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A. D. Buckingham<sup>a</sup>; P. W. Fowler<sup>a</sup>; A. J. Stone<sup>a</sup>

<sup>a</sup> Department of Theoretical Chemistry, University Chemical Laboratory, Cambridge, England

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## Electrostatic predictions of shapes and properties of Van der Waals molecules

by A. D. BUCKINGHAM, P. W. FOWLER and A. J. STONE

Department of Theoretical Chemistry, University Chemical Laboratory,  
Lensfield Road, Cambridge, CB2 1EW, England

The application of long-range models to shapes and dipole moments of Van der Waals complexes is reviewed. A simple model incorporating electrostatic interactions through distributed point multipoles, and short-range repulsion through hard spheres, has wide predictive power for the shapes of hydrogen-bonded and other complexes. Successes and limitations of the model are discussed. Inclusion of a distributed polarizability allows semiquantitative prediction of dipole moments of complexes.

### 1. Introduction

This paper reviews the understanding of Van der Waals molecules that can be gained from the long-range theory of intermolecular forces. Our particular interest is in modelling the shapes and properties of hydrogen-bonded complexes formed by polar (or quadrupolar) monomers.

In a Van der Waals molecule the monomer subunits retain to a large extent their separate identities, as shown by the geometrical structure and vibrational frequencies of the complex. It is natural, therefore, to describe the structure and bonding of weakly bound complexes in terms of the isolated monomers, treating the interaction as a perturbation. For large separations, there is a well established theory of intermolecular forces (Buckingham 1967, 1978) leading to a partitioning of the interaction energy into distinct long-range contributions: electrostatic, induction and dispersion. At short range, overlap repulsion and charge transfer become significant.

The electrostatic energy arises from the interaction of the two undistorted charge clouds; the induction (or polarization) energy arises from the distortion of each charge cloud in the field of the other; the dispersion energy comes from correlation between monomers of the quantum-mechanical fluctuations in electron positions. Overlap repulsion is caused by exchange effects and charge-cloud interpenetration. Charge-transfer energies come from donor-acceptor interaction between filled orbitals of one monomer and the virtual orbitals of the other.

Perturbation theory based on a multipole expansion of the interaction Hamiltonian may be used to express each long-range energy as a series in inverse powers of the separation, with expansion coefficients depending on the permanent moments (electrostatic), static polarizabilities (induction), and polarizabilities at imaginary frequencies (dispersion) of the monomers (Buckingham 1967, 1978).

The expansions are strictly valid only in regions of negligible overlap. At shorter distances the unexpanded energy contributions may still be defined, and various schemes for decomposition of the interaction energy are in use (Morokuma 1971, Hayes and Stone 1983 a, b). Although the series expansions are in principle subject to exchange and overlap corrections, they may still provide a very good approximation to

the attractive intermolecular potential, even at the potential minimum. In *ab initio* SCF calculations on the Ne–HF complex (Fowler and Buckingham 1983) it was found that, after elimination of basis-set superposition effects, the long-range induction energy matched the interaction energy all the way in to the minimum near  $R(\text{Ne} \dots \text{H}) = 2.9 \text{ \AA}$ . (Dispersion contributions are not present in an SCF calculation.) Similarly, a long-range expression fitted the interaction dipole moment of  $\text{Ne} \dots \text{HF}$  over the same range of distance.

## 2. A model for geometries

Morokuma-type decomposition of the SCF interaction energy for a variety of H-bonded dimers (Umeyama and Morokuma 1977, Kollman 1977 b) has shown that the electrostatic contribution is a large fraction of the binding energy; more importantly, it dominates the angular variation of the total energy. Calculations by Rendell *et al.* (1985) and Hurst *et al.* (1985) confirm this approximate cancellation of polarization and exchange repulsion.

A model for the shape of the H-bonded and other dimers therefore needs to include the electrostatic interaction (to give an angular minimum) and a repulsive potential (to give a radial minimum). Such a model has been proposed (Buckingham and Fowler 1983, 1985) and is discussed further in this article.

The charge distribution of a molecule is represented by a set of point multipoles determined from a *distributed multipole analysis* (DMA) of an *ab initio* wavefunction (Stone 1981). Each atom carries a charge, a dipole and a quadrupole calculated by a procedure analogous to the usual Mulliken population analysis of the charge density. Combination of the point multipoles recovers the total molecular charge, dipole and quadrupole moments of the given wavefunction.

The *distributed* nature of the multipoles is an important feature of the model. At large separations a single-centre multipole expansion of the electrostatic energy is adequate, where only the longest-range term involving the lowest-order non-vanishing moment is significant, e.g. for a pair of HF molecules this would be the dipole–dipole energy varying as  $R^{-3}$ . At the distances characteristic of Van der Waals complexes, higher molecular multipoles are required and convergence problems are found. Brobjer and Murrell (1981) observed that the logarithm of the  $2^n$ -pole moment of a molecule grows approximately linearly with  $n$ . A multi-site expansion gives a better description of the molecular electrostatic potential at shorter range (Stone 1981) and is also compatible with familiar valence concepts. A multipole moment describes a departure from spherical symmetry, and thus an atomic multipole describes the distortion of an atom from local spherical symmetry when that atom forms part of a molecule. Features such as lone pairs and bonding pairs which are revealed by density difference (molecule– $\Sigma$  atoms) maps (Steiner 1976) are thus *represented* by atomic multipoles. An anisotropic bonding density such as that of the  $\pi$  orbitals in  $\text{C}_2\text{H}_4$  is represented by a bond quadrupole. It is clear that a single-site expansion is a relatively clumsy way of describing *local* distortions of atoms on the periphery of a molecule and will require higher orders of spherical harmonic than a distributed, multi-site expansion (Stone 1981).

Other workers have used sets of point charges to model the electrostatic potential around a molecule. Brobjer and Murrell (1981, 1982) fit the values and positions of the charges to experimental total multipole moments. In order to mimic, e.g., the three non-bonding pairs on F in HF or the lone pairs on O in  $\text{H}_2\text{O}$ , Kollman (1977 a) places off-axis charges at positions determined by the assumed hybridization and the Van der

Waals radii. Off-axis charges predict, for example, the correct bent geometry of  $(\text{HF})_2$ , whereas using axial charges it is necessary to fit to molecular multipoles up to hexadecapole to obtain a bent equilibrium geometry (Brobjer and Murrell 1982). Our model automatically includes the non-bonding density through the dipole and quadrupole on F. The multipoles are calculated directly from an *ab initio* wavefunction, thus avoiding the arbitrariness inherent in a fitted point-charge model. However, there is considerable scope for choice in the means of describing the intermolecular electrostatic potential; for example one could select a variety of sites or include local octupoles; but we believe that the approach through distributed atomic multipoles gives a reliable, convenient and transferable representation at distances appropriate to the equilibrium separation in a Van der Waals molecule (Stone and Alderton 1985).

The second important ingredient of the model is the way it treats the shapes of the monomer molecules. Short-range repulsive forces define the size and shape of the monomers. In the present model, hard spheres are placed on the atomic centres to simulate the repulsion. Pauling's (1960) values of the Van der Waals radii  $\sigma(\text{X})$  are used for heavy atoms.  $\text{CH}_2$  and  $\text{CH}_3$  groups are treated as spheres of radius  $2\text{ \AA}$ . Protons attached to heavy atoms are assumed to lie within the hard sphere of their bonded neighbour. Thus the distance  $R(\text{X} \dots \text{H-Y})$  in hydrogen-bonded complexes is approximated by assuming that the spheres X and Y are in contact. This is often accurate to within  $0.1\text{ \AA}$  (Buckingham and Fowler 1985). Use of hard-sphere radii is of course a crude approximation, and may lead to difficulties for non-hydrogen-bonded complexes. Other representations of the repulsion could be used; for example, it would be possible to parameterize the repulsion using atom-atom potentials fitted from crystallographic data.

The equilibrium structure of a complex  $\text{A} \dots \text{B}$  is predicted by a constrained minimization of the electrostatic interaction energy of the two assemblies of point multipoles, subject to the condition that no atoms approach closer than the sum of their hard-sphere radii. The total energy is a sum of pair terms:

$$U = \sum_{a \in \text{A}} \sum_{b \in \text{B}} U_{ab}$$

where (in atomic units)

$$U_{ab} = q^a q^b / R - R_\alpha (\mu_\alpha^b q^a - \mu_\alpha^a q^b) / R^3 + (3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}) (q^a \theta_{\alpha\beta}^b + q^b \theta_{\alpha\beta}^a - 3\mu_\alpha^a \mu_\beta^b) / 3R^5$$

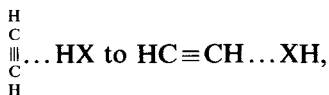
$\mathbf{R}$  is the vector from site  $a$  in A to site  $b$  in B,  $q$ ,  $\mu$ ,  $\theta$  are site charge, dipole and quadrupole moments, respectively, and

$$R \geq \sigma(a) + \sigma(b)$$

### 3. Results and discussion

In spite of its simplicity, this model is successful in predicting the shapes of Van der Waals complexes. Buckingham and Fowler (1983, 1985) report angular geometries of over 50 complexes. In 29 cases where an experimental structure is known, the predictions are qualitatively, and often quantitatively, correct. Thus the model predicts that  $\text{HF} \dots \text{HF}$  is bent whereas  $\text{OC} \dots \text{HF}$  is linear. (See the 1985 paper for a list of references to the experimental structures.) Hydrogen halides and hydrogen cyanide attach in  $\text{C}_{3v}$ -fashion to  $\text{NH}_3$  and  $\text{PH}_3$ , i.e.  $\text{H}_3\text{N} \dots \text{H-X}$  for HF, HCl, HCN. The model

distinguishes correctly between alternative hydrogen-bonded structures, e.g. finding that HF...HCl is preferred to HCl...HF,



and OC...HX to CO...HX.

The bond angles for low-symmetry complexes are often in quantitative agreement with experiment. Two cases of striking agreement are H<sub>2</sub>CO...HF (predicted COF=110°; experimental value 109.5° (Baiocchi and Klemperer 1983)), and H<sub>2</sub>S...HF (HF predicted to make an angle of 80° with the H<sub>2</sub>S plane; experimental value 89° (Viswanathan and Dyke 1982)).

It is important to note that pure dipole-dipole interaction favours linear HF...HF and the C<sub>2v</sub> structures  $\overset{\text{H}}{\text{H}} \text{>O} \dots \text{HF}$  and  $\overset{\text{H}}{\text{H}} \text{>C=O} \dots \text{HF}$ , for example. Although the dipole-dipole term is the *longest*-range term, others are significant in the long-range expansion when applied at typical Van der Waals separations, and these are implicitly included by a distributed multipole model. Predicted geometries are the result of an interplay of the electrostatics and molecular shape. At very long range a T-shaped dimer of CO<sub>2</sub> is favoured by quadrupole-quadrupole interactions, but the elongated shape of the molecules favours a skew-parallel shape where opposite atomic charges approach as closely as allowed by the repulsive forces. There is some experimental evidence that the parallel structure is correct (Barton *et al.* 1979) but this is a subject of debate (Lobue *et al.* 1984).

An empirical rule has been proposed by Legon and Millen (1982) to rationalize the geometries of hydrogen-bonded complexes. It states that the geometry of a gas-phase dimer B...HX can be obtained from the location of non-bonding and  $\pi$  bonding electron pairs on B by assuming that the axis of HX coincides with the axis of a non-bonding pair on B. If B has no non-bonding pairs but has  $\pi$ -bonding pairs, the axis of HX intersects the  $\pi$ -bond and is perpendicular to the nodal plane of the  $\pi$ -orbital. In other words the proton acts as a probe for lone pairs, or, in their absence, for  $\pi$ -bonds in the proton acceptor. The rule gives results in qualitative agreement with experiment and with our model. In high-symmetry cases agreement is complete, e.g. HCN...HCN, H<sub>3</sub>N...HF, where the hydrogen bond is linear. In lower-symmetry examples, e.g. H<sub>2</sub>CO...HF, HF...HF, the hydrogen bond is not exactly linear, the hydrogen-halide axis lying at a few degrees to the line of heavy atoms and the direction of attack of HX is not quite along the direction of the lone pairs expected from simple hybridization arguments. Our model predicts such deviations, but the Legon-Millen rule would require refinement, perhaps along the lines of valence-shell-electron-pair repulsion theory. Del Bene's 'Generalized hybridization model' (1973, 1975 a, b) permits small deviations for linearity of hydrogen bonds as a result of long-range dipole-dipole interactions.

Although at first sight the Legon-Millen rule is a 'chemical' rationalization, and not connected with electrostatics, it can be interpreted as a qualitative electrostatic model. The rule implies that the proton in HX seeks out electron-rich regions of the charge density of B; as noted above, these are described by the distributed multipoles, hence the qualitative agreement of the two approaches.

This comparison shows that the success of the simple DMA + hard-sphere model depends on having a satisfactory description of the overall charge density, rather than highly accurate values of the total molecular multipoles, and explains why SCF

wavefunctions are adequate. One case where the SCF multipoles might be expected to be unreliable is the CO molecule. At the Hartree–Fock limit the total dipole of CO has the (incorrect) sense  $C^+O^-$  and correlation effects must be included to give the observed  $C^-O^+$  direction. Even so, SCF distributed multipoles correctly predict that hydrogen halides and cyanide coordinate to the carbon ( $OC \dots HX$ ) rather than to the oxygen ( $CO \dots HX$ ) (Buckingham and Fowler 1985). Inclusion of correlation by Møller–Plesset perturbation theory increases the energy difference in favour of C coordination. Similarly, the complex of CO and  $BF_3$  is correctly predicted to be  $C_{3v} OC \dots BF_3$  at both SCF and correlated levels. For an *ab initio* comparison of the  $OC \dots HF$  and  $CO \dots HF$  structures, see Curtiss *et al.* (1985).

Although the model is successful in predicting the geometry of hydrogen-bonded and some non-hydrogen-bonded complexes (e.g. the halogen dimers), it has limitations for some ‘anti-hydrogen-bonded’ structures (Baiocchi *et al.* 1983). The basic model predicts bent hydrogen-bonded structures for  $FH \dots FCl$  and  $FH \dots Cl_2$  when the  $F \dots Cl$  distance is fixed at 3.15 Å, the sum of the Van der Waals radii. But from experiment (Novick *et al.* 1976, Baiocchi *et al.* 1982) these dimers are known to adopt the ‘anti-hydrogen-bonded’ structures  $HF \dots ClF$  and  $HF \dots Cl_2$  with much shorter  $F \dots Cl$  distances, e.g. 2.76 Å in the  $ClF$  complex. Morokuma-analysis of SCF energies shows that the binding of the anti-hydrogen-bonded structures is still predominantly electrostatic (Umeyama and Morokuma 1977, Rendell *et al.* 1985) and that the electrostatic interaction is responsible for the greater stability of the anti-hydrogen-bonded structure. The assumption of hard spheres needs modification in this case, to allow closer approach of F and Cl. A study of complexes for which the basic model may be inadequate is in the press (Hurst *et al.* 1986).

As described so far, the model excludes the mutual distortion of the interacting molecules. The induction energy is usually not important for prediction of geometries of hydrogen-bonded complexes, but induction is the major source of the change of dipole moment on complex formation. Unlike electrostatic energy, induction energy is not pairwise additive and if included in a model of the hydrogen bond would allow non-additivity effects to be studied. Hydrogen bonding is a cooperative phenomenon; formation of one hydrogen bond polarizes the monomers in such a way as to make the formation of a second more favourable in some approach geometries. Kollman (1977 b) has noted that non-additivity in  $(H_2O)_n$  clusters is explicable in terms of changes induced in the electrostatic potential by complexation.

#### 4. A model for dipole moments of complexes

The dipole moment of an interacting pair of molecules may differ from the vector sum of the permanent dipoles of the monomers for three distinct reasons: (i) dipoles are induced in each molecule by the non-uniform electric field of the neighbour; (ii) the charge distribution may be distorted by dispersion forces; (iii) the electron distribution and nuclear configuration may be distorted by short-range forces. Large enhancements of dipole on formation of Van der Waals complexes have been measured, e.g.  $\Delta\mu = 0.60$  D for  $H_3P \dots HCN$  (Legon and Willoughby 1984), 0.60 D for  $CO_2 \dots HF$  (Baiocchi *et al.* 1981), and 0.49 D for  $OC \dots BF_3$  (Janda *et al.* 1978, Altman *et al.* 1983 a).

As the dimer geometries are successfully predicted by an electrostatic model, we expect that the first, inductive effect will largely explain the dipoles. A model to test this hypothesis is described in the present section.

The electric field around a molecule is well represented by distributed multipoles; for similar reasons the response of a molecule to a non-uniform field should be

described by a distributed polarizability. Stone (1985) has developed an *ab initio* method for partitioning molecular polarizability into atomic contributions using an approach similar to his DMA (1981). We shall not describe the details of distributed polarizability analysis (DPA) here, but note that for each atom of a molecule in an external field there is a set of *induced* point multipoles related by a set of coefficients to the potential, field, field gradient... at *all* atomic sites. These response coefficients can be calculated by coupled-Hartree-Fock theory (Stone 1985) and can be combined to recover the molecular dipole polarizability and higher polarizabilities.

For a linear molecule lying along the field direction, an applied field induces a dipole through changes in the charge and dipole on each atom *i*. These may be expanded in terms of the electrostatic potential *V*, field  $F_z$  and field-gradient  $F_{zz}$  at all atoms *j*:

$$\Delta q^{(i)} = \sum_j \left\{ -\alpha_{00,00}^{(i,j)} V^{(j)} + \alpha_{00,10}^{(i,j)} F_z^{(j)} + \frac{1}{2} \alpha_{00,20}^{(i,j)} F_{zz}^{(j)} \dots \right\}$$

$$\Delta \mu^{(i)} = \sum_j \left\{ -\alpha_{10,00}^{(i,j)} V^{(j)} + \alpha_{10,10}^{(i,j)} F_z^{(j)} + \frac{1}{2} \alpha_{10,20}^{(i,j)} F_{zz}^{(j)} \dots \right\}$$

Table 1 gives the two site DPA models of five linear molecules calculated using large basis sets (Stone 1985).

Table 1. Distributed Polarizability Analysis for five linear molecules. A two-site model is used for each molecule (for CO<sub>2</sub> all the polarizability is placed on the O atoms). Each row represents the expansion of the induced atomic multipole in terms of the external potential *V*, field and field gradient at sites in the molecule. By charge conservation the coefficient of  $V^{(2)}$  is minus that of  $V^{(1)}$ , and  $\Delta q^{(2)} = -\Delta q^{(1)}$ . The quantities are in atomic units.

Molecule	Sites	Expansion	$\alpha_{l0,r0}(i,j)$					
			$j=1$ $l=0$	2 0	1 1	2 1	1 2	2 2
N <sub>2</sub>	1 ≡ N(z = -1.034)	$\Delta q^{(1)}$	1.694	-1.694	-0.366	-0.366	-1.147	1.147
	2 ≡ N(z = 1.034)	$\Delta \mu^{(1)}$	-0.366	0.366	2.276	-0.035	-2.898	-0.433
CO	1 ≡ C(z = -1.218)	$\Delta q^{(1)}$	1.402	-1.402	-0.202	-0.436	-0.863	0.611
		$\Delta \mu^{(1)}$	-0.202	0.202	3.422	-0.076	-7.351	-0.658
	2 ≡ O(z = 0.914)	$\Delta q^{(2)}$	-1.402	1.402	0.202	0.436	0.863	-0.611
		$\Delta \mu^{(2)}$	-0.436	0.436	-0.076	2.012	0.695	1.914
HCl	1 ≡ Cl(z = 0.0)	$\Delta q^{(1)}$	1.070	-1.070	-0.914	-0.187	0.698	1.166
		$\Delta \mu^{(1)}$	-0.914	0.914	6.014	-0.351	-5.941	-1.749
	2 ≡ H(z = 2.409)	$\Delta q^{(2)}$	-1.070	1.070	0.914	0.187	-0.698	-1.166
		$\Delta \mu^{(2)}$	-0.187	0.187	-0.351	1.076	0.668	0.505
HF	1 ≡ H(z = 1.732)	$\Delta q^{(1)}$	0.734	-0.734	0.150	0.336	-0.375	-0.202
		$\Delta \mu^{(1)}$	0.150	-0.150	0.378	-0.049	0.152	0.173
	2 ≡ F(z = 0.0)	$\Delta q^{(2)}$	-0.734	0.734	-0.150	-0.336	0.375	0.202
		$\Delta \mu^{(2)}$	-0.336	-0.336	-0.049	1.542	-0.325	-1.329
CO <sub>2</sub>	1 ≡ O(z = -2.196)	$\Delta q^{(1)}$	-0.613	-0.613	-0.113	-0.113	-0.346	0.346
	2 ≡ O(z = 2.196)	$\Delta \mu^{(1)}$	-0.113	0.113	5.159	-0.286	1.208	0.485

A model of the interaction dipole is constructed by using the DMA multipoles and DPA polarizabilities to calculate the dipole induced in each monomer by the proximity of the other. Using the DMA (Buckingham and Fowler 1985) and experimental geometries of the complexes, we compare the predictions of the DMA/DPA model with experiment for four hydrogen-bonded dimers in table 2. The good agreement shows that, for these complexes at least, the interaction dipole is predominantly inductive in origin. Previous discussions (Altman *et al.* 1982 b, 1983) of the 0.14 D difference between  $\Delta\mu$  for  $N_2 \dots HCl$  and  $OC \dots HCl$  neglected the dipole induced in HCl by its less polar partner; from table 2 it is seen that  $\Delta\mu^{HCl}$  is 40 per cent of the interaction dipole for  $OC \dots HCl$ . It is the dipoles induced in  $N_2$  and CO by the nearby HCl that scale approximately as the polarizabilities  $\alpha(N_2)$ :  $\alpha(CO)$ , rather than the total interaction dipoles. Table 2 also gives predicted dipole moments for the  $N_2 \dots HF$  and  $OC \dots HF$  dimers.

Table 2. Predictions of the DMA/DPA model for induced dipole moments of linear Van der Waals complexes.  $\Delta\mu^B$  is the dipole induced in monomer B. The experimental induced dipole is deduced from the second-order Stark effect after making allowances for the zero-point bending motion.† All dipoles are in debye.

B...HX	Predictions			Experimental $\Delta\mu^B \dots HX$
	$\Delta\mu^B + \Delta\mu^{HX} = \Delta\mu^B \dots HX$			
$N_2 \dots HCl$	0.210	0.055	0.265	0.25†
$N_2 \dots HF$	0.371	0.043	0.412	—
$OC \dots HCl$	0.245	0.136	0.381	0.39‡
$OC \dots HF$	0.454	0.096	0.550	—
$OCO \dots HCl$	0.320	0.121	0.441	0.45§
$OCO \dots HF$	0.548	0.069	0.617	0.60¶

† Altman *et al.* (1983 a).

‡ Altman *et al.* (1983 b).

§ Altman *et al.* (1982 a).

¶ Baiocchi *et al.* (1981).

### References

- ALTMAN, R. S., MARSHALL, M. D., and KLEMPERER, W., 1982 a, *J. chem. Phys.*, **77**, 4344.  
 ALTMAN, R. S., MARSHALL, M. D., and KLEMPERER, W., 1982 b, *Discuss. Faraday Soc.*, **73**, 116.  
 ALTMAN, R. S., MARSHALL, M. D., and KLEMPERER, W., 1983 a, *J. chem. Phys.*, **79**, 57.  
 ALTMAN, R. S., MARSHALL, M. D., KLEMPERER, W., and KRUPNOV, A., 1983 b, *J. chem. Phys.*, **79**, 52.  
 BAIOCCHI, F. A., DIXON, T. A., JOYNER, C. H., and KLEMPERER, W., 1981, *J. chem. Phys.*, **74**, 6544.  
 BAIOCCHI, F. A., DIXON, T. A., and KLEMPERER, W., 1982, *J. chem. Phys.*, **77**, 1632.  
 BAIOCCHI, F. A., and KLEMPERER, W., 1983, *J. chem. Phys.*, **78**, 3509.  
 BAIOCCHI, F. A., REIHER, W., and KLEMPERER, W., 1983, *J. chem. Phys.*, **79**, 6428.  
 BARTON, A. E., CHABLO, A., and HOWARD, B. J., 1979, *Chem. Phys. Lett.*, **60**, 414.  
 BROBJER, J. T., and MURRELL, J. N., 1981, *Chem. Phys. Lett.*, **77**, 601.  
 BROBJER, J. T., and MURRELL, J. N., 1982, *J. chem. Soc. Faraday Trans. II*, **78**, 1853; see also *Discuss. Faraday Soc.*, **73**, 128.  
 BUCKINGHAM, A. D., 1967, *Adv. chem. Phys.*, **12**, 107.  
 BUCKINGHAM, A. D., 1978, In *Intermolecular Interactions: From Diatomics to Biopolymers*, edited by B. Pullman (Wiley), chap. 1.  
 BUCKINGHAM, A. D., and FOWLER, P. W., 1983, *J. chem. Phys.*, **79**, 6426.  
 BUCKINGHAM, A. D., and FOWLER, P. W., 1985, *Canad. J. Chem.*, **63**, 2018.



- CURTISS, L. A., POCHATKO, D. J., REED, A. E., and WEINHOLD, F., 1985, *J. chem. Phys.*, **82**, 2679.
- DEL BENE, J. E., 1973, *J. chem. Phys.*, **58**, 3139.
- DEL BENE, J. E., 1975 a, *J. chem. Phys.*, **62**, 1314.
- DEL BENE, J. E., 1975 b, *J. chem. Phys.*, **63**, 4666.
- FOWLER, P. W., and BUCKINGHAM, A. D., 1983, *Molec. Phys.*, **50**, 1349.
- HAYES, I. C., HURST, G. J. B., and STONE, A. J., 1984 b, *Molec. Phys.*, **53**, 107.
- HAYES, I. C., and STONE, A. J., 1984 a, *Molec. Phys.*, **53**, 69, 83.
- HURST, G. J. B., FOWLER, P. W. STONE, A. J., and BUCKINGHAM, A. D., 1986, *Int. J. Quantum Chem.* (in the press).
- JANDA, K. C., BERNSTEIN, L. S., STEED, J. M., NOVICK, S. E., and KLEMPERER, W., 1978, *J. Am. chem. Soc.*, **100**, 8074.
- KOLLMAN, P. A., 1977 a, *Accts. chem. Res.*, **10**, 365.
- KOLLMAN, P., 1977 b, *J. Am. chem. Soc.*, **99**, 4875.
- LEGON, A. C., and MILLEN, D. J., 1982, *Discuss. Faraday Soc.*, **73**, 71, 127, 128.
- LEGON, A. C., and WILLOUGHBY, L. C., 1984, *Chem. Phys. Lett.*, **111**, 566.
- LOBUE, J. M., RICE, J. K., and NOVICK, S. E., 1984, *Chem. Phys. Lett.*, **112**, 376.
- MOROKUMA, K., 1971, *J. chem. Phys.*, **55**, 1236.
- NOVICK, S. E., JANDA, K. C., and KLEMPERER, W., 1976, *J. chem. Phys.*, **65**, 5115.
- PAULING, L., 1960, *The Nature of The Chemical Bond*, third edition (Cornell University).
- RENDELL, A. P. L., BACSKAY, G. B., and HUSH, N. S., 1985, *Chem. Phys. Lett.*, **117**, 400.
- STEINER, E., 1976, *The Determination and Interpretation of Molecular Wavefunctions* (Cambridge University Press).
- STONE, A. J., 1981, *Chem. Phys. Lett.*, **83**, 233.
- STONE, A. J., 1985, *Molec. Phys.*, **56**, 1065.
- STONE, A. J., and ALDERTON, M., 1985, *Molec. Phys.*, **56**, 1047.
- UMEYAMA, H., and MOROKUMA, K., 1977, *J. Am. chem. Soc.*, **99**, 1316.
- VISWANATHAN, R., and DYKE, T. R., 1982, *J. chem. Phys.*, **77**, 1166.