BH_3 and CO is less stable than the pyramidal complex due to an increase in the EX repulsion. The pyramidal BH_3 keeps its B–H bonds away from the CO group to minimize EX.

EDA Complexes[8,12,14–16]

By carrying out detailed analyses of energy and electron-density components as illustrated earlier, one should be able to obtain clues concerning the question of why molecules interact. Since absolute values of calculated components are rather sensitive to the approximation, it is often more meaningful to compare such analyses among varieties of complexes.

Results of such analyses for many so-called EDA complexes at their calculated equilibrium geometries are summarized in Table II. A classification for each complex is given in terms of the principal energy

(14) W. A. Lathan and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 3615 (1975).

(15) H. Umeyama, K. Morokuma, and S. Yamabe, *J. Am. Chem. Soc.*, **99**, 330 (1977).

(16) K. Morokuma, to be published.

Table III
Energy Components in kcal/mol at the Optimized Intermolecular Geometries[a]

Proton acceptor	Proton donor	R_e, Å	θ, deg	ΔE	ES	EX	PL	CT	MIX
H_3N	HF	2.68	0	−16.3	−25.6	16.0	−2.0	−4.1	−0.7
H_2O	HF	2.62	6	−13.4	−18.9	10.5	−1.6	−3.1	−0.4
HF	HF	2.71	60	−7.6	−8.2	4.5	−0.4	−3.2	−0.3
H_3N	HOH	2.93	0^b	−9.0	−14.0	9.0	−1.1	−2.4	−0.4
H_2O	HOH	2.88	60^b	−7.8	−10.5	6.2	−0.6	−2.4	−0.5
H_3N	HNH_2	3.30	0^b	−4.1	−5.7	3.6	−0.6	−1.3	−0.2
H_2O	HNH_2	3.22	60^b	−4.1	−4.6	2.5	−0.3	−1.5	−0.2
H_3N	HCH_3	4.02	0^b	−1.1	−0.6	0.5	−0.3	−0.7	−0.0
H_2O	HCH_3	3.80	60^b	−1.1	−0.5	0.5	−0.1	−0.9	−0.0

[a] All the complexes are linear, having a linear X--H—Y bond. θ is the angle between this bond and the molecular axis of the proton acceptor. [b] Assumed.

components and is meant to be only a very qualitative guide to the nature of the interaction. For instance, H_3N–ClF has been labeled as an ES complex, but may well be called an ES–CT or, better, an ES>CT complex.

We immediately recognize that these EDA complexes are in general not "charge-transfer" complexes. Not any single energy component emerges as the origin of the interaction. Rather one finds a collection of complexes of varying strengths with a different origin or origins. One common factor noticed in Table II is that ES, which includes all the permanent multipole interactions, plays an important role in almost all the complexes studied. For n–σ* type complexes three classes are recognized. A polar–polar complex has the shortest interatomic distance, R_e, is the strongest, and is dominated by a large ES, even though CT and PL are not negligible. One might interpret this class of complexes as the products of the following sequence of events. Large dipole moments of both the acceptor and the donor give rise to a large ES attraction, which causes R_e to be small. A small R_e, in turn, could enhance the short-range attractions CT and PL. OC–BH_3 is a strong CT–PL–ES complex, somewhat unique in its nature due to the CO's dual role in the CT interaction, acting both as a σ donor and a π* acceptor. NH_3 is a "harder" base than CO, and the H_3N–BH_3 is clearly an ES complex. A polar–nonpolar complex is intermediate to weak, with both ES and CT being major contributions. It is important to note that both the ES and CT contributions are smaller in magnitude here due to the long intermolecular separation. A nonpolar–nonpolar complex is very weak, with both DISP and CT contributing principally to the stabilization.

Only a limited number of complexes of π-electron systems have been studied. A polar n-donor–π*-acceptor complex such as R_2O—$OC(CN)_2$ and R_2O—$(NC)_2C$=$C(CN)_2$, where the n donor approaches perpendicularly to the planar π-electron system, seems to be an intermediate ES complex with a relatively large R_e. In this kind of approach, the dipole moment of the n donor is not usually aligned with the local dipole of the π acceptor, and consequently ES is only of intermediate strength. As a result the R_e is rather large, insuring that CT and PL contributions are small. For the benzene–$OC(CN)_2$ complex (π donor–π* acceptor) ES and DISP are the principal contributions, supplemented by PL and CT. Benzene–halogen complexes (π donor–σ* acceptor) are ES>CT–DISP for heteropolar ClF and DISP–CT>ES for homopolar Cl_2 and F_2.

It is not possible to make sweeping generalizations as to which energy components are dominant in de-

termining the equilibrium geometries of EDA complexes. It depends both on the nature of the distortion from equilibrium which one is considering and on the particular complex of interest.[12,15,16] In this review we simply mention that more often than not the deviation from the equilibrium accompanies a reduction in the ES stabilization.

Charge-transfer excited states of EDA complexes have been subjected to an energy-decomposition analysis.[14] As is expected the interaction between a cation D^+ and an anion A^- is almost exclusively ES in nature.

The geometry and nature—local excitation or charge transfer—of exciplexes are of a special interest in photochemistry. For the exciplex between R_2CO and NR'_3 (R = R' = H for actual calculations), the approach of N to the lone pair of O has been found to be most favorable, though it is not clear whether or not this exciplex is actually bound.[17,18] The energy components at R ~ 2.9 Å for the triplet exciplex are ΔE = 0.4, ES = −0.3, EX = 1.9, PL = −0.4, and CT + MIX = −0.9 kcal/mol, which can be compared with those for the ground state at the same geometry: ΔE = 6.1, ES = 4.5, EX = 2.6, PL = −0.4, and CT + MIX = −0.7 kcal/mol. The exciplex is essentially a complex between R_2CO^* and NR_3 and is more favorable than the analogous ground-state complex, principally due to its enhanced ES interaction, augmented somewhat by a slightly greater CT contribution and a smaller EX repulsion.

Hydrogen Bonding[3b,6,7,11]

The objective in this section is to review energy-decomposition results of hydrogen-bonded complexes in an effort to determine which components control the geometry, directionality, and linearity of hydrogen bonds. In the interest of simplicity, this discussion will be restricted to "normal" hydrogen bonding between neutral electronegative atoms such as N, O, and F and neutral proton donor groups such as F–H, O–H, N–H, and C–H. This excludes "ionic" or strong hydrogen bonding which is of a very different nature.[19]

Table III summarizes energy components for a variety of complexes possessing linear X--H—Y hydrogen bonds. Each of the calculations was performed at the calculated equilibrium geometry. Each of these com-

(17) K. Morokuma, G. H. Neems, and S. Yamabe, *Tetrahedron Lett.*, 767 (1977).

(18) U. Maharaj, I. G. Csizmadia, and M. A. Winnik, *J. Am. Chem. Soc.*, 99, 946 (1977).

(19) H. Umeyama, K. Kitaura, and K. Morokuma, *Chem. Phys. Lett.*, 36, 11 (1975).

Table IV
Comparison of Energy Components in kcal/mol at the
Calculated R_e for Three Structures of $(H_2O)_2$

Geometry:	Linear	Bifurcated	Cyclic
R_e(Å):	2.88	2.90	2.85
ΔE	−7.8	−6.4	−6.1
ES	−10.5	−7.4	−7.4
EX	6.2	2.3	4.7
PL	−0.6	−0.3	−0.3
CT	−2.4	−1.0	−2.8
MIX	−0.5	−0.1	−0.3

plexes is strongly ES in nature, with a small but significant contribution from CT, the relative importance of which varies from one complex to another. The N--H—F bond is the strongest and essentially ES. The weakest X--H—C bonds are CT-ES in nature, both components making an essential contribution to this weak bonding. The principal CT contribution has been found to come from the proton acceptor → proton donor CT through the σ-type interaction.[11] Neither the proton donor → acceptor back-donation nor the CT through π-type interaction is very significant. It is interesting to note that at R_e the total interaction energy ΔE is generally not very different from ES alone. We define the hydrogen-bond directionality as the relative orientation of approach of the donor Y–H bond to the hydrogen-acceptor molecule. Figure 6 shows the energy components of $(H_2O)_2$ as functions of θ, the angle between the hydrogen-bond axis O--H—O and the bisector T of the proton acceptor's HOH angle. In this particular case, as well as for many other examples, it has been found that the optimal approach is dictated by ES alone. Interestingly in this example ES is not the component which shows the largest angular dependence. The large increase in CT stabilization as θ increases cancels almost completely with the destabilization due to EX and PL. If CT alone is used to predict the geometry, an extremely large θ ($\gtrsim90°$) will result. This gives a general warning that one should not use a HOMO–LUMO orbital interaction argument for this kind of weak molecular complexes. The linearity of the hydrogen bond refers to the fact that the hydrogen bond X--H—Y is nearly collinear in most cases. The general preference for linear hydrogen bonds seems to be controlled principally by a balance between changes in ES and EX upon distortion. A deviation of the proton away from the hydrogen bond axis reduces ES stabilization because the H—Y dipole becomes misaligned with the electronegative center X. The same
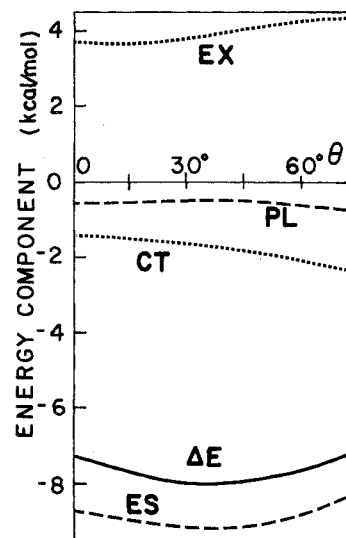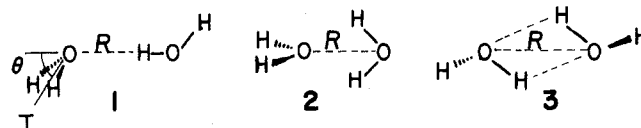

Figure 6. Energy components for linear $(H_2O)_2$ as functions of θ at $R = 2.98$ Å.

deviation also reduces the EX repulsion because the electron cloud on H is removed from the electron cloud of X.

The bifurcated **2** and cyclic **3** structures of $(H_2O)_2$ are less stable than the linear hydrogen bond structure **1**

because of a reduction in ES, as is seen in Table IV. A substantial (25–40%) loss in the ES stabilization cannot be compensated for by the large (30–60%) reduction in the EX repulsion. A point dipole model would have preferred the bifurcated structure where the dipoles are aligned. The fact that the linear structure has a larger ES stabilization suggests that an electrostatic model must include higher multipoles or consider local charge distributions.

One may now ask the ultimate question: what makes hydrogen bonding unique? A comparison between energy components for EDA complexes in Table II and for hydrogen-bonded complexes in Table III does not reveal any characteristic difference. A clue to its uniqueness comes from a comparison between the hydrogen-bonded complex $(HF)_2$ and analogous lithium-bonded complexes $(LiF)_2$ and $(LiH)_2$,[20] as shown in

Table V
Comparison of Energy Components in kcal/mol for Lithium and Hydrogen-Bonded Complexes

Compound	(LiF)$_2$			(LiH)$_2$			(HF)$_2$		
Geometry	Linear	Cyclic	Δ^a	Linear	Cyclic	Δ^a	Linear	Cyclic	Δ^a
Symmetry	$C_{\infty v}$	D_{2h}		$C_{\infty v}$	D_{2h}		$C_{\infty v}$	C_{2h}	
R_e^1, Å^b	1.560	1.729		1.633	1.804		0.916	0.916	
R_e^2, Å^b	1.800	1.729		1.630	1.804		1.965	2.464	
ΔE	−44.7	−75.4	30.7	−24.8	−44.6	19.8	−7.6	−5.6	−2.0
DEF^c		2 × 4.5	−9.1		2 × 1.6	−3.3			
ES	−44.5	−98.1	53.7	−33.8	−79.7	45.9	−8.2	−3.9	−4.3
EX	10.6	40.2	−29.6	17.3	51.7	−34.5	4.5	0.7	3.8
PL	−0.3	−8.6	8.3	−11.4	−13.0	1.7	−0.4	−0.5	0.1
CT	−6.1	−14.6	8.5	−8.7	−55.0	46.2	−3.2	−3.0	−0.2
MIX	−4.4	−3.3	−1.1	11.9	48.1	−36.2	−0.3	−0.1	−0.2

^{a} The difference between the linear and the cyclic structure. ^{b} In $(AB)_2$, R_e^1 is the shortest AB distance, and R_e^2 is the second shortest. ^{c} The energy required to stretch the monomer to the bond length in the cyclic dimer.

Table VI
Proton Affinity, Its Components (kcal/mol), and
Other Related Properties of Alkyl Amines

	NH_3	NH_2CH_3	$NH(CH_3)_2$	$N(CH_3)_3$
ΔE	−221.9	−230.4	−236.1	−239.7
ES	−99.8	−96.5	−91.2	−84.9
PL	−27.4	−40.2	−53.1	−65.4
CT	−88.3	−91.7	−95.1	−98.6
MIX	−6.5	−2.1	3.4	9.2
Q_N(calcd)[a]	7.93	7.81	7.72	7.65
μ_z(calcd),[b] D	1.99	1.70	1.38	1.05
IP(calcd),[c] kcal/mol	252.5	233.0	222.4	216.0

[a] The Mulliken gross population on the O atom. [b] Dipole moment along the direction of the proton approach, i.e., the C_{3v} axis in NR_3. [c] Ionization potential from the Koopmans theorem.

Table V.[11] One should note first that the cyclic form of $(LiF)_2$ and $(LiH)_2$ both have a D_{2h} symmetry, whereas $(HF)_2$ has a C_{2h} symmetry. The cyclic $(LiF)_2$ is much more stable than the linear form, because of an extremely favorable ES. The gain in ES is so large (∼55 kcal/mol) that one can form a stable cyclic (D_{2h}) form by overcoming the overcrowding of electrons (an increase in EX repulsion by ∼30 kcal/mol) and the energy loss DEF required to stretch two LiF molecules (∼9 kcal/mol). This small energy loss in stretching the LiF bond to a separation (1.729 Å) of the cyclic complex helps the cyclization process. On the other hand, for $(HF)_2$ ES is not large enough to accommodate the overcrowding and the stretching of the bonds necessary in forming a D_{2h} complex. The fact that HF has a rather short bond distance and requires a large energy to stretch to a comfortable distance also disfavors the cyclization.

Therefore one may propose that the uniqueness of normal hydrogen bonding lies in the basic fact that it always involves an only moderately polar, short, and strong H—Y bond as the proton donor. ES is not strong enough to allow geometry variation and bond stretching, which result in an additional EX and an extra DEF. The normal hydrogen bond can be considered as a special case of intermediate to weak EDA complex, with linear bonding and appropriate directionality, as discussed earlier.

Proton Affinity[21]

The interaction of a base and a proton can be considered a special case of strong, ionic hydrogen bonding. It is unique in the sense that the proton has no electron; therefore, there exists no exchange repulsion EX. Energy components for the proton affinity of amines are shown in Table VI. ES and CT are the largest contributions and PL is the smallest; the protonated complexes are CT–ES>PL complexes. ES is mainly due to the interaction between the unit charge of the proton and the dipole of the amine, and CT is due to the charge transfer from the amine to the proton. The situation is the same for the proton affinity of R_2O.

Of particular interest is the alkyl substituent effect. Successive methylation of ammonia increases the proton affinity ΔE. ES shows the opposite trend, which

is concordant with the decrease in the electron density on N and in the dipole moment of amines. The alkyl substituent effect is found to be principally controlled by a change in PL, which is the smallest contribution to the proton affinity itself. Alkyl groups act as a reservoir of electrons and make the amine more easily polarizable when a proton approaches it. This large alkyl substituent effect is in contrast with that for the R_3N–BH_3 complex.[12] In the latter complex, a similar increase in PL upon methylation is in part canceled by an increase in EX repulsion. For the proton affinity there is no EX, and as a consequence a large change in PL is observed as a change in ΔE without such a cancelation.

Conclusion

It is hoped that, through this review, coupled with our earlier publications, the reader has gained some insight into the nature of the interaction in molecular complexes. The following two conclusions are deserving of special emphasis. Adducts characterized as EDA complexes are in general not dominated by CT interactions, but rather encompass a wide variety of complexes of different strengths and origin. Neutral hydrogen bonds, on the other hand, are more easily generalized, being strongly ES in nature with a smaller but essential CT contribution.

The applicability of the energy-decomposition technique is not limited to molecular complexes of the type discussed here. It is, for example, well suited for examining the interaction of a transition metal and complexing ligands. A similar technique is also being used to elucidate the "origin" of chemical bonds and chemical reactions.

In hydrogen bonding we have found that at the equilibrium geometry ES is often not far from the total interaction energy ΔE and that ES also often dictates the most favorable approach. These offer a foundation for electrostatic theories of interaction.[22,23] Based on these findings, we have proposed a fractional charge model of solvation,[24] in which a few solvent molecules are included explicitly in the supermolecule, whereas additional solvent molecules are approximated by fractional charges, such as $H^{+\delta}$–$O^{-2\delta}$–$H^{+\delta}$. This model has been applied to solvation of ions, the proton affinity in aqueous solution, proton transfer reactions in solution, and hydrated electrons.[24]

Gordon and Kim's electron gas model predicts molecular interaction energy very accurately.[25] No systematic comparison of our results with theirs has been carried out. We expect a reasonable agreement between the two when the interaction is not strong. Since the charge-transfer effect is not taken into account in their theory, a substantial discrepancy is expected for stronger interactions where CT or MIX is large.

(20) (a) P. A. Kollman, J. F. Liebman, and L. C. Allen, *J. Am. Chem. Soc.*, 92, 1142 (1969); (b) P. A. Kollman, C. F. Bender, and S. Rothenberg, *J. Am. Chem. Soc.*, 94, 8016 (1972); (c) C. P. Baskin, C. F. Bender, and P. A. Kollman, *ibid.*, 95, 5868 (1973).

(21) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, 98, 4400 (1976).

(22) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif., 1960.

(23) R. Bonacconsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *Theor. Chim. Acta*, 20, 331 (1971).

(24) J. O. Noell and K. Morokuma, *Chem. Phys. Lett.*, 36, 465 (1975); *J. Phys. Chem.*, 80, 2675 (1976); unpublished results.

(25) R. G. Gordon and Y. S. Kim, *J. Chem. Phys.*, 56, 3122 (1971), and papers thereafter.