Theoret. Chim. Acta (Berl.) 43, 63–73

THEORETICA CHIMICA ACTA

A Representation of the Polarization Term in the Interaction Energy between a Molecule and a Point-Like Charge

Rosanna Bonaccorsi, Eolo Scrocco and Jacopo Tomasi

Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R.
Via Risorgimento 35, 56100 Pisa, Italy

The interaction energy of a molecule M with a point-like charge q can be partitioned into simpler contributions, two of which can be expressed in terms of the charge distribution ρ_M of the sole M. The first term, $qV(r)$, represents the interaction of q with the undistorted charge ρ_M^0 of M while the second $q^2P(r)$ gives the additional contributions due to the polarization of ρ_M^0 under the influence of the charge q placed at the point r. In this paper we investigate the possibility of getting an inexpensive and sufficiently accurate analytical representation of $P(r)$ over the whole space outside the van der Waals volume of M.

Key words: Polarization energy – Molecule-point charge interaction energy

1. Introduction

A useful tool for the rationalization of the complex problem of the interaction between two reacting molecules may be found in a suitable partition of the interaction energy into partial contributions, allowing easier manipulation. A larger number of people refer to electrostatic, polarization, exchange and charge transfer terms, a partition which has its origin in the perturbative approach to the problem but which can be correctly applied also in the SCF scheme [1, 2].

The relative importance of the various contributions obviously depends on the reaction we are considering, and for a given reaction it depends also on the mutual distance among partners. For example, in the protonation reaction $M + H^+ \rightarrow MH^+$, the interaction energy is mainly electrostatic at large distances, while polarization and charge transfer contributions begin to be appreciable when the two partners approach closer (see e.g. Fig. 3 of Ref. [3]), and the electrostatic contribution represents less than one-half of the interaction energy at the equilibrium distance. In the reaction $M + Li^+$ the electrostatic contribution is dominant even at the equilibrium distances, and polarization and exchange constitute but correcting terms.

In this paper we shall focus our attention on polarization terms, trying to find a suitable representation, simple and easy to use, in analogy with that which we have already proposed for the electrostatic term.

In fact useful information on the electrostatic interaction energy[1] may be obtained from the inspection of the electrostatic molecular potential of the isolated molecule M. This quantity directly gives the electrostatic interaction energy $V(r)$ of M with a point-like unit positive charge $q^+(H^+, Li^+ \ldots)$ placed at the point r. Besides, it has also been shown that it is possible to get information from V on the electrostatic interaction of M with more complex reactants than an atomic unpolarizable cation [4].

In analogy with the definition of $V(r)$, one may adopt a definition of the polarization energy $P(r)$ which relies on a SCF calculation of the supersystem $M + q^+$ having the point charge q^+ placed at point r. If E_0 is the SCF energy of the isolated M molecule and $E_1(r)$ is the energy obtained after a reoptimization of the wave function of M under the field of the point charge[2], then

$$P(r) = E_1(r) - E_0 - V(r) \tag{1}$$

2. Method

Obvious reasons of computer cost make it impractical to use directly Eq. (1) to get two-dimensional maps of $P(r)$ similar to those employed for examining the features of $V(r)$.

In order to overcome this difficulty we have tried to find an analytical approximation to $P(r)$ which may be suitable as an interpolation formula. Assuming an approximate group additivity for the polarization energy, one can consider the following analytical expression as a possible candidate:

$$P(r) = -\frac{1}{2}\sum_i^N \frac{(\widetilde{r - r_i})\boldsymbol{\alpha}^i(r - r_i)}{|r - r_i|^6} \tag{2}$$

In Eq. (2) the index i refers to a suitable group partition of the molecule M. Eq. (2) can be further simplified because the partition of M we have adopted is made in terms of bonds and lone pairs which, in general, have a fairly local symmetry. As for the molecules we have considered in this paper it has been found possible to assume for every group a cylindrical symmetry and to predetermine the orientation of the main tensor axes of the corresponding $\boldsymbol{\alpha}^i$s. In this case Eq. (1) assumes the form:

$$P(r) = -\frac{1}{2}\sum_i^N \frac{\alpha_\perp^i[(x - x_i)^2 + (y - y_i)^2] + \alpha_\parallel^i(z - z_i)^2}{|r - r_i|^6} \tag{3}$$

---

[1] The electrostatic interaction energy is the classical interaction energy between undistorted charge distributions.

[2] Point r must be at a sufficiently large distance from M in order to ensure that the resulting wave-function of $M + q^+$ does not contain contaminating charge transfer contributions. In fact the definition of polarization energy as given in Refs. [1, 2] tacitly assumes that the basis set for M is not so spread out as to allow charge transfer to q^+.

Of course for each group i there will be a different orientation of the axes[3].

Eq. (2) can give only a partial representation of $P(r)$ because it assumes the interactions among polarized groups and the contributions of higher terms in the expansion to be negligible. It is possible to introduce such refinements into the analytical expression of $P(r)$, but we will limit ourselves in this paper to the simple formulation of Eq. (2) which, as will be seen later, gives an approximation to the polarization energy sufficient to detect the main features of the spatial behaviour of $P(r)$.

3. Results

We report here some results obtained with Eq. (3), all referring to small molecules containing the N atom, namely N_2, HCN, NH_3, NH_2CH_3, $NH(CH_3)_2$ and $N(CH_3)_3$. The calculations have been performed at standard geometries [6] with a minimal basis of Gaussian functions, contracted from a (7*s*, 5*p*) set for C and N, and from a (4*s*) set for H [7].

It has been found that it is possible to get a sensible approximation of the polarization energy using a relatively small number of $P(r)$ values calculated by means of Eq. (1) at opportunely selected points r around the molecule. For the molecules considered here we report in Table 1, a) the number of independent α^i_{ll} parameters (the others being determined by symmetry), b) the minimal number of $P(r)$ values necessary to get a

Table 1. Numerical data concerning the determination of the parameters of Eq. (3)

Molecule	Parameters	Fitting Points	Check Points N	Mean Deviation[a, b] $\bar{\Delta}$
N_2	4	7	70	0.19
HCN	6	8	56	0.33
NH_3	4	9	38	0.30
NH_2CH_3	8	10	55	0.38
$NH(CH_3)_2$	8	11	62	0.31
$N(CH_3)_3$	6	12	81	0.37

[a] In kcal/mole.

[b] $\bar{\Delta} = \frac{1}{N}\sum_{i=1}^{N} |P(r_i),(\text{Eq. } 1) - P(r_i), (\text{Eq. } 3)|$ expressed in kcal/mole. N is the number of checking points.

---

[3] The values of the α^is found by means of Eq. (2) or (3) cannot be directly compared to group polarizabilities obtained from experimental data. A reliable appreciation of the molecular polarizability tensor by means of an *ab initio* method requires expansion basis sets having special features and being far larger than those employed in the present paper. Eq. (2) gives, however, an approximation to the polarization energy congruent with $V(r)$. In other words, both terms are calculated with similar procedures on the same basis set, permitting us to compare, as a consequence, numerical values of similar accuracy.

reasonable fitting, c) the number N of $P(r)$ values calculated according to Eq. (1) and employed as a test, d) the mean absolute deviation among the exact values and those obtained by means of Eq. (1).

In defining the i groups it has been found expedient to consider each bond as a group *in se*, no matter whether the bond is simple or triple, to define a two-electron group for each lone pair and to disregard the inner shell electrons. The midpoint between the two nuclei defining a bond has been selected as the centre of the bond group, while it has been found convenient to use as the centre for a lone pair the nucleus itself. For example in HCN we have three tensors with cylindrical symmetry, the first centred at the midpoint of the HC bond, the second at the midpoint of the CN bond, the third centred on the N nucleus.

The choice of the points r corresponding to the $P(r)$ values used for determining the α^i_{ll} parameters does not appear particularly critical, at least as far as the quality of the fitting on the whole space is concerned; with other reasonable selections of points one

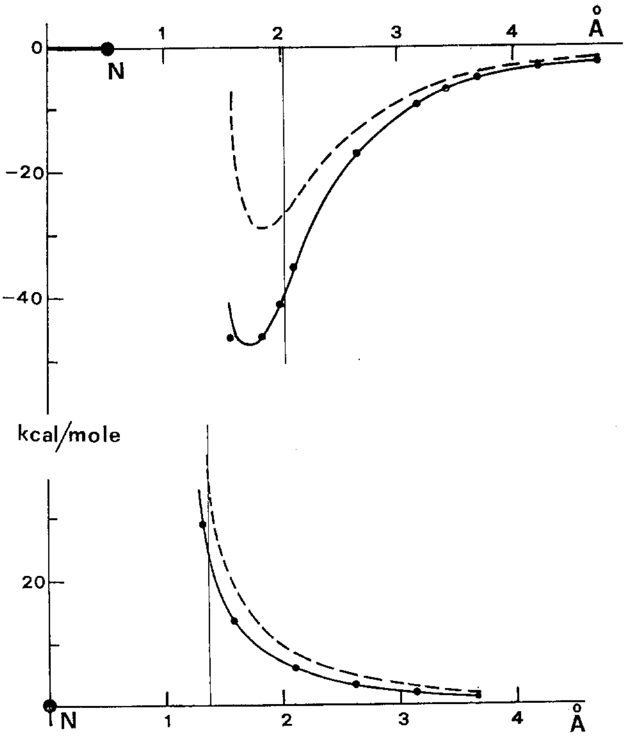

Fig. 1. Trend of $V + P$ energy (full line) for the approach of a positive unit charge to the N molecule. The points give the same quantity with $P(r)$ values calculated according to Eq. (1). The broken line gives the $V(r)$ contribution alone. The vertical line defines the van der Waals surface. a) Approach along the molecular axis, b) approach perpendicular to the molecular axis and pointing towards the N-N midpoint

practically finds the same deviations between exact and interpolated $P(r)$ values. We have checked the dependence of the quality of the results upon the number of points used in the fitting procedure, and the results here reported refer to the minimal number of points we have found possible to use. A change in the number of points or in their positions produces, however, changes in the numerical values of the α's.

The fitting and checks have been limited to a portion of space surrounding the molecule M and ranging from 0.8 to 3 van der Waals atomic radii. As noted above, for shorter distances the operative definition of $P(r)$ loses its meaning, while for points lying outside the portion of space here considered the $P(r)$ values are exceedingly small.

Figs. 1-3 permit a direct appreciation of the quality of the fitting: in each figure the full line gives the values of $V(r) + P(r)$ when the point charge approaches M along a given straight direction. The points in the figures are exact calculations of the same quantity and the broken line reports, for comparison, the trend of $V(r)$ alone.

Fig. 1a refers to the approach along the molecular axis of N_2 and Fig. 1b refers to the approach along the median axis of the same molecule. $P(r)$ is obviously negative every-

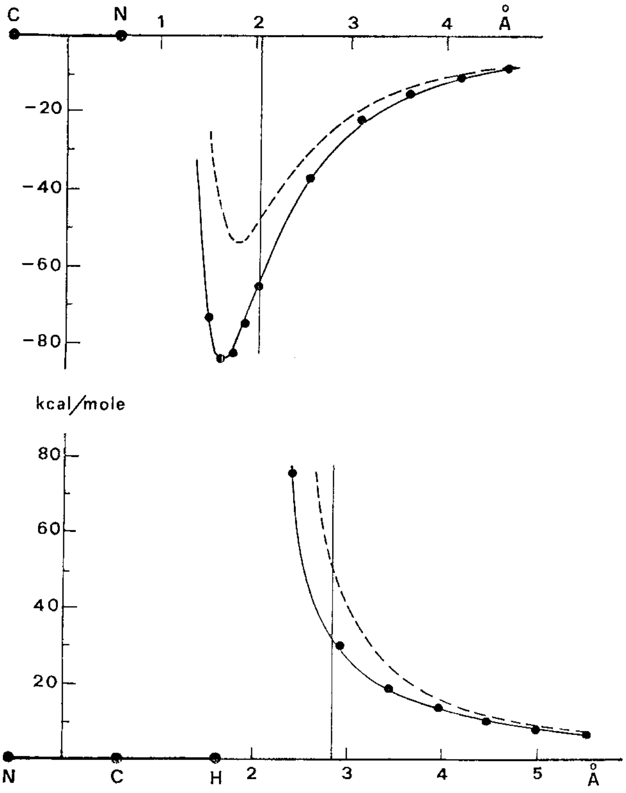

Fig. 2. Trend of $V + P$ for the approach of a positive unit charge to HCN. a) Approach along the molecular axis pointing at the N atom, b) approach along the molecular axis pointing towards the H atom

where and becomes larger in absolute value when r decreases. The minimum of $V(r)$ finds a counterpart in the $V+P$ curves: the minimum has only shifted to smaller r values. According to our experience (with limited basis sets and without geometry optimization) more complete calculations, including also charge transfer and polarization, give a minimum value of r placed midway between the one given by $V(r)$ and the other given by $V+P$.

Fig. 2 reports the same quantities as Fig. 1 for the approach of the point charge along the two opposite directions of the molecular axis of HCN. It is of some interest to remark that for every couple of points placed at the same distance from the centre of the CN group, the polarization energy is decidedly larger for the point placed on the C-H side (for instance at $r = 5$ a.u. one has $P = -20.7$ and -6.7 kcal/mole respectively). This fact is in accordance with an analysis, not yet published, of some molecules containing the C≡N group which shows a relatively low polarizability of the N lone pair (at least such as it is represented by a minimal basis set wave function).

Fig. 3 compares the same curves in the case of the approach along the N lone pair direction for NH_3, NH_2CH_3, $NH(CH_3)_2$ and $N(CH_3)_3$. The example offered by this set of molecules can be considered as a classical counter-example of the applicability of the electrostatic approximation. The relative order of the proton affinities experimentally found in the gas phase (the P.A. increases with increasing methylation) [8-10] is opposite to that predicted by the electrostatic approximation. As is possible to see by examining Fig. 3 and the numerical data reported in Table 2, the contribution given by $P(r)$ is not yet sufficient (within the minimal basis set used for the present calculations)

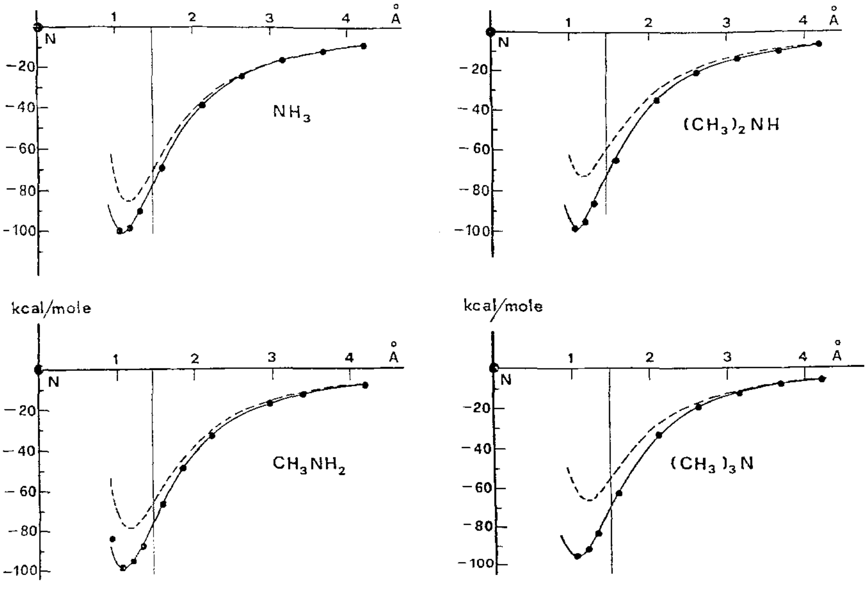

Fig. 3. Comparison of $V+P$ and V for approaches to ammonia and methylamines along to the fourth axis the tetrahedron defined by the NR bonds

Table 2. Proton affinity and its components for ammonia and the methylamines (kcal/mole)[a]

Molecule	NH_3	NH_2CH_3	$NH(CH_3)_2$	$N(CH_3)_3$
Experimental[b]	−207	−218.4	−224.9	229.1
[c]		216.3	222.4	226.6
V	−85.50	−79.55	−72.80	−65.73
P	−14.54	−19.48	−23.97	−28.04
$V+P$	−100.04	−93.03	−96.77	−93.77
Other Terms	−81.58	−87.42	−91.69	−94.76
ΔE	181.62	186.45	188.46	188.53

[a] The calculated values refer to a N . . . H^+ distance of 1.14 Å which is near to the equilibrium distance found with full SCF calculations by keeping rigid the internal geometry of the molecules.

[b] Ref. [8].

[c] Ref. [9].

to reverse the trend. Only when the other contributions to the interaction energy are added (the most important being the charge transfer term) is the correct order found. For a clear dissection of the proton affinities for this set of molecules, the reader is referred to two recent papers [11, 12].

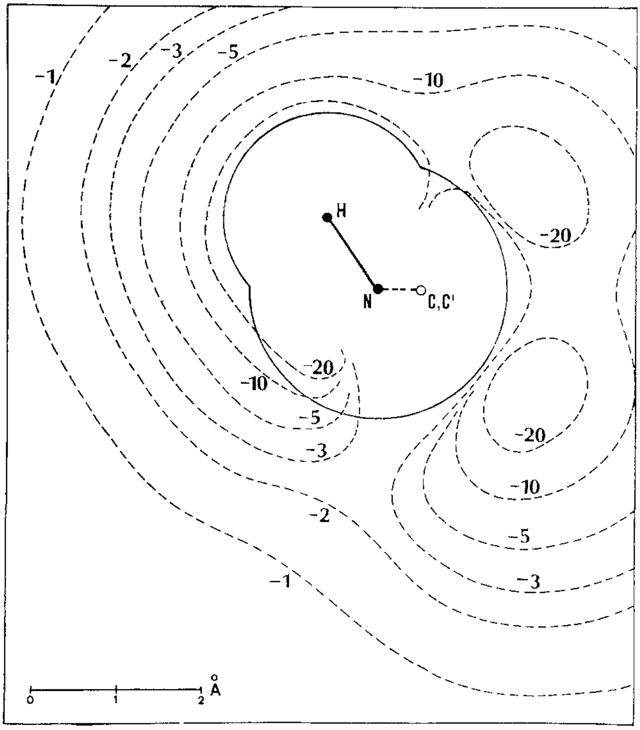

Fig. 4. Map of $P(r)$ for $NH(CH_3)_2$ in the symmetry plane. The iso-energy curves are given in kcal/mole

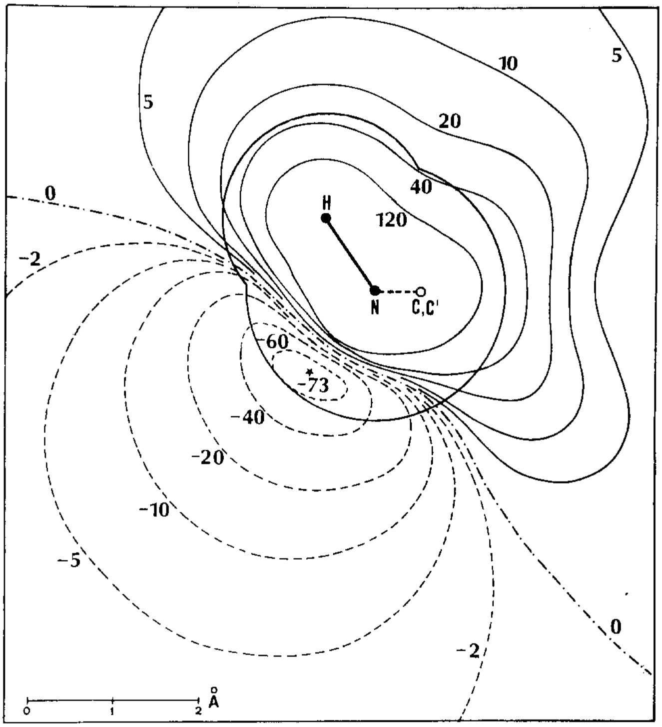

Fig. 5. Map of $V(r)$ for $NH(CH_3)_2$ in the same plane as Fig. 4. Iso-energy curves are given in kcal/mole

It can be of some interest to examine what two-dimensional maps of $P(r)$ give, even if the information on the protonation process they add to the corresponding $V(r)$ maps is not complete, as remarked above. In Fig. 4 we report the $P(r)$ maps for $NH(CH_3)_2$ in the molecular symmetry plane. The relatively large polarizability in the region corresponding to the N lone pair is well evidenced, but the most noticeable feature is perhaps given by the presence of two local minima which can be attributed to the polarization of the two CH_3 groups. The general shape of this map confirms, *a posteriori*, the opportunity of using a segmentation of the analytical expression of $P(r)$ into group contributions. The map of electrostatic contribution to the interaction energy, $V(r)$, is given in Fig. 5. Electrostatically, there is a unique channel for an incoming positive reactant, leading to an attack on the N lone pair. When $V(r)$ and $P(r)$ are added together (see Fig. 6) the reaction channel corresponding to an attack on the lone pair is still largely preferred, but there is also a hint that metastable associations of suitable positive reactants with the methyl groups could be possible.

All the results we have thus far exposed refer to a minimal basis set approximation. The passage to the next step in accuracy (i.e. to double-ζ basis approximation) probably gives more than a quantitative refinement. There are for instance some hints that the

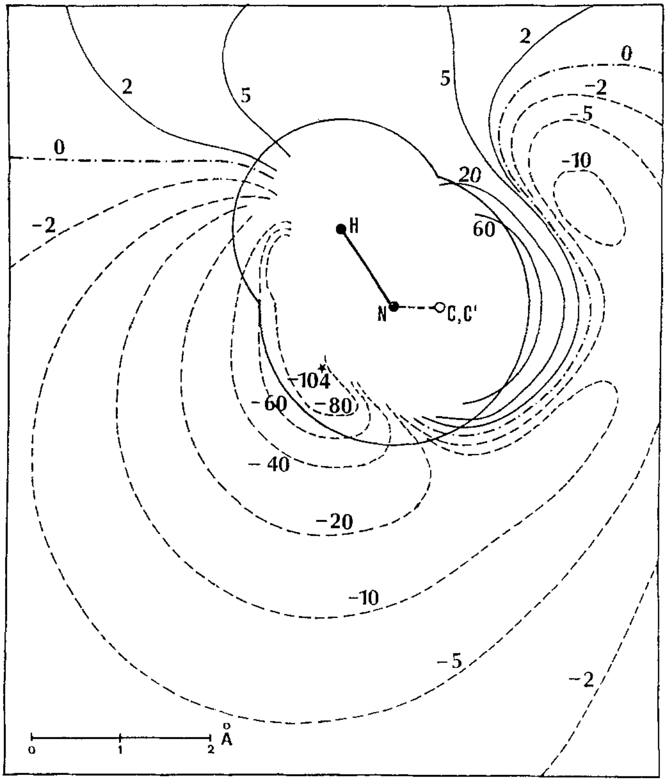

Fig. 6. Map of $V(r) + P(r)$ in the same plane as Figs. 4 and 5

differences in the interaction energy with H^+ of compounds related to ammonia and water (amines, alcohols and ethers) when hydrogen atoms are replaced by alkyl groups can be reproduced by the $V + P$ terms alone in the double-ζ approximation. The paper of Umeyama and Morokuma [12] offers a nice example in this sense: the differences in the experimental proton affinities of the same set of amines we have examined, as well in the set water-methyl alcohol-dimethyl ether, are well represented by the $V + P$ terms calculated with the 4-31G basis.

We have tried to find an analytical approximation to the $P(r)$ function calculated within the double-ζ approximation for a molecule alone, HCN, and in this case too we have found that it is possible to get a sensible analytical approximation to $P(r)$ using a quite limited number of "exact" $P(r)$ values. We report in Fig. 7 some results, corresponding to those of Fig. 2, obtained with the 4-31G basis.

4. Conclusions

A relatively inexpensive method of getting a representation of the polarization term of the interaction energy between a rigid reactant (bearing a net positive charge) and a molecule M has been shown. Such polarization energy directly derives from *ab initio*

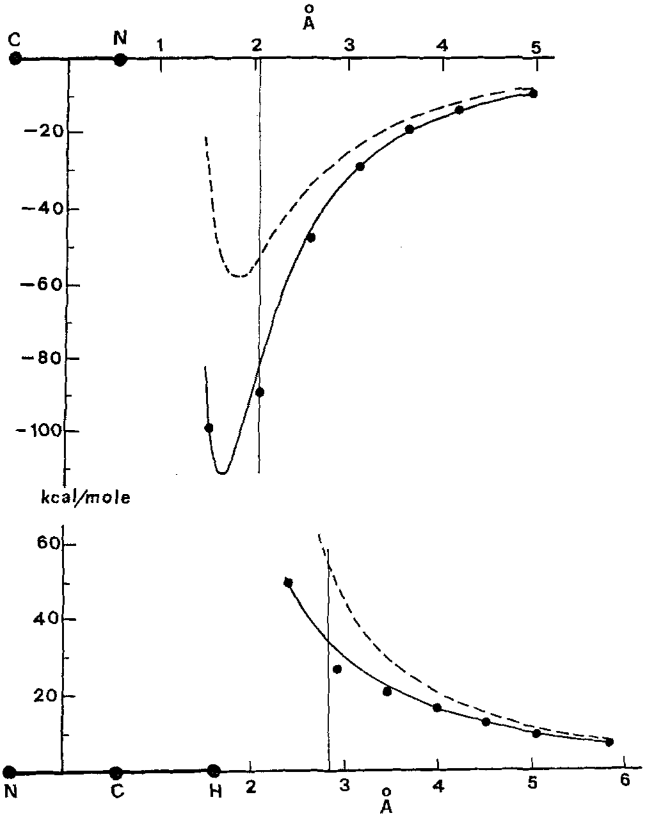

Fig. 7. Trend of V and $V + P$ for the approach of a positive charge to HCN. The approach directions are the same as in Fig. 2 but the results refer to 4-31G calculations

SCF calculations, thus permitting electrostatic and polarization terms at the same approximation level. The polarization contributions to the interaction energy are often calculated semiempirically by means of the polarizability coefficients deduced from experimental data. In the present case analogous coefficients are determined by means of a fitting procedure which relies on a certain number of polarization energies of the system $M + q^+$ obtained *via* SCF calculations. The number of "exact" values necessary to obtain a proper fit has proved to be very limited and consequently the computer time necessary for the whole procedure can be estimated to be around $2t$ where t is the time necessary for getting the SCF wavefunction of M.

The segmentation of the analytical formula into bond and lone pair contributions we have used can also be considered as the preliminary step to an investigation concerning the additivity and the transferability of such contributions, analogous to the research we have recently made for the electrostatic term of the same interaction energy, with promising results [13]. In the present paper we have not considered this aspect of the problem, contenting ourselves with a procedure which deals with each molecule separately

In analogy with the representation of the electrostatic part $V(r)$ of the interaction energy proposed some time ago, in the present case too we have used as a starting point the interactions of M with a unit positive charge. We think, however, that the usefulness of this representation of the polarization energy should not be limited to protonation reactions. The protonation reaction is just a limiting case where the charge transfer term plays an important role [3, 11, 12]. For other reactions the information obtainable from $V + P$ terms may reflect more closely the behaviour of the total interaction energy. There are for example good hints that even for the next atomic cation, Li^+, the charge transfer terms are of decidedly lower importance [14].

A last remark regards the dependence of the results upon the basis set. A minimal set underestimates $P(r)$ and the numerical values obtained from calculations with bases of this kind are of not too good quality. The method here outlined for getting an analytical representation can be used also with larger bases, there is the possibility that even at the next step in the enlargement of the basis (double-ζ level) the sole $V + P$ terms will give reliable information on the trend of the interaction process as for the protonation case too. For instance the changes in P.A. depending on increasing methylation of NH_3 and H_2O are well represented by the $V + P$ terms in the 4-31G approximation.

However, at present there are not sufficient data to permit a neater rationalization of the basis set dependency of $P(r)$.

References

1. Morokuma, K.: J. Chem. Phys. **55** 1236 (1971)
2. Pullman, A.: Chem. Phys. Letters **20**, 29 (1973)
3. Ghio, C., Tomasi, J.: Theoret. Chim. Acta (Berl.) **30**, 151 (1973)
4. Alagona, G., Cimiraglia, R., Scrocco, E., Tomasi, J.: Theoret. Chim. Acta (Berl.) **25**, 103 (1972)
5. Alagona, G., Pullman, A., Scrocco, E., Tomasi, J.: Intern. J. Peptide Protein Res. **5**, 251 (1973)
6. Pople, J. A., Gordon, M.: J. Am. Chem. Soc. **89**, 4235 (1967)
7. Clementi, E., André, M. C., Klint, D., Hahn, D.: Acta Phys. Hungarica **27**, 493 (1969)
8. Aue, D. H., Webb, H. M., Bowers, M. T.: J. Am. Chem. Soc. **94**, 4726 (1972)
9. Henderson, W. G., Taagepera, M., Holtz, D., McIver, R. T.: J. Am. Chem. Soc. **94**, 4728 (1972)
10. Briggs, J. P., Yamdagni, R., Kebarle, P.: J. Am. Chem. Soc. **94**, 5128 (1972)
11. Pullman, A., Broken, P.: Chem. Phys. Letters **34**, 7 (1975)
12. Umeyama, H., Morokuma, K.: J.Am. Chem. Soc., to be published
13. Bonaccorsi, R., Scrocco, E., Tomasi, J.: J. Am. Chem. Soc., **98**, 4049 (1976)
14. Pullman, A., Schuster, P.: Chem. Phys. Letters **24**, 472 (1974)

Received April 6, 1976/June 28, 1976