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Theoretical Models of Charge-transfer Complexes

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1 Definition of the Charge-transfer Interaction

Charge-transfer complexes are an electron donor/electron acceptor association for which an intermolecular electronic charge-transfer transition is observed. The nature of this transition will be made apparent in the theoretical discussion to follow, but experimentally, a charge-transfer complex is typically identified spectrally. If, when combining two compounds, absorption maxima appear that otherwise are not characteristic of either compound alone, it is suspected that a charge-transfer complex has formed between the components of the mixture. This is particularly true when one component is a good electron donor (has a low ionization potential) and the other is a good electron acceptor (has a high electron affinity). The current view is that the electronic transition is associated with the transfer of an electron from the donor to the acceptor.

Besides the charge-transfer complex which exists as a stable entity there are also what are known as contact charge-transfer spectra. In many instances there appear charge-transfer bands although no complexes are formed. The nature of these types of charge-transfer complexes is discussed in connection with the theory of the spectral transition but it might be mentioned here that the molecular interaction occurs when random collisions of the pair permit an overlap between the lowest virtual orbital of the acceptor and the donor molecular orbital. Since these pairs are not associated with each other for any long time, they do not form a stable complex, and therefore there is no minimum in the potential energy surface describing the ground state.

2 Historical Development of the Charge-transfer Theory

The classical experimental work which ultimately led to the modern theory of the charge-transfer complex is that of Benesi and Hildebrand[1,2] who studied the effect of various solvents on the absorption spectra of molecular iodine. It was noted that a mixture of aromatic hydrocarbons (*e.g.* benzene) and iodine possessed absorption maxima not present in the spectra of either benzene or iodine. They attributed this new band to the formation of an adduct between the two components and began to examine the nature of this complex by altering the substituents on benzene. From the spectral changes resulting from the addition of electron withdrawing or releasing groups to the benzene, it was concluded that these complexes were the result of an acid–base interaction in the Lewis sense. This systematic experimental

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[1] H. Benesi and J. Hildebrand, *J. Am. Chem. Soc.*, 1948, **70**, 3978.

[2] H. Benesi and J. Hildebrand, *J. Am. Chem. Soc.*, 1948, **71**, 2703.

investigation provided Mulliken[3] with data which enabled him to derive an acceptable theory of this phenomenon.

Prior to the work of Benesi and Hildebrand there was considerable activity in the study of molecular complexes although it is not often apparent that these are what we would today consider charge-transfer interactions. It was noted long ago that stable complexes existed which seemed to defy the rules of valency. That these complexes exhibited various new optical properties had also been noted (especially for transition metal complexes) and this feature was used as a criterion of molecular complex formation, as suggested by Pfeiffer.[4] In the early part of the twentieth century, however, the quantum theory was a relatively new concept and its application to the chemical properties of matter were as yet unknown. The early theoretical explanations of the complexes relied on the valance descriptions. It was then understood that new absorption properties meant that a new chemical entity was present and the only way to make a new chemical substance was through the formation of bonds. It is not surprising then that the first theories of Sudborough[5] made the suggestion that the complexes were covalent in nature.

The idea that complex formation was somehow linked to the formation of covalent bonds persisted for nearly thirty years in some form or another. The structure of co-ordination compounds was first explained in terms of the Bohr model of the atom by Sidgwick[6] who sought to derive a set of general valency rules that were applicable to both complexes and covalently bound molecules. In the same year the subject of valence was addressed at a meeting of the Faraday Society and, in a paper presented by Fowler,[7] the nature of the bond was discussed. The covalent nature of co-ordination compounds was stressed, and it was suggested that the complexation was the result of the sharing or the combination of orbitals (by this time the quantum mechanics was being applied to problems of atomic structure). The surmised role of bond formation becomes apparent in the subsequent discussions where Fowler[8] argues that complex formation is impossible in the situation where only one electron can be shared; this despite a contradictory remark by Bragg[9] who, on the basis of *X*-ray diffraction studies, stated that there are forces between organic molecules which are much weaker than valence (binding) forces. He noted that the distances between complexed molecules were greater than those between atoms in molecules and concluded that the forces between complexing molecules were weaker.

A variation of the covalency argument appeared in the book authored by Pfeiffer[4] which stated that the complexation was the result of 'residual valence forces'. In a molecule the valency of the constituent atoms changes and it was argued by Pfeiffer that this new 'valency' of the entire molecule must be considered. It is the satisfaction of molecular valencies that results in the formation of the

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[3] R. S. Mulliken, *J. Am. Chem. Soc.*, 1950, **72**, 610.

[4] P. Pfeiffer, 'Organische Molekulverbindung', Ferdinand Enke, Stuttgart, 1927.

[5] J. Sudborough, *J. Chem. Soc.*, 1901, **79**, 522.

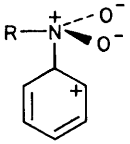
[6] N. Sidgwick, *J. Chem. Soc.*, 1923, **123**, 725.

[7] R. Fowler, *Faraday Trans.*, 1923, **19**, 459.

[8] R. Fowler, *Faraday Trans.*, 1923, **19**, 469.

[9] F. Bragg, *Faraday Trans.*, 1923, **19**, 469.

complex. Pfeiffer's theory was considered unacceptable by Bennett and Willis[10] who felt that there was no way that residual valence could account for the stoicheiometry of many complexes nor their stability in solution. What they advocated instead was that the linkage was indeed covalent, and gave as an example the complex between benzene and nitro-compounds:



Studies of the polarizabilities, refractive indices, and the molecular Kerr effect led Briegleb[11,12] to suggest that the interaction was of the dipole–dipole type. During complex formation the molecules align in such a way that the negative end lines up with the positive end of its neighbour. In a sense, then, the interaction is of an electrostatic type. A duality of the nature of the association is discussed in a study by Moore, Shepard, and Goodall[13] who concluded from an investigation of the colouration of complexes that both dipole and covalent forces were present and their degree of influence was reflected in the colouration (as an indication of strength) of the complex. It was suggested that weak associations (possessing little to no colouration) were of the interacting dipole type, and that strong (and highly coloured) associations were covalent. It followed from their argument that colouration could be used as an assay of covalency. At this juncture the multifarous nature of intermolecular forces was beginning to evolve.

Following the introduction of the interaction of dipoles, the further development of a theory of charge-transfer forces based on the notion of electrostatic interactions continued. Pauling[14] extended his theory of resonance to account for the properties of dyestuffs and included an explanation of some molecular complex properties. Pauling felt that the existence of numerous resonance forms (some of which being ionic) provided a true description of the actual complex. Since the true description was a combination of these various states, it was imagined that the molecule would have an uneven distribution of charge (*i.e.* regions of net positive and negative charge). It was these charge distributions that allowed for an electrostatic interaction to occur between the molecules in the complex.

The most extreme view holding electrostatic forces responsible for complex formation was that of Weiss[15] who considered the ionic forms of the molecules as the composite parts of the complex. The idea was essentially identical to that of Pauling except that only one resonance form was considered. His theory was based on experimental investigations of the quinone–hydroquinone system. The

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[10] G. Bennett and G. Willis, *J. Chem. Soc.*, 1929, 256.

[11] G. Briegleb, *Z. Phys. Chem. B*, 1932, **16**, 249.

[12] G. Briegleb and T. Schachowskoy, *Z. Phys. Chem. B*, 1932, **19**, 255.

[13] T. S. Moore, F. Shepard, and E. Goodall, *J. Chem. Soc.*, 1931, 1447.

[14] L. Pauling, *Proc. Nat. Acad. Sci. USA*, 1939, **25**, 577.

[15] J. Weiss, *J. Chem. Soc.*, 1942, 245.

importance of dipole and dispersion forces was de-emphasized and given the role of stabilizing initial encounters between pairs prior to electron transfer. Weiss proposed the following mechanism to describe the complex formation process:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons [\mathrm{AB}]_t \longrightarrow \mathrm{A}^+\mathrm{B}^- \qquad (1)$$

which involved a transition state composed of a van der Waals interaction followed by the transfer of an electron giving rise to the ionic complex. This theoretical exposition is important historically; it is one of the first attempts to explain donor–acceptor complexes in a quantum mechanical formalism, and is noteworthy on that merit alone. Weiss proposed that the total wavefunction of the complex could be written as a linear combination of wavefunctions describing the van der Waals system (London dispersion forces) and ionic interactions. The weighting factor determining which of the two contributions dominating was defined as the difference $I - E$, where I is the ionization potential and E the electron affinity of the donor and acceptor, respectively. In the situations in which $I - E$ was small, the complex was more ionic in character. These ideas were substantiated in a manner similar to the investigations later performed by Benesi and Hildebrand; that is, electron affinities and ionization potentials were systematically varied (in the actual experiments this was inferred from the redox properties, which reflect $I - E$). Opposition to Weiss' theory was made by Powell and Huse[16] who cited a number of *X*-ray diffraction studies to argue that the forces involved in complex formation were too weak to be strictly ionic and electrostatic in nature. It was argued that if the forces were indeed electrostatic then the spacings between interacting pairs of molecules would be much less than those observed (which were slightly less than the van der Waals distance).

It was not until the investigations of Benesi and Hildebrand that any new developments in the theory of charge-transfer complexes were made. Throughout the early period of the development of these theories, however, the modern quantum theory was being completed and knowledge of the physics describing spectroscopic transitions was accumulating. It is important to note the necessity of these advances to the ultimate derivation of a theory of charge-transfer.

The development of the theoretical interpretation of charge-transfer spectra closely paralleled the increased experience in interpreting spectra in general. This fact is reflected in the ultimate elucidation of an acceptable theory by a spectroscopist. One development in the theory of spectral interpretation was crucial in influencing the development of a theory of charge transfer was the discovery of a light-induced electron transfer. This phenomena was known well before an acceptable theory of charge-transfer had been derived and was known as Electron Affinity Spectra. These spectra were commonly observed for gaseous ionic molecules, ionic crystals, and ions in solution. The earliest identification of an electron-transfer spectrum was made by Kondratjew[17] who irradiated alkali halide vapours and observed fluorescence from the excited halide atom. It seemed from

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[16] H. Powell and G. Huse, *J. Chem. Soc.*, 1943, 435.

[17] V. Kondratjew, *Z. Phys.*, 1926, **39**, 191.

the data that the excited state was being excited to a state consisting of neutral atoms. Subsequent work by others (primarily in Franck's laboratory) identified many photochemical reactions involving electron transfer, and implicated a mechanism for the reaction:

$$X^+A^- \longrightarrow X + A \tag{2}$$

Following the excitation and transfer of the electron the atomic pair would dissociate (Franck, Kuhn, and Rollefson[18]) to give neutral atoms. The potential energy profiles representing this process are illustrated in Figure 1, and from this it can be seen that the transition energy, $h\nu$, is given by (Rabinowitch[19])

$$h\nu = E - I + \Delta, \tag{3}$$

where E is the electron affinity of the halide, I is the ionization potential of the alkali metal, and Δ represents the difference between the energy of formation of the ionic molecule from free ions and the energy of formation of the atomic molecule from free atoms. By changing the halide (thereby varying E), a correlation of calculated trends in the variation of $h\nu$ was made with experimental results, and the theoretical analysis verified. Calculation of Δ (and therefore $h\nu$) is not difficult since a good approximation can be made by simply considering the electrostatic energy of the lattice. Earliest calculations of this type were made by Born[20] and improved upon

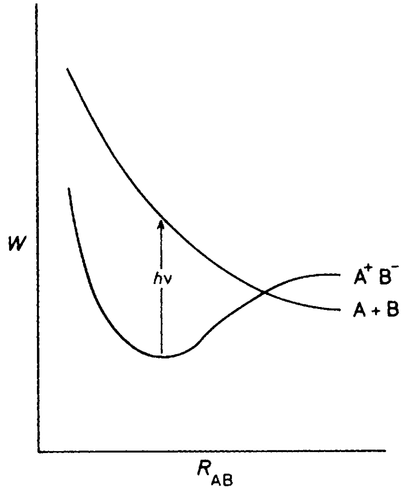

Figure 1 *Potential energy surface representation of a light-induced charge-exchange process leading to the dissociation of neutral atoms*
(*After ref. 17*)

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[18] J. Franck, H. Kuhn, and G. Rollefson, *Z. Phys.*, 1927, **43**, 155.
[19] E. Rabinowitch, *Rev. Mod. Phys.*, 1942, **14**, 112.
[20] M. Born, *Z. Phys.*, 1932, **79**, 62.

by Klemm[21] and von Hippel[22] who accounted for non-electrostatic interactions.

A similar advance in the study of diatomic spectra showed that the identification of dissociation products of excited states was possible. Through the analysis of excited states it was soon noted that there existed instances where the electronic transition resulted in the transfer of an electron between two neutral ground-state species. For example, it was noted that for the case of AgX (X = Cl, Br, I), excitation led to ionized dissociation products[23] as indicated in Figure 2.

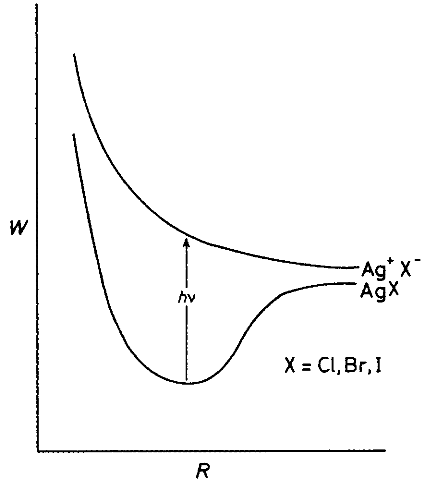

Figure 2 *Potential energy surface representation of a light-induced charge-exchange process leading to the dissociation of ions*
(*After ref. 23*)

3 Modern Theoretical Approaches to Charge Transfer

In an attempt to explain the results of Benesi and Hildebrand the modern theory of charge-transfer complexes was developed. This theory was first proposed by Mulliken[24–26] and was very successful in explaining the origin of the charge-transfer absorption band and also the variations in the spectra as the donor and acceptor properties of the components were varied. Mulliken had been previously involved in the interpretation of band spectra of diatomic molecules and decided to treat the problem of molecular complexes in a similar manner. As a result his theoretical treatment of the complex was very similar to the valence bond treatment of diatomic molecules.

[21] W. Klemm, *Z. Phys.*, 1933, **82**, 529.
[22] A. von Hippel, *Z. Phys.*, 1936, **101**, 680.
[23] R. S. Mulliken, *Phys. Rev.*, 1937, **51**, 310.
[24] R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811.
[25] R. S. Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.
[26] R. S. Mulliken, *J. Chim. Phys.*, 1964, **61**, 20.

In the valence bond treatment of molecular wavefunctions one writes the total wavefunction describing the molecule as a sum of terms representing various configurations of electrons about the nuclei. For example, if we consider the molecule H_2, the valence bond description of the wavefunction would be written as

$$\Psi = N[\{1S_A(1)1S_B(2) + 1S_A(2)1S_B(1)\} + \{1S_A(1)1S_A(2) + 1S_B(1)1S_B(2)\}] \quad (4)$$

The number of terms present in this treatment for an arbitrary molecule would depend on the number of electrons present and how many configurations one decided to consider. In principle, a wavefunction describing a diatomic molecule with a total of M electrons could be written

$$\Psi = A(i)B(j) + \sum [A^{(+n)}(i')B^{(-n)}(j') + A^{(-n)}(i')B^{(+n)}(j')] \quad (5)$$

In equation 5 A and B represent the atomic wavefunctions of the configuration indicated for the set of electrons i and j. The summation is over all ionized forms of A and B.

What Mulliken did in his treatment of molecular complexes was to consider each member of the complex as an 'atom' and the overall pair as a diatomic molecule of sorts. He then wrote a very simple diatomic-like bond wavefunction

$$\Psi_N(\mathrm{DA}) = a\psi_0(\mathrm{D,A}) + b\psi_1(\mathrm{D^+A^-}) \quad (6)$$

where D refers to the donor and A the acceptor. To be more general the equation should include terms of higher ionic character (which Mulliken later did) but the theory and its ramifications are best explained using the simple form above. Equation 6 states very simply that the complex may be considered as a mixture of two states, a non-ionic pair $\psi_0(\mathrm{D,A})$ which, in addition to describing the non-bonding pair, includes modifying terms due to polarization effects, and an ionic pair $\psi_1(\mathrm{D^+A^-})$ which describes a weak covalent bond between the pair and also includes some modifying terms. That this can be done is stipulated within the rules of quantum mechanics since we are regarding ψ_0 and ψ_1 as our basis functions with which we are to describe our system. The beauty of this assumption in describing the wavefunction of the complex is that from it all the properties of charge-transfer spectra can be derived even though we have no idea as to the form of ψ_0 and ψ_1.

Although it has been stated above that ψ_0 and ψ_1 are unknown, this is true in the absolute sense only. The physical nature can be inferred by constructing these states from the individual wavefunctions describing the donor and acceptor, $\Psi(\mathrm{D})$ and $\Psi(\mathrm{A})$ respectively. One can therefore express ψ_0 as a product wavefunction

$$\psi_0 = \mathscr{A}[\Psi(\mathrm{D})\,\Psi(\mathrm{A})]$$

where each component wavefunction describes the donor or acceptor with its full complement of electrons without actually exchanging electrons, in other words, two molecular centres on which there are localized separate electronic distributions. However, despite their being separate entities, the two electronic distributions on the donor and acceptor are mutually influenced by one another, and subject to exchange repulsion forces, dispersion, and classical electrostatic forces. It follows then that $\Psi(D)$ is not identical to the wavefunction which describes the donor *in vacuo*, but possesses some modification due to the nearby molecule; these modifications naturally would be more extreme as the strength of the interaction increased.

The dative basis function may be likewise written as a product of two ionic wavefunctions $\Psi(D^+)$, $\Psi(A^-)$. In this case however an electron is exchanged from the donor to acceptor and may be regarded as being delocalized over the entire donor–acceptor moiety. It is in this sense that the ionic form of the complex's basis is considered to contain some covalent character. It must be realized that for two molecules to exchange an electron, they must approach one another to the extent that orbitals localized on the individual molecules overlap. There follows exchange and delocalization of electrons which, in essence, constitutes a covalent interaction; the new species (*i.e.* the complex) is unique only in that charge density shifts from donor to acceptor. It is erroneous to consider the complex as two ions in close proximity.

In equation 6 the ground-state wavefunction has been written in terms of a basis consisting of a sum of functions ψ_0 and ψ_1. It is necessary that the excited state be written as a sum of the same basis functions. This excited state (also known as the virtual state) is then

$$\Psi_V(DA) = c\psi_0(D,A) + d\psi_1(D^+A^-) \tag{7}$$

Imposing orthonormality conditions upon Ψ_N and Ψ_V provides information regarding the nature of the charge-transfer transition. Orthonormality gives three relations involving the coefficients and integrals over ψ_0 and ψ_1:

$$\langle\Psi_N|\Psi_N\rangle = 1 = a^2 + b^2 + ab\langle\psi_1|\psi_0\rangle \tag{8a}$$

$$\langle\Psi_V|\Psi_V\rangle = 1 = c^2 + d^2 + cd\langle\psi_1|\psi_0\rangle \tag{8b}$$

$$\langle\Psi_N|\Psi_V\rangle = 0 = ac + bd + ac\langle\psi_1|\psi_0\rangle + bd\langle\psi_1|\psi_0\rangle \tag{8c}$$

which imply that $c = -b$ and that $d = a$. It is therefore apparent that during the excitation process the character of the complex changes; that is, if in the ground state the complex is predominantly non-ionic ($a \gg b$), then in the excited state it becomes ionic. The excitation process has associated with it a transfer of an electron (charge) from the donor to the acceptor; and as discussed above, this type of photochemically assisted charge-transfer was already known in the case of diatomic molecules.

The analogy of the treatment of the complex with the theory of diatomic molecules can be carried further in order to account for the experimental data. If one represents the interaction between the pair in terms of a potential energy profile (similar to that of diatomics) for the ground and excited states, it can be seen (Figure 3) that at infinite separation dissociation products D and A are obtained in the ground state, and ionic D^+ and A^- are the dissociation products of the excited state. This information follows from the orthogonality relations above. At infinite separation the difference in energy between the ground and excited states is $I_D - E_A$, where I_D is the ionization potential of the donor, and E_A is the electron affinity of the acceptor. Therefore the transition energy is approximated by

$$h\nu = I_D + E_A + \Delta \tag{9}$$

which is very nearly identical to the equation proposed by Rabinowitch for Electron Affinity Spectra; the difference being that the signs are reversed (which is to be expected since the transition described by Rabinowitch is that of an ionic ground state to a neutral excited state). In the above equation Δ is also a correction term which accounts for differences in the potential curves at $r = r_{eq.}$

At the time Mulliken reported his theory of charge transfer, the modern theory of quantum mechanics, including the method of molecular orbitals[27] was well developed. With the molecular orbital theory Mulliken was able to approximate Δ by more sophisticated means. Since he was able to write the wavefunction in a meaningful (albeit not calculable) form, an application of the variational principle of quantum mechanics was possible. By substituting the approximate wavefunction $\Psi_N(DA) = a\Psi_0(D,A) + b\Psi_1(D^+A^-)$ into the Schrödinger equation and requiring that $\partial W/\partial a$ and $\partial W/\partial b$ (where W designates energy) be zero, a secular determinant of the form

$$\begin{vmatrix} W_0 - W & H_{01} W S_{01} \\ H_{01} - W S_{01} & W_1 W \end{vmatrix} = 0 \tag{10}$$

was obtained, which when solved, gives a quadratic equation in W with two roots as solutions. One of these roots corresponds to the ground-state energy

$$W_N \simeq W_0 - \frac{(H_{01} - S_{01}W_0)^2}{(W_1 - W_0)} \tag{11a}$$

whereas the second root yields the excited-state energy

$$W_V \simeq W_1 + \frac{(H_{01} - S_{01}W_1)^2}{(W_1 - W_0)} \tag{11b}$$

In the above equations H_{01} is the expectation value $\langle\psi_0|H|\psi_1\rangle$ and $S_{01}$is the overlap integral $\langle\psi_0|\psi_1\rangle$.

To obtain $h\nu$ in the form of equation 9 one starts from its definition

$$h\nu = W_V - W_N$$

which, following substitution from equations 11a and 11b, yields

$$h\nu_{CT} = W_1 - W_0 - \frac{(H_{01} - S_{01}W_0)^2 - (H_{01} - S_{01}W_1)^2}{(W_1 - W_0)} \tag{12}$$

The form of equation 9 is obtained if the expressions for W are written as energies at infinite separation plus a correction term. For example, the ground-state energy is

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[27] C. Roothan, *Rev. Mod. Phys.*, 1951, **23**, 69.

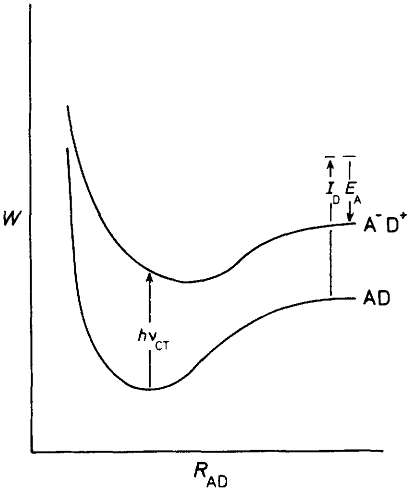

Figure 3 *Potential energy surface representation of the charge-transfer transition and its dependence upon* I_D *and* E_A

expressed as $W_0 = W_\infty - G$ and from this the excited-state energy can be written as $W_1 = W_\infty + I_D - E_A - G'$. Substitution into equation (12) gives

$$h\nu_{CT} = I_D + E_A - G' + G - \frac{(H_{01} - S_{01}W_1)^2}{(W_1 - W_0)} \tag{13}$$

which is the desired form expressing the functional dependencies upon I_D and E_A. Mulliken offered an explanation as to the possible nature of the terms G and G'. He suggested that G was a non-bonding stabilization term which largely consisted of contributions from London dispersion forces. G' was a term which had to include major contributions from coulombic and exchange forces due to the nature of the excited state. What is important is that not only has this valence bond approach agreed with the diatomic molecule analogue (and could be directly applied to the ionic molecule problem), but it successfully predicts experimental trends in the variation of $h\nu_{CT}$ as a function of the ionization potential and electron affinity of the donor and acceptor respectively as illustrated by the experimental data plotted in Figure 4.

In the variational treatment of the charge-transfer problem the coefficients a and b were the parameters with respect to which the energy was minimized. The results of this procedure can be used to obtain a ratio of the coefficients, b/a, by the application of second-order perturbation theory.[28] In the application of the perturbation methods to the complexes the dative wavefunction is considered as a perturbation to the non-bonding pair, which ultimately gives for b/a:

$$b/a = -(H_{01} - S_{01}W_0)/(W_1 - W_0) \tag{14}$$

[28] L. I. Schiff, 'Quantum Mechanics', McGraw Hill, New York, 1968.

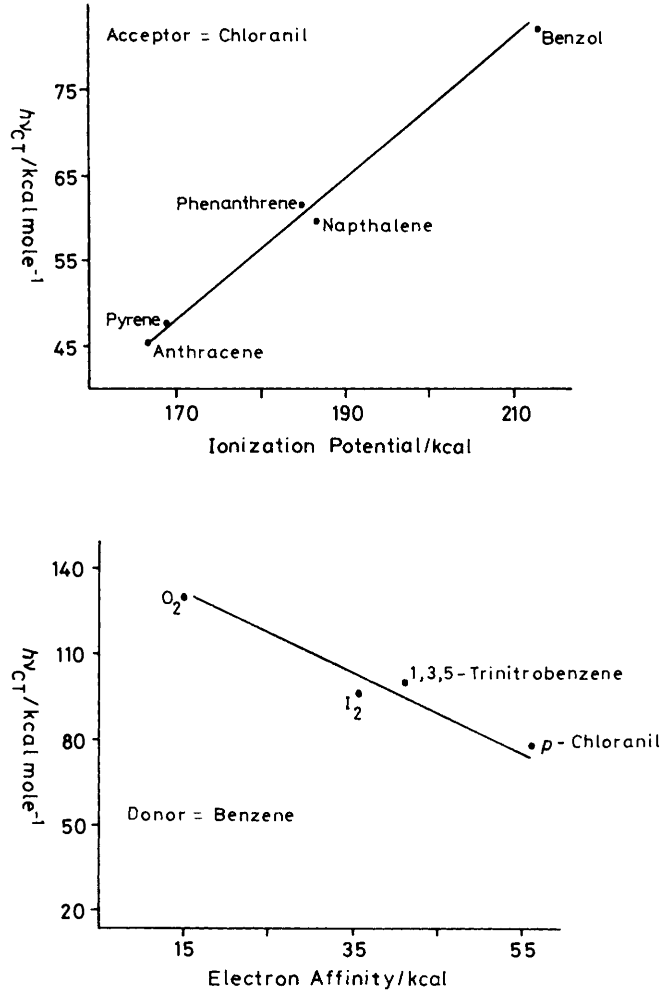

Figure 4 *The linear dependence of* $h\nu_{CT}$ *upon the ionization potential of the donor or the electron affinity of the acceptor*

The importance of this equation has been discussed in detail by Mulliken,[29] however a few of its more important features will be mentioned here. It should be noted that complex formation (resonance interaction between the two wavefunctions) is not predicted to occur based on this theory unless the wavefunctions describing the no-bond and dative forms are of the same symmetry. If Ψ_0 and Ψ_1 are not of the same symmetry then the integrals H_{01} and S_{01} both

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[29] R. S. Mulliken and W. Person, 'Molecular Complexes: A Lecture Note and Reprint Volume', Wiley, New York, 1969.

vanish, making $b/a = 0$, meaning that $b = 0$, or in other words, there is no interaction. A second feature is that the wavefunction must also possess the same orbital species under the group theoretical classification corresponding to the overall symmetry of the complex. This orbital requirement is relaxed in the case of molecules possessing no symmetry, or when there is considerable spin–orbit coupling (most common for heavy atoms).

The actual magnitude of the ratio b/a is usually not evaluated, however in a qualitative sense it can be seen that in the case of a loose complex $a \gg b$, and as the association between the pair becomes stronger, the ratio would approach unity. BF_3–NMe_3 is one adduct commonly associated with those very strong complexes having b/a ratios in excess of unity. Although both individual components are gases, their combination results in the formation of a white powder which is quite stable. This complex is formed through a dative bond between the vacant p-orbital of boron and the non-bonding electron pair of nitrogen in a manner reminiscent of a HOMO/LUMO interaction. This bond gives an ionic character to the complex and hence suggests that in this case b is greater than a. Weak complexes are typically composed of pairs of closed-shell (all valencies filled) molecules; a simple example being associations between rare-gas atoms. It is now somewhat easier to perform the necessary calculations of equation 14 through self-consistent field methods, and this will be discussed in a later section in connection with the quantum mechanical energy decomposition scheme.

The charge-transfer process has been described by most researchers as an interaction between molecular orbitals of the donor and acceptor. The conceptual descriptions of this process is due largely to the notion of orbital interactions[30,31] and the concept of highest occupied molecular orbitals of the donor (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the acceptor. Electron exchange from HOMO to LUMO was suggested as the physical process responsible for complex formation in charge-transfer interactions. Mulliken recognized the importance of the interaction between the orbitals now referred to as HOMO and LUMO, stating that the geometry of the complex was dependent upon the conformation giving maximal overlap of the pair. In his orbital description[32] of the interactions Mulliken makes use of this orbital notion to deal with the process. Recalling that the approximate wavefunctions are given by

$$\Psi_N = a\psi_0 + b\psi_1 + c\psi_2 + \cdots \tag{15a}$$

and

$$\Psi_V = a^*\psi_0 + b^*\psi_1 + c^*\psi_2 + \cdots \tag{15b}$$

in their most general form, with higher order basis functions included, the basis

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[30] R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, 1968, **8**, 781.

[31] K. Fukui, *Acc. Chem. Res.*, 1971, **4**, 57.

[32] R. S. Mulliken and W. B. Person, *J. Am. Chem. Soc.*, 1969, **91**, 3409.

functions ψ_0 and ψ_1 can be expressed as products of molecular orbitals localized on the separate molecules:

$$\psi_0 = \mathscr{A}[\varphi_d(1)\alpha(1)\varphi_d(2)\beta(2)\cdots \\ \cdots\varphi_a(M+1)\alpha(M+1)\cdots \quad (16a)$$

$$\psi_1 = \mathscr{A}'\frac{N}{2(1+S)^2}\{[\varphi_d(1)\alpha(1)\varphi_{a'}(2)\beta(2) + \varphi_d(2)\beta(2)\varphi_{a'}(1)\alpha(1)] \\ \varphi_d(3)\alpha(3)\cdots\varphi_a(M+1)\alpha(M+1)\cdots\} \quad (16b)$$

In the above equation φ_a, is the lowest lying virtual orbital (LUMO) of the acceptor and the sum within the square braces of the excited-state wavefunction is necessary because it is not known whether an α or β spin electron is involved in the transfer, so a linear combination of all possibilities is used (a common trick of quantum theory, and permitted since the only meaningful relations are probabilities, $|\Psi|^2$). The variable $\mathscr{A}$ represents the antisymmetry operator.

Just as in the quantum theory of molecules where there are two methods of writing the wavefunction (valence bond *vs.* molecular orbital theories), there is a second way to treat the description of the charge-transfer complex, and this method is reminiscent of the molecular orbital method in which orbitals delocalized over the entire complex are used (once again it helps to imagine the complex as a type of diatomic molecule). The molecular orbital treatment of the complex differs from the resonance structure description in that the electrons partaking in the transfer between the molecules are assigned to an orbital (or orbitals if multiple charge-transfer effects are to be described) which is delocalized over the nuclei of both interacting molecules. In this way the complex is regarded as a supermolecule and the charge-transfer excitation is simply an excitation from an occupied delocalized molecular orbital to a virtual molecular orbital.

In a modified molecular orbital treatment Mulliken (1969) writes an MO wavefunction which looks similar to the resonance structure description

$$\Psi_N = \mathscr{A}[\varphi_{da}(1)\varphi_{da}(2)S_{12}]\varphi_3(3)\alpha(3)\cdots \quad (17)$$

where the $\varphi_{i\text{'s}}$ are molecular orbitals delocalized over either the donor or acceptor and the function φ_{da} is a bridging molecular orbital which contains those electrons involved in the charge transfer. This bridging molecular orbital is written as a sum of orbitals localized on the acceptor and donor

$$\varphi_{da} = m\chi_d + n\chi_a \quad (18a)$$

and these orbitals can be approximated by $\chi_d = \varphi_d$ and $\chi_a = \varphi_a$. The ratio m/n is an indication of the strength of the complex (approaching unity as the strength of the interaction increases). There also exists an excited-state bridging molecular orbital

$$\varphi_{da}^* = m^*\chi_d + n^*\chi_a \quad (18b)$$

which corresponds to the charge-transfer state. The orthonormality relations dictate that the ratio n^*/m^* is similar in form to n/m. With this the total wavefunction for the excited state of the complex can be written as

$$\Psi_{\mathrm{V}} = \frac{\mathscr{A}}{\sqrt{2}} [\varphi_{\mathrm{da}}(1)\varphi_{\mathrm{da}}(2) + \varphi_{\mathrm{da}}(1)\varphi_{\mathrm{da}}(2)]S_{12}\varphi_3(3)\alpha(3)\cdots \qquad (19)$$

and the similarity with the Resonance Structure Theory wavefunction discussed above can be seen. The equivalence of these two approaches has been demonstrated,[32] although the resonance theory is considered preferable except in the case of very strong complexes in the singlet charge-transfer state. The significant difference is in the sign of the exchange term, which in turn causes a difference in the energies which would vary with intermolecular distance. For the ground state both approaches are equally acceptable although the molecular orbital method is more easily dealt with computationally.

As an alternative to the molecular orbital theory of charge-transfer interactions a perturbational approach[33] to the problem was taken. In this particular application the system is treated as a few-electron problem in terms of overlap and electron transfer. The perturbation of the system is obtained from the potential field produced by the donor ion D^+, making the perturbation expansion a function of matrix elements depicting the effect of the potential and overlap. From this standpoint Murrell was able to demonstrate the behaviour of the wavefunction as a result of charge transfer and also the nature of the charge distribution function with increasing overlap. Furthermore, by using an explicit function expressing the relationship between the intensity of the charge-transfer band and the overlap of orbitals belonging to A and D, the feasibility of the suggested origin of contact charge-transfer interactions is illustrated.

Murrell's perturbation approach does not derive new or independent results but instead uses Mulliken's theory to obtain approximate wavefunctions for analysis. The general theory begins with the assumption that the wavefunction can be written as the antisymmetrized product of the eigenfunctions of A and D

$$\Psi_{\mathrm{r}} = \mathscr{A}\varphi_{\mathrm{dr}}(i)\varphi_{\mathrm{ar}}(j) \qquad (20)$$

where

$$H_{\mathrm{d}}\varphi_{\mathrm{dr}}(i) = W_{\mathrm{dr}}\varphi_{\mathrm{dr}}(i)$$

and

$$H_{\mathrm{a}}\varphi_{\mathrm{ar}}(j) = W_{\mathrm{ar}}\varphi_{\mathrm{ar}}(j)$$

As D and A approach one another this total wavefunction is no longer an eigenfunction of the complete Hamiltonian

$$H = H_{\mathrm{a}} + H_{\mathrm{d}} - \sum_{\mathrm{i}}(Z_{\mathrm{a}}/r_{\mathrm{ai}}) - \sum_{\mathrm{j}}(Z_{\mathrm{d}}/r_{\mathrm{dj}}) + \sum_{\mathrm{ij}} r_{\mathrm{ij}}^{-1} + (Z_{\mathrm{a}}Z_{\mathrm{d}}/r_{\mathrm{ad}})$$

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[33] J. Murrell, *J. Am. Chem. Soc.*, 1959, **81**, 5037.

nor do they form an orthogonal set. The perturbed wavefunction is given by

$$\Psi' = \Psi_r + \sum a_{rs}\Psi_s \tag{21}$$

where $\Psi_s' = \varphi_{as}(i')\varphi_{ds}(j')$. Here the primes indicate that the number of electrons on D and A differ from those of the function Ψ_r which consists of an orthogonal set of functions with Z_a electrons on A and Z_d electrons on D. These functions can be localized or delocalized over the complex. The coefficients of equation 21 are found to be

$$a_{rs} = \frac{H_{rs} - S_{rs}H_{rr}}{H_{rr} - H_{ss}} \tag{22}$$

The significance of these coefficients is that they permit the determination of the extent of mixing of ionized states Ψ_s' with the non-bonding function as the degree of overlap changes (the functional dependence seen here as involving matrix elements H_{rs} and S_{rs}).

The method is illustrated using a one-electron approximation for which the ground-state wavefunction is written

$$\Psi(\mathrm{D,A}) = \varphi_d \tag{23}$$

and the charge-transfer state wavefunction is

$$\Psi(\mathrm{D^+A^-}) = \varphi_a \tag{24}$$

These one-electron functions describe the orbital of the electron transferred during the transition. The total Hamiltonian for the one-electron system is

$$H = V(\mathrm{D^+}) + V(\mathrm{A}) \tag{25}$$

where the functions V represent the electrostatic field of the molecular configuration indicated. When subjected to the external perturbation of the electrostatic field, the wavefunction for the donor and acceptor states are written as

$$\varphi_d' = \varphi_d + a_{ad}\varphi_a \tag{26a}$$

and

$$\varphi_a' = \varphi_a + a_{da}\varphi_d \tag{26b}$$

The coefficients for the system described in this manner are thereby found to be

$$a_{ad} = \frac{H_{ad} - S_{ad}\,H_{dd}}{W_d - W_a} \tag{27a}$$

and

$$a_{da} = \frac{H_{ad} - S_{ad}\,H_{aa}}{W_a - W_d} \tag{27b}$$

which permits one to write these coefficients in terms of matrix elements. Expressed as

$$a_{ad}(W_d - W_a) = \langle\varphi_a|V(A)|\varphi_d\rangle - S_{ad}\langle\varphi_d|V(A)|\varphi_d\rangle \tag{28a}$$

and

$$a_{da}(W_a - W_d) = \langle\varphi_a|V(D^+)|\varphi_d\rangle - S_{ad}\langle\varphi_a|V(D^+)|\varphi_a\rangle \tag{28b}$$

it becomes possible to determine the effect of overlap and thereby the degree of charge exchange for the ground and excited state. The normalized charge-density is given by $\varphi_a\varphi_d/S_{ad}$, making the following expressions valid for the coefficients:

$$a_{ad}(W_d - W_a) = S_{ad}\langle(\varphi_a\varphi_d/S_{ad}) - \varphi_d^2|V(A)\rangle \tag{29a}$$

$$a_{da}(W_a - W_d) = S_{ad}\langle(\varphi_a\varphi_d/S_{ad}) - \varphi_a^2|V(D^+)\rangle \tag{29b}$$

It is apparent that $a_{ad} \neq a_{da}$; the major difference being the potential field over which the system is integrated. Because $V(D^+)$ is essentially an electrostatic potential, it decreases as r^{-1} whereas $V(A)$ falls off exponentially and vanishes outside the electronic orbitals of A. This fact implies that the integral of equation 29b is greater than that of 29a, leading to the conclusion that $|a_{da}| \gg |a_{ad}|$. It follows then that there is more ground-state character introduced into the charge-transfer state than the other way around.

Another factor which influences the relative size of the coefficients is the relative magnitude of the functions φ_a and φ_d. Using approximate wavefunctions of the form $\varphi = (\zeta^3/\pi)\exp(\zeta r)$, and by varying ζ, Murrell demonstrated that the electron density is greatest on the centre whose wavefunction is smaller. The function φ_a is generally larger than φ_d because it describes a negative ion; and this leads to the same condition as described in the preceding paragraph.

4 The Charge-transfer Transition Process

From the above descriptions it appears that in the process of photon absorption there is a simultaneous physical movement of an electron from one molecule to another. When described in this manner the phenomenon of charge-transfer resembles a scattering process; a photon in some way encounters the complex and perhaps in the encounter transfers momentum to an electron and knocks it into an energy state which can be captured by an acceptor. If not a collision process, then one still has to contend with rationalizing what appears to be movement of an electron between donor and acceptor during the annihilation of a photon. In proposing a mechanism for the charge-transfer transition a process has been described which seems to defy some of the accepted concepts of physics and particularly special relativity. The problem is associated with the nature of the apparent motion of the electron during photon absorption, yet the results of the spectral studies (particularly those of Kondratjew[17]) indicate that the excitation process does involve charge transfer.

The problem in this apparent paradox may be due to an error in the interpretation of the theory; in particular, an attempt to read more from the equations than is justified. It is made clear in all introductory texts of quantum mechanics that the wavefunction is a meaningless expression, while it is actually from the probability density that we can obtain information of a physical nature. Even for a system as simple as a free particle in one dimension the solution to the eigenvalue equation tells us nothing about the physics of the particle. It is only from the probability function that we can predict a distribution for the location of the particle. A more familiar experimental example of this limitation in wavefunction descriptions of physical systems is found in discussions of diffraction and the double slit experiment, which is discussed in numerous texts[34] on the quantum theory. In the solution of the hydrogen atom problem, a set of eigenstates are obtained and designated as *s*, *p*, *d*, *etc.*, each set possessing a different set of eigenvalues (*e.g.* momentum). It is conceded that the eigenfunctions describing these states are in themselves meaningless since one cannot draw a parallel between the equations of motion for classical orbits and these quantum equations of state; however, from the square moduli of these eigenfunctions it is possible to plot electronic charge-density of the atom or molecule. The distribution of an *s* state is different from that of a *p* state, and therefore an excitation of a hydrogen atom from an *s* to *p* state would seem to require the reordering of the charge, giving a situation analogous to the charge-transfer paradox.

It may have been noticed that in the discussion of the hydrogen atom system above, the electronic charge-density was the property which was altered during excitation when it is often considered that it is the electron which is transferred during a charge-transfer transition. The latter statement concerning charge transfer is actually in error. The classical concept of the electron transfer is not accurate in describing the process; it does however provide us with a useful basis function with which to describe the electronic configuration of the complex. Returning to the Mulliken description of the complex given in equations 6 and 7, the dative form is only used as a basis function to describe the total wavefunction. The probability density of this total wavefunction is what is then found to have a charge-density shift in a manner similar to that derived for the hydrogen atom or any system of electrons in general. In reconciling this theoretical description with the observations of Kondratjew and others it must be realized that the excited state is characterized by an electronic probability (or charge density) which is greater on the acceptor. If the excited state is unstable and has a propensity towards dissociation, then the dissociation products will reflect the charge distribution of the excited state. In actual computational studies of charge-transfer complexes, electron densities can be used as a measure of the extent of charge transfer.[35]

From the above discussion it appears that this reordering of charge is a quantum effect arising from changes in the probability distribution of the eigenfunctions. The time evolution of these changes can be studied through the application of

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[34] R. P. Feynman and A. R. Hibbs, 'Quantum Mechanics and Path Integrals', McGraw-Hill, New York, 1965.

[35] G. Del Re, *Isr. J. Chem.*, 1980, **19**, 265.

perturbation theory to the time-dependent wavefunctions. The concept of a discontinuous process is unknown in quantum mechanics since temporal changes occur continuously. It is the measurement which determines the state.[36] The change in the nature of the state as initiated by the interaction of a photon with the complex can be followed in time as will now be outlined theoretically. The wavefunctions derived by Mulliken for a complex are both stationary states (solutions of the time independent Schrödinger equation):

$$H_0\Psi_N = W_N\Psi_N \tag{30a}$$

$$H_0\Psi_V = W_V\Psi_V \tag{30b}$$

These stationary states are stable in the sense that once the system is in either of these two states, it remains in that state for all subsequent time unless subjected to a perturbation. The electromagnetic radiation (light) impinging upon the complex supplies a time-dependent perturbation (due to the oscillation of the electrical and magnetic fields) from which we can define a total Hamiltonian as

$$H = H_0 + H(t)$$

and write the wavefunction as non-stationary states. If the frequency of the light is that of the charge-transfer transition ν_{CT}, only the two states need be included in the description of the process; and the total wavefunction for the time-dependent process need only be written as a linear combination of the two stationary states:

$$\Phi(r,t) = C_N(t)\Phi_N(r,t) + C_V(t)\Phi_V(r,t) \tag{31}$$

In the above equation the time-dependent forms of Ψ_N and Ψ_V have been used; namely $\Phi(r,t) = \Psi(r)\exp(-iWt/\hbar)$. The time-dependent Schrödinger equation using the wavefunction and Hamiltonian described yields

$$H(C_N(t)\Phi_N + C_V(t)\Phi_V) = i\hbar\left(\Phi_N\frac{\mathrm{d}C_N}{\mathrm{d}t} + \Phi_V\frac{\mathrm{d}C_V}{\mathrm{d}t}\right) \tag{32}$$

after common terms containing W are cancelled. From this equation it is now possible to derive differential forms from which C_N and C_V may be obtained. Multiplication of this equation by Φ_N^* and integrating gives

$$C_N\langle\Phi_N|H|\Phi_N\rangle + C_V\exp(i\frac{W_N - W_V}{\hbar}t)\langle\Phi_N|H|\Phi_V\rangle = i\hbar(\mathrm{d}C_N/\mathrm{d}t) \tag{33}$$

which is equivalent to (because $W_V - W_N = h\nu_{CT}$)

$$C_N\langle\Phi_N|H'|\Phi_N\rangle + C_V\exp(-\nu_{CT}t)\langle\Phi_N|H|\Phi_V\rangle = i\hbar(\mathrm{d}C_N/\mathrm{d}t) \tag{34a}$$

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[36] W. Pauli, 'Handbuch der Physik', Vol. 5, Springer, Berlin, 1958, 1.

A similar procedure involving multiplication by Φ_V^* gives a second equation

$$C_N\exp(-i\nu_{CT}t)\langle\Phi_V|H|\Phi_N\rangle + C_V(\Phi_V|H|\Phi_V\rangle = i\hbar(dC_V/dt) \qquad (34b)$$

which together with the first may be solved for the coefficients C and also Φ. Knowledge of $\Phi(r,t)$ can be used to find the electron density $-e|\Phi(r,t)|^2$ and observe its variation with time.

5 Criticism and Alternative Theories of Charge Transfer

Although the theory of Mulliken is the most widely known description of the charge-transfer process it has received some criticism. In the development of the theory Mulliken did acknowledge that there exist contributions by various intermolecular forces (*e.g.* dispersion, inductive, coulombic, *etc.*) to the stability of the complex; however the major cause of the stability was, in his opinion, due to the resonance interaction between the non-bond state and the dative state. It was this idea which drew criticism from several researchers who felt that in reality, these complexes differed little from other known complexes including those of rare-gas atoms. By the latter part of the 1960's the perturbation method had been applied to the problem of molecular interactions and had yielded a convenient decomposition of the forces involved in complex formation. Since this method was generalized, it seemed appropriate to consider the charge-transfer phenomenon in terms of it. Since a term corresponding to charge-transfer arose from the decomposition a measure of the relative importance of the various forces could be made. Dewar was perhaps the first who openly questioned the importance of charge transfer in this way and suggested that it was simply the close proximity of the molecules which was responsible for the charge-transfer transition.

The alternative model presented by Dewar and Lepley[37] proposes that the close encounter of the interacting molecules permits the excitation of electrons from the donor to a virtual orbital on the acceptor. That more than one virtual orbital on the acceptor may be involved was suggested as the origin of multiple charge-transfer bands, and further, it was demonstrated by Dewar that it is possible to obtain the observed functional dependence of $h\nu_{CT}$ on I_D and E_A since these parameters roughly correspond to the energies of the HOMO of the donor and the LUMO of the acceptor respectively. In support of this model a correlation between charge transfer frequency and orbital energies is demonstrated. In a later study Dewar[38] suggests that, like contact charge-transfer in which no complex is formed, these interactions in general owe their transitions to their proximity due to van der Waals interactions. According to this scheme the major contribution to the stability of the complex comes from electrostatic forces; both of the dipole–dipole type and of the polarization (*i.e.* dipole–induced-dipole type). This was in agreement with the view of Briegleb.[11,12]

Dewar emphasized that the success of Mulliken's theory lies not in the correct use of a term representing the transfer of an electron, $\Psi(D^+A^-)$, but rather because

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[37] M. J. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, 1961, **83**, 4560.

[38] M. J. Dewar and C. C. Thompson, *Tetrahedron*, 1966, Suppl. 7, 97.

such dative terms $\Psi_1(D^+A^-)$, $\Psi_2(D^{2+}A^{2-})$, *etc.* formed a reasonable basis set which represents the polarization and dipole effects (*cf.* the terms obtained by perturbation theory below). The actual charge-transfer process is thus a special case of polarization, and charge-transfer complexes (or electron donor/acceptor complexes) are just one type of molecular complex. These types of complexes differ only in the particular force which predominates, that is, contributes most to the stabilization of the complex. According to this scheme it might be expected that a pair of polar molecules would be stabilized primarily by dipole–dipole interactions, whereas a pair of closed shell molecules might interact through dispersion interactions. From a perturbational analysis of this problem Dewar was able to derive an approximate relationship between the interaction energy ΔW and the frequency of the charge-transfer band:

$$\Delta W = c/\nu + D$$

from which it was found possible to obtain a functional dependence between the frequency of the charge-transfer transition and the equilibrium constant of complex formation. Following Dewar's theoretical proposal and comparison of charge-transfer energies with molecular orbital properties there appeared papers which reported direct calculations of some of the forces obtained in the perturbative decomposition. Mantione[39] was one of the first to perform these calculations and showed that polarization effects were important in the stabilization of TCNE containing charge-transfer complexes.

Hanna and co-workers[40,41] also felt that the role of charge-transfer interactions was minimal in the stabilization of the ground state of the complex. This had already been suggested by Mulliken when he stated that for many systems, his parameter b in equation 6 was very small and that the non-bonding basis function $\psi_0(D,A)$ included many terms of intermolecular forces. Hanna did suggest that the dominant forces responsible for formation and stabilization of the complex were electrostatic, and introduced the quadrupolar effect as an important contribution to the total interaction energy. He does however retain the charge-transfer resonance interaction of Mulliken to account for the spectral observations, and goes so far as to say that this resonance is a '. . . necessary and sufficient condition to explain the unique spectral features'.[41] These theoretical discussions of Hanna are more consistent with the views of Mulliken than those of Dewar since they retain most of Mulliken's ideas while changing only the nature of the force believed to stabilize the ground state. Another contribution made by Hanna was his argument on behalf of the importance of orientation in determining the relative contributions of various forces. This idea was also advocated by Rice[42] who distinguished, by a kinetic approach, categories of complexes which showed charge-transfer properties

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[39] M. Mantione, *Theor. Chim. Acta*, 1968, **11**, 119.

[40] M. Hanna, *J. Am. Chem. Soc.*, 1968, **90**, 285.

[41] M. Hanna and J. Lippert, in 'Molecular Complexes', ed. R. Foster, Crane, Russack, and Company, New York, 1973, V. 1, 1.

[42] O. Rice, *Int. J. Quantum Chem.*, 1968, **2S**, 219.

dependent upon the orientation of the pair at a given instant of time. It would seem then that the relative contributions of forces is a dynamic parameter related to molecular dynamics.

6 Charge-transfer and Generalized Theories

It was previously mentioned that the perturbation theory gave a natural decomposition of terms when applied to the problem of molecular interactions, one of these terms corresponding to charge-transfer interactions. A similar treatment based on the variational method was developed several years later and greatly simplified the computational aspects of intermolecular force calculations. It is the latter variational approach which dominates current research in the theoretical aspects of charge-transfer interactions and molecular interactions in general. I would like to conclude this review by introducing some aspects of generalized molecular interactions and decomposition schemes in the context of charge-transfer complex formation. It was this generalized theory upon which much of the criticism of Mulliken's theory was based.

Decomposition of energy terms is actually a mental exercise which is based on an intuitive notion of the physics of the system. In a classical system of charged particles (*e.g.* nuclei and electrons) decomposition might resolve the purely coulombic forces between the charges and a dynamic inductive effect caused by the changing electric field due to the motion of these particles. Within the realm of quantum systems the situation is somewhat more difficult since the quantum mechanics possesses phenomena that defy our intuitive grasp of reality (*e.g.* the Pauli exclusion principle). Although subject to some difficulties in its interpretation, the decomposition scheme is still a useful concept in understanding the physical nature of molecular interactions.

Before proceeding with the decomposition of a quantum mechanical system's energetics *via* perturbational procedures, it should be pointed out that the first example of interactions between atoms (*i.e.* the H_2^+) yielded types of decomposed energy terms in the form of overlap, exchange, and coulombic integrals. For a more detailed discussion of the nature of these integrals and their manifestation in terms of electron density profiles the reader is referred to the original paper of Heitler and London[43] and a later article by Berlin.[44] The perturbation theory similarly yields sets of integrals which are then assigned some physical significance based on their mathematical behaviour or origins. It is in this way that a natural decomposition of the total energy is derived from the solution of a given problem. One other similarity to the chemical bond theory of molecules is the tacit assumption of the Born–Oppenheimer approximation which permits the decoupling of fast and slow subsystems, thereby allowing the computation of electronic energy at a given nuclear configuration. A chapter by Teller[45] is strongly recommended for its detailed analysis of the Born–Oppenheimer approximation and its limitations. In

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[43] W. Heitler and F. London, *Z. Phys.*, 1927, **46**, 455.

[44] T. Berlin, *J. Chem. Phys.*, 1951, **19**, 208.

[45] E. Teller and H. Sabin, in 'Physical Chemistry: An Advanced Treatise', Vol. 1, ed. H. Eyring, D. Henderson, and W. Jost, Academic Press, New York, 1970, p. 1.

the present discussion the Born–Oppenheimer approximation will only be used as justification for isolating the electronic system in the subsequent analysis.

The fundamental difficulty which arises in the derivation of interactions is that no generalized means of mathematically treating the problem exists which is applicable over the entire range of molecular distances. The wavefunction necessary to describe the interaction of a pair of molecules whose orbitals may overlap is considerably different from that required to describe the situation in which there is no overlap. The wavefunction of the former system must be antisymmetrized with respect to all electrons, whereas the latter case need not meet this requirement. Since most quantum mechanical descriptions are constructed from product wavefunctions, the difference between the long range (no orbital overlap) and short range (orbital overlap) amounts to where the antisymmetrization operator is located in the product function:

$$\Psi = \mathscr{A}A(i)\mathscr{A}B(j) \tag{35}$$

for the long range interactions, and

$$\Psi = \mathscr{A}A(i)B(j) \tag{36}$$

for the short interactions. As might be expected, the mixing of electrons in the case of short range interactions permits one to account for the possibility of charge-transfer effects. This is accomplished mathematically by incorporating ionized forms of the pair into the basis set used to describe the perturbational wavefunction (much like the valence bond-like approach used by Mulliken). Perturbation theory applied in the long range case yields terms corresponding to the coulombic, inductive, and dispersion energies of interaction, charge transfer being absent since electron exchange is unlikely without orbital overlap.

The primary aim of any perturbational approach to the problem of interactions is that an approximation to the true wavefunction describing the interaction be written as an expansion of the wavefunction describing the system in the absence of interaction. Mathematically, it makes sense to write the expansion in terms of the other orthogonal functions of the set to which the unperturbed function belongs. In the case of a simple quantum mechanical system, if the unperturbed wavefunction is the ground state representation of the system then an expansion could be constructed from the excited state representations of the system. If the sets $\{A_u(i)\}$ and $\{B_v(j)\}$ are the set of functions describing the molecules A and B respectively such that A_0 and B_0 are the ground states, then the unperturbed and perturbed wavefunctions for the interaction of A and B can be written:

$$\Psi_0 = \mathscr{A}A_0(i)\mathscr{A}B_0(j) \tag{37}$$

and

$$\Psi = \mathscr{A}A_0(i)\mathscr{A}B_0(j) + \sum_{u,v} c_{uv}\mathscr{A}A_u(i)\mathscr{A}B_v(j) \tag{38a}$$

$$= \Psi_0 + \sum_t c_t\Psi_t \tag{38b}$$

respectively. In the above definitions i and j refer to the collective electrons on A and B respectively. This representation as described above is valid for long-range interactions. However, for a more accurate approximation to the situation in which electronic exchange is permitted the basis used in the expansion should include terms of the type

$$A_u^+(i)B_v^-(j)$$

and

$$A_u^-(i)B_v^+(j)$$

which are called 'charge transfer' terms by those who originally derived[46–48] the decomposition terms for the small orbital overlap system.

With the introduction of new basis functions the approach taken in the examination of short-range forces begins to deviate from that of long-range interactions. A second modification to the perturbational approach[46,49] deals with the nature of the perturbation itself. The situation is complicated by the supplementing of the electrostatic forces by exchange interactions which necessitates the use of a double perturbation expansion. The resulting expansion of the interaction energy is composed of terms which are mth order in electrostatic energy and nth order in exchange. In their original papers the authors[46–48] retained terms to second order only. The Hamiltonian used in the double perturbation is identical to that used for long-range forces (*i.e.*, $H = H_A + H_B + U$, where U represents electrostatic forces); the second aspect of the perturbation is derived from the antisymmetry operator $\mathscr{A} = [N_i!N_j!/(N_i + N_j)!]^{\frac{1}{2}}(1 + P_{ij})$ where P_{ij} is the operator representing permutation of electrons of the set i and j on A and B respectively.

Following the usual method of perturbation theory equation 38b is inserted into the Schrödinger equation $(H - W)\Psi = 0$ and multiplied by $\langle\Psi_0|$ to obtain

$$(H_{00} - WS_{00}) + \sum_t c_t(H_{0t} - WS_{0t}) = 0 \tag{39}$$

with matrix elements defined as $H_{00} = \langle\Psi_0|H|\Psi_0\rangle$, $H_{0t} = \langle\Psi_0|H|\Psi_t\rangle$, *etc.* Examination of these matrix elements determines the nature of the resolved energy terms. The terms S_{00}

$$S_{00} = \langle\mathscr{A}A_0(i)B_0(j)|\mathscr{A}A_0(i)B_0(j)\rangle$$

can be rewritten by pulling the operator out in front of the integral

$$S_{00} = \langle(1 + P_{ij})A_0(i)B_0(j)|A_0(i)B_0(j)\rangle$$

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[46] J. Murrell, M. Randic, and D. Williams, *Proc. R. Soc., London, Ser. A*, 1965, **264**, 566.

[47] L. Salem, *Discuss. Faraday Soc.*, 1965, **40**, 150.

[48] J. I. Musher and L. Salem, *J. Chem. Phys.*, 1966, **44**, 2943.

[49] J. N. Murrell and G. Shaw, *J. Chem. Phys.*, 1967, **46**, 1768.

In this form it is possible to note that for each pair of electrons permuted the integral obtained increases by order two. Taking the first two terms of the expansion yields

$$S_{00} = 1 + S_{00}^{02}.$$

Similar machinations with the expectation value H_{00} give

$$\begin{aligned} H_{00} &= W_0 S_{00} + \langle (1 + P_{ij}) A_0(i) B_0(j) | U | A_0(i) B_0(j) \rangle \\ &= W_0(1 + S_{00}^{02}) + H_{00}^{10} + H_{00}^{12} \end{aligned}$$

The superscripts 10 and 12 indicate the matrix elements are first order in electrostatic energy. Each permutation of electrons in the H_{00} term also increases the order of the integral by two, hence H_{00}^{10} and H_{00}^{12}.

The off-diagonal elements are obtained by multiplying the expression $(H - W)\Psi = 0$ by $\langle \Psi_p|$ where Ψ_p is an element of the set $\{\Psi_t\}$. This ultimately yields the terms

$$S_{t0} = S_{t0}^{02}$$

and

$$H_{t0} = W_0 S_{t0}^{02} + H_{t0}^{10} + H_{t0}^{12}$$

These terms are valid for those basis functions taken from the set of excited-state wavefunctions: for the basis functions of the charge-transfer type, however, these terms are not valid because the antisymmetry operator must be altered for functions in which electrons are transferred. The changes are actually minor and the outcome of the change is that instead of the expansion of the integrals in even powers, expansion is in the odd powers of $\langle A_u(i') B_v(j') | A_0(i) B_0(j) \rangle$ giving

$$S_{t0} = S_{t0}^{01}$$

and

$$H_{t0} = W_0 S_{t0}^{01} + H_{t0}^{11}$$

terms. Here i' and j' indicate that the set of electrons on A and B have been altered in number. From the matrix elements the energy terms are obtained in a manner similar to ordinary perturbation theory; as a result the charge-transfer basis functions in the double perturbation scheme provide the additional term

$$\sum_{t \neq 0} \frac{(H_{t0}^{11} - S_{t0}^{01} H_{00}^{10})^2}{(W_0 - W_t)} \tag{40}$$

which was assigned by Murrell as the representation of charge-transfer interaction energy.

The usefulness of equation 40 is for the most part limited to the theoretical realm of quantum mechanics; for practical calculations perturbational approaches are notoriously unwieldy. The other popular method of approximation in quantum mechanics is the variational method; this is much more useful as a computational method since the introduction of the Self-consistent Field technique as a form of the variational method made computer applications relatively easy. In applications to problems describing molecular interactions one starts with the basic premise that the interaction energy ΔW can be described in much the same way that binding energy is defined for a chemical bond, *i.e.*

$$\Delta W_{\text{interaction}} = W_{\text{AB}} - (W_{\text{A}} + W_{\text{B}})$$

The disadvantage of this approach is that in performing an SCF calculation on a given molecular pair there is no natural decomposition of various energy contributions. One basically has to scrounge among the sets of integrals and cull those which correspond to pairs of electrons obtained from separate molecules. One also has to contend with the errors of the Hartree–Fock method of SCF theory which are attributed to a term known as the correlation energy, *i.e.* $W_{\text{exact}} = W_{\text{HF}} + W_{\text{correlation}}$. Since the correlation energy can be calculated by various methods the interaction energy can be written as

$$\Delta W_{\text{interaction}} = \Delta W_{\text{HF}} + \Delta W_{\text{correlation}}$$

A careful analysis of the correlation energy terms for both general cases and interacting molecules[50–54] has demonstrated that the difference in correlation energy $\Delta W_{\text{corr.}}$ is equivalent to the dispersion energy with ΔW_{HF} being composed of other contributions. The following decomposition of the variational energy (ΔW_{HF}) by Kitaura and Morokuma[55] is an extension of earlier attempts to decompose the variational energy:

$$\Delta W_{\text{HF}} = W_{\text{es}} + W_{\text{pl}} + W_{\text{exch}} + W_{\text{CT}} + \text{W}_{\text{mix}}$$

where terms corresponding to electrostatic, polarization, exchange, charge transfer, and coupling interactions are resolved.

As alluded to above, this scheme had its origin in some earlier investigations of the SCF density matrix.[54,56] In a calculation of a molecular pair[57] the unperturbed wavefunction for the molecular pair appears as a diagonalized combination of the individual density matrices of A and B

[50] O. Sinanoglu, *J. Chem. Phys.*, 1962, **36**, 706.

[51] O. Sinanoglu, in 'Modern Quantum Chemistry', Vol. 2, ed. O. Sinanoglu, Academic Press, New York, 1965, 99.

[52] O. Sinanoglu, *J. Chem. Phys.*, 1962, **36**, 3198.

[53] N. Kestner, *J. Chem. Phys.*, 1968, **48**, 252.

[54] E. Kochanski, in 'Intermolecular Forces', ed. B. Pullman, Reidel, Boston, 1981, p. 15.

[55] K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, 1976, **10**, 325.

[56] E. Kochanski and J. Gouyet, *Mol. Phys.*, 1975, **29**, 693.

[57] S. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.

$$\overline{AB} = \begin{vmatrix} A & 0 \\ 0 & B \end{vmatrix}$$

in which one can impose antisymmetry on either the entire matrix AB or each of its component matrices. A single calculation of the energy of this matrix representation yields a value $W^{(1)}$ such that $W^{(1)} = H\Psi_{AB}$, and can be used to obtain the electrostatic energy contribution (if the individual A and B matrices alone are antisymmetrized):

$$W_{es} = W^{(1)} - (W_A + W_B)$$

When the entire density matrix AB is antisymmetrized the exchange of electrons means that a single iteration of the SCF for this density matrix yields an energy $W^{(2)}$ which includes exchange interaction, *i.e.*

$$W_{exch} = W^{(2)} - W^{(1)}$$

Continuation of the SCF process and subsequent optimization of the density matrix is accompanied by delocalization of charge (mixing of molecular orbitals) giving non-zero values where there were formerly none. The additional energy decrease due to further optimization is called the delocalization energy and includes contribution from induction, charge transfer, *etc.*

In the more complete decomposition scheme the definitions of W_{es} and W_{exch} are retained, and further resolution of the delocalization energy is attempted. The polarization energy is obtained by allowing the density matrix coefficients written as a composite of A and B density matrices to be optimized without delocalization. This procedure results in another energy $W^{(3)}$ which contains the polarization energy and is resolved as

$$W_{pl} = W^{(3)} - W^{(1)}$$

The charge-transfer energy was originally not included in a direct computational scheme[55] and assigned as part of a remainder term

$$W_{CT} + W_{mix} = W_{HF} - (W_{es} + W_{exch} + W_{pl})$$

More recently a direct computational scheme[58] has been devised which manipulates the basis functions such that the energies of ionic states are calculated from the density matrix. The energies are combined to give the total charge-transfer interaction energy. The remainder term in this revised scheme is the mixing energy and is attributed to coupling interaction.

The variational decomposition scheme has been successful in a number of

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[58] K. Morokuma, *Acc. Chem. Res.*, 1977, **10**, 294.

applications (*cf.* Morokuma[58,59] and references therein). The method has been adapted to the GUASSIAN[60] system of molecular orbital programs, and permits the resolution of molecular interaction energy profiles into their various components, thus allowing an evaluation of the relative importance of each of the components. The *ab initio* SCF method of computing molecular interactions suffers from the problem that these energies are derived from the subtraction of energies which are comparable in magnitude. The total energies obtained in the SCF calculations are orders of magnitude greater than the interaction energies which are obtained from their differences. In consideration of these errors, the perturbation method approach has the advantage that each individual interaction is individually computed and the total interaction energy obtained from their sum. The price one pays for the more facile application of variational methods then, is the need to perform SCF computations to a very high degree of accuracy. The requirements of performing accurate SCF computations[57] of interacting systems place great demands on the computational facilities available to the researcher, particularly when investigating systems of polyatomic molecules. To deal with the interactions of larger molecules, including some of biological interest, Pullman[61] developed an energy decomposition scheme for use with a semi-empirical computational method known as the Perturbative Configuration Interaction using Localized Orbital (PCILO) method. Although the approach does not yield highly accurate calculations by virtue of its semi-empirical nature, it makes up for this deficiency by determining the interaction energy by an additive procedure.[62]

7 Conclusion

Charge transfer, hydrogen bonds, London dispersion (or van der Waals) forces are types of molecular interaction which have been distinguished more due to historical reasons than any other. A given interaction was usually emphasized as being responsible for the forces between molecules because of the particular system chosen for study by the investigator. In general, types of molecular interacting systems can be readily discerned in day to day observations made in any laboratory or in any environment. Spectroscopists first became familiar with changes in colour as a clue to interactions, others such as organic chemists may have noticed the effect of hydrogen bonding on reactivity; depending on what system caught his attention, the researcher developed a theory based on his system and this theory evolved rather independently of theories of different systems. The intensified interest in molecular interactions since the early 1960s has unified the seemingly disparate types of intermolecular forces into the various manifestations of molecular interactions. This renewed interest in molecular interactions has had wide ranging effects in spectroscopy, molecular acoustics, pharmacology, and numerous other

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[59] K. Morokuma and K. Kitaura, in 'Molecular Interactions', H. Ratajczak and W. J. Orville-Thomas, ed., Wiley, New York, 1980, p. 21.

[60] J. Binkley, R. Whiteside, R. Krishnan, R. Seeger, D. DeFrees, H. Schlengel, S. Topiol, L. Kahn, and J. Pople, GAUSSIAN 80, Carnegie-Mellon University, Pittsburg.

[61] N. Gresh, P. Claverie, and A. Pullman, *Int. J. Quantum Chem.*, 1982, **22**, 199.

[62] N. Gresh, P. Claverie, and A. Pullman, *Int. J. Quantum Chem.*, 1979, **13S**, 243.

fields. For the reader interested in the many aspects of intermolecular forces many new books have appeared recently dealing with current trends in theory[63–66] and applications.[67,68]

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[63] 'Intermolecular Forces', ed. B. Pullman, Reidel, Boston, 1981.

[64] 'Molecular Interactions', in three volumes, ed. H. Ratajczak and W. Orville-Thomas, Wiley, New York, 1980.

[65] P. Hobza and R. Zahradnik, 'Weak Intermolecular Interactions in Chemistry and Biology', Elsevier, Amsterdam, 1980.

[66] G. Maitland, M. Rigby, E. Smith, and W. Wakeman, 'Intermolecular Forces, Their Origin and Determination', Oxford University Press, New York, 1982.

[67] P. Arrighini, 'Intermolecular Forces and their Evaluation by Perturbation Theory', Springer Verlag, Berlin, 1982.

[68] N. Matoga and T. Kubota, 'Molecular Interactions and Electronic Spectra', Dekker, New York, 1970.