CROATICA CHEMICA ACTA CCACAA 56 (3) 461—476 (1983)

CCA-1392

YU ISSN 0011 1643
UDC 539.19
*Authors' Review*

# Point-charge Description of some Molecular Properties*

*Zvonimir B. Maksić*** *and Krešimir Rupnik*

*Theoretical Chemistry Group, The »Ruđer Bošković« Institute, 41001 Zagreb, Croatia, Yugoslavia*

Received August 30, 1982

The notion of formal atomic charges in molecules is probably the most debated issue in quantum chemistry. Although atomic charge can not be rigorously defined in a unique way, conclusive evidence is given here which shows that it provides semiquantitative information about a number of molecular properties in a very simple and transparent way. In particular, the calculations of ESCA chemical shifts, diamagnetic shielding of nuclei and diamagnetic part of the molecular magnetic susceptibility are well described and thoroughly discussed. Finally, a relation between the effective atomic charges and total molecular SCF energies is illustrated by numerical examples. The point-charge description of the mentioned molecular properties is particularly useful if it is employed within the framework of semiempirical theories because the computational costs are then negligible. The most successful semiempirical scheme in this respect seems to be the SCC-MO (self-consistent charge MO) method.

## INTRODUCTION

The role of charged parts or even particles (atoms) in chemical compounds has been recognized in the beginning of the 19th century by Davy and Berzelius[1]. Pauling defined the electronegativity of atoms in order to describe intramolecular charge transfer and its consequences on molecular properties[2]. This concept proved very useful in discussing behaviour of electrons in molecular systems. The quantum mechanical definition of electronegativity was given by Mulliken[3] and recently by Parr et al.[4] by using density functional theory. The underlying assumption of the concept of electronegativity is the idea that each atom in a molecule is a carrier of the partial effective charge. The partitioning of the total electronic density to certain atomic regions is arbitrary and the definition of formal atomic charges within the MO model is probably the most debated problem in quantum chemistry so far. This question is outside the framework of this work. Instead we shall adopt the Mulliken population analysis[5], which is the simplest one, aiming to show that atomic charges in conjunction with slight empirical adjustments are capable to provide semiquantitative and sometimes even quantitative information

---

about a number of molecular properties. In particular we shall discuss: (a) electrostatic potentials at the nuclei which in turn are closely related to ESCA chemical shifts and the average diamagnetic shielding of the nuclei, (b) the second moments of the molecular charge distribution and the corresponding elements of the diamagnetic susceptibility tensor, and (c) total molecular energies and their relation to effective atomic charges. It will appear that the notion of atomic charge, although it can not be rigorously and unambiguously defined, provides a useful bonding parameter. It does have a certain meaning within the adopted theoretical model as evidenced by the successful description of some molecular properties.

## THE METHOD OF CALCULATIONS

The validity of the point-charge description of the particular molecular property is assessed the best if the corresponding ab initio expectation values are compared with results of approximate formulas involving atomic charges. For this purpose we shall use Snyder-Basch ab initio DZ results[6], i. e. wavefunctions, atomic charges and average values of some one-electron operators, which represent the most extensive compendium of ab initio data for polyatomic molecules computed with the same basis set. In this way the results are obtained within the same approximations and the bias of different basis sets is avoided. However, the point--charge description of molecular properties makes little sense in the ab initio approach, unless it is used for interpretative purposes, because the rigorous expectation values are calculated with relatively little additional effort once the wavefunctions are known. The great potential usefullness of the point-charge concept lies in the field of semiempirical theories of chemical bonding since the computation time for the rigorous average values of the corresponding operators may well exceed the time for obtaining semiempirical wavefunctions by an order of magnitude. On the contrary, the point-charge approximation yields the desired information immediately offering in the same time simple, albeit very approximate, physical picture. In this review we discuss exclusively the SCC-MO (self-consistent charge) method[7] which is a variation of Hoffmann's EHT approach[8]. It was conclusively shown in the previous extensive calculations that the SCC-MO method gives substantionally better results for molecular quadrupole moments[9,10] and ESCA chemical shifts[11] than the semiempirical theories based on the various ZDO schemes.

The calculation of one-electron properties $\langle 0 | 1/r_A | 0 \rangle$ and $\langle 0 | r_\alpha^2 | 0 \rangle$ ($\alpha = x, y, z$) in the point-charge approach deserves some more comments. Let's consider first the potential at the nucleus A. The expectation value

$$-\langle 0 | 1/r_A | 0 \rangle = -\sum_{\mu, \nu} P_{\mu\nu} \langle \Phi_\mu | 1/r_A | \Phi_\nu \rangle \tag{1}$$

is given in the single-determinant ground state approximation as a double sum, each extended over all AOs of the basis set. Here $P_{\mu\nu}$ are the elements of the first order density matrix. Employing Mulliken approximation[12] $\Phi_\mu \Phi_\nu = (1/2) S_{\mu\nu} (\Phi_\mu^2 + \Phi_\nu^2)$ for integrals involving mixed densities and using Taylor expansion of the $1/r_A$ operator, which terminates after the first term, one straightforwardly obtains the following approximate formula*

$$-\langle 0 | 1/r_A | 0 \rangle = -\sum_{\mu}^{A} Q_\mu \langle \Phi_\mu | 1/r_A | \Phi_\mu \rangle - \sum_{B}{}' Q_B/r_{AB} \tag{2}$$

where the second sum encompasses all nuclei. Here $Q_\mu = P_{\mu\mu} + \sum_B \sum_\nu{}' P_{\mu\nu} S_{\mu\nu}$ and $Q_B = \sum_\mu^B Q_\mu$ are gross orbital and atomic populations, respectively. If all one-center integrals $\langle \Phi_\mu^A | 1/r_A | \Phi_\mu^A \rangle$ are equal, then first sum reduces to a single term $-Q_A \langle \Phi_\mu^A | 1/r_A | \Phi_\mu^A \rangle$. However, provision will be made for the difference in screening of s- and p-type AOs, since we shall use Clementi-Raimondi atomic functions[13]. It should be mentioned that neglect of higher order terms in the Taylor $1/r_A$ expansion does not lead to serious error. Their inclusion did not significantly improve the ESCA chemical shifts for INDO wavefunctions[14]. Taking into account the influence of the nuclei ($B \neq A$), the electrostatic potential exerted on the nucleus of atom A reads

$$V_A = -\sum_{\mu}^{A} Q_\mu \langle \Phi_\mu | 1/r_A | \Phi_\mu \rangle + \sum_{B}{}' (Z_B - Q_B)/r_{AB} \tag{3}$$

Thus the potential is expressed in terms of formal atomic charges $Z_B - Q_B$ which combine the conceptual and computational advantage. The last term in the formula (3) is customarily called the Madelung potential in analogy with the term appearing in solid state theory.

The second moments of the electronic charge distribution $\langle 0 | r_\alpha^2 | 0 \rangle$ ($\alpha = x, y, z$) refer usually to the center of mass of a molecule. Employing the MO-LCAO approximation, the second moment is easily broken down into three contributions

$$\langle r_\alpha^2 \rangle = \sum_{A} \sum_{\mu}^{A} P_{\mu\mu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\mu \rangle + 2 \sum \sum_{\mu<\nu}^{A\,A} P_{\mu\nu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\nu \rangle +$$
$$+ 2 \sum \sum \sum \sum \sum_{A<B\ \mu\ \nu}^{A\,B} P_{\mu\nu} \langle \Phi_\mu | r_\alpha^2 | \Phi_\nu \rangle \tag{4}$$

The integrals appearing in the expression (4) involve several different centers. It is gratifying that a series of consecutive coordinate translations $r_\alpha = r_{A\alpha} + r_{A\alpha}(i)$ ($\alpha = x, y, z$), where $r_{A\alpha}$ is the $\alpha$-th coordinate of the nucleus A relative to the center of mass and $r_{A\alpha}$ (i) refers to the corresponding coordinate of the electron i with respect to the host nucleus A, brings the formula (4) to a one-center form:

$$\langle r_\alpha^2 \rangle \cong \sum_{A} [Q_A r_{A\alpha}^2 + \sum_{\mu}^{A} Q_\mu \langle \Phi_\mu(i) | r_{A\alpha}^2(i) | \Phi_\mu(i) \rangle] \tag{5}$$

It is tacitly assumed again that the Mulliken approximation $\Phi_\mu \Phi_\nu = (1/2) S_{\mu\nu} (\Phi_\mu^2 + \Phi_\nu^2)$ holds with a fair accuracy. Extensive semiempirical calculations have shown that the second term in the formula (5) is roughly a constant for each atom belonging to the same row of the periodic system of elements. This finding was rationalized by the fact that the more electronegative atoms have larger populations $Q_\mu$ but at the same time the larger electron attractive power means that atomic orbitals are more compact, giving rise to the smaller values of the corresponding one-center integrals $\langle \Phi_\mu(i) | r_{A\alpha}^2(i) | \Phi_\mu(i) \rangle$. Their products lead to roughly constant values. Hence the approximate formula (5) assumes a very compact form[15]

$$\langle r_\alpha^2 \rangle \cong \sum_{A} Q_A r_A^2 + \sum_{p} N_p k_p \tag{6}$$

where $N_p$ is the number of atoms of the p-th row and $k_p$ are empirical parameters. It is interesting to mention that $k_p$ adjustable parameters correspond to $(1/3) \langle 0 | r^2 | 0 \rangle$ ab initio values for free atoms averaged over the p-th period of the Mendeleev system[16]. Results are discussed in the forthcomming sections.

---

* Atomic units are used throughout this paper unless stated otherwise.

## RESULTS AND DISCUSSION

### *ESCA Chemical Shifts*

It was shown by theoretical consideration[17] and by actual ab initio calculations[18] that inner-shell binding energies are affected mostly by the average molecular potentials at the nuclei under consideration. In the ionization process measured by the ESCA spectroscopy one has to take into account the effect of the final state reflected by the electron reorganization arising from the creation of the positive hole. This is accomplished approximately by the equivalent core (EC) concept advanced by Jolly[19] and formulated at the semiempirical level of sophistication by Shirley[20]. By using the expression for the electrostatic potential at the nucleus A in the point-charge approximation (3) the final formula for ESCA inner-shell binding energy shifts $\Delta BE$s reads

$$\Delta BE_A = k_1(\zeta_A Q_A + \zeta_{\tilde{A}} Q_{\tilde{A}}) + k_2(M_A + M_{\tilde{A}}) + k_3 \tag{7}$$

where $Q_A$ is the gross electron valence population of the host atom A, $\zeta_A$ is its effective nuclear charge and $M_A$ is the Madelung term. The equivalent core atom is denoted by $\tilde{A}$. The adjustable weighting factors $k_i$ (i = 1, 2) take into account the approximate nature of the equivalent core approach and put the electrostatic potentials in line with the binding energies. The additive constant $k_3$ is related to the reference level of the BEs. An analogous formula is obtained if the transition potential (TP) formalism[21] is adopted. By using EC and TP concepts and SCC-MO atomic formal charges, we obtained very good agreement with experimental ESCA chemical shifts for boron, carbon, nitrogen, oxygen, silicon and germanium atoms in large varieties of their bonding situations both in gaseous and solid states[11]. The standard deviations are considerably lower than those obtained by e. g. CNDO/2 method. The latter semiempirical theory employs sometimes different empirical parameters $k_i$ for different families of compounds while in the SCC-MO approach the single set $k_i$ (i = 1, 2, 3) is used. Here we shall discuss in some detail $\Delta BE$s binding energy shifts of sulfur S $(2p_{3/2})$ levels. The SCC-MO results obtained by the formula (7) and the equivalent TP expression are displayed in Table I for some characteristic examples. The semiempirical values are in good accordance with experimental data, the agreement being less satisfactory for the solid state shifts. This is presumably due to larger experimental errors and/or the influence of the extramolecular relaxation which is not explicitly considered in present calculations. The EC and TP methods give strikingly similar ESCA shifts expected from general analysis[22]. We found that the following relations between the charges and Madelung potentials

$$Q_A^{TP} \cong (Q_A^{GP} + Q_A^{EC})/2 \quad \text{and} \quad M_A^{TP} \cong (M_A^{GP} + M_A^{EC})/2 \tag{8}$$

hold to a good approximation. Here GP stands for the ground state charge distribution.

The relaxation energies $E_A^r$ are interesting per se because they are related to proton affinities[23]. The SCC-MO estimates of $E_A^r$, obtained either by EC or TP model, are in fair accordance with ab initio results[24]. The relaxation energies occurring upon the X-ray photoionization of 2p electrons of sulfur atoms are listed in Table II. They can be conveniently broken down into three contributions[24] (in eV):

$$E_A^{\,r}\,(\text{contr.}) = 13.6\; Q_A\,(\zeta_A - \zeta_{\bar{A}})/n \tag{9a}$$

$$E_A^{\,r}\,(\text{flow}) = 7.2\;(M_{\bar{A}} - M_A) \tag{9b}$$

$$E_A^{\,r}\,(\text{mix.}) = 13.6\;\zeta_{\bar{A}}\;(Q_{\bar{A}} - Q_A)/n \tag{9c}$$

TABLE I

*Comparison of ESCA Chemical Shifts for Sulfur Atoms ($2p_{3/2}$ level) in Various Chemical Environments as Calculated by the SCC-MO Method Employing Equivalent* Core Concept and Transition Potential Formalism with Available Experimental Data *(in eV).**

| Molecule | EC | TP | EXP. |
|---|---|---|---|
| $CS_2$ | —0.8 | —0.8 | —0.4 |
| $C_4H_4S$ | —0.1 | —0.1 | —0.4 |
| $SO_2$ | 4.4 | 4.4 | 4.6 (4.4) |
| $SOF_2$ | 6.0 | 6.0 | 6.0 |
| $SF_6$ | 10.3 | 10.3 | 10.2 |
| $H_2S$ | 0.1 | 0.1 | 0. (per. def.) |
| $CH_3SH$ | —0.6 | —0.7 | —0.7 |
| OCS | 0.3 | 0.3 | 0.3 |
| $S(CH_3)_2$ | —1.1 | —1.1 | —1.2 |
| $Cl_2SO$* | —1.7 | —1.7 | —1.9 |
| $S_8$* | —6.1 | —6.1 | —6.8 |
| $SOF_2$ | 0.9 | 0.9 | 0.0 (per. def.) |
| 1-methyl-2-thiouracil* | —8.3 | —8.3 | —7.7 |
| 1-methyl-4-thiouracil* | —8.0 | —8.0 | —7.9 |

* Gaseous shifts are measured relative to $H_2S$. The solid state results are denoted by an asterisk. Their reference point is given by the S ($2p_{3/2}$) level in $SO_2$.

TABLE II

*Breakdown of the Relaxation Energies into Three Contributions $E_r$ (contr.) $E_r$ (flow) and $E_r$ (mix.) for Sulfur Atoms as Estimated by the SCC-MO Method (in eV).*

| Molecule | $E_r$ (contr.) | | $E_r$ (flow) | | $E_r$ (mix.) | | $E_r$ (tot.) | |
|---|---|---|---|---|---|---|---|---|
| | EC | TP | EC | TP | EC | TP | EC | TP |
| $CS_2$ | —5.8 | —5.8 | 2.1 | 2.1 | —5.6 | —5.3 | —9.4 | —9.1 |
| $C_4H_4S$ | —5.7 | —5.7 | 2.3 | 2.3 | —6.1 | —5.8 | —9.5 | —9.2 |
| $SO_2$ | —5.2 | —5.2 | 2.7 | 2.7 | —5.0 | —4.7 | —7.5 | —7.3 |
| $SOF_2$ | —5.0 | —5.0 | 3.0 | 3.0 | —5.9 | —5.6 | —7.8 | —7.5 |
| $SF_6$ | —4.3 | —4.3 | 3.7 | 3.7 | —7.4 | —7.1 | —8.1 | —7.7 |
| $H_2S$ | —5.9 | —5.9 | 2.0 | 2.0 | —3.5 | —3.3 | —7.3 | —7.1 |
| $CH_3SH$ | —5.9 | —5.9 | 1.9 | 1.9 | —4.8 | —4.5 | —8.7 | —8.5 |
| OCS | —5.7 | —5.7 | 2.2 | 2.2 | —5.4 | —5.1 | —8.9 | —8.7 |
| $S(CH_3)_2$ | —5.9 | —5.9 | 2.1 | 2.1 | —5.6 | —5.3 | —9.3 | —9.0 |
| $S_8$ | —5.8 | —5.8 | 1.9 | 1.9 | —5.6 | —5.3 | —9.6 | —9.3 |
| $Cl_2SO$ | —5.3 | —5.3 | 2.6 | 2.6 | —5.9 | —5.6 | —8.6 | —8.3 |
| 1-methyl-2-thiouracil | —6.0 | —6.0 | 2.0 | 2.0 | —6.8 | —6.4 | —10.8 | —10.4 |
| 1-methyl-4-thiouracil | —6.0 | —6.0 | 2.0 | 2.0 | —7.1 | —6.7 | —11.1 | —10.7 |

where n stands for the principal quantum number of the valence shell electrons. Each of these contributions has simple physical meaning. The first term (9a) arised obviously from the contraction of the valence orbitals of the host atom, since the positive charge of the nucleus is effectively increased. The charge flow relaxation term (9b) is a consequence of the electron density migration toward the positive hole and the concomitant redestribution of the charge in the molecular ion. The mixed term describes additional stabilization due to the contraction and the increase in effective electron population of the ionized host atom due to the charge transfer. Perusal of the data in Table II shows that relaxation energies are by no means negligible. However their variation is almost an order of magnitude smaller. Thus the ground state potential involving the charge distribution of the neutral molecule only, gives in most cases reasonable results. The relaxation effects should be taken into account explicitly if better accuracy is desired particularly in compounds possessing special bonding characteristics. The largest relaxation energy is found in methyl-thiouracil due to the mobile $\pi$-electrons. The smallest reorganization effect appears in $H_2S$ which is a rather small molecular system. The mixed term assumes here the lowest value. One observes that the relaxation energies $E_A^r$ (tot.) are determined to the large extent by the $E_A^r$ (contr.) and $E_A^r$ (mix.) terms. It is interesting to point out that EC and TP estimates of $E_A^r$ (contr.) and $E_A^r$ (flow) are virtually the same. Slight variations are noticed in the $E_A^r$ (mix.) term.

Summarizing our extensive semiempirical calculations[11] we can say that point-charge formula (7) provides a good description of the inner-shell binding energy shifts in molecules and molecular crystals, provided that, a reliable semiempirical theory is applied. We found that the SCC-MO method serves this purpose. Although the results are approximate, they do have predictive power if high accuracy is not required. For example, the SCC-MO calculations of inner-shell energy levels were found very useful in studying keto-enol tautomerism[25]. It should be mentioned that gas phase and solid state levels differ as given in eq. (10)

$$BE_A\,(\text{gas}) - BE_A\,(\text{solid}) = \varphi + E_A^r\,(\text{extra}) \tag{10}$$

the difference being a sum of the work function $\varphi$ and extramolecular reorganization energy $E_A^r$ (extra). By using appropriate weighting factors in the formula (7), one can get theoretical estimates of $\varphi + E_A^r$ (extra). It appears that they are fairly constant in a series of the related compounds[11]. Finally, one obtains fair estimates of the relaxation energies which in turn are easily interpreted in simple terms.

### *Diamagnetic Shielding of Nuclei*

Ramsey has shown[26] that the spherically average magnetic shielding can be split into two contributions

$$\sigma_{\text{av.}}\,(\text{A}) = \sigma_{\text{av.}}^{\text{d}}\,(\text{A}) + \sigma_{\text{av.}}^{\text{p}}\,(\text{A}) \tag{11}$$

where the superscripts *d* and *p* refer to diamagnetic and paramagnetic contributions, respectively. We shall consider the former because it is directly related to the potential at the nucleus A:

$$\sigma_{\mathrm{av.}}{}^{d} = (e^2/3\,\mathrm{mc}^2)\,\langle 0 \,|\, 1/r_{\mathrm{A}} \,|\, 0 \rangle \tag{12}$$

Flygare and Goodisman[27] suggested a very simple formula for the calculation of the average diamagnetic shielding

$$\sigma_{\mathrm{av.}}{}^{d}\,(\mathrm{A}) = \sigma_{\mathrm{av.}}{}^{d}\,(\mathrm{FA}) + (e^2/3\mathrm{mc}^2) \sum_{\mathrm{B}}{}' Z_{\mathrm{B}}/R_{\mathrm{AB}} \tag{13}$$

where the first term corresponds to the free-atom value. It is clear that Flygare-Goodisman formula (13) gives the $\sigma_{\mathrm{av.}}{}^{d}$ values in the point-charge approximation if the intramolecular charge migration is neglected. In other words, in this approach it is supposed that the molecule is formed by neutral atoms. Despite this apparent oversimplification, the formula (13) yields quite reasonable results (vide infra). By using the point-charge approach including the intramolecular charge transfer (3) and some adjustable parameters, the diamagnetic shielding takes the form[28]

$$\sigma_{\mathrm{av.}}{}^{d}\,(\mathrm{A}) = K_{\mathrm{A1}} \sum_{\mu}^{\mathrm{A}} (\xi_{\mathrm{A}\mu}\, Q^{\mathrm{A}}/n_{\mathrm{A}\mu}) + K_{\mathrm{A2}} \sum_{\mathrm{B}}{}' Q_{\mathrm{B}}/R_{\mathrm{AB}} + K_{\mathrm{A3}} \tag{14}$$

Since the plain point-charge approximation ($K_{\mathrm{A1}} = K_{\mathrm{A2}} = 1$ and $K_{\mathrm{A3}} = 0$) gives more than 90% of the diamagnetic shielding, the use of empirical parameters in order to increase performance and predictability of this simple model is fully justified. The weighting factors $K_{\mathrm{Ai}}$ ($i = 1, 2, 3$) depend only on the nature of the atom A and were determined by the least squares fitting of the DZ ab initio $\langle 0 \,|\, 1/r_{\mathrm{A}} \,|\, 0 \rangle$ expectation values of Snyder and Basch[6]. The formula (14) is quite general holding for ab initio as well as semiempirical wavefunctions. In the latter case, the inner-shells are treated as highly localised nonpolarizable cores possessing maximal electron occupancy. The results obtained by the SCC-MO method and ab initio DZ wavefunctions[6] employing the formula (14) are compared with DZ expectation values in table III. Survey of the results reveals that SCC-MO and ab initio DZ point charges yield very good $\sigma_{\mathrm{av.}}{}^{d}$ (A) values. The neutral-atom formula (13) has surprisingly good performance being rarely in error as high as 4 ppm like in the case of central nitrogen atom in NNO. It should be mentioned for the sake of completeness that free-atom $\sigma_{\mathrm{av.}}{}^{d}$ (FA) values were approximated by the atomic Hartree-Fock results of Fischer-Froese[29]. Very good agreement of the Flygare-Goodisman formula with the sophisticated ab initio method is obviously a consequence of a cancellation of errors. Let's suppose that the atom A is more electronegative than its neighbours. Then the first term in the formula (13) increases but the second term decreases in the same time because the number of electrons residing on the neighbouring atoms is smaller. Even better results with Flygare-Goodisman formula could be obtained by appropriate empirical parametrisation in the sense of the formula (14). Then the quantitative prediction of the average diamagnetic shielding is easily made by a simple pencil-and-paper calculation provided the molecular geometry is known. Finally, it should be mentioned that the simple relation between the derivatives of the total energy over the nuclear charges, molecular electronegativity and diamagnetic shielding was recently found by Ray and Parr[30]. It was concluded that the molecular electronegativity has rather small influence on $\sigma_{\mathrm{av.}}{}^{d}$ concomitant with the very good performance of the Flygare-Goodisman formula (Table III).

TABLE III

*Comparison of the Diamagnetic Shielding of Various Nuclei as Calculated by the SCC-MO Method and ab Initio 2ξ Results Obtained in the Point-Charge Approximation and the Corresponding 2ξ ab Initio Expectation values.* The Neutral-Atom Point-Charge Estimates Obtained by the Flygare-Goodisman Formula (6) are Also Included (in ppm, All Values Multiplied by —1)*

| Molecule | | Point-charge approximation | | | Ab initio |
|---|---|---|---|---|---|
| | Atom | Neutral atoms | SCC-MO | ab initio | 2ξ results |
| $H_2O$ | H | 102.4 | 102.1 | 102.4 | 102.1 |
| | O | 414.7 | 416.8 | 416.2 | 416.8 |
| $NH_3$ | H | 94.1 | 95.6 | 95.8 | 95.1 |
| | N | 353.2 | 354.0 | 354.3 | 354.4 |
| HCN | H | 100.3 | 100.6 | 99.1 | 99.6 |
| | C | 326.4 | 326.7 | 326.3 | 326.6 |
| | N | 378.5 | 378.9 | 378.8 | 378.6 |
| $N_2H_2$ | H | 120.5 | 121.2 | 121.1 | 120.9 |
| | N | 393.1 | 392.8 | 392.9 | 392.8 |
| $N_2H_4$ | H1 | 128.0 | 129.1 | 129.3 | 129.0 |
| | H2 | 129.3 | 130.8 | 131.3 | 129.9 |
| | N | 397.1 | 396.9 | 396.6 | 396.5 |
| $H_2O_2$ | H | 142.2 | 141.0 | 141.5 | 141.4 |
| | O | 461.1 | 461.3 | 461.4 | 462.0 |
| CO | C | 327.3 | 326.8 | 325.4 | 326.1 |
| | O | 445.0 | 445.5 | 446.9 | 445.1 |
| $CO_2$ | C | 390.1 | 387.2 | 387.7 | 386.8 |
| | O | 476.0 | 475.1 | 475.2 | 476.2 |
| $H_2CO$ | H | 110.1 | 110.4 | 110.9 | 112.3 |
| | C | 339.7 | 338.8 | 339.3 | 338.8 |
| | O | 451.0 | 453.0 | 543.2 | 452.7 |
| $N_2$ | N | 385.4 | 384.4 | 384.9 | 384.1 |
| $CH_4$ | H | 85.0 | 87.3 | 87.7 | 87.2 |
| | C | 295.1 | 296.7 | 296.7 | 296.7 |
| $C_2H_6$ | H | 115.7 | 118.3 | 118.5 | 118.1 |
| | C | 335.7 | 337.1 | 337.3 | 337.2 |
| $C_2H_2$ | H | 98.6 | 100.4 | 98.6 | 99.1 |
| | C | 320.6 | 322.2 | 321.0 | 321.5 |
| NNO | N1 | 416.3 | 413.6 | 412.5 | 414.4 |
| | N2 | 447.2 | 443.3 | 443.9 | 443.1 |
| | O | 479.1 | 479.2 | 479.2 | 479.6 |

* The results of Snyder and Basch, ref. [6].

To conclude, the diamagnetic part of the NMR chemical shift can be satisfactorily estimated at the semiempirical level of sophistication (SCC-MO) within the point-charge approximation.

## *Diamagnetic Susceptibility of Molecules and the Second Moments of the Electronic Charge Distribution*

The temperature independent part of the magnetic susceptibility has two contributions[31]:

$$\chi_{aa} = \chi_{aa}^{d} + \chi_{aa}^{p} \tag{15}$$

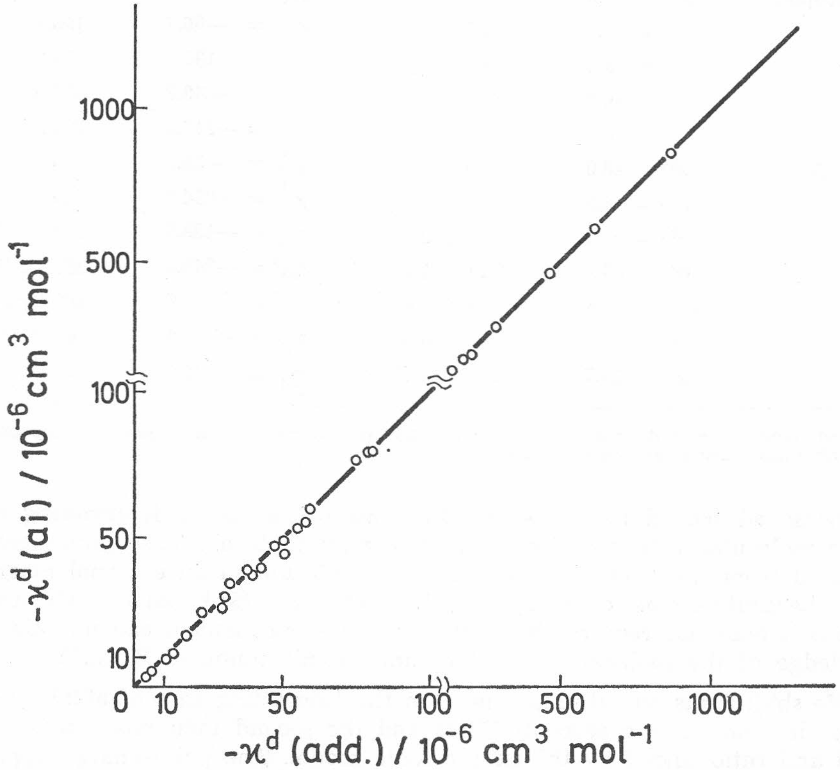
where the first part designated by $\chi_{aa}^{d}$ is the Langevin's diamagnetic term and $\chi_{aa}^{p}$ is the Van Vleck's paramagnetic term. The former will be of our concern here. By using eq. (6) it can be conveniently expressed in the point-charge approximation as follows:

$$\chi_{aa}{}^{d} \cong (Ne^2/4mc^2)\,[\sum_{A} Q_A\,(b_A{}^2 + c_A{}^2) + \sum_{p} 2k_p\,N_p] \tag{16}$$

where $b_A$ and $c_A$ are inertial coordinates of the atom A. Other constants have their usual meaning. If the intramolecular charge migration is disregarded, the formula (16) takes a form

$$\chi_{aa}{}^{d} \cong (Ne^2/4mc^2)\,[\sum_{A} Z_A\,(b_A{}^2 + c_A{}^2) + \sum_{p} 2k_p\,N_p] \tag{17}$$

where $Z_A$ is atomic number which actualy determines here the number of electrons residing on the nucleus A. In both expressions (16) and (17) the first term is large and geometry dependent whilst the second term is relatively small and isotropic. It represents a correction to the point-charge approximation arising due to the spatial extension of atomic orbitals. The neutral-atom formula (17) has good performance as evidenced by the comparison with large number of ab initio and experimental results[10,15,16,32]. We shall mention a few typical examples. The results of eq. (17) for diatomics $H_2$, HF, HCl, $F_2$, ClF, BrF, HBr, HI, IF, $Cl_2$, BrCl, $Br_2$, IBr and $I_2$ were checked against the ab initio values[33]. They are depicted in Figure 1. Good accordance between these two sets of data is evident. It should be pointed out that the simple neutral-atom approach has high predictive power and has led to the



Comparison of the diamagnetic susceptibilities for a number of diatomics as calculated by the simple additive point-charge formula and the ab initio DZ method.

better interpretation of experimental measurements for FClCO[34]. If the results obtained by the formulas (6), (16) and (17) are in serious discrepancy with the experimental results, the experiment should be reinvestigated. For example, our estimated second moments and diagonal elements of the $\chi^d$ tensor for $PF_3$ indicate that the experimental findings of Stone et al.[35] are in error. This conclusion is supported by the ab initio caluclations of Hyde et al.[36] (Table IV). Thus the formula (6) can be used as a simple check of the measured second moments and as a useful means in determining signs of the molecular g-tensor elements, since only their absolute values can be extracted from the microwave spectra of a molecule in an external magnetic field. The neutral-atom counterpart of the expression (6) is particularly simple, because it does not require the actual quantum mechanical calculations. The knowledge of the molecular geometry and atomic numbers $Z_A$ suffices.

TABLE IV

*Comparison of the Second Moments and Diamagnetic Susceptibilities Obtained by the Neutral-Atom Point-Charge Approach and the Corresponding ab Initio or Experimental Results**

| Molecule | Neutral-atom point-charge | Exp. or Ab initio | Neutral-atom point-charge | Exp. or Ab initio |
|---|---|---|---|---|
| $CH_4$ | $\langle x^2 \rangle = 3.3$ | 3.3* | $\chi_{xx}^{d} = -27.8$ | —27.8* |
| $C_2H_6$ | $\langle x^2 \rangle = 18.0$ | 18.1* | $\chi_{xx}^{d} = -53.5$ | —52.6* |
| | $\langle y^2 \rangle = 6.3$ | 6.2 | $\chi_{yy} = -103.1$ | —103.0 |
| | $\langle z^2 \rangle = 6.3$ | 6.2 | $\chi_{zz}^{d} = -103.1$ | —103.0 |
| cyclopropene | $\langle x^2 \rangle = 17.5$ | 17.8 | $\chi_{xx}^{d} = -80.6$ | —82.3 |
| | $\langle y^2 \rangle = 13.7$ | 13.5 | $\chi_{yy}^{d} = -96.7$ | —100.4 |
| | $\langle z^2 \rangle = 5.3$ | 5.8 | $\chi_{zz}^{d} = -132.4$ | —133.3 |
| ClCN | $\langle z^2 \rangle = 46.3$ | 47.3 | $\chi_{\|}^{d} = -38.2$ | —39.0 |
| | $\langle x^2 \rangle = 4.5$ | 4.6 | $\chi_{\perp}^{d} = -215.5$ | —220.2 |
| O=C=S | $\langle z^2 \rangle = 46.0$ | 45.9 | $\chi_{\|}^{d} = -38.2$ | —39.0 |
| | $\langle x^2 \rangle = 4.5$ | 4.6 | $\chi_{\perp}^{d} = -214.2$ | —214.2 |
| FClCO | $\langle a^2 \rangle = 52.1$ | 55.9 ± 2.3 | $\chi_{aa}^{d} = -134.9$ | —156.6 ± 7.6 |
| | $\langle b^2 \rangle = 26.3$ | 31.1 ± 1.7 | $\chi_{bb}^{d} = -244.4$ | —261.7 ± 10.0 |
| | $\langle c^2 \rangle = 5.5$ | 5.8 ± 0.6 | $\chi_{cc}^{d} = -332.6$ | 369.1 ± 21.1 |
| $PF_3$ | $\langle z^2 \rangle = 11.0$ | 10.7*; 8.5 | $\chi_{\|}^{d} = -252.0$ | —249.5*; 297.8 |
| | $\langle x^2 \rangle = 29.7$ | 29.4* 35.1 | $\chi_{d}^{\perp} = -172.7$ | —170.1*; 185.0 |

* Second moments and diamagnetic susceptibilities in $10^{-16}$ cm$^2$ and $10^{-16}$ cm$^3$/mol respectively. The ab initio results are denoted by an asterisk.

We shall focus our attention now on the interesting case of alkali halides where the diamagnetic susceptibilities and the second moments can be computed and rationalized by the simple ionic model. The point-charge approximation gives values which compare favourably with the ab initio second moments of Matcha[37] (Table V). The neutral-atom approach is apparently less

TABLE V

*Comparison of Second Moments of Alkali-Halides Obtained by Assuming Ionic Point-Charge Model and the Corresponding ab Initio Results (in $10^{-16}$ cm$^2$)*

| Molecule | Second moment | Neutral | Ionic | Ab initio* |
|---|---|---|---|---|
| NaF | $\langle z^2 \rangle$ Na = | 44.0 | 38.9 | 38.99 |
| | $\langle z^2 \rangle$ F = | 36.7 | 38.9 | 38.28 |
| | $\langle x^2 \rangle$ = | 5.5 | 2.0 | 2.02 |
| NaCl | $\langle z^2 \rangle$ Cl = | 66.3 | 59.2 | 60.58 |
| | $\langle z^2 \rangle$ Na = | 99.7 | 103.8 | 103.42 |
| | $\langle x^2 \rangle$ = | 5.0 | 3.5 | 3.95 |
| KF | $\langle z^2 \rangle$ K = | 94.1 | 88.4 | 88.87 |
| | $\langle z^2 \rangle$ F = | 46.9 | 50.7 | 49.58 |
| | $\langle x^2 \rangle$ = | 4.5 | 3.5 | 3.25 |
| KCl | $\langle z^2 \rangle$ K = | 126.8 | 132.9 | 131.40 |
| | $\langle z^2 \rangle$ Cl = | 141.0 | 132.9 | 133.97 |
| | $\langle x^2 \rangle$ = | 6.0 | 5.0 | 5.13 |
| RbF | $\langle z^2 \rangle$ F = | 203.9 | 196.6 | 197.82 |
| | $\langle z^2 \rangle$ Rb = | 54.5 | 57.8 | 56.85 |
| | $\langle x^2 \rangle$ = | 6.5 | 4.5 | 4.37 |

* Ab initio results of Matcha, ref. [31].

satisfactory here. On the contrary, the ionic bond involving complete transfer of the alkali valence electron to the halide atom provides a simple interpretation of the ab initio results. In particular, the $\langle z^2 \rangle_{\mathrm{Na}}$ and $\langle z^2 \rangle_{\mathrm{F}}$ in NaF are equal although the second moment is generally origin dependent. This finding is easily understood if it is recalled that NaF is represented by the homonuclear pseudomolecule $Ne_2$ in the ionic model. Consequently, it is immaterial which Ne atom in the hypothetical $Ne_2$ molecule is taken as the origin of the coordinate system. The same conclusion holds for KCl, which can be represented by the noble gas pseudo-diatomic $Ar_2$. The slight difference between $\langle z^2 \rangle_{\mathrm{K}}$ and $\langle z^2 \rangle_{\mathrm{Cl}}$ ab initio values indicates the limits of the adopted ionic model. These examples illustrate rather nicely the usefullness and beauty of the conceptual approach in quantum chemistry despite its qualitative nature.

## *Total Molecular Energy and Formal Atomic Charges*

Politzer has recently shown[38] that the total energy of a molecular system in a single determinant approximation can be expressed as a sum of potentials exerted on the nuclei

$$E_t = \sum_{A} k_A Z_A V_A \tag{18}$$

where $k_A$ are adjustable parameters. This approximate formula is a simplified form of the more general and exact expression of Politzer and Parr[39]. The formula (18) is capable to reproduce the total molecular SCF energy to within 0.5% if the potentials are calculated in an ab initio fashion[40]. We shall use[41] the eq. (18) in the point charge approximation which in turn will be checked against the DZ (one-determinant) ab initio $\langle 0 | H | 0 \rangle$ expectation values of Snyder and Basch[6]. The potential $V_A$ is given by eq. (19)

$$V_A = -\sum_{\mu}^{A} (\xi_{A\mu} Q_{\mu}^{A} / n_{A\mu}) + \sum_{B}{}' (Z_B - Q_B)/R_{AB} \tag{19}$$

The formal point-charges are deduced from the semiempirical SCC-MO and DZ ab initio[6] wavefunctions. The weighting factors $k_A$ are determined by the least square fit procedure employing ab initio total energies[6]. The results are shown in Table VI. It appears that SCC-MO and ab initio point-charges reproduce nicely total (one determinant) ab initio energies. The standard deviation for both sets of charges are 0.1 a. u. This is by no means negligible but it is encouraging because only Coulomb interactions are taken into account in the approximate formula (18). Since the exchange energy is fairly well described by local hybrid orbitals and their overlapping[42,43] a very simple and attractive model emerges which could give good, although approximate, estimates of molecular Hartree-Fock energies. It is based on hybrid orbitals which rationalize directional properties of chemical bonds by describing asym-

TABLE VI

*Comparison of the Total Energies Calculated as the Expectation Values Over the ab Initio 2 ξ Wavefunctions* and the Corresponding Entities Obtained in the Point--Charge Approximation Employing SCC-MO and ab Initio Formal Atomic Charges* (in a. u.)*

| Molecule | Point-charge approximation<br>SCC-MO | <br>ab initio 2 ξ | Ab initio 2 ξ average energy |
|---|---|---|---|
| $H_2O$ | —76.086 | —75.940 | —76.004 |
| $NH_3$ | —56.129 | —56.009 | —56.171 |
| $N_2H_4$ | —111.238 | —111.226 | —111.126 |
| $H_2O_2$ | —150.848 | —150.694 | —150.737 |
| $CH_3OH$ | —115.201 | —115.239 | —115.006 |
| CHOOH | —188.771 | —188.882 | —188.689 |
| HCN | —93.005 | —92.769 | —92.829 |
| $C_2H_4$ | —78.047 | —77.969 | —78.005 |
| $N_2H_2$ | —110.073 | —110.127 | —109.942 |
| $H_2$ | —0.992 | —0.858 | —1.127 |
| $CH_4$ | —39.963 | —39.989 | —40.182 |
| $C_2H_2$ | —76.964 | —76.842 | —76.792 |
| $H_2CO$ | —114.001 | —113.906 | —113.821 |
| $C_2H_6$ | —78.921 | —79.189 | —79.198 |
| $CO_2$ | —187.221 | —187.304 | —187.538 |
| CO | —112.705 | —112.641 | —112.676 |
| NNO | —183.334 | —183.521 | —183.576 |
| $N_2$ | —108.799 | —108.749 | —108.870 |

| | Point-charge approximation<br>SCC-MO | <br>ab initio 2 ξ |
|---|---|---|
| Weighting factors | $k_H = 0.4150$ | 0.3679 |
| | $k_C = 0.4317$ | 0.4309 |
| | $k_N = 0.4252$ | 0.4266 |
| | $k_O = 0.4191$ | 0.4233 |

* Snyder and Basch wavefunctions, ref. [6].

well accounted for by the potentials exerted at the respective nuclei calculated in the point-charge approximation. Formal atomic-charges are useful for the calculation of molecular properties in particular within semiempirical quantum chemical schemes. The most successful semiempirical method in this respect seems to be the SCC-MO approach. The concept of point-charges combines in the same time practical and interpretative advantages, since it can rationalize a number of physical and chemical features of molecules in a very transparent way.

Finally, a word of caution is in place here. One should not imagine a molecule as a mere distribution of fractional point charges because any static arrangement of point charges is electrostatically unstable according to the Earnshaw's theorem. Instead, the formal atomic charge is a difference between the number of protons in the nucleus and the electron charge density integrated over the loge ascribed to the atom in question. It is tacitly assumed that the center of this electron charge coincides with the nucleus. This is somewhat arbitrary as well as the definition of the loge. Thus, the point--charge model should be taken »cum grano salis«. It is remarkable how many molecular properties are well reproduced by the atomic point-charge model supporting thus the »atoms in molecule« picture of chemical compounds. However, the errors in estimating molecular energies being as large as 60 kcal/mol indicate the limit of the model. Apparently, one should take into account explicitly directional properties and exchange effects. The simplest model corresponding to the »distorted atoms in molecule« picture consists of local hybrid orbitals which form the bond pairs by the strong overlapping. The latter is able to describe the exchange interactions while the potentials at the nuclei would reproduce the bulk of the molecular energy. This intuitively appealling model is worth of further elaboration.

## REFERENCES

1. A. Julg, *Topics in Current Chemistry* **58** (1975) 1.
2. L. Pauling, *The Nature of the Chemical Bond,* 3rd ed., Cornell Univ. Pres, Ithaca, New York, (1960).
3. R. S. Mulliken, *J. Chem. Phys.* **2** (1934) 782; **3** (1935) 573.
4. R. G. Parr, R. A. Donnelly, M. Levy and W. E. Palke, *J. Chem. Phys.* **68** (1978) 3801.
5. R. S. Mulliken, *J. Chem. Phys.* **23** (1955) 1841, 2338, 2343.
6. L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties,* John Wiley and Sons, New York (1972).
7. W. D. White and R. S. Drago, *J. Chem. Phys.* **52** (1970) 4717.
8. R. Hoffmann, *J. Chem. Phys.* **39** (1963) 1397.
9. J. E. Bloor and Z. B. Maksić, *Mol. Phys.* **22** (1971) 351; **26** (1973) 397.
10. A. Graovac, Z. B. Maksić, K. Rupnik, and A. Veseli, *Croat. Chem. Acta* **49** (1977) 695.
11. Z. B. Maksić and K. Rupnik, *Croat. Chem. Acta* **50** (1977) 307; *Theoret. Chim. Acta* **54** (1980) 145; *Z. Naturforsch.* **35a** (1980) 988; *Croat. Chem. Acta* **53** (1980) 413; *Nouv. J. Chim.* **5** (1981) 515; *J. Organomet. Chem.* **219** (1981) 21.
12. R. S. Mulliken, *J. Chem. Phys.* **23** (1955) 1833.
13. E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38** (1963) 2686.
14. Z. B. Maksić, K. Kovačević, and H. Metiu, *Croat. Chem. Acta* **46** (1974) 1.
15. Z. B. Maksić and J. E. Bloor, *J. Phys. Chem.* **77** (1973) 1520.
16. Z. B. Maksić and N. Mikac, *Mol. Phys.* **40** (1980) 455.
17. H. Basch, *Chem. Phys. Letters* **5** (1970) 337.
18. M. E. Schwartz, *Chem. Phys. Letters* **6** (1970) 631.

19. W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.* **92** (1970) 1863.
20. D. W. Davis and D. A. Shirley, *Chem. Phys. Letters* **15** (1972) 185; *J. El. Spectry Rel. Phenom.* **3** (1974) 137.
21. O. Goscinski, G. Howat, and T. Åberg, *J. Phys.* **B8** (1975) 11; *G.* Howat and O. Goscinski, *Chem. Phys. Letters* **30** (1975) 87.
22. O. Goscinski and H. Siegbahn, *Chem. Phys. Letters* **48** (1977) 568.
23. R. L. Martin and D. A. Shirley, *J. Amer. Chem. Soc.* **96** (1974) 5299; D. W. Davis and J. W. Rabalais, *J. Amer. Chem. Soc.* **96** (1974) 5305.
24. Z. B. Maksić and K. Rupnik (to be published).
25. Z. B. Maksić, K. Rupnik, and M. Eckert-Maksić, *J. El. Spectry Rel. Phen.* **16** (1979) 371.
26. N. F. Ramsey, *Phys. Rev.* **78** (1950) 699; **86** (1952) 243.
27. W. H. Flygare and J. Goodisman, *J. Chem. Phys.* **49** (1968) 3122.
28. Z. B. Maksić and K. Rupnik, *Theoret. Chim. Acta* **62** (1983) 397.
29. C. F. Fischer-Froese, *The Hartree-Fock Method for Atoms*, John Wiley and Sons, New York, 1977.
30. N. K. Ray and R. G. Parr, *J. Chem. Phys.* **73** (1980) 1334.
31. J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1932.
32. Z. B. Maksić, *Croat. Chem. Acta* **45** (1973) 431; *J. Mol. Structure* **20** (1974) 41; *Croat. Chem. Acta* **48** (1976) 309.
33. P. A. Straub and A. D. McLean, *Theoret. Chim. Acta* **32** (1974) 227.
34. F. Scappini and A. Guarnieri, *Z. Naturforsch.* **36a** (1981) 1393.
35. R. G. Stone, J. M. Pochan, and W. H. Flygare, *Inorg. Chem.* **8** (1969) 2647.
36. R. G. Hyde, J. B. Peel, and K. Terauds, *J. Chem. Soc. Faraday II* **69** (1973) 1563.
37. R. L. Matcha, *J. Chem. Phys.* **47** (1967) 4995 and the series of papers in this journal.
38. P. Politzer, *Isr. J. Chem.* **19** (1980) 224.
39. P. Politzer and R. G. Parr, *J. Chem. Phys.* **61** (1974) 4258.
40. P. Politzer, *J. Chem. Phys.* **64** (1976) 4239; **69** (1978) 491; **70** (1979) 1067.
41. Z. B. Maksić and K. Rupnik, *Theoret. Chim. Acta* **62** (1983) 219.
42. K. Kovačević, M. Eckert-Maksić, and Z. B. Maksić, *Croat. Chem. Acta* **46** (1974) 249; *J. Mol. Structure* **21** (1974) 335.
43. Z. B. Maksić, K. Kovačević, and A. Moguš, *J. Mol. Structure Theochem* **85** (1981) 9; M. Eckert-Maksić and Z. B. Maksić, *J. Mol. Structure Theochem* **86** (1982) 325.
44. S. W. Benson and M. Luria, *J. Amer. Chem. Soc.* **97** (1975) 707; *J. Amer. Chem. Soc.* **97** (1975) 3337.
45. S. W. Benson, *Angew. Chem.* **90** (1978) 868.
46. H. Henry, S. Fliszár, and A. Julg, *Can. J. Chem.* **54** (1976) 2085; H. Henry, G. Kean, and S. Fliszár, *J. Amer Chem. Soc.* **99** (1977) 5889.
47. K. Ruedenberg, *J. Chem. Phys.* **66** (1977) 375.
48. L. J. Schaad, B. H. Robinson, and B. A. Hess, Jr., *J. Chem. Phys.* **67** (1977) 4616; T. Anno and Y. Sakai, *J. Chem. Phys.* **67** (1977) 4772; A. B. Sannigrahi, B. R. De, and B. G. Niyogi, *J. Chem. Phys.* **68** (1978) 784; G. I. Plindov and S. K. Pogrebnya, *Chem. Phys. Letters* **59** (1978) 265; E. A. Castro, *Int. J. Quant. Chem.* **15** (1979) 355; J. F. Mucci and N. H. March, *J. Chem. Phys.* **71** (1979) 1495; K. D. Sen, *J. Chem. Phys.* **74** (1981) 1500; Z. B. Maksić and K. Rupnik, *Z. Naturforsch.* **38a** (1983) 313.
49. R. G. Parr and R. F. Borkman, *J. Chem. Phys.* **49** (1968) 1055.
50. R. G. Parr and J. E. Brown, *J. Chem. Phys.* **49** (1968) 4849.
51. R. F. Borkman, *Chem. Phys. Letters* **9** (1971) 624; R. F. Borkman and F. A. Settle, Jr., *J. Amer. Chem. Soc.* **93** (1971) 5640.
52. R. Rein, G. R. Pack, and J. R. Rabinowitz, *J. Mag. Res.* **6** (1972) 360; J. R. Rabinowitz and R. Rein, *Int. J. Quant. Chem.* **6** (1972) 669.
53. S. Huzinaga and S. Narita, *Isr. J. Chem.* **19** (1980) 242.
54. J. Wasilewski, *Mol. Phys.* **44** (1981) 1297.
55. A. T. Amos and J. A. Yoffe, *Theoret. Chim. Acta* **40** (1975) 221; J. A. Yoffe, *Theoret. Chim. Acta* **52** (1979) 147.
56. G. G. Hall, *Chem. Phys. Letters* **6** (1973) 501.

57. L. L. Shipman, *Chem. Phys. Letters* **31** (1975) 361.
58. H. Bethe, *Ann. Phys. (Leipzig)* **3** (1929) 133.
59. T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.* **94** (1972) 331.
60. F. L. Hirshfeld, *Theoret. Chim. Acta* **44** (1977) 129.

## SAŽETAK

### Opis nekih molekularnih svojstava pomoću točkastih naboja

*Z. Maksić i K. Rupnik*

Naboj atoma u molekuli ne može se definirati na jedinstven način. Međutim, u ovom radu je pokazano da se, unatoč tome, točkasti naboji mogu uspješno koristiti pri opisu nekih molekulskih svojstava. Posebno dobri rezultati dobivaju se za ESCA kemijske pomake, dijamagnetsko zasjenjenje jezgri i dijamagnetsku susceptibilnost molekula. Konačno, prodiskutirana je veza između formalnih naboja atoma i ukupne SCF energije molekula. Model točkastog naboja vrlo je koristan u okviru semiempirijskih kvantno-kemijskih metoda, pri čemu najbolje rezultate daje SCC-Mo tehnika.