Theory of the Chemical Bond. 1. Implicit Perturbation Theory and Dipole Moment Model for Diatomic Molecules

Robert L. Matcha*[1a,b] **and Stephen C. King, Jr.**[1c]

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77004, and Battelle Memorial Institute, Columbus, Ohio 44201.

Received August 27, 1974

Abstract: A perturbation formalism is developed for studying intramolecular forces and constructing models of molecular properties. Some characteristics of the theory are: (1) Zeroth-order wave functions can be conveniently chosen on physical grounds. (2) Knowledge of the zeroth-order Hamiltonian corresponding to the zeroth-order wave function is not required in order to get higher order corrections. (3) The theory can be applied to the study of intermolecular interactions without the necessity of assuming distinguishable electrons in the Hamiltonian. The formalism is used to obtain a model relating diatomic dipole moments to bond lengths, charge distributions, and charge polarizabilities.

During the period immediately following the inception of quantum mechanics, many qualitative empirical concepts related to chemical bonds and properties were developed. These have proven quite useful to chemists and physicists. This development was restricted to some extent by available experimental data which were often faulty and misleading.

In recent years highly accurate and reliable molecular data from both experimentalists and theoreticians have become available which makes possible considerably more detailed and reliable analysis of molecular interactions. Trends can be identified with some confidence and certain qualitative concepts can be made semiquantitative.

The extraction of detailed information about atomic interactions and properties from experimental molecular data is facilitated by the use of models relating a particular property to bond parameters and charge distributions. In many cases the available data exceed in quality the corresponding models.

Models are usually obtained qualitatively using classical electrodynamical arguments. Consequently they frequently neglect important effects explainable only by recourse to quantum mechanics. Prime examples of such models are the highly successful Rittner potential curve and dipole moment models.[2] These models describe interactions between two polarizable spheres with charges ±1.

Brumer and Karplus[3] have attempted to obtain and perhaps improve upon the Rittner models using a quantum mechanical formalism known as exchange perturbation theory.[4] Although they showed that these could be derived by making certain quantum mechanical approximations, they failed to improve upon them significantly. This was due primarily to the fact that the formalism they applied assumed that the electrons in the Hamiltonian were distinguishable and could thus be associated with a particular nucleus. This assumption effectively precludes inclusion of partial charge transfer effects, a major limitation of the Rittner theory.

In this paper we develop a perturbation formalism suitable for studying inter- and intra-molecular interactions which does not require an artificial division of the Hamiltonian into atomic components and an interatomic interaction potential. This formalism, implicit perturbation theory, has three essential characteristics:

(1) The zeroth-order wave function is chosen on physical grounds rather than with respect to an explicit perturbation.

(2) The perturbation series is obtained without partitioning the Hamiltonian into perturbed and unperturbed components.

(3) Kinetic energy operators are treated on an equal footing with potential energy operators.

This formalism in conjunction with empirical analysis gives us a procedure for obtaining and testing molecular models and relating them to charge distribution bond parameters and atomic properties. We apply the formalism here to obtain a dipole moment model for diatomic molecules; in the second paper of this series we test the model and compare it with the earlier models of Rittner,[2] Brumer and Karplus,[3] and DeWijn.[5]

Implicit Perturbation Theory

Conventional perturbation theory is designed to deal systematically with effects of small perturbations on physical systems when exact solutions of the appropriate Schrödinger equation are difficult to obtain and the properties of the unperturbed system are known with sufficient accuracy. In conventional perturbation theory the total Hamiltonian is expressed as a sum of a zeroth-order operator $H^{(0)}$ and a perturbation V. Normally it is assumed that the complete set of zeroth-order eigenfunctions $\psi_k{}^{(0)}$ and corresponding eigenvalues $E_k{}^{(0)}$ are known. Corrections to these are obtained, in the Rayleigh-Schrödinger (RS) scheme, by solving the set of equations

$$\bar{H}^{(0)}\psi_k{}^{(n)} + \bar{V}\psi_k{}^{(n-1)} = \left(\sum_{j=2}^{n-1} E_k{}^{(j)}\right) \psi_k{}^{(n-j)} \qquad (1)$$

where $\bar{H}^{(0)} = H^{(0)} - E^{(0)}$ and $\bar{V} = V - E^{(1)}$. This approach we term an explicit perturbation theory since the Hamiltonian is partitioned into zeroth order and perturbing operators in an explicit way.

Certain physical problems which logically call for a perturbation solution do not lend themselves to conventional approaches. For example, in the treatment of molecular interactions we may have available an approximate wave function $\tilde{\psi}$ chosen on the basis of physical considerations. If it is desired to treat $\tilde{\psi}$ as a zeroth-order wave function and to use an explicit perturbation theory to improve it, it is necessary to construct an unperturbed Hamiltonian corresponding to $\tilde{\psi}$ and to develop procedures for solving nth order equations.[6] Although the problem for obtaining $H^{(0)}$ and V can be solved formally,[6] the formal solution is frequently intractable. Furthermore, the decomposition of the Hamiltonian may be state dependent.

Thus, a perturbation theory not requiring an explicit partition of the Hamiltonian yet preordained by an appropriate wave function is desirable. Such a theory is developed below. We term it implicit perturbation theory.

Let $H(x)$ be a Hamiltonian operator for a system of particles functionally dependent on a parameter x in addition to appropriate coordinates and momenta. Let $\psi(x)$ be an exact eigenfunction with corresponding energy, $E(x)$, and $\tilde{\psi}(x)$ an approximate eigenfunction assumed expressible as a sum

$$\tilde{\psi}(x) = \sum_j g_j(x)h_j(x) \tag{2}$$

where g_j and h_j are well behaved functions of x. We define a zeroth-order wave function

$$\psi^{(0)}(x,x_0) = \sum_j g_j(x_0)h_j(x) \tag{3}$$

where x_0 is a particular choice of x. Clearly $\psi^{(0)}(x_0,x_0) = \tilde{\psi}(x_0)$.

Let $\{\chi_m(x,x_0)\}$ be a set of basis functions in the Hilbert space of functions occupied by the exact eigenfunctions of H. Then

$$\psi = \psi^{(0)}(x,x_0) + \sum_m c_m(x,x_0)\chi_m(x,x_0) \tag{4}$$

We wish to extract from the coefficients, c_m, in a well defined and systematic fashion, a series of progressively smaller corrections to $\psi^{(0)}$ such that

$$\psi = \sum_{n=0}^{\infty} \psi^{(n)} \tag{5}$$

Substituting eq 4 into the Schroedinger equation, premultiplying by $\chi_n{}^*$, and integrating leads to the set of equations

$$-\sum_m c_m(H_{nm} - ES_{nm}) = H_{n0} - ES_{n0} \tag{6}$$

where $H_{nm} = \langle \chi_n|H|\chi_m\rangle$ and $S_{nm} = \langle \chi_n|\chi_m\rangle$ with $\chi_0 \equiv \psi^{(0)}$

Using the definitions $(\mathbf{H} - E\mathbf{S})_{nm} = H_{nm} - ES_{nm}$, $(\mathbf{h} - E\mathbf{s})_n = H_{n0} - ES_{n0}$, $(\boldsymbol{\chi})_n = \chi_n$, and $(\mathbf{c})_n = c_n$ we can write

$$\mathbf{c} = -(\mathbf{H} - E\mathbf{S})^{-1}(\mathbf{h} - E\mathbf{s}) \tag{7}$$

with the corresponding eigenfunctions ψ expressible as

$$\psi = \psi^{(0)} + \mathbf{c}_{\mathrm{T}}\boldsymbol{\chi} \tag{8}$$

The subscript on $\mathbf{c}_{\mathrm{T}}$ indicates the transpose vector. To obtain an appropriate expansion of ψ we define a diagonal matrix $\mathbf{D}$ with elements $D_{nm} = \delta_{nm}(\epsilon_m - \epsilon)$ where the ϵ_m and ϵ comprise a set of energy values chosen to ensure that the diagonal elements of the matrix

$$-\mathbf{W} = (\mathrm{H} - E\mathrm{S}) - \mathbf{D} \tag{9}$$

are small compared to the elements of $\mathbf{D}$. We then expand $(\mathbf{H} - E\mathbf{S})^{-1} = (\mathbf{D} - \mathbf{W})^{-1}$ in a Taylor-like series,

$$(\mathrm{H} - E\mathbf{S})^{-1} = \mathbf{D}^{-1} + \mathbf{D}^{-1}\mathbf{W}\mathbf{D}^{-1} + \mathbf{D}^{-1}\mathbf{W}\mathbf{D}^{-1}\mathbf{W}\mathbf{D}^{-1} + \ldots \tag{10}$$

Assuming the series converges, the adroitness of the choice of the ϵ_n and ϵ affects the rate of convergence. Criteria for convergence of both this and Rayleigh-Schroedinger expansions are derived in paper 3 of this series. Equations 10 and 7 in some respects define a perturbation-like expansion of the wave function. However, since the total energy appears in each term, the expansion is not particularly useful except as a semiempirical scheme. Thus a further partitioning of terms is desirable. To obtain this we express the energy in the form

$$E = \sum_{n=1}^{\infty} E(n) \tag{11}$$

where successive terms in the series will be energy corrections corresponding to successive terms in the series eq 5. To obtain this correspondence we first partition $\mathbf{h} - E\mathbf{s}$ in eq 7 into the sum

$$\mathbf{h} - E\mathbf{s} = \mathbf{v} + \boldsymbol{\delta} \tag{12}$$

where

$$\mathbf{v} = \mathbf{h} - E(1)\mathbf{s} \tag{13}$$

and

$$\boldsymbol{\delta} = -\sum_{n=2}^{\infty} E(n)\mathbf{s} \tag{14}$$

We choose $E(1)$ to maximize the rate of convergence of eq 11. The best noniterative value of $E(1)$ extractible from $\psi^{(0)}$ is $E(1) = \langle\psi^{(0)}|H|\psi^{(0)}\rangle$. This corresponds to the sum $E^{(0)} + E^{(1)}$ in conventional perturbation theory but requires no partitioning of the Hamiltonian. We next express $-\mathbf{W}$ in eq 9 as the sum of a large component $\mathbf{V}$ and a small correction $\boldsymbol{\Delta}$:

$$-\mathbf{W} = \mathbf{V} + \boldsymbol{\Delta} \tag{15}$$

where

$$\mathbf{V} = \mathbf{H} - E(1)\mathbf{S} - \mathbf{D} \tag{16}$$

and

$$\boldsymbol{\Delta} = -\sum_{n=2}^{\infty} E(n)\mathbf{S} \tag{17}$$

Substituting eq 10–17 into eq 7 and ordering with respect to $\mathbf{V}$, $\mathbf{v}$, and $E(n)$, treating $\mathbf{V}$ and $\mathbf{v}$ as first-order terms, allows us to write $\mathbf{c}$ in the form

$$\mathbf{c} = \sum_{n=1}^{\infty} \mathbf{c}^{(n)} \tag{18}$$

with

$$\mathbf{c}^{(1)} = -\mathbf{D}^{-1}\mathbf{v} \tag{19}$$

$$\mathbf{c}^{(2)} = -\mathbf{D}^{-1}\mathbf{V}\mathbf{c}^{(1)} + E(2)\mathbf{D}^{-1}\mathbf{s} \tag{20}$$

while for $n > 2$,

$$\mathbf{c}^{(n)} = -\mathbf{D}^{-1}\mathbf{V}\mathbf{c}^{(n-1)} + \sum_{k=1}^{n-2} E(n-k)\mathbf{D}^{-1}\mathbf{S}\mathbf{c}^{(k)} + E(n)\mathbf{D}^{-1}\mathbf{s} \tag{21}$$

The nth order wave function is thus given by

$$\psi^{(n)} = \mathbf{c}_{\mathrm{T}}{}^{(n)}\chi \tag{22}$$

In summation form we have for the first few orders

$$\psi^{(1)} = -\sum_n \frac{V_{n0}\chi_n}{\epsilon_n - \epsilon} \tag{23}$$

and

$$\psi^{(2)} = \sum_{nm} \frac{V_{mn}V_{n0}\chi_n}{(\epsilon_m - \epsilon)(\epsilon_n - \epsilon)} + E(2)\sum \frac{S_{n0}\chi_n}{\epsilon_n - \epsilon} \tag{24}$$

where $V_{mn} = (\mathbf{V})_{mn}$ and $V_{n0} = (\mathbf{v})_n$. These equations are generalizations of the Rayleigh–Schrödinger equations, to which they reduce under conditions discussed in the next section. Singular terms are excluded from the sums.

The D Matrix and Energy Expansions

There is a flexibility associated with the manner in which the energy $E(n)$ can be determined from the wave functions through order $\psi^{(n-1)}$, energies through $E(n-1)$, and the total Hamiltonian.

A satisfactory relationship must be consistent with eq 11. An adroitly chosen correspondence should result in a rapidly converging series. The relationship, furthermore, may be dictated by physical or mathematical expediencies.

One possibility is the identification $E(n) = E^{(n)}$, where $E^{(n)}$ is the nth order Rayleigh–Schrödinger energy. It is of course necessary to express $E^{(n)}$ in terms of the total Hamiltonian since we are not assuming that the partitioning of the Hamiltonian associated with the zeroth-order wave function is known. This is easily accomplished. We simply multiply eq 1 by $\psi^{(0)*}$, integrate over all space, note that $\langle 0|H^{(0)}|m\rangle = 0$, and solve for $E^{(n)}$ to obtain

$$E^{(n)} = \langle 0|\bar{H}|n-1\rangle - \sum_{k=2}^{n-1} E^{(k)}\langle 0|n-k\rangle \qquad (n > 2) \quad (25)$$

where for convenience in notation we assume $\langle 0|0\rangle = 1$ and have defined

$$\bar{H} = H - E(1) \quad (26)$$

and

$$\langle n|\hat{O}|m\rangle = \int \psi^{(n)*}\hat{O}\psi^{(m)}\,\mathrm{d}\tau \quad (27)$$

For the special case, $n = 2$,

$$E^{(2)} = \langle 0|\bar{H}|1\rangle \quad (28)$$

The advantage of this choice is that results can be compared directly with calculations based on Rayleigh–Schrödinger perturbation theory, provided the **D** matrix is constructed appropriately.

Within RS theory it is well known that the wave function through order n can be used to calculate the energy through order $2n + 1$. The appropriate equations for $n > 1$ assuming $\langle\psi|\psi\rangle = 1$ and defining $\bar{V} = V - E^{(1)}$ are

$$E^{(2n)} = \langle n-1|\bar{V}|n\rangle - \sum_{k=2}^{n} E^{(k)} \sum_{j=0}^{k-1} \langle n+j-k|n-j\rangle \quad (29)$$

and

$$E^{(2n+1)} = \langle n|\bar{V}|n\rangle - \sum_{k=2}^{n} E^{(k)} \sum_{j=0}^{k-1} \langle n+1+j-k|n-j\rangle \quad (30)$$

These equations as written require a functional form for V. However, equivalent expressions can be written in terms of matrix elements of the total Hamiltonian. To obtain these we first add $\bar{V}|n\rangle$ to both sides of eq 1 and rearrange to obtain the recursion formula

$$\bar{V}|n\rangle = \bar{V}|n-1\rangle + \bar{H}|n\rangle - \sum_{k=2}^{n-1} E^{(k)}|n-k\rangle \quad (31)$$

Successive application of this equation yields

$$\bar{V}|n\rangle = \sum_{k=0}^{n} \bar{H}|k\rangle - \sum_{m=2}^{n}\sum_{k=2}^{m} E^{(k)}|m-k\rangle \quad (32)$$

Direct substitution into eq 29 and 30 then leads to $E^{(3)} = \langle 1|\bar{H}|1\rangle + E^{(2)}$ and, for $n > 1$

$$E^{(2n)} = \sum_{k=0}^{n} \langle n-1|\bar{H}|k\rangle - \sum_{m=2}^{n}\sum_{k=2}^{m} E^{(k)}\langle n-1|m-k\rangle - \sum_{k=2}^{n} E^{(k)} \sum_{j=0}^{k-1} \langle n+j-k|n-j\rangle \quad (33)$$

and

$$E^{(2n+1)} = \sum_{k=2}^{n} \langle n|\bar{H}|k\rangle - \sum_{m=2}^{n}\sum_{k=2}^{m} E^{(k)}\langle n|m-k\rangle - \sum_{k=2}^{n} E^{(k)} \sum_{j=0}^{k-1} \langle n+j+1-k|n-j\rangle \quad (34)$$

It is thus possible, using eq 33 and 34, to obtain energy corrections associated with a particular $\psi^{(0)}$ utilizing the total Hamiltonian H rather than a perturbation V.

A certain flexibility is associated with the construction of the **D** matrix. It is clear, for example, from eq 9 that if χ is an approximation to the nth state eigenfunction then ϵ_n should approximate the nth energy state. One approximation is given by

$$\epsilon_n = \langle \chi_n|\bar{H}|\chi_n\rangle \quad (35)$$

yielding an $\epsilon_n - \epsilon$ equivalent to a difference in energies through first order in the sense of conventional perturbation theory. If the set of states $\{\psi_n{}^{(0)}\}$ and corresponding eigenvalues are known these serve as satisfactory choices of ϵ_n.

Dipole Moment Model

In this section we apply implicit perturbation theory to the problem of obtaining a dipole moment equation which relates the dipole moment of diatomic molecules to bond lengths, charge distributions, charge polarizabilities, and charge overlap.

The procedure for obtaining a dipole moment model for a molecule AB with nuclear charges Z_{A} and Z_{B} involves analyzing the expectation value of the dipole moment operator,

$$\langle\mu\rangle = \frac{\langle\psi|\hat{\mu}|\psi\rangle}{\langle\psi|\psi\rangle} \quad (36)$$

where $\hat{\mu} = \mu_n + \mu_E$ and $\psi = \psi^{(0)} + \psi^{(1)} + \ldots$ with

$$\mu_N = \frac{(Z_{\mathrm{A}} - Z_{\mathrm{B}})}{2}\mathbf{R} + (Z_{\mathrm{A}} + Z_{\mathrm{B}})\mathbf{R}_c \quad (37)$$

and $\mu_E = \Sigma_k \mathbf{r}_k$. The vector $\mathbf{R} = (\mathbf{R}_{\mathrm{A}} - \mathbf{R}_{\mathrm{B}})/2$ is a vector connecting the two nuclei while $\mathbf{R}_{\mathrm{c}} = (\mathbf{R}_{\mathrm{A}} + \mathbf{R}_{\mathrm{B}})/2$ is a position vector to the geometric center of the molecule with $\mathbf{R}_{\mathrm{A}}$, $\mathbf{R}_{\mathrm{B}}$, and $\mathbf{r}_k$ position vectors to nuclei A and B and electron k, respectively. The choice of $\psi^{(0)}$ is made on physical grounds. The first-order correction to the wave function is obtained following the procedures outlined in the Implicit Perturbation Theory section.

An appropriate choice of $\psi^{(0)}$ is based on the following considerations. As two ground state neutral atoms approaching from infinity enter the curve-crossing region, the ground state becomes degenerate with the state corresponding to approaching ions; the matrix elements connecting the two states become nonnegligible. As a result, the atoms emerge from the region in a ground state a portion of the time and an excited state the remainder, with the relative probability determined by the interaction matrix. Because of the nonvanishing off-diagonal matrix elements connecting the initial states, the final states correspond neither to pure ionic nor pure neutral atom states but to mixtures of the two. As the atoms go through the curve-crossing region, charge is redistributed throughout the molecule. An effective charge f is transferred from one atom toward the other resulting in a rapid increase in the dipole moment from zero to fR. (This is not to say that the atoms acquire charges of $\pm f$ but that half the difference between the two charges is f.)

A proper description of changes occurring in the curve-crossing region requires degenerate perturbation theory. Since we are interested primarily in models of properties accurate near R_{e}, this complication can be avoided by an adroit choice of the zeroth-order wave function. Let R_0 be a value of R somewhat less than the curve-crossing separation, such that final state interactions are small, but greater than R_{e}, so that the distortion polarization effect is also small. The zeroth-order wave function $\psi^{(0)}$ then has atomic charge distributions frozen in shape at R_0, but centered on the nuclei and movable with them. The charge transfer effect appears in the zeroth order, but other effects such as polarization are effectively excluded until higher orders. Note that this choice of $\psi^{(0)}$ is R dependent.

Thus we let $\{\psi_n(R_0)\}$ be a complete orthonormal set of molecular states with corresponding eigenvalues $E_n(R_0)$. We assume these are approximately expressible in the form of single determinant SCF functions $\tilde{\psi}_n(R_0) = \mathcal{A}\chi_n \approx \psi_n(R_0)$ where

$$\chi_n = \Phi_n{}^1(1)\Phi_n{}^2(2)\ldots\Phi_n{}^N(N) \quad (38)$$

Here, $\mathcal{A}$ is an antisymmetrizer. The functions $\Phi_n{}^k = \phi_n{}^{Ak} + \phi_n{}^{Bk}$ are molecular spin orbitals with

$$\phi_n{}^{\alpha k} = \sum_j c_{nj}{}^{\alpha k}\,(R_0)\chi_j{}^{\alpha}(R_0) \tag{39}$$

linear combinations of basis functions, $\chi_j{}^{\alpha}$, centered on nucleus α. The $\Phi_n{}^j$ are assumed to satisfy the orthonormal conditions $\langle \Phi_n{}^j | \Phi_n{}^k \rangle = \delta_{jk}$ at $R = 0$. In the context of eq 3 we let R, c_{nj}, and χ_j play the roles of x, g_j, and h_j, respectively, and define a zeroth-order set of functions

$$\psi_n{}^{(0)}(R, R_0) = A \prod_{i=1}^{N} \Phi_n{}^i(i;R;R_0) \tag{40}$$

where

$$\Phi_n{}^i(i;R;R_0) = \sum_{j,\alpha} c_{nj}{}^{\alpha k}(R_0)\chi_j{}^{\alpha}(R) \tag{41}$$

The zeroth-order ground state $\psi^{(0)} = \psi_0{}^{(0)}$ then describes a hypothetical state of two converging interpenetrating charge clouds whose shapes are determined by the distribution at R_0. The charge distributions are thus not allowed to polarize as R decreases. We can now proceed to evaluate eq 36.

Let us first examine the integrals $\langle\psi|\psi\rangle = 1$ at $R = R_0$. As R decreases, additional overlapping of charge clouds occurs. Since overlap integrals vary exponentially with R, $\langle\psi|\psi\rangle \approx 1 + \epsilon(R)$ indicates an exponential dependence on R with $\epsilon(R_0) = 0$. An analysis of $\epsilon(R)$ suggests that it is the sum of two types of terms: those describing valence electron intermediate range attractive overlapping and those describing short-range Pauli Exclusion inner shell repulsive overlapping. The latter dies off quickly, dominating only at distance S less than R_e.

Since $\boldsymbol{\mu}_N$ is independent of electron coordinates, $\langle\boldsymbol{\mu}_N\rangle = \boldsymbol{\mu}_N$; furthermore, $\langle\psi|\boldsymbol{\mu}_E|\psi\rangle \approx \boldsymbol{\mu}_E{}^{00} + \boldsymbol{\mu}_E{}^{01}$ where $\boldsymbol{\mu}_E{}^{00} = \langle\psi^{(0)}|\boldsymbol{\mu}_E|\psi^{(0)}$ and $\boldsymbol{\mu}_E{}^{01} = 2\langle\psi^{(0)}|\boldsymbol{\mu}_E|\psi^{(1)}\rangle$. Since $\boldsymbol{\mu}_E$ is a one-electron operator its expectation value is conveniently expressed as

$$\boldsymbol{\mu}_E{}^{00} = \langle\chi_0|\boldsymbol{\mu}_E|\chi_0\rangle + \langle P\chi_0|\boldsymbol{\mu}_E|\chi_0\rangle \tag{42}$$

The operator P is a permutation operator representing all permutations of χ with appropriate signs. The second term on the right is zero at R_0. It increases rapidly at values of R less and R_e and represents an effect on the dipole moment due to Pauli Exclusion charge cloud overlapping.[3,8] This behavior is expected to be exponentially dependent on R and approximately describable by a function of the form $ke^{-\gamma R}\hat{\mathbf{R}}$ where k and γ are constants and $\hat{\mathbf{R}} = \mathbf{R}/R$ is a unit vector in the direction of $\mathbf{R}$.

The first term on the right-hand side of eq 42, to the extent that we can ignore the departure from orthonormality of the $\langle\Phi_m{}^k|\Phi_n{}^k\rangle$, can be written as

$$\langle\chi_0|\boldsymbol{\mu}_E|\chi_0\rangle = -\sum_k [\langle\phi_0{}^{Ak}|\mathbf{r}_k|\phi_0{}^{Ak}\rangle + 2\langle\phi_0{}^{Ak}|\mathbf{r}_k|\phi_0{}^{Bk}\rangle + \langle\phi_0{}^{Bk}|\mathbf{r}_k|\phi_0{}^{Bk}\rangle] \tag{43}$$

The one-center terms can be evaluated by replacing $\mathbf{r}_k$ by $\mathbf{R}_\alpha + \mathbf{r}_{k\alpha}$ and noting that the charge distributions are cylindrically symmetric; thus

$$\langle\phi_0{}^{\alpha k}|\mathbf{r}_k|\phi_0{}^{\alpha k}\rangle = \mathbf{R}_\alpha \left[n_\alpha{}^k \left\langle \phi_0{}^{\alpha k} \left| \frac{z_{k\alpha}}{R} \right| \phi_0{}^{\alpha k} \right\rangle \right] \tag{44}$$

where $n_\alpha{}^k = \langle\phi_0{}^{\alpha k}|\phi_0{}^{\alpha k}\rangle$ can be roughly regarded as the probability of finding the electron in the kth molecular spin orbital about center α and $z_{k\alpha} = z_k - z_\alpha$. To evaluate the two-center matrix elements in eq 43 we set $\mathbf{r}_k = \mathbf{R}_c + \mathbf{r}_{kc}$ and again apply cylindrical symmetry. Hence

$$2\langle\phi_0{}^{\mathrm{A}k}|\mathrm{r}_k|\phi_0{}^{\mathrm{B}k}\rangle = \mathbf{R}_c\left[n_{\mathrm{AB}}{}^k + 2\left\langle \phi_0{}^{\mathrm{A}k} \left| \frac{z_{kc}}{R} \right| \phi_0{}^{Bk} \right\rangle \right] \tag{45}$$

where $n_{\mathrm{AB}}{}^k = 2\langle\phi_0{}^{\mathrm{A}k}|\phi_0{}^{\mathrm{B}k}\rangle$ can be considered as approximating the charge in orbital ϕ^k shared by the two atoms. The matrix element on the far right of eq 44 represents a zeroth-order polarization contribution to the dipole moment. It reflects the departure from spherical symmetry of the $\phi_0{}^{\alpha k}$ functions at R_0. We thus designate the sum of these terms as $\boldsymbol{\mu}_{\mathrm{pol}}{}^{00}$.

Adding the contributions from $\boldsymbol{\mu}_E{}^{00}$ and $\boldsymbol{\mu}_N$, defining $q_\alpha = Z_\alpha - \sum_k n_\alpha{}^k$, and replacing $\mathbf{R}_{\mathrm{A}}$ by $\mathbf{R}/2 + \mathbf{R}_c$ and $\mathbf{R}_{\mathrm{B}}$ by $-(\mathbf{R}/2) + \mathbf{R}_c$, gives

$$\boldsymbol{\mu}_N + \boldsymbol{\mu}_E{}^{00} = \frac{q_{\mathrm{A}} - q_{\mathrm{B}}}{2}\mathbf{R} + ke^{-\gamma R}\hat{\mathbf{R}} + \boldsymbol{\mu}_{\mathrm{pol}}{}^{00} - 2\sum_k \langle\phi_0{}^{Ak}|z_{ck}|\phi_0{}^{Bk}\rangle\,\hat{\mathbf{R}} \tag{46}$$

The quantity q_α represents the charge on center α. Replacing z_{ck} by $z_{cv} + z_{vk}$ where $\mathbf{R}_v$ indicates the approximate center of overlap charge buildup and making the assumption that $\langle\phi_0{}^{\mathrm{A}k}|z_{vk}|\phi_0{}^{\mathrm{B}k}\rangle \approx 0$, i.e., the covalent overlap is symmetric about the point indicated by $\mathbf{R}_v$, leads to the result.

$$\boldsymbol{\mu}_N + \boldsymbol{\mu}_E{}^{00} = f\mathbf{R} + ke^{-\gamma R}\hat{\mathbf{R}} + \boldsymbol{\mu}_{\mathrm{pol}}{}^{00} + q_{\mathrm{AB}}\,z_{cv}\hat{\mathbf{R}} \tag{47}$$

where

$$f = (q_{\mathrm{A}} - q_{\mathrm{B}})/2 \tag{48}$$

with $q_{\mathrm{AB}} = -\sum_k n_{\mathrm{AB}}{}^k$, roughly the electronic charge shared by atoms A and B. According to eq 47, the dipole moment in zeroth order consists of an effective charge $\pm f$ separated by a distance R, a constant term representing the polarization present at R_0, an exponentially dependent term representing the Pauli Exclusion overlap effect on the dipole moment, and a term representing a covalent contribution to the dipole moment. The latter is proportional to the covalent charge buildup and to the difference in radii of the reacting atoms. Thus if the atoms are approximately the same size and if the bond is almost completely ionic this term is small. On the other hand, this term can be important if the reacting atoms are dissimilar in size or if the bond is largely covalent.

The remaining term to be considered is $\boldsymbol{\mu}_E{}^{01}$. To evaluate this we require a first-order wave function. According to eq 23

$$\psi^{(1)} = -\sum_n \frac{V_{n0}\chi_n}{\epsilon_n - \epsilon} \tag{49}$$

where the ϵ's are elements of the $\mathbf{D}$ matrix (Eq. 9), the χ_n are basis functions and

$$V_{n0} = H_{n0} - E(1)S_{n0} \tag{50}$$

with $H_{n0} = \langle\chi_n|H|\psi^{(0)}\rangle$, $S_{n0} = \langle\chi_n|\psi^{(0)}\rangle$, and $E(1) = \langle\psi^{(0)}|H|\psi^{(0)}\rangle$. Based on the discussion in the $\mathbf{D}$ Matrix and Energy Expansions section we make the identification $\epsilon_n = E_n(R_0)$, $\epsilon = E_0(R_0)$, and $\chi_n = \psi_n(R,R_0)$. Thus, substituting for $\psi^{(1)}$ in $\boldsymbol{\mu}_E{}^{01}$ gives

$$\boldsymbol{\mu}_E{}^{01} = \sum_n \frac{V_{n0}\boldsymbol{\mu}_{n0}}{E_n - E_0} \tag{51}$$

where $\boldsymbol{\mu}_{n0} = \langle\psi_n|\boldsymbol{\mu}_E|\psi_0\rangle$. To simplify the analysis of this term we assume $S_{n0} = 0$, an exact result at R_0 and an approximation at smaller R's. We next note that $V_{n0}(R_0)$ approaches zero as R approaches R_0. Furthermore by expanding the matrix elements into one- and two-center components we may write $V_{n0} = V_{n0}{}^{\mathrm{AA}} + V_{n0}{}^{\mathrm{BB}} + V_{n0}{}^{\mathrm{AB}}$. Thus $V_{n0}{}^{\mathrm{AA}} + V_{n0}{}^{\mathrm{BB}} = -V_{n0}{}^{\mathrm{AB}}(R_0)$. It follows that

$$V_{n0}(R) = H_{n0}{}^{\mathrm{AB}}(R) - H_{n0}{}^{\mathrm{AB}}(R_0) \tag{52}$$

The matrix element of the total Hamiltonian can be expressed as a sum of a kinetic energy term, $T_{n0}{}^{\mathrm{AB}}$, and a potential energy term, $U_{n0}{}^{\mathrm{AB}}$

$$H_{n0}{}^{\mathrm{AB}}(R) = T_{n0}{}^{\mathrm{AB}}(R) + U_{n0}{}^{\mathrm{AB}}(R) \tag{53}$$

The kinetic energy term has the form

$$T_{n0}{}^{\mathrm{AB}} = -\tfrac{1}{2}\sum_{k} \left[\langle \phi_n{}^{\mathrm{A}k}|\nabla^2|\phi_0{}^{\mathrm{B}k}\rangle + \langle \phi_n{}^{\mathrm{B}k}|\nabla^2|\phi_0{}^{\mathrm{A}k}\rangle\right] \quad (54)$$

since the dipole moment operator only couples single-particle excitations. Thus we may write $\boldsymbol{\mu}_E{}^{01}$ as a sum of two terms, $\boldsymbol{\mu}_{ET}{}^{01}$ and $\boldsymbol{\mu}_{EU}{}^{01}$, with

$$\boldsymbol{\mu}_{ET}{}^{01} = -2\sum_{n} \frac{T_{n0}{}^{\mathrm{AB}}(R) - T_{n0}{}^{\mathrm{AB}}(R_0)}{E_n - E_0}\boldsymbol{\mu}_{n0} \quad (55)$$

and

$$\boldsymbol{\mu}_{EU}{}^{01} = -2\sum_{n} \frac{U_{n0}{}^{\mathrm{AB}}(R) - U_{n0}{}^{\mathrm{AB}}(R_0)}{E_n - E_0}\boldsymbol{\mu}_{n0} \quad (56)$$

The first of these represents a dynamic rather than static contribution to the dipole moment. It is a quantum mechanical effect completely missing in classical models of the Rittner type. From an examination of eq 54 it appears that the R dependence of this term is strongly coupled to the R dependence of charge overlap. However, the virial theorem suggests that its R dependence closely approximates that of the potential energy in form.

The second term, $\boldsymbol{\mu}_{EU}{}^{01}$, is a static factor related primarily to the electromagnetic response of the charge clouds to charges on opposite centers. To extract the R dependence we expand $U_{n0}{}^{\mathrm{AB}}$ in the form

$$U_{n0}{}^{\mathrm{AB}} = -\sum_{k,\gamma}\sum_{\alpha\neq\beta} \left\langle \phi_n{}^{\alpha k}\left|\frac{Z_\gamma}{r_{k\gamma}}\right|\phi_0{}^{\beta k}\right\rangle - \sum_{k,\alpha\neq\beta} \left\langle \phi_n{}^{\alpha k}\left|\frac{Z_\beta}{r_{k\beta}}\right|\phi_0{}^{\alpha k}\right\rangle + M_{\mathrm{coul}} + M_{\mathrm{hyb}} + M_{\mathrm{exc}} \quad (57)$$

where

$$M_{\mathrm{coul}} = \sum_{\alpha\neq\beta}\sum_{k\neq l}\left[\left\langle \phi_n{}^{\alpha k}(1)\phi_n{}^{\beta l}(2)\left|\frac{1}{r_{12}}\right|\phi_0{}^{\alpha k}(1)\ \phi_0{}^{\beta l}(2)\right\rangle - \left\langle \phi_n{}^{\alpha k}(1)\phi_n{}^{\beta l}(2)\left|\frac{1}{r_{12}}\right|\phi_0{}^{\beta k}(2)\phi_0{}^{\alpha l}(1)\right\rangle\right] \quad (58)$$

with similar definitions for the hybrid and exchange matrix elements, M_{hyb} and M_{exc}. Three terms in eq 57 depend on charge overlap: the first, M_{hyb}, and M_{exc}.

We next introduce expansions of the form

$$\frac{1}{r_{k\alpha}} = \sum_{lm}\frac{4\pi}{2l+1}\frac{r_<{}^l}{r_>{}^{l+1}}Y_l{}^m(\hat{\mathbf{r}}_{k\beta})Y_l{}^{m*}(\hat{\mathbf{R}}) \quad (59)$$

and

$$\frac{1}{r_{ij}} = \sum_{lm}\frac{4\pi}{2l+1}\frac{r_<{}^l}{r_>{}^{l+1}}Y_l{}^m(\hat{\mathbf{r}})Y_l{}^{m*}(\hat{\mathbf{R}}_{\alpha\beta}) \quad (60)$$

where $\mathbf{r} = \mathbf{r}_{i\beta} - \mathbf{r}_{j\alpha}$ and $\mathbf{R}_{\alpha\beta} = \mathbf{R}_\alpha - \mathbf{R}_\beta$. To a good approximation, since most electron density associated with a given center is found within a sphere of radius $r \leq R$, we can write

$$\frac{1}{r_{k\alpha}} = \frac{1}{R} + \frac{z_{k\beta}}{R^2} + \frac{P_2{}^0(\hat{\mathbf{r}}_{k\beta})}{R^3} + \ldots \quad (61)$$

and

$$\frac{1}{r_{ij}} = \frac{1}{R} + \frac{z}{R^2} + \frac{P_2{}^0(\hat{\mathbf{r}})}{R^3} + \ldots \quad (62)$$

where we let $\mathbf{R}$ lie in the z,direction pointing from B to A. Introducing expansions 61 and 62 into integrals in eq 57 leads to the result

$$U_{n0}{}^{\mathrm{AB}} = -\frac{q_{\mathrm{A}}z_{\mathrm{B}}{}^{n0} - q_{\mathrm{B}}z_{\mathrm{A}}{}^{n0} + q_{\mathrm{AB}}z_{\mathrm{AB}}{}^{n0}(R)}{R^2} \quad (63)$$

where $z_{\mathrm{AB}}{}^{n0}(R)$ incorporates contributions due to M_{hyb} and M_{exc} and

$$z_\alpha{}^{n0} = \sum_k \langle \phi_n{}^{\alpha k}|z_{k\alpha}|\phi_0{}^{\alpha k}\rangle \quad (64)$$

To obtain eq 63, we have assumed that the term proportional to $1/R$ is negligible due to the factor $\langle \phi_n{}^{\alpha k}|\phi_0{}^{\alpha k}\rangle$ appearing in the numerator. We have also neglected terms higher than $1/R^2$ and effects due to Pauli Exclusion overlapping. Similarly we can expand $\boldsymbol{\mu}_{n0}$ as

$$\boldsymbol{\mu}_{n0} = (z_{\mathrm{A}}{}^{0n} + z_{\mathrm{B}}{}^{0n} + z_{\mathrm{AB}}{}^{0n})\hat{\mathbf{R}} \quad (65)$$

Introducing eq 65 and 63 into eq 56 and identifying the term in $U_{n0}{}^{\mathrm{AB}}(R_0)$ with a zeroth-order polarization, $\boldsymbol{\mu}_{\mathrm{pol}}{}^{01}(R_0)$, yields

$$\boldsymbol{\mu}_{EU}{}^{01} = -\frac{2}{R^2}\sum_n\left[\frac{(q_{\mathrm{A}}z_{\mathrm{B}}{}^{n0} - q_{\mathrm{B}}z_{\mathrm{A}}{}^{n0} + q_{\mathrm{AB}}z_{\mathrm{AB}}{}^{n0})}{E_n - E_0} \times (z_{\mathrm{B}}{}^{n0} + z_{\mathrm{B}}{}^{n0} + z_{\mathrm{AB}}{}^{n0})\hat{R}\right] + \boldsymbol{\mu}_{\mathrm{pol}}{}^{01}(R_0) \quad (66)$$

To simplify further we assume that the excitations can be associated primarily with one center or the other. Thus the set $\{n\}$ reduces to sets $\{n_{\mathrm{A}}\}$ and $\{n_{\mathrm{B}}\}$. Furthermore $E_{n\mathrm{A}} - E_0 \approx E_n{}^{\mathrm{A}} - E_0{}^{\mathrm{A}}$ and $E_{n\mathrm{B}} - E_0 \approx E_n{}^{\mathrm{B}} - E_0{}^{\mathrm{B}}$ are approximately differences in atomic energies. Equation 66 then reduces to

$$\boldsymbol{\mu}_{EU}{}^{01} = \left[\frac{q_{\mathrm{B}}\alpha_{\mathrm{A}} - q_{\mathrm{A}}\alpha_{\mathrm{B}}}{R^2} + \epsilon_{\mathrm{AB}}(R)\right]\hat{R} \quad (67)$$

with

$$\epsilon_{\mathrm{AB}}(R) = -\frac{2}{R^2}\sum_n\frac{z_{\mathrm{AB}}{}^{n0}}{E_n - E_0}[q_{\mathrm{A}}z_{\mathrm{B}}{}^{n0} - q_{\mathrm{B}}z_{\mathrm{A}}{}^{n0} + q_{\mathrm{AB}}(z_{\mathrm{B}}{}^{n0} + z_{\mathrm{B}}{}^{n0} + z_{\mathrm{AB}}{}^{n0})] \quad (68)$$

and

$$\alpha_{\mathrm{A}} = 2\sum_n\frac{(z_{\mathrm{A}}{}^{n0})^2}{E_n{}^{\mathrm{A}} - E_0{}^{\mathrm{A}}} \quad (69)$$

The term ϵ_{AB} is proportional to the overlap between zeroth order and excited orbitals while α_{A} represents the polarizability of atom A. If we further note that $q_{\mathrm{A}} + q_{\mathrm{B}} + q_{\mathrm{AB}} = 0$ for uncharged molecules we can write

$$\boldsymbol{\mu}_{EU}{}^{01} = \left[-f\frac{\alpha_{\mathrm{A}} + \alpha_{\mathrm{B}}}{R^2} + q_{\mathrm{AB}}\frac{\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}}}{2R^2} + \epsilon_{\mathrm{AB}}(R)\right]\hat{R} \quad (70)$$

The first term represents the mutual polarization of two hypothetical ions whose charges are $\pm f$. The second is equivalent to a polarization of opposite ions by an overlap charge situated at the center of the molecule. In rare gas molecules where $f \approx 0$, terms of this type account for the fact that collision induced moments vary exponentially with R and are proportional to differences in atomic polarizabilities.[8] The term ϵ_{AB} contains similar interactions. An analysis of the remaining terms yields in the lowest approximation the term $4q_{\mathrm{AB}}(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})/R^3$.

Collecting, absorbing the zeroth-order polarization contribution into the $1/R^3$ terms, and incorporating the kinetic energy contribution into the exponential term leads to the dipole moment model

$$\mu = fR\left(1 - \frac{\alpha_{\mathrm{A}} + \alpha_{\mathrm{B}}}{R^3}\right) + cR\left(2\frac{z_{cv}}{R} - 7\frac{\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}}{R^3}\right) + ke^{\gamma R} \quad (71)$$

where $c = -q_{\mathrm{AB}}/2 = (q_{\mathrm{A}} + q_{\mathrm{B}})/2$. According to this model the dipole moment of a diatomic molecule can be resolved into three principal components. The first of these corresponds to the dipole moment associated with two hypothetical charges $\pm f$ centered on the respective nuclei. The second represents the dipole moment due to a covalent charge centered in the overlap region. This charge polarizes the charge clouds centered on the two nuclei. The third primarily represents short-range overlapping effects.

In highly polar molecules the first term should predominate at large R. In very covalent molecules, whose component atoms are quite different in size, the second term should contribute significantly to the dipole moment. The model should apply equally well to molecules ranging from highly polar to homonuclear. In the latter case the dipole moment given by eq 71 reduces to zero as it should. This model in conjunction with experimental data can be used to explain trends in charge distributions in diatomic molecules across the periodic table. This possibility is explored in part 2 of this series.

Acknowledgment. The authors wish to thank Dr. Luis Kahn, Dr. C. W. Kern, and Mr. Rudolf Goldflam for helpful comments. They also wish to acknowledge the support of Battelle Memorial Institute and the Robert A. Welch Foundation through Grant No. E-397.

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Theory of the Chemical Bond. 2. Dipole Moments of Alkali Halide Molecules, Bond Polarity, and Differential Charge Affinity

Robert L. Matcha*[1a,b] and Stephen C. King, Jr.[1c]

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77004, and Battelle Memorial Institute, Columbus, Ohio 44201.
Received August 27, 1974

Abstract: An accurate dipole moment model is used to analyze dipole moments of alkali halide molecules. It is found that for these molecules the effective charge transferred during molecular formation, f, ranges systematically from 0.76 to 0.99 in an order predictable from the periodic table. The f's are related to atomic parameters by the equation $f = (q_M - q_X)/2$ where q_α is the ideal charge of atom α. The model is found to predict equilibrium dipole moments and slopes for alkali halides which differ on the average from experimental values by 0.33 and 1.5%, respectively. A complete table of alkali halide dipole moments is constructed; given are coefficients in the equation $\mu_{v,J} = \mu_0 + \mu_1(v + \frac{1}{2}) + \mu_{11}(v + \frac{1}{2})^2 + \mu_0{}^J J(J + 1) + \mu_1{}^J J(J + 1)(v + \frac{1}{2})$, where v and J are vibrational and rotational quantum numbers, respectively. The model is compared with several other dipole moment models. The model leads to a plausible interpretation of the signs of equilibrium dipole moments for such molecules as CF which have appeared to violate chemical intuition. A quantitative procedure for resolving chemical bonds into ionic and covalent components is proposed. The method derives from an analysis of alkali halide dipole moment measurements. Bonds are classified according to their polarity $f = (q_A - q_B)/2$ and their covalency $c = (q_A + q_B)/2$. A new concept, the differential charge affinity, is introduced to explain trends in the bond polarities of alkali halide molecules. The relationship of this property to ionization potentials and electron affinities is explored. A comparison of bond polarities and differential charge affinities with the older concepts of ionic character and electronegativity is given.

The relationship of atomic interactions and molecular properties to bond parameters and charge distributions can be studied with the aid of appropriate models in conjunction with experimental data. Models of molecular properties are usually based on qualitative classical electrodynamic arguments and are self limiting in that they frequently do not incorporate important quantum mechanical effects. It is therefore desirable to derive models within the framework of a quantum mechanical formalism.

One procedure for facilitating this endeavor was developed in the first paper[2] of this series (1). There, a model relating dipole moments to bond lengths in diatomic molecules was derived using a formalism termed implicit perturbation theory. The model has the form

$$\mu = fR\left(1 - \frac{\alpha_A + \alpha_B}{R^3}\right) + cR\left(2\frac{z_{cv}}{R} - 7\frac{(\alpha_A - \alpha_B)}{R^3}\right) + ke^{-\gamma R} \qquad (1)$$

The first term represents the dipole moment associated with two hypothetical polarizable charges $\pm f$ located at the two nuclei. The second term describes the dipole moment associated with an overlap charge $-2c$ located a distance $-z_{cv}$ toward A from the geometric center of the molecule. This charge induces moments in the partially charged ions. The third term approximates collision-induced moments at distances less than R_e in addition to effects due to kinetic energy variations with R.

In this paper we introduce a dipole moment model appropriate to highly polar molecules and evaluate it by analyzing experimental dipole moment data. The functional form we adopt is suggested both by the quantum mechanical model and the classical arguments of Rittner.[3a] Constants are obtained empirically by demanding the best possible fit with experimenta alkali halide data. Trends among the fitted constants are examined graphically to determine the correlation between actual and expected behavior.

Based on an analysis of the constants, we attempt to deduce new information pertaining to bond formation and to evaluate