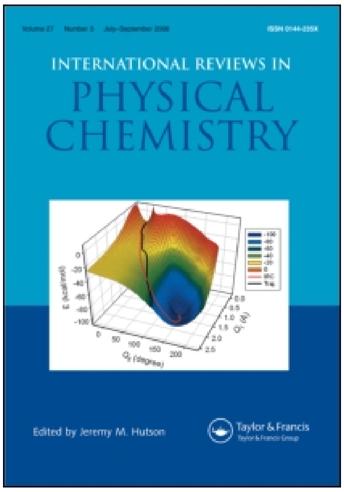


International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

The role of electrostatics in molecular interactions: prediction of shapes and electronic properties of weakly bound complexes

Peter L. Cummins[a]; Alistair P. L. Rendell[a]; David J. Swanton[a]; George B. Bacskay[a]; Noel S. Hush[a]
[a] Department of Theoretical Chemistry, The University of Sydney, Australia

To cite this Article Cummins, Peter L. , Rendell, Alistair P. L. , Swanton, David J. , Bacskay, George B. and Hush, Noel S.(1986) 'The role of electrostatics in molecular interactions: prediction of shapes and electronic properties of weakly bound complexes', International Reviews in Physical Chemistry, 5: 2, 139 — 146

To link to this Article: DOI: 10.1080/01442358609353375

URL: http://dx.doi.org/10.1080/01442358609353375

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1986, VOL. 5, NOS. 2 & 3, 139–146

The role of electrostatics in molecular interactions: prediction of shapes and electronic properties of weakly bound complexes

by PETER L. CUMMINS, ALISTAIR P. L. RENDELL, DAVID J. SWANTON, GEORGE B. BACSKAY and NOEL S. HUSH

Department of Theoretical Chemistry, The University of Sydney, N.S.W., 2006, Australia

Using *ab initio* self-consistent field molecular orbital methods the validity and potential predictive capabilities of electrostatic methods are explored with specific reference to the determination of the shapes of weakly bound molecular complexes and the changes in electronic properties that occur on the formation of a dimer, cluster or crystal. The Van der Waals dimers $(H_2O)_2$, Cl_2-HF, ClF-HF and N_2O-HF are studied from the structural point of view while for water other properties, such as dipole moment, dipole moment derivatives and ^{17}O nuclear quadrupole coupling constant are also investigated. In all cases, except for the dipole moment derivatives, the electrostatic effects are shown to account for the major part of the observed effects. Finally, the results of a purely electrostatic calculation of the vapour to solid shift of the ^{14}N nuclear quadrupole coupling constant in ammonia are discussed.

1. Introduction

An understanding of molecular interactions is the crucial first step towards the elucidation of the properties of bulk matter. However, in order to model bulk matter efficiently the fundamental intermolecular forces must be cast into a sufficiently simple, preferably analytical, form (see for example, Karlström *et al.* 1983). Thus it is hardly surprising that electrostatic models have been explored and applied to a large body of problems, most notably those that involve hydrogen-bonded systems (see for example, Politzer and Truhlar 1981, Brobjer and Murell 1982, Scrocco and Tomasi 1973).

It has become customary to analyse molecular interactions in terms of five distinct, physically meaningful mechanisms, viz. electrostatic (ES), exchange (EX), charge transfer (CT), polarization (PL) and dispersion (Margenau and Kestner 1971, Morokuma 1971, Kollman 1977). The electrostatic force between two molecules is expressible as dipole–dipole, dipole–quadrupole, etc. interactions and is just the coulombic interaction between two non-spherical charge distributions. Exchange, a repulsive force, exists between closed shells of electrons as a result of the Pauli exclusion principle, while charge transfer results in an increased attraction due to the intermolecular electron density reorganization, i.e., charge transfer. Polarization too results in increased attraction that is brought about by the intramolecular rearrangement of electron distribution. The above four effects can be modelled within the framework of Hartree–Fock self-consistent field (SCF) theory, while the fifth force, viz. dispersion, is an electron correlation effect that reflects the increased correlation in the interacting system. While perturbation theory is the most direct way to obtain quantitative estimates of each of the above components (Murrell *et al.* 1965, Fueno *et al.* 1972, Daudey *et al.* 1974), a widely used alternative method rests on the partitioning of the interaction energy within the Hartree–Fock SCF formalism, as developed by

Morokuma and co-workers (Morokuma 1971, Kitaura and Morokuma 1976). The limitation of such a scheme is the implicit neglect of electron correlation; hence, dispersion is not accounted for.

Utilizing such an SCF decomposition scheme, numerous studies of molecular dimers have been reported that have generally confirmed the notion that the electrostatic energy is the dominant term in the binding of many dimers, especially the hydrogen-bonded ones (Lathan *et al.* 1975, Umeyama and Morokuma 1976 a, b, Umeyama *et al.* 1977, Morokuma and Kitaura 1981). Obvious exceptions are the dimers that involve rare-gas atoms where the very small binding energies are mostly dispersive.

Morokuma's work has largely centred on the calculation and analysis of binding energies and the conclusion emerged that in many dimers, especially hydrogen-bonded ones, the attractive charge transfer and polarization energies are approximately cancelled by the exchange energy. Consequently at the equilibrium geometries the total interaction energies are closely paralleled by the respective electrostatic components, suggesting that the binding energy of a complex could be estimated by a purely electrostatic calculation provided its equilibrium geometry is known.

Buckingham and Fowler (1983, 1985) have extended the model, showing that the shape of a complex, that is, its intermolecular angles, can be quite accurately predicted by the use of electrostatics, provided a reasonable value is used for the intermolecular separation. That proposition has certainly aroused some spirited opposition (Baiocchi *et al.* 1983); nevertheless, a system is yet to be found where the breakdown of the model has been demonstrated.

Recent work of ours has explicitly addressed the question of validity of electrostatic predictions of the shapes of Van der Waals dimers (Rendell *et al.* 1985). We were led to the conclusion that accurate electrostatic calculations yield results that agree well with the SCF predictions for a number of fairly diverse systems. Other problems that we have investigated concern the effects of complex formation on molecular properties such as dipole moments, electric polarizabilities and their geometrical derivatives and electric field gradients (efg). In particular we looked at the water dimer molecule (Swanton *et al.* 1983, 1984) as well as clusters of H_2O molecules up to pentamers (Cummins *et al.* 1985 a), clusters of ammonia molecules as well as other complexes such as $(HCN)_2$ and HCN-NH_3, with particular reference to the importance of electrostatic polarization effects on the above properties. Model calculations have also been performed for H_2O and NH_3 where a single central molecule (treated quantum mechanically) is surrounded by point charges chosen so as to give an adequate representation of the crystalline environment in an effort to calculate the gas→solid phase shifts in efgs that are experimentally observed.

In this paper we give a brief overview of aspects of our theoretical work on some of the above systems and discuss specifically: (*a*) the prediction of the shapes of Van der Waals dimers and (*b*) changes in electronic properties that occur on dimerization and/or formation of hydrogen-bonded solid. Where appropriate, the effects of binding are analysed into electrostatic, exchange, polarization and charge transfer terms, so that the potential validity and applicability of a purely electrostatic model can be assessed.

2. Theory and computational methods

Our standard SCF program, driven by the MOLECULE supermatrix program (Almlöf 1974), has been modified so that the electrostatic (ES), exchange (EX), polarization (PL) and charge transfer (CT) contributions to the interaction energy of a dimer A–B could be evaluated using the methods suggested by Morokuma (1971) and Kitaura and Morokuma (1976). The electrostatic interaction energy E_{ES} in A–B is calculated from the equation

$$E_{ES} = \langle \psi_A^0 \psi_B^0 | \hat{V}_{AB} | \psi_A^0 \psi_B^0 \rangle \tag{1}$$

where $\psi_A^0 \psi_B^0$ denotes a non-antisymmetrized, i.e., Hartree product of the unperturbed monomer SCF wavefunctions ψ_A^0 and ψ_B^0 and $\hat{V}_{AB}$ is the operator that contains all the potential terms of interaction. Thus the electrostatic interaction energy E_{ES} is calculated exactly, given the (approximate) charge distribution of A and B as predicted by SCF. The evaluation of the EX, PL and CT terms is carried out by SCF type schemes which allow the monomeric SCF orbitals of A and B to mix subject to well defined restrictions. Thus the effect of polarization is estimated by allowing the occupied and virtual monomeric SCF orbitals to mix, that results in a mutually polarized wavefunction $\psi_A \psi_B$ that minimizes the total energy of A–B without allowing for exchange or charge transfer. The latter terms result from the antisymmetrization of the monomeric wavefunctions so that *intermolecular* orbital mixing can take place: $\{\phi_i^A\}|\{\phi_i^B\}$ and $\{\phi_a^A\}|\{\phi_a^B\}$ respectively in the case of exchange, $\{\phi_i^A\}|\{\phi_a^B\}$ and $\{\phi_i^B\}|\{\phi_a^A\}$ for charge transfer, where $\{\phi_i^A\}$, $\{\phi_a^A\}$ refer to the occupied and virtual unperturbed SCF orbitals of A, with $\{\phi_i^B\}$, $\{\phi_a^B\}$ being the analogous sets for B.

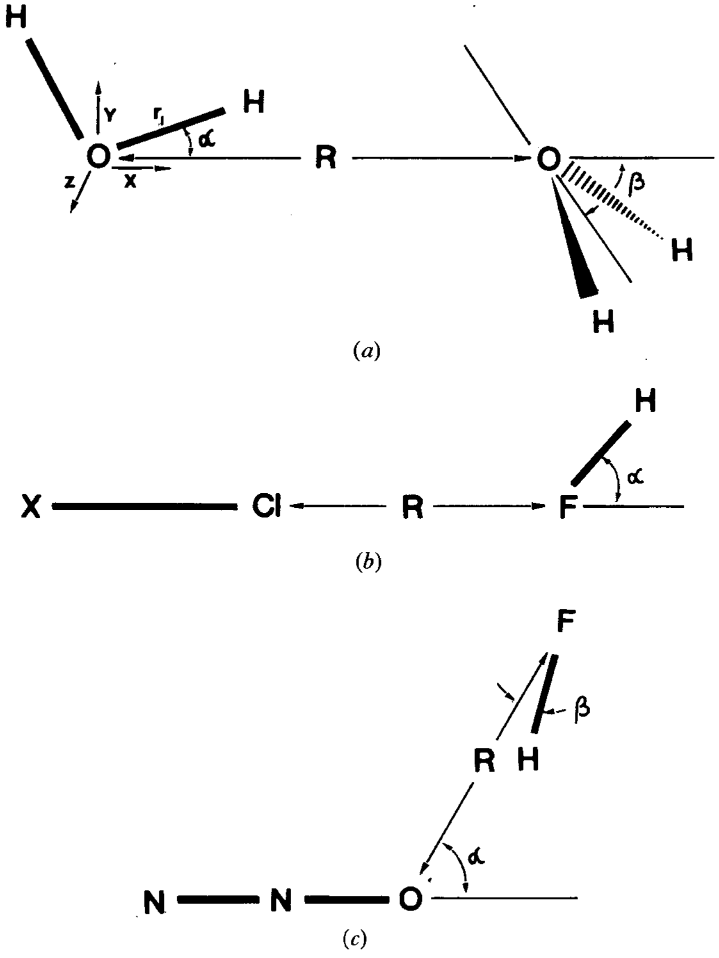
The use of finite viz. incomplete basis sets in the calculation of interaction energies and changes in electronic properties does result in a basis-set superposition error (BSSE), which is mainly manifested in an overestimate of the charge transfer term but also affects the exchange contribution (Karlström 1981, Sokalski *et al.* 1983). In our work we use the counterpoise correction of Boys and Bernardi (1970) to correct the interaction energies for BSSE. Thus far we have not applied analogous corrections to other properties, mainly because, as will be demonstrated in the following sections, the BSSE in the electronic properties we are most interested in are expected to be very small.

The Gaussian basis sets used in our calculations are generally of double zeta + polarization functions quality; details are given in the relevant sections.

The calculations have been performed on the University of Sydney's Cyber 720 and 825 and VAX11/780 computers.

3. Prediction of shapes of Van der Waals molecules

Four different Van der Waals dimers have been studied from the energetic point of view of test the validity and potential usefulness of electrostatic models in predicting molecular shapes, that is, the intermolecular angles of the dimers. The systems are H_2O/H_2O, Cl_2/HF, ClF/HF and NO_2/HF; their structure are shown in the figure. For each dimer, the intramolecular geometries were fixed as the experimental monomer structure, as well as using the experimental value for the intermolecular separation, i.e., only the appropriate angles α, β were optimized. The results are summarized in table 1. The agreement between the electrostatic predictions of the angles and experiment is remarkably good, given the inherent approximations in the model. In some cases the ES calculations seem to yield actually better results than the full ES + EX + PL + CT, i.e., SCF treatment, although that is purely fortuitous. The general trend is that the PL and CT contributions oppose and approximately cancel the EX term. The level of agreement is not so good for the interaction energies, although there too some cancellation occurs between the repulsive EX and attractive PL and CT terms, as



Geometries of the Van der Waals dimers (*a*) $(H_2O)_2$; (*b*) XCl/HF (X = Cl or F); and (*c*) N_2O/HF.

emphasized by Morokuma and co-workers (Umeyama and Morokuma 1975, 1976 a, b, 1977, Lathan and Morokuma 1975).

The role of the EX and CT terms in the determination of intermolecular angles in the above systems is discussed elsewhere (Rendell *et al.* 1985). In summary, the electrostatic method appears to have reasonable predictive power with regard to the shapes of Van der Waals complexes and seems to work well even for such systems as the 'anti' hydrogen-bonded FCl-FH and Cl_2-FH. The strength of the method lies in its potential simplicity and ease of application, as demonstrated by Buckingham and Fowler (1983, 1985), since one only requires accurate monomeric charge distributions which can then be used to investigate all possible pairs of molecules, etc.

4. Predictions of electronic properties

The spectroscopic properties of any given substance generally show a strong phase dependence; for example, the infrared spectrum of water in the vapour phase is quite different from its spectra in the various crystalline forms of ice or in the liquid phase.

Table 1. Optimized intermolecular angles and interaction energies.

System	Basis†	Calculation	R(Å)	α(deg.)	β(deg.)	Energy (kcal mol^{-1})‡
H_2O/H_2O	[5s, 3p, 1d; 3s, 1p]	ES	2·980	0·0	53·1	−7·85
		ES+EX		−1·1	31·5	−3·23
		SCF		0·4	44·1	−4·46
		Experiment		−1·3	58·0	−5·40
Cl_2/HF	[6s, 4p, 1d; 5s, 3p, 1d; 3s, 1p]	ES	2·960	59·5		−1·51
		ES+EX		44·6		−0·34
		SCF		54·7		−0·65
		Experiment		55·0		
ClF/HF	[6s, 4p, 1d; 5s, 3p, 1d; 3s, 1p]	ES	2·760	55·1		−3·36
		ES+EX		42·6		−1·30
		SCF		52·4		−2·05
		Experiment		55·0		
N_2O/HF	4–31G	ES	2·865	51·4	8·2	−6·07
		ES+EX		48·8	18·3	−3·05
		SCF		47·6	7·4	−4·44
		Experiment		63·7	14·2	

† Full details of basis sets given by Rendell *et al.* (1985).
‡ SCF energies corrected for BSSE.

Table 2. Analysis of the dipole moment and dipole moment derivative for the water dimer.†

Calculation‡	$\mu_x(ea_0)$	$\mu_y(ea_0)$	$\partial\mu_x/\partial r_1(e)$	$\partial\mu_y/\partial r_1(e)$
Monomers	0·9755	−0·0597	0·1502	−0·0642
Monomers+PL	1·1655	−0·0788	0·1902	−0·0581
Monomers+PL+EX	1·1700	−0·0800	0·2243	−0·0608
Monomers+PL+EX+CT≡SCF	1·1854	−0·0799	0·5012	−0·0892

† See the figure for definitions of coordinate system and r_1.
‡ [5s, 4p, 1d; 5s, 1p] basis, details given by Swanton *et al.* (1983).

Nevertheless, many of the interesting properties in a bulk phase could still be expressed as the sum of individual properties, provided the perturbing effect of the crystalline or liquid environment is properly accounted for. For example, one can still identify the intramolecular I.R. modes, such as an OH stretch, in ice.

In an effort to understand the changes in the intensities of intramolecular I.R. fundamentals, we carried out a series of SCF calculations on the H_2O dimer and analysed the change in dipole moment and dipole moment derivatives that occur on dimerization. The results are summarized in table 2. Note that for properties that depend purely on charge distribution there is no electrostatic contribution. For the dipole moment components the single most important term is due to polarization, while CT and EX make contributions smaller by an order of magnitude. Consequently, if one could model the crystalline environment around a given water molecule by a suitably chosen point-charge distribution, the changes in properties such as the dipole and higher moments could be successfully calculated. Unfortunately the same does not hold for the dipole moment derivative $\partial\mu/\partial r_1$ where r_1 is the distance between the H-bonding proton and the oxygen of the parent molecule (see the figure). The main contribution for the latter property comes from charge transfer which is largely responsible for the order of magnitude change in the intensity of the stretch that occurs on liquid water or ice formation. Consequently, an electrostatic model does not seem appropriate when changes in I.R. intensities are sought. As a result, the dipole moment derivatives and I.R. intensities of the water dimer molecules were calculated by the SCF method (Swanton *et al.* 1983).

A very interesting property that is often gauged by solid-state measurements is the electric field gradient (efg) at a given nucleus N, that can be quantified if the nucleus is quadrupolar since the quadrupole coupling constant (nqcc) χ and asymmetry parameter η are related to the efgs by the equation

$$\chi \equiv eQV^{\mathrm{P}}_{zz}(\mathrm{N})/h \tag{2}$$

$$\eta \equiv (V^{\mathrm{P}}_{xx}(\mathrm{N}) - V^{\mathrm{P}}_{yy}(\mathrm{N}))/V^{\mathrm{P}}_{zz}(\mathrm{N}) \tag{3}$$

where eQ is the nuclear quadrupole moment, h is Planck's constant and $V^{\mathrm{P}}_{ii}(i = x, y, z)$ is a given component of the efg tensor in the principal axis system. We have carried out a series of SCF calculations for water, calculating the efgs at the O and H sites for a number of different clusters. The pentamer calculations generally recovered about three-quarters of the decrease in the oxygen efg that is observed between H_2O vapour and ice. What is very interesting, however, is that most of the calculated change can be shown to be due to polarization, so that essentially the same results could in principle be obtained by an electrostatic calculation. The results of our analysis for $(H_2O)_5$ are given in table 3. The discrepancy between the calculated values of $V^{\mathrm{P}}_{zz}(^{17}\mathrm{O})$ and experiment greatly diminishes when a larger basis set is used and electron correlation is taken into account (Cummins *et al.* 1985 a).

Calculations are currently in progress on crystalline H_2O, where up to $\sim 10^4$ polarizing molecules are taken into account. Such a calculation has already been carried out for crystalline ammonia which is a somewhat easier system to set up on the computer. Initially, crystalline ammonia is modelled by a heptamer cluster, using the neutron diffraction results of Hewat and Riekel (1979) to fix the geometry of the system. The six nearest neighbours of the central, reference, NH_3 molecule are modelled by point charges chosen so as to reproduce the experimental dipole moment and the calculated higher multipole moments of the free molecule up to hexadecapole exactly.

Table 3. Analysis of the electric field gradient V^{P}_{zz} and asymmetry parameter η for $(H_2O)_5$.

Calculation†	$\lvert V^{\mathrm{P}}_{zz}(^{17}\mathrm{O})\rvert$	$\eta(^{17}\mathrm{O})$
Monomer	2·220	0·872
Monomer + ES	2·192	0·877
Monomer + ES + EX	2·234	0·863
Monomer + ES + EX + PL	1·688	0·887
Monomer + ES + EX + PL + CT ≡ SCF	1·566	0·905
Experiment‡ (vapour)§	1·636	0·75
Experiment‡ (ice Ih)¶	1·037	0·93

† [4s, 3p; 2s] basis, details given by Cummins *et al.* (1985 a).

‡ Efgs calculated from experimental nqccs using $Q(^{17}\mathrm{O}) = -2{\cdot}63\,\mathrm{fm}^2$ (Kelly 1969).

§ Nqccs from Verhoeven *et al.* (1969).

¶ Nqccs from Edmonds and Zussman (1972).

The resulting shift in the efg at the central N atom, $\Delta V_{zz}(\mathrm{N})$, is given to first order by the equation

$$\Delta V_{zz}(\mathrm{N}) = \gamma_z(\mathrm{N}) V_z(\mathrm{ext}) + [1 + \gamma_{zz}(\mathrm{N})] V_{zz}(\mathrm{ext}) \tag{4}$$

where γ_z and γ_{zz} are the Sternheimer (anti) shielding components for N which have been calculated by the electrostatic perturbation method of Engström *et al.* (1977), and $V_z(\mathrm{ext})$ and $V_{zz}(\mathrm{ext})$ are the external field and field gradient components that result from the six molecules that surround the reference molecule. Equation (4) accounts, to first order, for the polarization of the reference molecule. A quantum mechanical (SCF) calculation on the reference molecule in the presence of the point charges gives a better estimate of the polarization and its effect on the efg and also provides a straightforward measure of such polarization on the charge distribution of a given NH_3 molecule in the form of an improved set of multipole moments, which could then be used to improve the point-charge distribution in an iterative fashion. The results are summarized in table 4, indicating the type of calculation used as well as the source of the point-charge distribution and giving the calculated efg shifts. For a crystal, modelled by ~20 000 NH_3 molecules, the perturbation result for ΔV_{zz} is 0·151 a.u. Noting, however, the closeness of the perturbation results for $(NH_3)_7$ and the crystal of NH_3, we anticipate that the SCF results would agree to a similar extent, i.e., the figure of 0·151 a.u. should be corrected to give a value of ~0·176 a.u. The agreement with experiment is excellent.

5. Conclusions

The results reported here provide good evidence for the potential usefulness of electrostatic methods in describing certain features of intermolecular interactions in molecular dimers and also in condensed phases. Nevertheless, we feel that one must proceed cautiously and evaluate the validity and behaviour of the model as thoroughly as possible. Thus far our work has mainly dealt with the analysis of molecular interactions but we are increasingly concerned with the application of calculations to such problems as the properties of molecular solids.

As we have pointed out, purely electrostatic methods are expected to be inadequate in the predictions of quantities such as dipole moment derivatives, especially when taking a derivative implies the movement of a H-bonding proton or an atom in an analogous 'bonding' environment. This situation correlates with the inapplicability of electrostatic models in the prediction of intermolecular separations, although for

Table 4. External electric fields $V_z(\mathrm{ext})$, field gradients $V_{zz}(\mathrm{ext})$ and efg shifts ΔV_{zz} for ammonia (all results in atomic units).

System	Calculation†	Charge distribution	$V_z(\mathrm{ext})$	$V_{zz}(\mathrm{ext})$	ΔV_{zz}
$(NH_3)_7$	Perturbation	NH_3	−0·0241	0·0103	0·139
$(NH_3)_7$	SCF	NH_3	−0·0241	0·0103	0·159
$(NH_3)_7$	Perturbation	$(NH_3)_7$ iterated	−0·0287	0·0126	0·169
$(NH_3)_7$	SCF	$(NH_3)_7$ iterated	−0·0287	0·0126	0·194
NH_3 crystal‡	Perturbation	$(NH_3)_7$ iterated	−0·0254	0·0113	0·151
NH_3 crystal	Experiment§				0·20

† [4s, 3p, 1d; 2s, 1p] basis, details given by Cummins *et al.* (1985 b).

‡ Crystal modelled by ~20 000 molecules.

§ Efg shift extrapolated to 0 K and includes vibrational effects, see Lehrer and O'Konski (1965). Efgs calculated using $Q(^{14}\mathrm{N}) = 1{\cdot}93\,\mathrm{fm}^2$ (Winter and Andrä 1980).

dipole derivatives it is the charge transfer term that seems most important, rather than exchange, even though charge transfer may be relatively unimportant as far as the absolute value of the dipole moment is concerned. Nevertheless, one could envisage model calculations for condensed phases where the nearest neighbours are included in the quantum mechanical calculations while the rest of the crystal is treated by a simplified method. We plan to test this contention as well as carry out more research along the lines of our work presented in this paper for a number of molecular crystals.

References

Almlöf, J., 1974, *MOLECULE* USIP Report 74–29 (University of Stockholm).
Baiocchi, F. A., Reiher, W., and Klemperer, W., 1983, *J. chem. Phys.*, **79**, 6428.
Boys, S. F., and Bernardi, F., 1970, *Molec. Phys.*, **19**, 553.
Brobjer, J. T., and Murrell, J. N., 1982, *J. chem. Soc.*, *Faraday Trans.* II, **78**, 1853.
Buckingham, A. D., and Fowler, P. W., 1983, *J. chem. Phys.*, **79**, 6426.
Buckingham, A. D., and Fowler, P. W., 1985, *Can. J. Chem.*, **63**, 2018.
Cummins, P. L., Bacskay, G. B., Hush, N. S., Halle, B., and Engstrom, S., 1985 a, *J. chem. Phys.*, **82**, 2002.
Cummins, P. L., Bacskay, G. B., and Hush, N. S., 1985 b, *J. phys. Chem.*, **89**, 2151.
Daudey, J. P., Claverie, P., and Malrieu, J. P., 1974, *Int. J. quant. Chem.*, **8**, 1.
Edmonds, D. T., and Zussman, Z., 1972, *Phys. Lett.* A, **41**, 167.
Engström, S., Wennerström, H., Jönsson, B., and Karlström, G., 1977, *Molec. Phys.*, **34**, 813.
Fueno, T., Nagase, S., Tatsumi, K., and Yamaguchi, K., 1972, *Theoret. Chim. Acta*, **26**, 43.
Hewat, A. W., and Riekel. C., 1979, *Acta crystallogr.* A, **38**, 569.
Karlström, G., Linse, P., Wallqvist, A., and Jönnson, B., 1983, *J. Am. chem. Soc.*, **105**, 3777.
Karlström, G., 1981, in *Proceedings from the 5th Seminar on Computational Methods in Quantum Chemistry, Groningen* (Max Planck Institut für Physik und Astrophysik, München), p. 353.
Kelly, H. P., 1969, *Phys. Rev.*, **180**, 55.
Kitaura, K., and Morokuma, K., 1976, *Int. J. Quant. Chem.*, **10**, 325.
Kollman, P. A., 1977, *Applications of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum Press), p. 109.
Lathan, W. A., and Morokuma, K., 1975, *J. Am. chem. Soc.*, **97**, 3615.
Lathan, W. A., Pack, G. R., and Morokuma, K., 1975, *J. Am. chem. Soc.*, **97**, 6624.
Lehrer, S. S., and O'Konski, C. T., 1965, *J. chem. Phys.*, **43**, 1941.
Margenau, H., and Kestner, N. R., 1971, *Theory of Intermolecular Forces* (Pergamon Press).
Morokuma, K., 1971, *J. chem. Phys.*, **55**, 1236.
Morokuma, K., and Kitaura, K., 1981, in *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, edited by P. Politzer and D. G. Truhlar (Plenum Press).
Murrell, J. M., Randic, M., and Williams, D. R., 1965, *Proc. R. Soc.* A, **284**, 566.
Politzer, P., and Truhlar, D. G., 1981, *Chemical Applications of Atomic and Molecular Electrostatic Potentials* (Plenum Press).
Rendell, A. P. L., Bacskay, G. B., and Hush, N. S., 1985, *Chem. Phys. Letts.*, **117**, 400.
Scrocco, E., and Tomasi, J., 1973, *Topics Curr. Chem.*, **42**, 95.
Sokalski, W. A., Roszak, S., Hariharan, P. C., and Kaufman, J. J., 1983, *Int. J. Quant. Chem.*, **23**, 847.
Swanton, D. J., Bacskay, G. B., and Hush, N. S., 1983, *Chem. Phys.*, **82**, 303.
Swanton, D. J., Bacskay, G. B., and Hush, N. S., 1984, *Chem. Phys.*, **83**, 69.
Umeyama, H., and Morokuma, K., 1976 a, *J. Am. chem. Soc.*, **98**, 7208.
Umeyama, H., and Morokuma, K., 1976 b, *J. Am. chem. Soc.*, **98**, 4400.
Umeyama, H., Morokuma, K., and Yamabe, S., 1977, *J. Am. chem. Soc.*, **99**, 330.
Verhoeven, J., Dymanus, A., and Bluyssen, H., 1969, *J. chem. Phys.*, **50**, 3330.
Winter, H., and Andrä, H. J., 1980, *Phys. Rev.* A, **21**, 581.