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Principal Components of Ionicity

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Conventionally, numerical values of effective partial charges are assigned to atoms in molecules and crystals in order to economically describe the ionicity or polarity of chemical bonds. However, quite different values are obtained when applying the various experimentally or theoretically based recipes or definitions of atomic charges. A factor analysis has been performed on atomic partial charge values from about two dozen different approaches. Only a single principal component of ionicity has been found, which is common to all the various operational charge definitions. It covers more than 90% of the variances. Apart from quite different scale units, the remaining discrepancies between different charge scales are due to individual factors for every charge recipe.

1. Introduction

The scientific framework of chemistry is based on many qualitative, intuitive and empirical concepts, which are often rather vaguely defined such as chemical bonding, aromaticity, polarity, etc. Different operational schemes have been suggested to make each of these concepts unique and quantitative. However different schemes turn out not to be equivalent. Statistical approaches like cluster analysis, factor analysis, concept analysis, etc.[1-6] can help to elucidate the anticipated physical concepts behind these intuitive ideas.

For example, Katritzky et al.[7,8] have shown that aromaticity is not a linear scale but is an at least two- (or even three-) dimensional concept. That is, values of aromaticity represent linear combinations of two independent orthogonal aromaticity factors, namely classical (energetic) and magnetic aromaticity. Similarly, it has been shown[9-11] that the polarity of solvents cannot be ordered on a linear scale; it is a property in an at least two-dimensional space; the main axes are called anion- and cation-solvating tendency. In such cases the two-dimensional real quantity might be mapped onto a complex scalar.

One of the most basic concepts in chemistry is the concept of the chemical bond. Bonding is due to the specific distribution of electron density and electron pair density. Accordingly, the distribution of electrons among the atoms determines many chemical properties, static as well as reactive ones. A fruitful simplification of the representation of electron density distributions is achieved with the help of charge values associated with the individual atoms. This helps to classify and order systems; complex phenomena can now be explained in a pedagogical, simple manner.

The idea that chemical interactions are caused or at least influenced by electric charges on atoms has a long history.[12-15] The concept of the homopolar electron pair bond in the classical[16-18] and in the quantum chemical framework[19-21] was extended to the concept of polar covalencies by Pauling's introduction of electronegativity.[22] The earliest forerunners of such scales were those of Geoffroy et al.[23-25]

The introduction of one-dimensional charge and electronegativity scales is a useful simplification but also a drastic reduction of reality. Furthermore the projection of the charge density distribution onto atomic point charges is not unique. One may use different weighting schemes in space. Bonded atoms overlap and the overlapping and deformed charge density may in different ways be related to the point charges on the atom and its neighbors. Finally, many chemical properties depend not only on the static charge distribution but also on its sensitivity to perturbations.

Therefore the response properties of the density distribution are often assumed to contribute to the effective point charges which are used to simulate the corresponding phenomenon. Different chemists, focusing their interests on different classes of compounds or classes of phenomena, will favor different projections of the multidimensional reality onto that linear scale, which seems most efficient in order to classify their specific collection of data and to make predictions in their field of interest.

The question arises of how many different or independent concepts are hidden behind the different scales associated with the same phrase of "bond polarity" or "ionicity". We note that the phrase "ionic" has two completely different meanings in the framework of the VB approach, for instance, namely

$$\Psi_{\text{ionic}}^{(1)} = (A^-B^+ \leftrightarrow A^+B^-) = (|\varphi_a\bar{\varphi}_a| + |\varphi_b\bar{\varphi}_b|) = (|\varphi\bar{\varphi}| + |\varphi^*\bar{\varphi}^*|)$$

$$\Psi_{\text{ionic}}^{(2)} = (A^-B^+) = |\varphi_a\bar{\varphi}_a| = (|\varphi\bar{\varphi}| + |\varphi^*\bar{\varphi}^*|) + (|\varphi\bar{\varphi}^*| + |\varphi^*\bar{\varphi}|)$$

φ, φ^* are the MO's $(\varphi_a + \varphi_b)$ and $(\varphi_a - \varphi_b)$, respectively. $\Psi_{\text{ionic}}^{(1)}$ and $\Psi_{\text{ionic}}^{(2)}$ are linearly independent but not orthogonal:

$$\langle \Psi_{\text{ionic}}^{(1)} | \Psi_{\text{ionic}}^{(2)} \rangle = \sqrt{(1 + S^2)/2} \qquad \in [0.7, 1.0]$$

$S = \langle \varphi_a \varphi_b \rangle$. Furthermore covalency and ionicity are also nonorthogonal VB concepts, as exhibited by the nonzero overlap:

$$\langle \Psi_{\text{ionic}}^{(1)} | \Psi_{\text{covalent}} \rangle = 2S/(1 + S^2) \qquad \in [0, 1.0]$$

That two charge scales a and b yield different values for a series of atoms in a set of compounds may have two different reasons (see Figure 1). Either, the underlying property may be of two-dimensional character on scales a and b or the measured property may be a one-dimensional scalar on scale c but afflicted with different specific deviations when measured on scales a or b.

The aim of the present paper is to determine how many linearly independent scales are covered by the different concepts of ionicity. To this end we apply factor analysis (principal component analysis, PCA) to about two dozen different atomic charge scales. The mathematics of PCA is reviewed in section 2. It will be rederived in the appendix, where we point out the mathematical similarities with the Hartree–Fock formalism. In section 3 we briefly describe about three dozen of different charge scales. A majority of them was used as basic material for the factor analysis. The results and our conclusions on atomic charge scales are presented in section 4.

2. Theory

Only a part of the formalism of statistical factor analysis[1-5] is needed in this work. We present here only the basic definitions
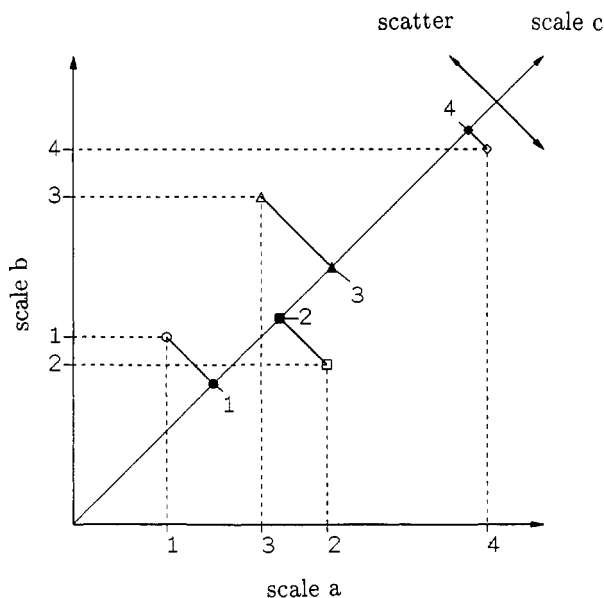
Figure 1. Different order of property values obtained by various methods (scales *a* and *b*) may be different because of two different reasons, either (1) the property is a two-dimensional one, scales *a* and *b* measure two linear independent properties, or (2) the property is a one-dimensional one on scale *c*, the values on measuring scales *a* and *b* being afflicted by different errors. Note the different order of compounds on scales *a*, *b*, and *c*.

and the working formulas. A brief derivation of the following equations in terms, which are familiar to quantum chemists, is given in the Appendix.

Different definitions of atomic charges, i.e., different schemes or recipes to determine the corresponding parameter or property values (experimentally or theoretically), will be indexed by

$$p = 1, ..., P$$

The different chemical compounds, investigated objects or individuals will be denoted by

$$i = 1, ..., I$$

The value of property p for individual i is V_{pi}. The V_{pi} are obtained from the original data X_{pi} by a simple rescaling concerning the zero and the unit, so that the average value $\bar{V}$ and the variance Σ of the V values for each property p are zero and one, respectively:

$$V_{pi} = (X_{pi} - \bar{X}_p)/\Sigma_p \tag{1}$$

with

$$\bar{X}_p = I^{-1}\sum_i X_{pi} \tag{2}$$

$$\Sigma_p^{\ 2} = h\sum_i (X_{pi} - \bar{X}_p)^2 \tag{3}$$

where $h = 1/(I - 1)$ so that

$$\sum_i V_{pi} = 0, \qquad \sum_i V_{pi}^{\ 2} = h^{-1} \tag{4}$$

In the present context, the assumption of *linear* relations between the different property scales seems very natural in view of the manner in which charge and electronegativity scales are defined. So we may assume that there are F underlying linear factors, denoted by

$$f = 1, ..., F$$

which determine all the V_{pi} in an approximately linear manner:

$$V_{pi} \approx \sum_f L_{pf}S_{fi} \quad \text{or} \quad \mathbf{V} \approx \mathbf{L \cdot S} \tag{5}$$

The contribution or loading of factor f on property scale p is L_{pf}, and the strength or score of factor f in the individual i is S_{fi}. The loadings and scores are obtained as eigenvectors of the correlation matrices. The correlation matrix $\mathbf{C}$ between the *properties* is defined as

$$\mathbf{C} = \mathbf{V}h\mathbf{V}^+ \tag{6}$$

so that the correlation coefficient between two completely independent properties V_p and V_q vanishes, $C_{pq} = 0$, and between two identical properties is unity, $C_{pp} = 1$. An analogous measure D_{ij} of the similarity of *molecules* i, j is

$$\mathbf{D} = \mathbf{V}^+h\mathbf{V} \tag{7}$$

Then the loadings and scores are obtained from

$$\mathbf{C}\vec{L}_f = \vec{L}_f\lambda_f \tag{8}$$

$$\mathbf{D}\vec{S}_f^+ = \vec{S}_f^+\cdot\lambda_f \tag{9}$$

The *main component(s)* f are those eigenvector(s) $\vec{L}_f$ of eq 8 with large eigenvalue(s) λ_f, which contribute strongly to $\mathbf{V}$ according to eq 5. If there are only one or two main components, the individuals can be represented by a scalar on a line or by a vector in a plane, which form a one- or two-dimensional subspace of the P-dimensional space, generated by all the different properties.

We note that the L_{pf} are the slopes of the linear correlations between the property values V_{pi} and the scores S_{fi}, see eq 5. The corresponding correlation coefficients K_{pf} are also identical with the L_{pf}.

The presented formulas hold in this simple form only provided all data V_{pi} are known. In general, however, there are many holes in the data set. Either appropriate estimates of the missing data V_{pi}, or of the resulting correlation matrix elements $C_{pp'}$ must be generated, or a mathematically different procedure must be applied. Among the large number of possible procedures[9,26,27,28] we found the prediction of missing data by multiple linear regression or by the so-called complete-pairs-only approach to be quite reliable.

3. Atomic Charge Scales

In the following, five groups of charge scales, a total of about three dozen scales, which have been considered in the present work, are briefly described. They by far do not exhaust the set of charge recipes suggested in the literature.

3.1. Population Analysis of Wave Functions. A common means to represent and approximate wave functions is the linear combination of atomic basis orbitals χ_i (LCAO). Such an approach suggests to allocate the density described by orbital products $\chi_i\chi_j$ to the respective atoms and pairs of atoms.

3.1.1. Mulliken's atomic gross charges: The most influential procedure of this kind has been proposed by Mulliken:[29]

$$q_a^{\text{Mul}} = Z_a - \sum_{i,j\in a} P_{ij}S_{ji}$$

where q_a^{Mul} is the charge assigned to atom a, and Z_a is its nuclear charge. S_{ij} and P_{ij} are the overlap integrals and the one-electron density matrix elements, respectively, with respect to the basis orbitals i, j, the $j \in a$ ones being somewhat artificially assigned to atom a. The resulting nonuniqueness and artifacts are well-known.[30]

3.1.2. Coulson's charges: Coulson et al.[31,32] applied this approach to approximate MO and VB functions and related his charges q_a^{Coul} to the polarity and the dipole moment of bonds.

3.1.3. Jug's charges: Jug determines atomic charges q_a^{Jug} in a similar manner, using an explicitly orthogonalized AO basis,[33] thereby circumventing the problem of assigning overlap charge contributions to the atoms. Another recipe to correct the Mulliken populations for the overlap terms has been suggested by Gussoni.[34]

3.1.4. Natural charges: To remedy the arbitrariness of the chosen AO basis as reference, Weinhold et al.[35] suggested to analyze the one-particle matrix with respect to "natural atomic orbitals in the given molecule". While the definition of the latter ones is still somewhat artificial, the corresponding charges q_a^{nat} are much less basis set dependent.

3.1.5. Further approaches: Further recipes for population analyses, which will not pursued here, have been suggested by Löwdin and many others.[36] We note that all population analysis schemes don't have unique basis set limits, i.e., they are nonobservables even in the extended quantum mechanical sense of Cioslowski.[37] Finally the LCAO-based recipes may be applied to ab initio (SCF or correlated) as well as to semiempirical (from Hückel to NDO-CI types) approaches,[38] also yielding somewhat different atomic charge values. All the following scales are obtained by applying more or less arbitrary rules to observable properties and are thus observables of the generalized sense.

3.2. Partitioning of Electron Density Distributions. Different schemes have been proposed to allocate the total electron density distribution (EDD) of a molecule or crystal to its constituent atoms. One may decompose the molecular EDD into overlapping or into nonoverlapping atomic contributions. Such partitionings represent multicenter multipole expansions, where different unique recipes are possible. Different sets of monopole charges are thereby assigned to the atoms, which are consistent with different sets of the higher atomic multipoles. At first, we will mention two schemes of the overlapping kind.

3.2.1. Hirshfeld charges: The promolecule or procrystal is defined as the superposition of the EDDs ρ_a of overlapping, neutral, spherically averaged atomic ground states, $\rho_{\text{pro}} = \sum_a \rho_a$. The molecular density can be split up into its atomic components with the help of the weight function $w_a = \rho_a/\rho_{\text{pro}}$.[39] The atomic charge on atom a in the molecule or crystal with ρ_{mol} is then calculated by

$$q_a^{\text{Hir}} = Z_a - \int \mathrm{d}r^3\, w_a \rho_{\text{mol}}$$

If one applies this recipe to ρ_{pro} instead of ρ_{mol}, one gets back the neutral independent atoms with $q_a = 0$.

3.2.2. Density fitted atomic charges: Several different approaches of fitting overlapping atomic densities to ρ_{mol} according to a Gauss' least-squares procedure have been proposed:

$$\int \mathrm{d}r^3\, w(r)\left(\rho_{\text{mol}} - \sum_a \rho_a(x)\right)^2 = \text{Min}_x$$

$$q_a^{\text{dfc}} = Z_a - \int \mathrm{d}r^3\, \rho_a(x=x_{\text{Min}})$$

$w(r)$ is an appropriate weight factor. The parameters x which are optimized may be the populations of atomic basis functions for the valence density as in the crystallographic multipole refinement procedures[40,41] (where the minimization is usually performed in the reciprocal space of X-ray scattering amplitudes). So this approach is also basis set dependent.

Or x may be the populations and orientations of the valence shells of atomic ground state ensembles as in the oriented atoms fitting approach (performed in either the real position space or in the reciprocal momentum space).[42,43] x may also be the linear mixing parameter of a neutral and an ionic promolecular density:[44–46]

$$\rho_{\text{mol}} \approx x\rho_{\text{pro}}^{\text{ionic}} + (1-x)\rho_{\text{pro}}^{\text{atomic}}$$

$$q_a^{\text{fit}} = q_a^{\text{form}}x$$

where q_a^{form} is the formal charge of the respective atomic ion. All these fitting recipes yield somewhat different charge values. The latter two fitting procedures yield rather low effective charges, reflecting the fact that a superposition of neutral atomic densities reproduces the molecular or crystal densities of even strongly polar compounds quite well.[44–47]

3.2.3. Bader charges: Bader[18] suggested splitting the molecular density up into *nonoverlapping* pieces by separating surfaces through the density minima along gradient lines from one nucleus to another (zero flux surfaces). A similar definition is common in solid state physics (compare, e.g., refs 49 and 50 and others). Bader argues that this special choice of a multicenter multipole expansion is specially justified, because several quantum-mechanical relations hold not only in the whole space but also in every atomic compartment of space created by the above mentioned zero flux surfaces. The atomic monopole Bader charges are given by

$$q_a^{\text{Bad}} = Z_a - \int\limits_{\text{compartment } a} \mathrm{d}r^3\, \rho_{\text{mol}}$$

Since a high density on an atom repels the zeroflux surface, the Bader-charge values will exaggerate the atomic charges. Therefore we expect Bader charges to be remarkably big.

3.2.4. Maslen's corrected Bader charges: Contrary to Hirshfeld's recipe, Bader's recipe yields significant charges on atoms for a promolecule of two different neutral atoms. This effect is due to significant interpenetration of atomic charge distributions and even of the ionic charge distributions of typically ionic compounds (compare, e.g., refs 44 and 49). Maslen[51] suggested to cure this unpleasant feature by subtracting the promolecular Bader charges from the molecular Bader charges:

$$q_a^{\text{Mas}} = q_a^{\text{Bad}}(\rho_{\text{mol}}) - q_a^{\text{Bad}}(\rho_{\text{pro}})$$

3.2.5. Politzer's charges: Politzer et al.[52,53] cut out the atoms in a molecule by vertical planes through the bonds, the positions of which were chosen so that the charges q_a^{Pol} of the neutral atomic promolecule vanish as for the Maslen charges.

3.2.6. Further approaches: Another kind of partitioning the space of a molecule is Daudel's loge theory[53] which will not be pursued here. Atomic charges may also be determined in the $X\alpha$ or improved density functional approaches within the somewhat arbitrary muffin-tin compartmentalization of space[38] or on the basis of the electron count number.[50]

3.3. Charges Derived from Density-Dependent Properties. Instead of adapting atomic charges to the wave function or to the density distribution directly, one may also adjust them to properties derived from the density distribution. All examples from the previous and from the present paragraph may be looked upon as density fitting procedures using different weight functions.

3.3.1. Potential derived charges: Here the multicenter multipole expansion of ρ_{mol} is made unique by using only those very first terms of the multipole expansions at the nuclear positions R_a which are just sufficient for a "reasonable approximation" of the electrostatic potential $V(r)$ "outside the molecular volume".[54–57] If only the monopole charges are included, they are derived by minimizing the difference between $V(r)$ and a sum of point charge potentials centered at the atomic positions R_a:

$$\left\| \sum_a (q_a^{\text{epd}}/|R_a - r|) - V(r) \right\| = \text{Min}_{q_a}$$

Somewhat different sets of q_a^{epd} values are obtained for different

weighting functions and for different volumes used in the definition of the norm $\|\delta V(r)\|$. Different q_a^{epd} values are also obtained if bond and/or lone-pair charges or atomic dipoles etc. are included in the sum of eq 10. $V(r)$ may be calculated by ab initio or semiempirical methods, e.g., AM1.[55] In the field of solid, crystalline compounds a very similar recipe has been used: point charges are adjusted so that their Madelung potential reproduces the electrostatic potential in the crystal.[49,58]

3.3.2. Dipole charges: The behavior of the electrostatic potential in the asymptotic region $r \to \infty$ is determined, to the lowest order, by the molecular dipole moment μ.[59-61] For a diatomic molecule with internuclear distance R, the atomic charges may be obtained from the simple relation:

$$q_a^{dip} = \mu/R$$

3.3.3. Dipole derivative charges: Cioslowski[62] defines charges with the help of dipole derivatives, i.e., the generalized atomic polar tensor (GAPT), $\mathbf{P_a} = \partial\vec{\mu}/\partial\vec{R}_a$:

$$q_a^{Cio} = {}^1/_3 \, \mathrm{tr} \, \mathbf{P_a} = {}^1/_3 \vec{\nabla}_{R_a} \cdot \vec{\mu}$$

So these charges represent response properties of the electron density distribution.

3.4. Charges Derived from Spectroscopic Data. Most spectroscopic parameters depend both on the EDD and on the response properties of the EDD. That is, the corresponding charge scales attach significance not only to different regions of the density but also to the responses of the density to different perturbations.

3.4.1. Charges from infrared intensities: Nuclear vibrations are apparent in the IR spectrum if the dipole moment μ changes during the vibration. An effective *dynamical* charge q^{IR} may be defined for diatomics by[63]

$$|q^{ir}| = \sqrt{(d\mu/dR)^2} = \mathrm{const} \cdot \sqrt{I\nu}$$

and can be obtained, up to the sign, from the integrated intensity I and the frequency ν. These charges may be split up in two contributions:

$$q_a^{ir} = q_a^{dip} + q_a^{flux}$$

where the first term is the dipole charge at equilibrium and q_a^{flux} represents the charge flux to atom a upon bond length variation. Also other partitionings are common.[63] The charges q^{ir} are very similar to the q^{Cio} ones (section 3.3.3), except that the present ones are given by the mean square root of the dipole derivative, $\sqrt{{}^1/_3 \, \mathrm{tr} \, \mathbf{P_a}\mathbf{P_a^+}}$.

3.4.2. Charges from XPS (ESCA): The chemical shift of core ionization energies (IP) depends on the environment of the respective atom. An electron-withdrawing neighbor atom shifts the core IPs of the respective atom to higher energies in comparison to the neutral species. Atomic charges may accordingly be calculated from[64,65]

$$k_a q_a^{esca} = IP_a - l_a - \sum_{a'}{}' q_{a'}/R_{aa'} \quad \mathrm{with} \quad \sum_a q_a = 0$$

l_a and k_a are semiempirical parameters and $\sum'_{a'} q_{a'}/R_{aa'}$ is the Madelung energy. We note that these charges correspond to Slater's transition state[66] between the neutral and ionized systems, i.e. to the ground state's charge distribution and to its modification due to the inner-shell ionization process. We further note that energy differences E of stationary states are, due to the virial theorem for Coulomb potentials ($|E| = E_{kin} = 0.5|E_{pot}|$), just one-half of the change of the electrostatic Coulomb energy $|E_{pot}|$ of the whole system. If the IP is approximated, according to

Koopman's theorem, by the Hartree–Fock core orbital energy ϵ, one should note that according to the general virial theorem, the relation $|\epsilon| \ll |\epsilon_{kin}| \approx |\epsilon_{pot}|$ holds for orbitals in Hartree–Fock potentials.[67] Therefore, we expect that the ESCA approach will yield especially small effective charge values.

3.4.3. Charges from X-ray emission spectroscopy: Inner shell hole creation on atom a leads to intraatomic electronic transitions, where the Madelung contribution cancels out in the X-ray emission energy ΔE_a:

$$k'_a q_a^{x-em} = \Delta E_a - l'_a$$

This approach has been applied both, to solids and free molecules.[65,68,69]

3.4.4. Charges from X-ray absorption spectra: Choosing a simple LCAO model, both the energies and the intensities of electronic excitations from atomic inner shells to unoccupied molecular or crystal orbitals may be related to effective atomic charges q_a^{x-abs}.[68,69]

3.4.5. Charges from solid-state infrared spectra: Different models have been developed to describe the whole body of mechanical, electrical, and optical properties of solids with the help of a few parameters. The frequency splitting between the transversal (TO) and longitudinal (LO) optical modes in solid-state vibrational spectra has been related to effective atomic charges assumed to vibrate with the nuclei.[70-73] The so-called transverse or Born charge is defined by

$$q_a^{tra} = \sqrt{(\omega_{LO}^2 - \omega_{TO}^2)\epsilon_{opt}(MV/4\pi)}$$

ω_{LO} and ω_{TO} are the optical mode IR frequencies at the center of the Brillouin zone, with $\omega_{LO} = \omega_{TO}\sqrt{\epsilon_{stat}/\epsilon_{opt}}$; ϵ_{stat} and ϵ_{opt} are the static dielectric constant, and the optical one in the long IR wavelength limit, respectively. M is the reduced mass, and V is the volume of the vibrating ion pair. Because the vibrating effective charges vary with frequency and mode, other charges can also be defined, which depend on the model assumed for the lattice dynamics. So for instance the longitudinal charge

$$q_a^{lon} = q_a^{tra}/\epsilon_{opt}$$

the Szigeti charge[72]

$$q_a^{Szi} = q_a^{tra} \cdot 3/(2 + \epsilon_{opt})$$

the local charge

$$q_a^{loc} = \sqrt{(\omega_0^2 - \omega_{TO}^2) \cdot 3MV/4\pi}$$

or other effective charges. ω_0 is the mechanical frequency corresponding to the elastic modulus B, $\omega_0^2 = 3BV/MR^6$.[74]

3.4.6. Charges from ligand field splittings: In the crystal field model one assumes point charges surrounding a transition element atom, which causes splittings of the energy levels of d-element complexes. These effective point charges q^{cfs} are then derived from the crystal field splittings and Racah parameters.[69,75]

3.4.7. Charges from vis–UV intensities of transition metal complexes: Within a simple minimal basis MO model, one can derive AO populations from the spectroscopic intensities and from them determine apparent charges q_a^{spint}.[69]

3.4.8. Charges from other spectroscopies: NMR chemical shifts have been related to the magnetic shielding by the electron density on the respective atom. Assuming point charge models, AO population values and/or atomic charges have also been estimated from NQR spectra, from EPR spectra, from electronic g factors, from nuclear hyperfine splittings etc.[69]

3.5. Charges from Other Experimental Data. Atomic charges have also been determined from many other properties, which do not show a direct relation to the EDD.

3.5.1. Charges from bandgaps or dielectric constants: Phillips[76,77] determines ionicities from the bandgap ΔE_g of solid compounds. ΔE_g is split up into two parts, the covalent (ΔE_c) and the ionic (ΔE_i) one:

$$\Delta E_g = \sqrt{\Delta E_c{}^2 + \Delta E_i{}^2}$$

$$q_a^{gap} = q_a^{from} \Delta E_i{}^2 / \Delta E_g{}^2$$

ΔE_g may be determined by different methods, for instance from the plasma frequency ω_p ($\omega_p = \sqrt{4\pi\bar{n}}$, $\bar{n}$ = average valence electron density) or from the optical dielectric constant ϵ_{opt}: $\Delta E_c = \hbar\omega_p/\sqrt{\epsilon_{opt} - 1}$. ΔE_c is obtained from a nonpolar isoelectronic reference compound.

3.5.2. Apparent charges from the piezoelectric effect: The polarization in the piezoelectric effect may also be used to calculate apparent atomic charges:[78]

$$q_a^{piez} = c \cdot \pi_e V / \zeta a$$

where π_e is the longitudinal piezoelectric coefficient, ζa the internal displacement per unit cell and c some crystallographic geometric parameter. Because π_e is significantly reduced by atomic deformations, the q_a^{piez} are comparatively small.

3.5.3. Charges derived from adiabatic potential energy curves: Assuming that purely covalent bonds give rise to a "universal potential energy curve" for diatomic molecules, Ferrante et al.[79] derived atomic charges q_a^{uni} by analyzing deviations of the real potential curve from the universal one, using Pauling's concept of covalent–ionic resonance.

3.5.4. Charges fitting molecular energy curves: Molecular potential energy surfaces may also be fitted by a simple Coulombic energy expression corresponding to point charges q^{efit} at the nuclear positions.[80]

3.5.5. Electronegativity (EN) based charges: The ionicity of a bond is usually related to the difference of the ENs of the atoms forming the bond. Pauling suggested the formula

$$q_a^{en} = q_a^{form}(1 - \exp(-0.25\Delta EN^2))$$

where his EN's were based on thermochemical data, i.e., on bond energy differences between covalent and polar bonds.[22]

There exist other, slightly different EN scales,[81] being based on ionization potentials,[21] orbital energies and their derivatives,[61,82,83] the principle of electronegativity equalization (see q^{Gast}[85] in Table 1),[84–87] atomic orbital density functions,[88] atomic average electron densities,[86,89] solubility products,[90] etc. Commonly used relations for defining effective charges are (q^{Hin},[84] q^{Sz}[87]):

$$q = \Delta EN/\Sigma\eta$$

where η is the atomic hardness.[91]

3.5.6. Atomic charges from other chemical data:[92] Equilibria and rate constants and inductive constants of organic chemistry have also been used to order the ionicity of bonds and attach charges to the atoms. Harrison has applied a very simple bond orbital model[71,93] to solid compounds and has derived atomic charges q_a^{Har} corresponding to different observable properties mentioned above.

3.5.7. Formal charges: A vast body of chemical experience can already be systematized with the help of the concept of formal charges q_a^{form}.[14,15]

4. Results and Conclusions of the Factor Analysis

Several of the above-mentioned atomic charge scales are related to the electron density distributions rather directly, though in

TABLE 1: Different Atomic Charge Scales[a]

charge scale	type of comp[b]	section	no. of data	b_p	K_p	$\sigma_p{}^2/\Sigma_p{}^2$
form	MS[f]	3.5.7	244	1.51	0.87	0.25
tra	S[g]	3.4.5	95	1.45	0.96	0.07
Bad	M[c]	3.2.3	148	0.95	0.94	0.12
Coul	M[e]	3.1.2	49	0.86	0.98	0.04
gap	S[g]	3.5.1	101	0.86	0.99	0.02
lon	S[g]	3.4.5	95	0.78	0.99	0.02
piez	S[g]	3.5.2	95	0.78	0.99	0.02
uni	M[e]	3.5.3	49	0.73	0.99	0.02
Szi	M[c]	3.5.5	56	0.73	0.99	0.02
x-em	S[c]	3.4.3	18	0.70	0.98	0.04
nat	M[c]	3.1.4	150	0.69	0.95	0.10
dip	M[c]	3.3.2	41	0.66	1.00	0.01
Cio	M[d]	3.3.3	46	0.60	0.92	0.16
epd	M[d]	3.3.1	32	0.60	0.97	0.07
ir	M[d]	3.4.1	57	0.58	0.97	0.05
en	MS[f]	3.5.5	244	0.49	0.89	0.21
Mul	M[c]	3.1.1	150	0.42	0.96	0.09
Pol	M[c]	3.2.5	24	0.35	0.97	0.06
Hir	M[c]	3.2.1	79	0.35	0.95	0.10
Mas	M[c]	3.2.4	74	0.30	0.95	0.10
Hin	M[d]	3.5.5	23	0.27	0.93	0.14
Jug	M[d]	3.1.3	17	0.22	0.95	0.11
Gast	M[d]	3.5.5	14	0.21	0.96	0.08
esca	MS[f]	3.4.2	244	0.19	0.94	0.11
dfc	M[e]	3.2.2	49	0.16	0.87	0.24

[a] b_p = slope of charge scale p with respect to the general charge score S_1; K_p = correlation coefficient between charge scale p and general score; $\sigma_p{}^2/\Sigma_p{}^2$ = fraction of quadratic variance of atomic charges, which is not reproduced by the general score. [b] Type of compounds: data for molecules or molecular crystals = M, data for ionic, covalent and metallic solids = S. [c] Various small molecules. [d] Mainly organic molecules. [e] Inorganic molecules. [f] Many different types. [g] Inorganic solids.

different manners. Different weighting and partitioning schemes test the EDD in different parts of space. Since the electron densities in different regions (e.g., near to or far from the nucleus, etc.) are only indirectly related to each other through the Schrödinger equation and the normalization condition (charge conservation), one expects several factors determining the different charge scales. Other charge scales have a rather intricate connection with the charge distribution of the molecular ground state, and even others are related to quite different properties, such as response properties of the EDD, bond or excitation energies, intensities, or thermodynamic data. So the question arises as to how many linearly independent factors are covered by these charge scales and which physical meanings can be attached to the underlying factors.

It is for this reason that we have performed a factor analysis. We have used the common SPSS software package.[94] Since the compounds are from many different areas of chemistry, our selection of compounds is not seriously biased. However, the data set is nearly blocked concerning solid compounds and solid physicists charge scales on one hand, and molecular compounds and typically chemical charge scales on the other hand (see below).

The main result of our investigation is that there exists just one common factor in all charge scales, which accounts for 90–93% of the whole variance in the data set. The results vary by 1% or so depending on how the holes in the data set were treated. To investigate the stability of the results against uncertainties in the original data X_{pi}, we have added random numbers to them. The comparatively large statistical errors of $0.1\Sigma_p$ reduce the eigenvalue of the common factor by not more than 2%.

The second and third factors contribute only 4–3% to the data variance. The structure of these factors, i.e., the loading vector $\bar{L}_p$, depends somewhat on the statistical errors. However, what is more important is the fact that the loadings are sensitive to the inclusion of further data sets p. That is, the variance of the data not described by the common factor is mainly due to specific factors of *each* method. We did not find any second factor of

ionicity which is common to many empirical scales, except perhaps to the charges in solids based on bandgaps (section 3.5.1), piezoelectric constants (section 3.5.2), phonon spectra, and dielectric constants (section 3.4.5). A factor analysis of different electronegativity scales (see section 3.5.5) also yielded only one main factor[95] which covers more than 95% of the total variance. The general electronegativity score correlates highly with all individual electronegativity scales p ($L_{p1} > 0.97$).

The slopes b_p of the linear relation between the general factor score S_{1i} of the individual atom in a given molecule, and the charge value X_{pi} on specific scale p:

$$X_{pi} \approx b_p \cdot S_{1i} \qquad (10)$$

are listed in Table 1. This linear relation does not contain a constant term, since, because of the overall neutrality of chemical matter, $\bar{X}_p$ and $\bar{S}_f$ are zero. K_{p1} in the table is the correlation coefficient of the linear relation 10 between $\bar{X}_p$ and $\bar{S}_f$. The ratio of σ_p (the standard deviation of atomic charge values X_{pi} from the first general score, eq 10), and Σ_p (the total variance of charge values on scale p, eq 3), is independent of the empirical normalization of scale p and is also given in Table 1. If there are no holes in the data set, the following relations hold: $b_p = \Sigma_p \cdot L_{p1}$, $K_{p1} = L_{p1}$, and $\sigma_p/\Sigma_p = \sqrt{1 - L_{p1}^2}$.

The single dominant factor indicates the physical essence which is behind all the intuitively defined empirical charge scales. The main differences between them are the units b_p with which the atomic charges are measured. The smallest charge values are the ESCA charges with $b = 0.19$ and the atomic density fitting charges *dfc* with $b = 0.16$. The largest charge values are the formal charges with $b = 1.51$ and the transverse optical charges with $b = 1.45$. That is, different charge scales may differ by up to an order of magnitude. If $K_p \ll 1$ and $\sigma_p/\Sigma_p \gg 0$, then another factor also contributes significantly to charge scale p. Individual specific factors are especially important for the formal charges (section 3.5.7), the electronegativity charges (section 3.5.5) and the density fitted charges (section 3.2.2), where σ^2/Σ^2 is about 1/4.

During the long period of empirical experience, many chemists gained the strong impression that an important natural cause of many chemical phenomena is something which might be called "charges on the atoms". Many different experimental charge scales have been suggested, and many different theoretical scales have been defined which are in more or less accord with each other. This is contrary to the concepts of solvent polarity or of aromaticity, where different definitions describe linear combinations of at least two general independent properties.

The puzzling fact that it is impossible to define charges *uniquely* in typical ionic compounds[44] has evoked the suspicion that a property of "atomic charges", the operational definition of which has only to be searched for and found, is an illusionary concept. The concept of atomic charges was looked upon to be nothing more than a *simple* model concept of the human brain which is *useful* in a restricted domain of chemistry[96] *without* any real basis in nature.[45] The opposite extreme standpoint is that only one unique definition of atomic charges is the one which is appropriate to, and given by, reality.[48]

Of course, a purely statistical analysis can never prove the existence of a physical determinant. But the fact that there is just one single main factor in all the more or less intuitively defined empirical charge and electronegativity scales, of both measured or calculated type, forms a strong indication that there indeed *exists* something in nature which corresponds to the vague charge concepts of the chemists and physicists. So, our factor analysis proves that the "definitions of atomic charges are relevant since they can be used to correlate or predict physical and chemical properties".[85] At the moment we cannot say what an atomic charge is in terms of mathematical physics, except that it is the dominant factor contained in all the suggested charge scales. Atomic charges are no observables in the strict sense, since they are not measured directly but are deduced from observable quantities on the basis of some more or less arbitrary, more or less simplified (some say oversimplified) model. So, they depend on both the model and on reality. The present factor analysis indicates that there is the same real physics behind all these models. However there is no support for the view that there exists a unique natural scale unit or that only one scale with one b value is the "true" one.

After we completed our work, Wiberg and Rablen[97] published a paper where they compare seven different atomic charge scales. Slopes and correlation coefficients were given there in Table X. They agree satisfactorily with ours. The present work represents an extension of these correlations to many other charge scales, including also the factor analysis.

Appendix

As mentioned in section 2, the scaled values V are assumed to be approximately given by scalar products of the socalled loadings and scores (eq 5). The loadings and scores are to be determined by a Gaussian least-squares procedure:

$$G = \sum_{p,i} (V_{pi} - \sum_f L_{pf} S_{fi})^2$$

$$= \text{tr}[(V - LS)\cdot(V - LS)^+] = \min \qquad (A1)$$

that is

$$\partial G/\partial L^+ = LSS^+ - VS^+ = 0 \qquad (A2)$$

$$\partial G/\partial S = S^+L^+L - V^+L = 0 \qquad (A3)$$

Equations A2 and A3 form a coupled system of equations of third degree in the unknowns L and S, comparable to the Hartree–Fock equations. Inserting eqs A3 and then A2 into (6) yields

$$CL = L\cdot(SS^+hL^+L) \qquad (A4)$$

Inserting eqs A2 and then A3 into eq 7 yields

$$DS^+ = S^+\cdot(L^+LhSS^+) \qquad (A5)$$

According to eq 5 only the matrix product LS matters. That is, any nonsingular square transformation matrix T yields an equivalent solution $\tilde{L}$, $\tilde{S}$ according to

$$LS = (LT^{-1})(TS) = \tilde{L}\tilde{S} \qquad (A6)$$

T transforms eqs A4 and A5 to

$$C\tilde{L} = \tilde{L}(\tilde{S}\tilde{S}^+h\tilde{L}^+\tilde{L}) = \tilde{L}\Lambda \qquad (A7)$$

$$D\tilde{S} = \tilde{S}^+(\tilde{S}\tilde{S}^+h\tilde{L}^+\tilde{L})^+ = \tilde{S}^+\Lambda \qquad (A8)$$

where

$$\Lambda = (\tilde{S}\tilde{S}^+h\tilde{L}^+\tilde{L}) = T\cdot(SS^+hL^+L)\cdot T^{-1} \qquad (A9)$$

As in the case of the transformation of the Hartree–Fock equations to canonical form, we choose T so that $(\tilde{S}\tilde{S}^+h\tilde{L}^+\tilde{L})$ becomes diagonal, $\Lambda_{fg} = \lambda_f\delta_{fg}$, with eigenvalues λ_f. It then follows that

$$C\tilde{L}_f = \tilde{L}_f\lambda_f \qquad (A10)$$

$$D\tilde{S}_f^+ = \tilde{S}_f^+\cdot\lambda_f \qquad (A11)$$

where we have omitted the tilde. These are the basic eqs 8 and 9. Note that C and D have the same eigenvalues. In general I is larger than P; therefore, the dimension of D is larger, and the additional eigenvalues of D are zero. Let us now normalize the orthogonal eigenvectors $\vec{L}_f$ of C so that $\langle \vec{L}_f \vec{L}_f \rangle = \lambda_f$.

$$L^+L = \Lambda \qquad (A12)$$

From eq A10 then follows

$$C = L\Lambda L^{-1} = LL^+LL^{-1} = LL^+ = \sum_f L_{pf} L_{p'f} \quad (A13)$$

that is, a few main components with large λ are sufficient to reproduce the correlation matrix with high accuracy. The normalization of the eigenvectors of D, which is compatible with eqs 5 and A12, is

$$ShS^+ = 1 = \delta_{fg}$$

as can be seen from

$$LL^+ = C = VhV^+ = LShS^+L^+$$

The statement of section 2 that L_{pf} is also the correlation coefficient K_{pf} of the linear regression (eq 5) follows from the following set of equations:

$$K_{pf} = \sum_i V_{pi}S_{fi} / \left(\sum_i V_{pi}{}^2 \sum_i S_{fi}{}^2\right)^{1/2} = h\sum_i V_{pi}S_{fi}$$

i.e.

$$K = hVS^+ \qquad (A14)$$

$$CK = hCVS^+ = h^2VV^+VS^+ = hVDS^+$$

$$= hVS^+\Lambda = K\Lambda \qquad (A15)$$

$$K^+K = h^2SV^+VS^+ = hSDS^+ = hSS^+\Lambda = \Lambda \qquad (A16)$$

References and Notes

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