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Application of the GAPT Population Analysis to Some Organic Molecules and Transition Structures

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Abstract: Atomic charges in ozone, carbon monoxide, silylene, silaketene and dimethylsilaketene (for both the pyramidal minimum and the planar transition state), 2-methyl-2-silacyclopropanone, ethylenebromonium cation (open and bridged), (*Z*)-1,3-butadiene, 1,3-cyclopentadiene, cyclopropene, methylenecyclopropene, the transition state for the Diels–Alder reaction between 1,3-cyclopentadiene and cyclopropene, and (*E*,*E*,*E*,*E*,*E*)-1,3,5,7,9-decapentaene have been calculated within the recently introduced GAPT population analysis. Effects of different basis sets and electron correlation on the atomic charges have been examined. On the basis of these studies it is found that the GAPT population analysis should be recommended as a standard tool for analyzing the electronic structure of organic molecules and transition states.

The importance of atomic charges in the interpretation of the results of electronic structure calculations cannot be overestimated. Therefore, it is not surprising that as early as in 1955 the first population analysis was proposed by Mulliken.[1] Since then, criticism of the original approach has resulted in a plethora of proposals[2–6] aiming at improving Mulliken analysis. Unfortunately, with Bader's atomic charges[7] being the remarkable exception, all of the published schemes are incapable of providing atomic charges without explicit reference to the basis sets used in the actual calculations. This has important theoretical and practical consequences. First, the computed charges are not true atomic properties for they cannot be extracted from the electronic wave function alone. Hence they cannot be assigned any explicit physical meaning. Second, one should expect significant sensitivity of the computed charges to the basis sets. Although the atomic charges calculated by Bader's definition[7] do not suffer from the above shortcomings, their calculation is computationally very demanding because of the use of numerical integration.

Recently, a population analysis that uses isotropically averaged atomic polar tensors as effective atomic charges has been pro-

$$Q_A = \tfrac{1}{3}\left(\frac{\partial \mu_x}{\partial x_A} + \frac{\partial \mu_y}{\partial y_A} + \frac{\partial \mu_z}{\partial z_A}\right) \qquad (1)$$

posed.[8,9] In eq 1 μ_x, m_y, and μ_z are the components of the dipole moment vector and x_A, y_A, and z_A are the Cartesian coordinates of the atom A. Such a definition of atomic charge has been used for some time in IR spectroscopy,[10] but its application in the interpretation of the results of electronic structure calculations has remained unexplored. In fact, some authors[11] have attempted to interpret the generalized atomic polar tensor (GAPT) charges, eq 1, in terms of Mulliken charges!

The calculation of Q_A's requires the solution of the coupled perturbed Hartree–Fock (CPHF) equations and therefore is more expensive than the computation of Mulliken charges. However, most modern electronic structure calculations construct the energy Hessian matrix to find and characterize stationary points on the potential energy hypersurface. In such instances, the GAPT charges are obtained as a byproduct without substantial increase in computing time. Preliminary calculations[9] with a set of 34 molecules of various size have shown that GAPT charges are quite insensitive to the quality of basis set used and have signs and magnitudes in accordance with the chemical rules of thumb.

In the present paper we report results of the GAPT population analysis for 16 (mostly organic) systems, including two cations and three transition structures. Our goals are threefold: First, we provide further evidence of the computational feasibility and the basis set insensitivity of GAPT charges. Second, we examine the effects of electron correlation on computed atomic charges. Third, the main goal of our study is to convince the chemical community to accept the GAPT charges as a standard tool for the interpretation of the electronic structure of molecules.

Results

The GAPT atomic charges are displayed in Table I. All molecular geometries were optimized within the quoted basis sets at the given level of theory. For the correlated methods used, the dipole moment was calculated as the respective energy derivative. The numbering of atoms is given in Figure 1.

We begin our presentation with the ozone molecule (**1**). It is well-known that the SCF method grossly overestimates the ionicity of this system.[12] This is reflected in the calculated atomic charges that are reduced by about 25% at the CCSD level of theory. The SCF charges calculated with the DZP basis set compare favorably with those obtained previously with the 4-31G and 6-31G* basis sets.[9]

The next system we discuss is the carbon monoxide molecule (**2**). The effect of electron correlation on the GAPT atomic charges has been reported previously.[9] Again, at both the SCF and CISD levels, the atomic charges are very close to those

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Table I. GAPT Atomic Charges in Selected Molecules[f]

molecule/atoms	basis set/level of theory[a]			
O_3 (**1**)	DZP[b]	DZP[b]		
	SCF	CCSD		
O1, O3	-0.5941	-0.4493		
O2	1.1883	0.8985		
CO (**2**)	DZP[c]	DZP[c]		
	SCF	CISD		
C1	0.3806	0.2400		
O2	-0.3806	-0.2400		
SiH_2 (**3**)	DZP[c]	DZP[c]		
	SCF	CISD		
Si1	0.4214	0.4205		
H2, H3	-0.2107	-0.2103		
H_2SiCO (**4**)[g]	DZP[c]	DZP[c]		
	SCF	CISD		
Si1	0.3192	0.1998		
C2	0.8143	0.8137		
O3	-0.6849	-0.6303		
H4, H5	-0.2243	-0.1916		
H_2SiCO (**5**)[h]	DZP[c]			
	SCF			
Si1	-0.0490			
C2	1.2743			
O3	-1.1343			
H4, H5	-0.0455			
$(CH_3)_2SiCO$ (**6**)[g]	DZP/DZ[c]			
	SCF			
Si1	0.4259			
C2	0.7649			
O3	-0.6994			
C4, C5	-0.1832			
H6, H7	-0.0126			
H8 H9	-0.0485			
H10, H11	-0.0014			
$(CH_3)_2SiCO$ (**7**)[h]	DZP/DZ[c]			
	SCF			
Si1	0.3119			
C2	1.0475			
O3	-1.1466			
C4, C5	-0.1024			
H6, H7	-0.0026			
H8, H9, H10, H11	-0.0007			
C_3H_6SiO (**8**)	DZP/DZ[c]			
	SCF			
O1	-0.8915			
C2	0.7347			
C3	-0.4121			
Si4	1.1119			
C5	-0.2684			
H6	0.0127			
H7	0.0084			
H8	-0.3052			
H9	0.0046			
H10	-0.0061			
H11	0.0111			
$C_2H_4Br^+$ (**9**)[i]	DZ/DZ[d]	DZP/DZ[d]	TZ2P/DZP[d]	
	SCF	SCF	SCF	
C1	0.4841	0.5192	0.5045	
C2	-0.1183	-0.0229	-0.0344	
H3	0.1678	0.1514	0.1577	
H4	0.1249	0.1188	0.1298	
H5, H6	0.1414	0.1098	0.1230	
Br7	0.0461	0.0140	-0.0035	
$C_2H_4Br^+$ (**10**)[j]	DZ/DZ[d]	DZP/DZ[d]	TZ2P/DZP[d]	
	SCF	SCF	SCF	
C1, C2	0.2454	0.3105	0.3346	
H3, H4, H5, H6	0.1422	0.1093	0.1053	
Br7	-0.0597	-0.0580	-0.0905	
C_4H_6 (**11**)[k]	6-31G*[e]			
	SCF			
C1, C2	0.0601			
C3, C4	-0.1089			
H5, H6	0.0308			
H7, H8	0.0215			
H9, H10	-0.0035			
C_5H_6 (**12**)	6-31G*[e]			
	SCF			
C1	0.0708			
C2, C3	-0.0847			
C4, C5	-0.0050			
H6, H7	-0.0053			
H8, H9	0.0307			
H10, H11	0.0288			
C_3H_4 (**13**)	6-31G*[e]			
	SCF			
C1	0.1523			
C28 C3	-0.1062			
H4, H5	0.0913			
H6, H7	-0.0613			
C_4H_4 (**14**)	4-31G[e]	6-31G[e]	6-31G[e]	6-31G**[e]
	SCF	SCF	MP2	SCF
C1	-0.3540	-0.3685	-0.2176	-0.3765
C2	0.4751	0.4870	0.3397	0.5331
C3, C4	-0.2175	-0.2248	-0.1843	-0.2069
H5, H6	0.00249	0.0297	0.0229	0.0181
H7, H8	0.1321	0.1359	0.1004	0.1104
C_7H_{10} (**15**)[l]	6-31G*[e]			
	SCF			
C1, C2	0.0216			
C3, C4	-0.0305			
C5, C6	-0.0254			
C7	0.0296			
H8, H9	0.0061			
H10, H11	0.0057			
H12, H13	0.0142			
H14, H15	0.0437			
H16	-0.0601			
H17	-0.0404			
$C_{10}H_{12}$ (**16**)[m]	6-31G[e]			
	SCF			
C1, C10	0.2054			
C2, C9	-0.0987			
C3, C8	0.0470			
C4, C7	-0.0216			
C5, C6	0.0097			
H11, H22	-0.0161			
H12, H21	-0.0463			
H13, H20	-0.0126			
H14, H19	-0.0246			
H15, H18	-0.0197			
H16, H17	-0.0224			

[a] SCF = self-consistent field (Hartree-Fock), CISD = configuration interaction involving single and double excitations, CCSD = coupled cluster including all single and double excitations, MP2 = the second-order Møller-Plesset perturbation theory. [b] Reference 19. [c] DZP = double-ζ + polarization, DZP/DZ = as DZP, but with double-ζ basis on the hydrogen atoms. See ref 15 and 19 for more details. [d] DZ/DZ = double-ζ, DZP/DZ = double-ζ + polarization functions on non-hydrogen atoms, TZ2P/DZP = triple-ζ + 2 sets of polarization functions on non-hydrogen atoms/double-ζ + polarization functions on the hydrogen atoms. See refs 17 and 19–21 for more details. [e] 4-31G, ref 22; 6-31G, ref 23; 6-31G* and 6-31G**, ref 24. [f] See Figure 1 for atom numbering. [g] Pyramidal minimum. [h] Planar transition state. [i] Open. [j] Bridged. [k] C_2 minimum. [l] Transition state. [m] C_{2h} minimum.

calculated within the 4-31G and 6-31G* basis sets. Analogous effects of electron correlation on the ionicity of the C=O bond in the formaldehyde molecule have been observed within Bader's formalism.[13]

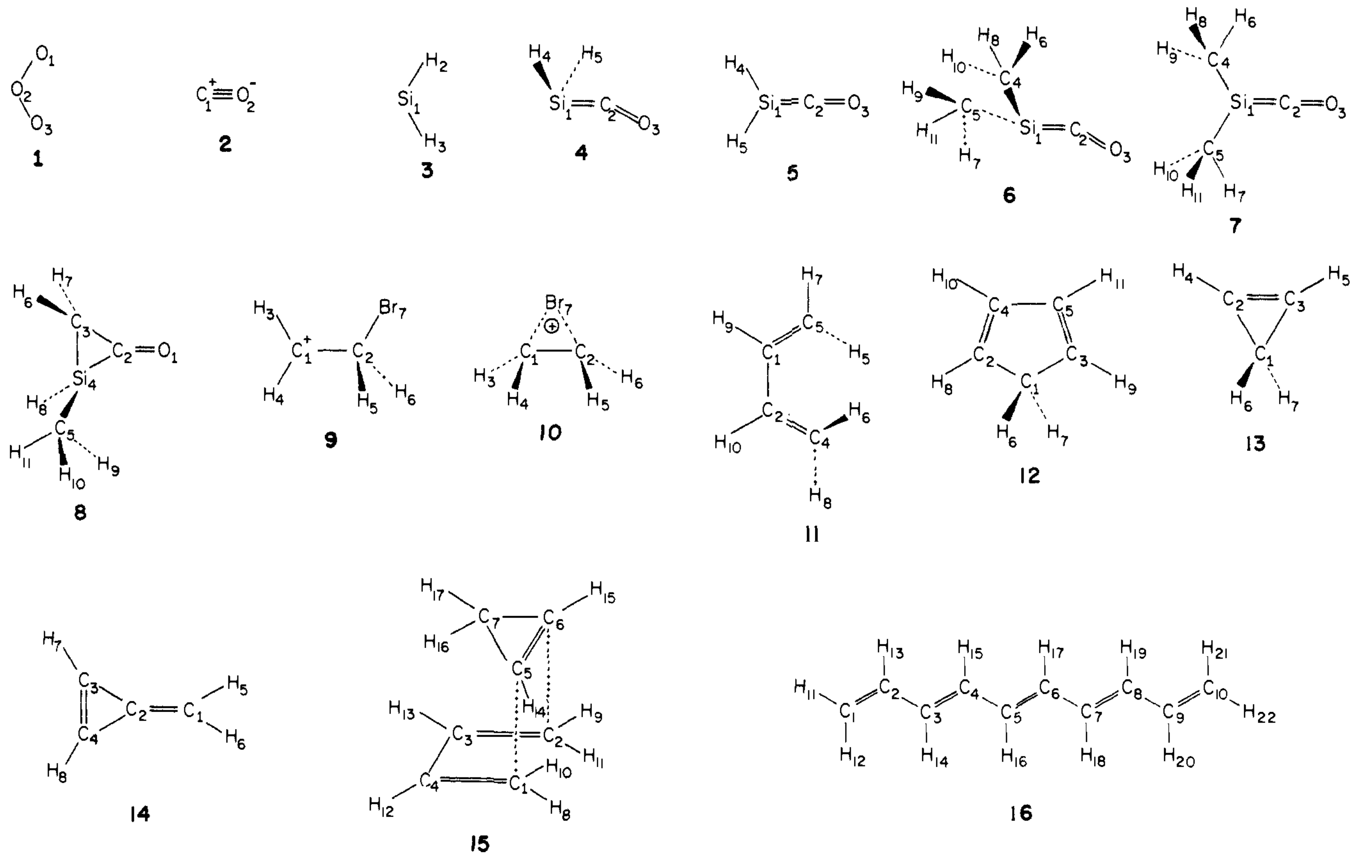

Figure 1.

The behavior of atomic charges in the silylene molecule (**3**) is markedly different from the previous examples. Upon the inclusion of electron correlation effects, the charges remain almost unchanged, at least at the CISD level of theory. This is consistent with the trends observed in Bader's charges.[14] Interaction between carbon monoxide and silylene yields the silaketene molecule. Unlike the ketene molecule, silaketene has a nonplanar geometry (**4**), whereas the planar arrangement of atoms corresponds to the transition state (**5**).[15] The polarities of the Si–H bonds in **3** and **4** are quite similar. The C=O bond in **4** is less polarized than in the ketene molecule,[9] and as expected, the polarity decreases (although slightly) upon the inclusion of electron correlation. Similar observations are relevant to the dimethylsilaketene system (**6** and **7**). The 2-methyl-2-silacyclopropanone molecule (**8**) possesses a variety of bonds. As in **6**, the Si–C and Si–H bonds are strongly polarized. At the same time, the C–H bond is almost nonpolar.

The ethylenebromonium cation is of great importance in the electrophilic addition of bromine to olefins.[16] It can exist in either open (2-bromoethyl cation, **9**) or bridged (bromiranium, **10**) form. The bridged form is energetically lower according to recent calculations.[17] In either case, the GAPT atomic charges indicate the presence of an almost neutral bromine atom. In the open form, the positive charge is spread over the C_1 atom and all the hydrogens. In the bridged form, the carbon atoms bear about 65% of the positive charge. The atomic charges change by less than ±0.02 upon going from the DZP/DZ to the TZ2P/DZP basis sets.

The unsaturated hydrocarbons are represented in our study by the molecules **11**–**16**. The carbon atoms in the (*Z*)-1,3-butadiene molecule (**11**) have small negative and positive charges. A similar pattern of charges is observed in the 1,3-cyclopentadiene molecule (**12**). Even if the internal stress in the cyclopropene molecule (**13**) appears to amplify the atomic charges to some extent, the ionicity of both the C–C and C–H bonds remains quite small. This is not the case, however, in the methylenecyclopropene molecule (**14**), which represents one of the simplest examples of a nonalternant hydrocarbon. Even the crude π-electron Hückel theory predicts a significant dipole moment for this molecule, and this is confirmed by experimental measurements.[18] Both the direction of the observed dipole moment and the calculated atomic charges indicate the electron transfer from the cyclopropene ring to the methylene moiety. Although inclusion of the electron correlation effects through the MP2 level of theory does not significantly decrease the calculated dipole moment,[18] it reduces the magnitude of atomic charges by a substantial amount. Again, the calculated GAPT charges are found to be rather insensitive to the choice of basis set.

The GAPT population analysis is suitable for computing atomic charges for transition structures as well. In the transition structure (**15**) for the Diels–Alder reaction between cyclopentadiene and cyclopropene, the atomic charges span the range of values typical of nonpolar hydrocarbons.

Finally, we present the GAPT atomic charges for the all-trans isomer of 1,3,5,7,9-decapentaene (**16**). All of the hydrogen atoms bear small negative charges. The carbon atoms exhibit a pattern of alternating charges. The amplitude of these charges decreases

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toward the inward portion of the molecule. This is in full agreement with the predictions based on the arguments of chemical graph theory.[25]

Conclusions

On the basis of the aforementioned examples we believe that the GAPT atomic charges can be a useful tool in the analysis of the electronic structure of molecules. The computed atomic charges are remarkably insensitive to the basis sets used for computing the wave function. Electron correlation effects can be significant in molecules possessing multiple bonds; however, they are predictable since they tend to decrease the atomic charges. This effect is especially pronounced in unsaturated molecules. It should be mentioned that similar observations concerning the influence of electron correlation on natural atomic charges[6] have been published very recently.[26]

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Barrier Widths, Barrier Heights, and the Origins of Anomalous Kinetic H/D Isotope Effects

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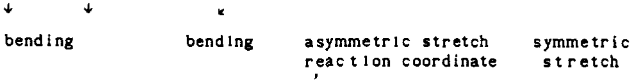
Abstract: Proton transfer between MeO^- and HOMe has been studied using ab initio molecular orbital theory. At the highest level employed (MP2/6-31+G(d)//6-31G(d) + ZPE), $-\Delta H^{298}$ and $-\Delta G^{298}$ for the formation of the ion-molecule complex $MeO^- \cdots HOMe$ from the separated reactants are 26.3 and 15.2 kcal/mol, respectively. At the 6-31G(d)//6-31G(d) level of theory, the $(MeO-H-OMe)^-$ transition structure is 2.19 kcal/mol higher in energy than the ion-molecule complex ($\Delta E^* =$ 2.19), but this barrier disappears when zero-point energies are taken into account. The performance of AM1 on this system is quantitatively different ($-\Delta H^{298} = 13.3$; $-\Delta G^{298} = 6.9$; $\Delta E^* = 4.91$; $k_H/k_D = 5.13$, increasing to 5.79 when quantum mechanical tunneling is invoked) but appears to be acceptable for the research envisaged in the title. The effect of an enforced separation of the heavy atoms upon proton transfer barriers and isotope effects (which simulates "steric effects") has been studied briefly at the 6-31G(d) level and in some detail using AM1. As predicted by a simplified two-parabola model of the barrier, ΔE^* increases linearly as the square of the heavy atom distance, and such plots extrapolate to the heavy atom distances of the fully optimized transition structures. The increase in the barriers is accompanied by a small increase in the semiclassical kinetic isotope effect, as expected from KIE theory, and a much larger increase in the tunneling correction, using Bell's treatment, in which the correction factor Q_H/Q_D depends upon the height of the barrier. Because of the relationship between barrier heights and widths, this correction becomes substantial when "steric hindrance" exists. Thus, in proton transfer between pyrrole anions and pyrroles, the KIE including the tunneling correction increases progressively from 6.6 to 9.0 to 15.6 as methyl groups are attached to the 2,5-positions and coplanarity of the two rings is enforced; for proton transfer between pyridinium cations and pyridines, the KIE's including the tunneling correction change from 5.2 to 4.6 to 5285(!) as methyl groups are attached to the 2,6-positions and coplanarity of the two rings is enforced. The energetics of proton transfer between pyridines conform to the Marcus equation, but the isotope effect and tunneling correction are smaller in the exoergic direction. The implications of the present findings for effects of pressure upon proton tunneling and tunneling effects in enzymatic hydrogen-transfer reactions are noted.

It has been the practice for some time to derive conclusions concerning the positions of transition states along the reaction coordinates of hydrogen-transfer reactions on the basis of experimentally determined slopes of Brönsted plots[1] and magnitudes of kinetic H/D isotope effects (KIE).[2] However, since the use of a Brönsted slope to deduce transition-state structure has recently come under attack,[3] the interpretation of a KIE and the factors that contribute to this effect have acquired renewed significance.

If quantum mechanical tunneling were unimportant for the case of a proton-transfer reaction, e.g., eq 1, most of the KIE would originate[2,4] in a zero-point energy difference (dZPE) between H- and D-substituted hydrogen-(deuterium-) bonded reactants (shown as their hydrogen-bonded complexes), which is only partly overcome by a residual dZPE in the transition state. The magnitude of the observed KIE would depend, inter alia, upon the degree of proton (deuteron) transfer in the transition state, and this would depend, in turn, on the separation between the proton donor and proton acceptor (X and Y in eq 1). As this separation increases, ZPE's and dZPE's of hydrogen-(deuterium-) bonded reactants will remain approximately the same. However, since the trans-

Scheme I



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