VOLUME 111, NUMBER 22
OCTOBER 25, 1989

JOURNAL
OF THE
AMERICAN
CHEMICAL
SOCIETY

A New Population Analysis Based on Atomic Polar Tensors

J. Cioslowski

Contribution from the Los Alamos National Laboratory, Theoretical Division, Group T-12, MS-J569, Los Alamos, New Mexico 87545. *Received September 26, 1988*

Abstract: A new population analysis which provides values of atomic charges in molecules is proposed. The atomic charge is related to trace of the corresponding atomic polar tensor (tensor of the derivatives of dipole moment with respect to atomic Cartesian coordinates). The resulting electron populations do not require any direct reference to the basis set used, and they can be calculated for both HF and correlated wave functions. The charges are computed for several molecules and compared with the results of Mulliken population analysis.

Electronic structure calculations (both ab initio and semiempirical) yield the wave function and the corresponding energy of a molecule in a particular electronic state. The wave function itself is not very suitable for interpretation, as it is a function of Cartesian coordinates of several electrons. A much clearer picture is provided by the electron density which depends only on three Cartesian coordinates. One can gain some insight into the electronic structure of molecules from the electron density plots. Yet chemists need even more simplified characteristics of the wave function in order to predict chemical reactivity and other properties of molecules in a semiquantitative way.

The notion of the electron population of a given atom (the atomic charge in the molecule) has been put forward a long time ago.[1] However, there are serious problems with the electron population schemes currently used by chemists. Most approaches are based on projecting the electron density onto some reference basis set. The population analyses of Mulliken,[2] Löwdin,[3] Roby,[4] and Mayer,[5] among others, fall into this category. In these approaches the reference basis set is related directly to the AO basis set used in actual calculations. On the other hand, Davidson[6] proposed a projection of the density onto a minimal AO basis set. Finally, the dependence of the computed atomic populations on the basis sets has been reduced to some degree in the analysis proposed by Weinhold et al.[7] through the use of atomic natural orbitals.

In principle, one could expand the molecular orbitals into a complete set of basis functions centered at any atom in the molecule under consideration. In such calculations, all the aforementioned population analyses would assign all electrons to this particular atom. One quickly realizes that classical methods of the electron distribution analysis yield atomic charges that reflect mostly properties of the basis sets used in calculations rather than the distribution itself.

The practical consequences of the above observation are widely known and will not be discussed here. The failure of Mulliken analysis in the case of lithium compounds can serve as a typical example.[8]

An elegant approach that provides a remedy for the above problems is based on a numerical integration of the electron density. The technique designed for linear molecules[9,10] was subsequently extended to systems of an arbitrary shape.[11-14] Space

---

[1] Mulliken, R. S. *Phys. Rev.* **1932**, *41*, 66; *J. Chem. Phys.* **1935**, *3*, 573.
[2] Mulliken, R. S. *J. Chem. Phys. 23* (1955) 1833, 1841, 2338, 2343.
[3] Löwdin, P. O. *J. Chem. Phys.* **1955**, *21*, 374.
[4] Roby, K. R. *Mol. Phys.* **1974**, *27*, 81.
[5] Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270. Mayer, I. *Chem. Phys. Lett.* **1984**, *110*, 440.
[6] Davidson, E. R. *J. Chem. Phys.* **1967**, *46*, 3320.
[7] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.
[8] See, for example, discussion in ref 10.
[9] Streitwieser, A., Jr.; Collins, J. B.; McKelvey, J. M.; Grier, D.; Sender, J.; Toczko, A. G. *Proc. Natl. Acad. Sci. U.S.A* **1979**, *76*, 2499.
[10] Collins, J. B.; Streitwieser, A. Jr. *J. Comput. Chem.* **1980**, *1*, 81.
[11] Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.
[12] Bader, R. F. W. Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.
[13] Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893.
[14] Biegler-König, F. W.; Nguyen-Dang, T. T.; Tal, Y.; Bader, R. F. W.; Duke, A. J. *J. Phys. B: At. Mol. Phys.* **1981**, *14*, 2739.

0002-7863/89/1511-8333$01.50/0

is divided into loges that enclose the atoms, and the total electronic charge within a particular loge is assigned to the corresponding atom. There are two major disadvantages of this scheme. First, the numerical integration is costly and requires careful programming.[14] Second, there is a possibility of the existence of "empty" loges that are not associated with any particular atom.[15]

Before proposing a new approach to calculating the atomic charges in molecules, we postulate here that a good population analysis should have the following properties: (1) the atomic charges should be invariant with respect to rotations and translations of the molecule; (2) they should sum up to the total electric charge of the molecule; (3) they should reflect the symmetry of the molecule; (4) they should tend to a well-defined limit as the basis set becomes complete; (5) they should have a definite physical interpretation; (6) they should be feasible for computing from both the HF and correlated wave functions, obtained from both AO and floating basis sets (the definition of atomic charges should be valid for both the ground and excited states); (7) they should be feasible for computing in an economical way, preferably directly from the data provided by standard quantum-mechanical programs. Certainly, postulates 1–4 are necessary to guarantee the calculated charges to be physically meaningful. The seventh postulate reflects the practical point of view of the computational chemist.

Atomic Polar Tensors and GAPT Atomic Charges

The atomic polar tensor $\mathbf{V}^{\mathrm{A}}$[16,17] of atom A is defined by its components that are the first derivatives of the dipole moment of the molecule with respect to the Cartesian coordinates, A_x, A_y, A_z:

$$V_{pq}^{\mathrm{A}} = \partial\mu_p/\partial A_q \qquad p, q = x, y, z \tag{1}$$

The components of $\mathbf{V}^{\mathrm{A}}$ are not invariant with respect to rotations of the coordinate system, but all its norms are:

$$\|\mathbf{V}^{\mathrm{A}}\|_k = \mathrm{Tr}(\mathbf{V}^{\mathrm{A}})^k \tag{2}$$

Thanks to invariance of the dipole moment with respect to translations of the origin of the coordinate system,[18] a unique condition is satisfied by the norm of rank one:

$$\sum_{\mathrm{A}} Q^{\mathrm{A}} = Q \tag{3}$$

where

$$Q^{\mathrm{A}} = (1/3)\|\mathbf{V}^{\mathrm{A}}\|_1 \tag{4}$$

and Q is the total charge of molecule. One should note that this property is not shared by the "effective charges" derived from IR intensities,[19] for they are related to $\|\mathbf{V}^{\mathrm{A}}\|_2$.

If the molecule under consideration were just a collection of fractional charges Q^{A}, Q^{B}, ... centered at the nuclei A, B, ..., respectively, the fractional charges could be calculated exactly from eq 4. We propose here to accommodate eq 4, or more explicitly

$$Q^{\mathrm{A}} = (1/3)\left(\frac{\partial\mu_x}{\partial x_{\mathrm{A}}} + \frac{\partial\mu_y}{\partial y_{\mathrm{A}}} + \frac{\partial\mu_z}{\partial z_{\mathrm{A}}}\right) \tag{5}$$

as a new definition of the atomic charges in molecules. For the sake of brevity, we will refer to Q^{A} as to GAPT (for "generalized atomic polar tensors") atomic charges. One should point out that even if the dipole moment of charged molecules is origin-dependent, the GAPT charges are not.

The GAPT atomic charges have all the desirable properties we have postulated in the previous section of this paper. They are invariant with respect to changes of the coordinate system, they sum up to the total electric charge of the molecule, and they are not directly related to the choice of a particular basis set. Their basis set dependence stems only from the fact that the basis set can be incomplete. For that reason, they approach a well-defined limit as the basis set becomes complete. Also, the GAPT atomic charges have a clear physical interpretation. Finally, one has to point out that they can be calculated for both the HF and correlated (CI, MBPT, CC, etc.) wave functions. The basis sets used in calculations can consist of atomic orbitals and/or floating and bond functions (see the next section for more details). One should add that a generalization of the above scheme to other electronic properties has been also proposed.[20]

Computational Considerations

Calculation of Q's requires solving the CPHF equations,[21] as the atomic polar tensor is a second-order response property. An alternative route involves computation of the geometry gradients in the presence of an electric field followed by a numerical differentiation.[22] The former approach is clearly preferable for ab initio HF wave functions, whereas the latter one is more practical for correlated wave functions and semiempirical Hamiltonians. In each case, it is a trivial task to incorporate computation of the GAPT charges into existing quantum-mechanical programs. For most ab initio packages it can be accomplished without any additional programming by just calling proper sequences of existing links.

Calculation of Q's in the case of floating basis functions requires an additional comment. Although the definition of charges allows for arbitrary molecular geometries, the positions of floating (and/or bond) functions have to be optimized. Moreover, one has to include a correction term in the definition of Q's to take into account the variation of these positions due to the external electric field.

Let $E(\epsilon_p,A_q,\mathbf{r})$ denote the total energy of the molecule in the presence of electric field ϵ_p directed along the p ($p = x, y, z$) axis. A_q is the q ($q = x, y, z$) coordinate of the atom A (=0 for the actual geometry) and r is the vector of Cartesian coordinates of the centers of floating functions. We have (note the absence of gradient of E with respect to $\mathbf{r}$):

$$E(\epsilon_p,A_q,\mathbf{r}) = E(0,0,\mathbf{0}) + \epsilon_p\frac{\partial E}{\partial\epsilon_p} + A_q\frac{\partial E}{\partial A_q} + (1/2)\epsilon_p{}^2\frac{\partial^2 E}{\partial\epsilon_{\mathrm{p}}{}^2} + (1/2)A_q{}^2\frac{\partial^2 E}{\partial A_q{}^2} + \epsilon_p A_q\frac{\partial^2 E}{\partial A_q\partial\epsilon_p} + \epsilon_p\mathbf{r}^{+}\cdot\mathbf{f}^{\mathrm{A}} + A_q\mathbf{r}^{+}\cdot\mathbf{g}^{\mathrm{A}} + (1/2)\mathbf{r}^{+}\mathbf{H}^{\mathrm{A}}\mathbf{r} \tag{6}$$

where

$$f_i{}^{\mathrm{A}} = \frac{\partial^2 E}{\partial\epsilon_p\partial r_i},\ g_i{}^{\mathrm{A}} = \frac{\partial^2 E}{\partial A_q\partial r_i},\ \text{and } H_{ij}{}^{\mathrm{A}} = \frac{\partial^2 E}{\partial r_i\partial r_j} \tag{7}$$

Requesting E to be stationary with respect to $\mathbf{r}$, we obtain:

$$\mathbf{r} = -(\mathbf{H}^{\mathrm{A}})^{-1}\,(\epsilon_p\mathbf{f}^{\mathrm{A}} + A_q\mathbf{g}^{\mathrm{A}}) \tag{8}$$

and

$$V_{pq}{}^{\mathrm{A}} = \frac{\mathrm{d}^2 E}{\mathrm{d}A_q\mathrm{d}\epsilon_p} = \frac{\partial^2 E}{\partial A_q\partial\epsilon_p} - (\mathbf{g}^{\mathrm{A}})^{+}(\mathbf{H}^{\mathrm{A}})^{-1}\,\mathbf{f}^{\mathrm{A}} \tag{9}$$

The correction (which vanishes when the AO basis set becomes complete) can be calculated easily. One should note that a similar formalism has been recently advocated by Almlöf et al. in the calculations of molecular polarizabilities.[23]

---

(15) There is no theorem that guarantees that the electron density has only one extremum along the bond between two atoms. Examples of a violation of this assumption are well known; see, for example: Gatti, C.; Fantucci, P.; Pacchioni, G. *Theor. Chim. Acta* **1987**, *72*, 433.

(16) Biarge, J. F.; Herranz, J.; Morcillo, J. *An. R. Soc. Esp. Fis. Quim. Ser. A* **1961**, *57*, 81.

(17) Person, W. B.; Newton, J. H. *J. Chem. Phys.* **1974**, *61*, 1040.

(18) Bogaard, M. P.; Haines, R. *Mol. Phys.* **1980**, *41*, 1281. Page, M.; Saxe, P.; Adams, G. F.; Lengsfield, B. H., III *Chem. Phys. Lett.* **1984**, *104*, 587.

(19) King, W. T.; Mast, G. B.; Blanchette, P. P. *J. Chem. Phys.* **1972**, *56*, 4440. King, W. T.; Mast, G. B. *J. Phys. Chem.* **1976**, *80*, 2521.

(20) Cioslowski, J. *Phys. Rev. Lett.* **1989**, *62*, 1469.

(21) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 225.

(22) Backsay, G. B.; Saebo, S.; Taylor, P. R. *Chem. Phys.* **1984**, *90*, 215.

(23) Almlöf, J.; Helgaker, T.; Taylor, P. R. *J. Phys. Chem.* **1988**, *92*, 3029.

Table I. Atomic Charges of Li Atom in LiF Molecule (Experimental Geometry, R_{LiF} = 1.564 Å

basis	μ [D]	Q_{Mull}	Q_{GAPT}	μ/R^a
STO-3G	3.6051	0.2277	0.5482	0.4799
4-31G	6.4308	0.7189	0.8396	0.8561
6-31G*	6.2099	0.6612	0.8379	0.8267
6-31G* PLUS[b]	6.1537	c	0.8245[d]	0.8192
6-31+G*	6.6022	0.7371	0.9033	0.8789

[a] Dipole moment/bond length. [b] The 6-31G* basis set with a ghost oxygen atom located on the Li–F bond. [c] Charges: Li +0.8228, F -0.5865, ghost -0.2363. [d] Charges without correction, eq 9: Li +0.8607, F -0.7883, ghost -0.0725.

In Table I we display the dependence of the calculated charges for the LiF molecule. The GAPT charges are well defined for the floating basis set ("6-31G* PLUS"). There is no simple way to assign the ghost Mulliken charges to the Li and F atoms.

Results of Test Calculations and Discussion

In Table II we present the GAPT atomic charges calculated for several molecules. For the purpose of comparison, we also quote the respective Mulliken charges.

The GAPT charges reflect the physical picture one would expect from the considerations based on the "chemical sense". The magnitudes of charges in the CH_4, C_2H_4, C_2H_6, and C_6H_6 molecules are very small. Mulliken analysis assigns large (unphysical) negative charges to the carbon atoms in hydrocarbons. As expected, the hydrogen atoms is the acetylene molecule bear positive charges which reflects the acidity of C_2H_2. The phenomenon of the C^+H^- polarization in alkanes versus the C^-H^+ polarization in alkenes and alkynes probably stems from the changes in the electronegativity of the C atoms due to different hybridizations. The results for the lithium compounds exhibit a decisive improvement over Mulliken analysis. The LiH molecule is predicted to be ionic, although less then LiF. Mulliken analysis predicts almost covalent bonding in LiH. The Li–C bond in CH_3Li is found to be as ionic as the Li–H bond, in agreement with the result of a direct integration of the electron density.[10] Again, Mulliken analysis fails to predict the correct magnitude of the atomic charges. The C–Li bonds in CLi_4 are found to be more covalent than in CH_3Li.

All the above calculations have been performed at optimized geometries in order to fully explore the basis set dependence of

Table II. Atomic Charges in Selected Molecules: Optimized Geometries Used. The STO-3G/4-31G/6-31G** Results

molecule		Q_{Mull}	Q_{GAPT}
CH_4	C	-0.2625/-0.6114/-0.4733	-0.0876/0.0049/0.0727
	H	0.0656/0.1529/0.1183	0.0219/-0.0012/-0.0182
C_2H_2	C	-0.1089/-0.2960/-0.2335	-0.1938/-0.2384/-0.2153
	H	0.1089/0.2960/0.2305	0.1938/0.2384/0.2153
C_2H_4	C	-0.1270/-0.3263/-0.2544	-0.0994/-0.0599/-0.0446
	H	0.0635/0.1631/0.1272	0.0497/0.0300/0.0223
C_2H_6	C	-0.1747/-0.4514/-0.3346	0.0117/0.1020/0.1446
	H	0.0582/0.1505/0.1115	-0.0039/-0.0337/-0.0482
$H_2C^aC^bC^aH_2$	C^a	-0.1698/-0.3831/-0.3855	-0.1937/-0.2021/-0.1795
	C^b	0.0285/0.0063/0.1646	0.1215/0.2062/0.1993
	H	0.0777/0.1899/0.1516	0.0665/0.0495/0.0399
$C_3H_3^+$	C	0.1014/-0.0336/0.0275	0.0404/0.0763/0.1007
	H	0.2319/0.3669/0.3058	0.2929/0.2571/0.2327
$C_5H_5^-$	C	-0.1638/-0.2588/-0.2099	-0.1455/-0.1412/-0.1389
	H	-0.0362/0.0588/0.0099	-0.0545/-0.0588/-0.0611
C_6H_6	C	-0.0629/-0.1894/-0.1477	-0.0556/-0.0279/-0.0218
	H	0.0629/0.1894/0.1477	0.0556/0.0279/0.0218
CH_3Li	C	-0.2416/-0.7584/-0.6173	-0.5610/-0.4386/-0.3880
	Li	0.1580/0.4613/0.4178	0.5681/0.6641/0.6667
	H	0.0279/0.0991/0.0662	-0.0024/-0.0752/-0.0929
CLi_4	C	0.0291/-0.7485/-0.5082	-0.9869/-0.6057/-0.6276
	Li	-0.0073/0.1871/0.1270	0.2467/0.1514/0.1569
HCN	N	-0.1614/-0.3365/-0.3858	-0.1315/-0.2535/-0.2766
	C	0.0118/0.0108/0.1177	-0.1364/-0.0558/0.0040
	H	0.1496/0.3258/0.2682	0.2679/0.3094/0.2727
HNC	C	0.1339/0.3020/0.1483	0.1981/0.2723/0.2256
	N	-0.3986/-0.7374/-0.5088	-0.6264/-0.8002/-0.7004
	H	0.2647/0.4354/0.3606	0.4283/0.5280/0.4748
$H_2CN^bN^a$	N^a	-0.0286/-0.0679/-0.1860	-0.3792/-0.6862/-0.7097
	N^b	-0.0576/-0.1899/0.1290	0.5385/0.9075/1.0223
	C	-0.0868/-0.1684/-0.2836	-0.3747/-0.4538/-0.5300
	H	0.0865/0.2131/0.1703	0.1077/0.1163/0.1087
CO	C	0.1989/0.3932/0.2683	0.1637/0.4031/0.3612
	O	-0.1989/-0.3932/-0.2683	-0.1637/-0.4031/-0.3612
CO_2	C	0.4439/0.9632/0.8925	0.9511/1.4559/1.5152
	O	-0.2220/-0.4816/-0.4463	-0.4756/-0.7280/-0.7576
$OC^aC^bC^aO$	O	-0.1953/-0.4784/-0.4143	-0.7446/-1.1447/-1.1386
	C^a	0.3180/0.5376/0.4030	1.6172/2.0251/2.0438
	C^b	-0.2453/-0.1185/0.0226	-1.7451/-1.7608/-1.8098
HCNO	O	-0.2143/-0.5228/-0.5659	-0.5524/-0.7360/-0.9141
	N	0.0018/-0.0115/0.2048	0.6323/0.7754/1.0491
	C	0.0376/0.1707/0.0655	-0.4268/-0.3964/-0.4645
	H	0.1749/0.3636/0.2956	0.3468/0.3570/0.3295
H_2CO	O	-0.1880/-0.4853/-0.4314	-0.2964/-0.6356/-0.6735
	C	0.0750/0.1760/0.2450	0.2802/0.6851/0.7899
	H	0.0565/0.1547/0.0932	0.0081/-0.0248/-0.0582
$H_2C^aC^bO$	O	-0.1864/-0.5249/-0.4376	-0.5091/-0.8760/-0.8889
	C^a	0.2596/0.5166/0.5508	0.8135/1.1792/1.2419
	C^b	-0.2464/-0.4545/-0.4868	-0.5408/-0.6060/-0.6161
	H	0.0866/0.2314/0.1868	0.1182/0.1514/0.1316
CH_3F	C	-0.0462/-0.0350/0.0866	0.2656/0.6076/0.7083
	F	-0.1460/-0.4643/-0.4071	-0.2269/-0.5336/-0.5484
	H	0.0641/0.1664/0.1068	-0.0129/-0.0247/-0.0533
CF_4	C	0.5652/1.4750/1.3133	1.3302/2.2017/2.2023
	F	-0.1413/-0.3688/-0.3283	-0.3326/-0.5504/-0.5506
FCN	N	-0.1775/-0.2163/-0.3836	-0.1775/-0.3068/-0.3740
	C	0.2191/0.5700/0.5884	0.2809/0.5727/0.7037
	F	-0.0416/-0.3536/-0.2048	-0.0855/-0.2659/-0.3297
F_2CO	O	-0.2352/-0.4437/-0.4592	-0.4412/-0.7408/-0.7753
	C	0.4766/1.1625/1.0308	1.0473/1.7950/1.8488
	F	-0.1207/-0.3594/-0.2858	-0.3030/-0.5271/-0.5367
LiH	Li	-0.0168/0.2642/0.1935	0.4578/0.6513/0.6470
	H	0.0168/-0.2642/-0.1935	-0.4578/-0.6513/-0.6470
NH_3	N	-0.4407/-0.9642/-0.7924	-0.2518/-0.7149/-0.4863
	H	0.1469/0.3214/0.2641	0.0839/0.2383/0.1621
H_2O	H	0.1653/0.4017/0.3353	0.0846/0.3234/0.2958
	O	-0.3306/-0.8034/-0.6706	-0.1691/-0.6467/-0.5916
$O^aO^bO^a$	O^a	-0.0701/-0.2116/-0.1630	-0.3254/-0.5338/-0.5585
	O^b	0.1402/0.4233/0.3261	0.6509/1.0676/1.1169
HNO	O	-0.0731/-0.3194/-0.2750	-0.0974/-0.3050/-0.3246
	N	-0.0622/-0.0023/0.0090	0.0207/0.1478/0.2160
	H	0.1353/0.3220/0.2659	0.0766/0.1572/0.1087
HF	H	0.1922/0.4792/0.3866	0.1173/0.4343/0.4199
	F	-0.1922/-0.1923/-0.3866	-0.1173/-0.4343/-0.4199
LiF	Li	0.2254/0.7189/0.6604	0.5099/0.8397/0.8373
	F	-0.2254/-0.7189/-0.6604	-0.5099/-0.8397/-0.8373
FNO	O	-0.0722/-0.2053/-0.1889	-0.1358/-0.3911/-0.3988
	N	0.1449/0.5649/0.5261	0.3309/0.9963/1.0043
	F	-0.0727/-0.3596/-0.3372	-0.1951/-0.6052/-0.6055
F_2O	O	0.0355/0.2427/0.3016	0.1147/0.3430/0.4265
	F	-0.0178/-0.1214/-0.1508	-0.0574/-0.1715/-0.2153
$BH_3 \cdots CO$	B	-0.0226/0.0283/0.0201	0.0194/0.1648/0.2428
	H	-0.0787/-0.0507/-0.0807	-0.1212/-0.1557/-0.1772
	C	0.3699/0.5278/0.5008	0.5635/0.9010/0.8510
	O	-0.1112/-0.4039/-0.2787	-0.2192/-0.5989/-0.5622
charge transfer		0.2587/0.1239/0.2221	0.3443/0.3021/0.2888
$BH^a_3 \cdots NH^b_3$	B	0.0644/0.2550/0.2081	0.4829/0.7605/0.7362
	H^a	-0.1338/-0.1511/-0.1571	-0.2101/-0.2843/-0.2810
	N	-0.3902/-0.9548/-0.7146	-0.4019/-0.6420/-0.5258
	H^b	0.2424/0.3843/0.3259	0.1831/0.2448/0.2108
charge transfer		0.3370/0.1983/0.2632	0.1474/0.0924/0.1066

Table III. Effect of Electron Correlation on the Computed GAPT Atomic Charges. The 6-31G** Basis Set and the Experimental Geometries Used

molecule		Q_{GAPT} HF	Q_{GAPT} MP2	Q_{GAPT} CISD
CH_4	C	0.0830	0.0119	0.0478
(R_{CH} = 1.092 Å)	H	−0.0208	−0.0030	−0.0120
CO	C	0.3712	0.1211	0.2437
(R_{CO} = 1.128 Å)	O	−0.3712	−0.1211	−0.2437
CO_2	C	1.4914	0.9061	1.2587
(R_{CO} = 1.162 Å)	O	−0.7457	−0.4531	−0.6294
HCN	H	0.2777	0.2444	0.2518
(R_{CH} = 1.065 Å)	C	−0.0077	−0.0784	−0.0431
(R_{CN} = 1.153 Å)	N	−0.2700	−0.1661	−0.2086
LiF	Li	0.8379	0.7727	0.7920
(R_{LiF} = 1.564 Å)	F	−0.8379	−0.7727	−0.7920

the computed charges. Our conclusion is that the GAPT charges do not change significantly going from the 4-31G to 6-31G** basis set (the only exception is the NH_3 molecule for which the optimized geometry changes substantially). In ref 20 we have computed the GAPT atomic charges in some lithium compounds using the 6-31++G** basis set. They compare very favorably to the present 6-31G** results. On the other hand, Mulliken net charges vary to a much larger extent. The STO-3G results underestimate ionicity as measured by the magnitude of the GAPT charges. This is caused by the inadequate flexibility of the minimal basis to provide correct dipole moments (see Table I). The STO-3G Mulliken charges have a sign reversed in several cases (CLi_4, HCNO, and LiH molecules).

Our population analysis predicts quite large atomic charges in molecules with multiple bonds (CO, CO_2, C_3O_2, O_3, HCNO, etc.). We found that this is an artifact of the HF wave function rather than an internal failure of our method. We recalculated the atomic charges in the CH_4, CO, CO_2, HCN, and LiF molecules using CISD and MP2 wave functions (with the dipole moments computed as the energy derivatives, Table III). Inclusion of electron correlation reduces the magnitude of atomic charges in all cases. The reduction is larger in the MP2 approach than in CISD. We trust the MP2 results more because CISD lacks the property of size extensivity and therefore might be incapable of accounting for the most part of the effect of the electron correlation on the calculated charges.

Electron correlation does not significantly change the charges in molecules with single bonds. This is true for both covalent (CH_4) and ionic (LiF) bonds. On the other hand, there is a large reduction of the charges in the CO, CO_2, and HCN molecules. The carbon monoxide molecule, which is predicted semipolar at the HF level, becomes almost homopolar according to the MP2 calculations. We conclude that electron correlation is essential for obtaining a correct picture of the electron distribution in molecules with multiple bonds.

In the present paper we have succeedced in proposing a new population analysis that provides insight into the electron distribution in molecules that is not distorted by an arbitrary choice of the reference basis set. Our procedure is simple and feasible for practical calculations. We have demonstrated its validity through numerical calculations on neutral and charged molecules, and molecular complexes.

We are planning to test our population analysis on semiempirical methods. Since they partially account for the electron correlation (through a numerical parametrization), we hope that they would provide reasonable GAPT atomic charges. The field of organometallic compounds and metal complexes can also benefit from our new definition of atomic charges.

Acknowledgment. This research has been performed under the auspices of U.S. D.O.E. All the computations have been carried out on the CRAY X-MP48 digital computer. The author acknowledges inspiring discussions with Drs. P. J. Hay and R. L. Martin.

Base-Initiated Aldol Condensations in the Gas Phase

Roger N. Hayes, Richard P. Grese, and Michael L. Gross*

Contribution from the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588. Received October 3, 1988

Abstract: The enolate anion $CH_2{=}CHO^-$ reacts with acetaldehyde in the gas phase at ca. 0.1 Torr to produce a "stable" adduct that is amenable to study by collisional activation and tandem mass spectrometry (MS/MS). The activated adduct and a reference ion $HCOCH_2CH(CH_3)O^-$ both decompose by elimination of methane and water and by a retro reaction to re-form $CH_2{=}CHO^-$. Although the kinetic energy releases associated with the decompositions and the charge reversed spectra of the adduct and reference are nearly identical, the extent of water and methane loss is considerably attenuated for the ion–molecule reaction adduct. These two losses are assigned to be characteristic of a species of tetrahedral geometry. The adduct undergoes these losses less abundantly because, in addition to existing as a tetrahedral complex, it also is formed as ion–dipole and proton-bound species. The enolate of acetone reacts in a similar way with neutral acetone to give also three adducts: ion–dipole, proton-bound, and tetrahedral complexes.

Aldol condensations, as first reported by Kane in 1838,[1] and later by Wurst in 1872,[2] constitute an important class of organic reactions. A study of the mechanism of the aldol reaction can to some extent lead to a clearer understanding of other condensation reactions that can be described by a priori similar mechanisms. For example, the Claisen, Knoevenagel, Doebner, Perkin, Stobbe, and Reformatsky reactions are all considered to be nucleophilic substitutions at carbonyl carbon.[3]

In the presence of dilute base or dilute acid, two molecules of an aldehyde or a ketone may condense to form a β-hydroxy aldehyde or β-hydroxy ketone. The generally accepted mechanism for the base-catalyzed aldol reaction in the condensed-phase is

---

[1] Kane, R. *Ann. Phys. Chem. 2* **1838**, *44*, 475. Kane, R. *J. Prakt. Chem.* **1838**, *15*, 129.

[2] Wurst, A. *Bull. Soc. Chim. Fr.* **1872** *17*, 436.

[3] House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin/Cummings: Menlo Park, CA, 1972; p 629. March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 849.

0002-7863/89/1511-8336$01.50/0