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Comprehensive Study of Density Functional Theory Based Properties for Group 14 Atoms and Functional Groups, $-XY_3$ ($X = C$, Si, Ge, Sn, Pb, Element 114; $Y = CH_3$, H, F, Cl, Br, I, At)

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All electron nonrelativistic and relativistic density functional theory calculations at the BP86/QZ4P (Slater type) level are reported for a set of fundamentally useful DFT based reactivity descriptors for group 14 elements (C, Si, Ge, Sn, Pb, Element 114 (abbreviated as Uuq)) and functional groups, $-XY_3$ ($X = C$, Si, Ge, Sn, Pb, Element 114 (Uuq); $Y = CH_3$, H, F, Cl, Br, I, At); these include electronegativity (χ), chemical hardness (η), global softness (S), and electrophilicity index (ω). This approach permits an evaluation of the discrepancies in electronegativity scales and associated properties at uniform levels affording a nonempirical analysis for the first time. The vital importance of the spin−orbit interaction, in addition to the scalar relativistic terms, is demonstrated in reproducing the experimental trends on going from top to bottom of the group. The order for isolated atoms is altered when passing to $-XY_3$ groups for all of the properties studied. For example, the calculated atomic electronegativities show a uniform decrease from C to Pb increasing again to Uuq as verified in the experimental data for C−Pb but at variance with several other scales. The sequence for functional groups is different and in accordance with experimental NMR data where available. The experimental hardness sequence for the isolated atoms (C > Pb > Si > Ge > Sn) is opposed to the trends of decreasing hardness on going down the periodic table as is found, e.g., in the halogen group and confirmed by this study. The $-XY_3$ functional groups however follow the C > Si > Ge > Sn > Pb sequence. The recently developed electrophilicity index (ω) has been shown to be highly correlated with the electron affinity rather than the electronegativity. Finally, regression analyses that discriminate between the properties are carried out to investigate the nature of additivity of atomic contributions in functional group properties.

Introduction

The periodic table has been of invaluable interest for discerning patterns of properties of elements thereby serving as a guide to discuss the synergic variations in geometry, structure, and reactivity of compounds.[1] Frequently, more insight is gained from the knowledge of the evolution in properties of different elements than from the specific numerical information.[2,3] Therefore, study of trends is of utmost importance in chemical research not only for properties directly obtainable from experiment (say ionization energy) but also for properties, not observable, emerging in concepts and principles presented (e.g., electronegativity) in the search for rationalizing chemistry. The chemical literature shows abundant examples of regular patterns for a wide variety of properties through the rows and columns of periodic table, albeit with, for some elements and some properties, some exceptions or deviations.

Reactivity descriptors finding a sharp definition in conceptual density functional theory[4] are important tools for explaining activity patterns of functional groups in chemistry. The most prominent of these descriptors is the electronegativity (χ), originally defined by Pauling[5] as the power of the atom in a molecule to draw electrons to itself. It has been the subject of intensive research initially for atoms[1,2,6−19] and later on also for functional groups.[20−30] Despite the relatively large number of scales, they mainly pertained to the first five rows, and heavier elements are often left out or given less importance. To state it alternatively, the care taken in searching accurate values for the lighter elements of a given column is not always found in their heavier congeners. The discussion of the evolution of a property (including sometimes nonmonotonic behavior) throughout a column is therefore sometimes difficult as not all relevant data are measured or derived with the same accuracy. Moreover, if the quantity considered is not sharply defined, different scales may be put forward. The electronegativity variation of the group 14 elements (the carbon group) and their functional groups, ubiquitous building blocks in all areas of chemistry, is a striking example. When looking at the data as given in Table 1, it turns out that there are important differences between the scales. The atomic sequences in the different scales can be summarized as follows.

χ**Pauling:**[1,5] C > Pb > Ge > Sn > Si
χ**Mulliken:**[6] C > Si > Ge > Sn > Pb
χ**Gordy:**[7] C > Si > Ge > Sn
χ**Allred−Rochow:**[9] C > Ge > Si > Sn > Pb
χ**Mulliken−Jaffe:**[10] C > Pb > Ge > Si > Sn
χ**Allen:**[13] C > Ge > Si > Sn
χ**Sanderson:**[15] C > Ge > Pb > Si > Sn

So, it is seen that all the scales agree only on one element: carbon, which is the most electronegative one in all scales. Other elements are found at various places depending on the choice

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TABLE 1: Comparison of Electronegativities from Various Scales[a]

	χPauling	χMulliken	χGordy	χAllred−Rochow	χMulliken−Jaffe	χAllen	χSanderson	χSuresh−Koga
C	2.55	6.43 (6.73)	2.52	2.50	2.48	2.54	2.75	2.55
Si	1.90	4.77 (4.96)	1.82	1.74	2.28	1.92	2.14	2.11
Ge	2.01	4.57 (4.71)	1.77	2.02	2.33	1.99	2.62	2.17
Sn	1.96	4.23 (4.31)	1.61	1.72	2.21	1.82	1.49	1.92
Pb	2.33	3.89 (3.85)		1.55	2.41		2.29	1.88
H	2.20	7.18 (7.26)		2.20	2.25	2.30	2.59	3.38
F	3.98	10.41 (10.84)	3.94	4.10	3.91	4.19	4.00	3.94
Cl	3.16	8.30 (8.43)	3.00	2.83	3.10	2.87	3.48	2.96
Br	2.96	7.59 (7.59)	2.68	2.74	2.95	2.68	3.22	2.69
I	2.66	6.76 (6.17)	2.36	2.21	2.74	2.36	2.78	2.49
At	2.2	6.17 (5.74)		1.90	2.85			

[a] Values in parentheses are from the present work.

of scale. Note that some of the scales have failed to give a value for the heaviest element (Pb). Such a situation is remarkable, as generally most chemists share the opinion that throughout the periodic table electronegativity increases from left to right of a period and decreases from top to bottom of a group, as described in most introductory general chemistry textbooks. This is found, e.g., for the halogens, where every scale predicts the same trend, i.e., decrease of electronegativity on moving down the group, except for the Mulliken−Jaffé scale, which predicts that astatine is more electronegative than iodine. The "anomalous" behavior of the electronegativity of the group 14 elements has been discussed by several authors of the mentioned scales, sometimes offering an interpretation, sometimes not. In our opinion the now classical 1958 paper by Allred and Rochow[9a] in which the Pauling order C > Pb > Ge > Sn > Si is modulated to C > Ge > Si ∼ Sn > Pb is one of the most elaborate discussions of electronegativity variation in rows and columns of the periodic table. In a subsequent paper,[9b] these authors have modified the electronegativity of Pb based on NMR studies: C > Pb > Ge > Si > Sn (see also the discussion by Drago[9d] and rebuttal by Allred and Rochow[9e]).

One can expect that problems similar to those encountered for group 14 elements are also met when one tries to incorporate the effect of the molecular environment on their electronegativity and passes on to the concept of group electronegativity, for which also a plethora of scales have been presented. Some scales for group 14 functional groups of formula XY_3 (X = Group 14, Y = H, Me, group 17) were reported and the results are summarized as follows.

χ**Clifford:**[21] Y = Me: X = C = Ge = Sn > Si
Y = H, F, Br: X = C > Ge > Sn > Si
Y = Cl, I: X = Ge > C > Sn > Si
X = C, Si, Ge, Sn: Y= F > Cl > Br > I > Me > H
χ**Bratsch:**[22] X = C: Y= F > Cl> H
χ**Huheey:**[23] Y = Me: X = Sn > C > Si > Ge
Y = H: X = Ge = Sn > C > Si
Y = F: X = C > Si > Ge > Sn
Y = Cl: X = C > Ge > Si > Sn
Y = Br: X = C > Ge = Sn > Si
Y = I: X = C = Ge > Sn > Si
X = C, Si: Y = F > Cl > Br > I > Me > H
X = Ge, Sn: Y = F > Cl > Br > I > H > Me
χ**Inamoto:**[24] Y = Me: X = Si > Ge > Sn > Pb
Y = F, Cl: X = C > Si > Ge
χ**Boehm-Schmidt:**[25] X = C: Y= F > Cl > H
χ**Suresh-Koga:**[30] X = C: Y = F > H
X = Si: Y= F > Cl > Br > Me
Y = Me: X = Ge > Si
Y = H: C > Ge > Si > Sn > Pb

In general, these data point out that for a given Y the sequence of XY_3 electronegativity values (X = C, Si, Ge, Sn, Pb) varies from scale to scale and that the sequence does not always parallel the isolated X electronegativity sequence. It can be seen from these scales that these are often incomplete for predicting periodicity in variations and that they do not always correlate with each other. The major drawback among many scales is that their evaluation is based on empirical quantities whose relation to electronegativity is obviously based on a model. Although Mulliken's approach of electronegativity as an average of ionization energy and electron affinity is widely acclaimed for its theoretical soundness, it was not directly suitable in the case of group electronegativity because the accuracy depends on the availability of accurate ionization energies and electron affinities. Therefore, many previous applications have led to spurious results. density functional theory (DFT) gave a boost to the Mulliken definition when it described electronegativity as the negative of the chemical potential, μ, which is in its turn defined as the first derivative of energy, E, with respect to total number of electrons, N, at constant external (i.e., due to the nuclei) potential $v(r)$[4]

$$\chi = -\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\mathrm{r})} \tag{1}$$

Using a quadratic $E = E(N)$ relationship, a finite difference approach then yields the working equation

$$\chi = \frac{I + A}{2} \tag{2}$$

i.e., Mulliken's definition.

Böhm and Schmidt had shown that the transition operator model converged to the same result.[25] As I and A can readily be calculated, eq 1 offers the opportunity for a nonempirical study of the variation of electronegativity of atoms and functional groups throughout the periodic table.

A "companion" fundamental property to the electronegativity is the chemical hardness put forward by Pearson in connection with Lewis acid−base reactions.[31−34] However, a sharp definition for hardness or softness has for a long time been lacking and therefore its use in the classification of acids and bases did not always turn out univocal. A breakthrough has been realized by Parr and Pearson identifying, within the context of conceptual DFT, the hardness as a second-order property[4]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathrm{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{v(\mathrm{r})} = -\left(\frac{\partial \chi}{\partial N}\right)_{v(\mathrm{r})} \tag{3}$$

i.e., the second derivative of the energy with respect to the number of electrons, measuring the resistance of the chemical potential to changes in number of electrons.

Within the mentioned parabolic model and the finite difference approximation, the hardness value is approximated as half the difference between ionization energy and electron affinity, i.e.

$$\eta = \frac{I - A}{2} \tag{4}$$

Subsequently, the global softness S was defined as an inversely related property to hardness as

$$S = \frac{1}{2\eta} \tag{5}$$

Latest among the properties that tried to explain charge distributions and their rearrangements upon perturbations in number of electrons or external potential of fundamental interest, for example, in physical organic chemistry, is the electrophilic capacity of atoms or functional groups. Both experimentalists and theoreticians tried to define a quantity, electrophilicity, for that purpose.[35−41] A noteworthy suggestion among various attempts was made by Maynard and co-workers based on experimental data.[42] It was proposed that electrophilicity is the ratio of the square of electronegativity and chemical hardness, affording a simple calculation of the property. Recently, Parr and co-workers gave a definitive theoretical validation and proposed that[43] the electrophilicity, ω, should be written as

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{6}$$

Despite evident correlations between ω and electron affinity, as both measure electron accepting ability, they differ because electron affinity accounts just for a single electron acceptance while ω accounts for the energy lowering of an atom or a functional group due to maximal electron flow between the atom or group and the rest of the molecule.

A quantitative discussion of all of the quantities discussed above requires knowledge of accurate (vertical) ionization energies and electron affinities. It should be noted that vertical ionization energy[44] and vertical electron affinities[45] are related to the energies of HOMO and LUMO, respectively.

The theoretical concepts and the calculational methodology sketched above enable us to gain more insight, on a nonempirical basis, on major concerns arising from our initial discussion on the behavior of the group 14 elements (vide supra). First, we would like to study the effect of moving down the periodic table for the properties of $-XY_3$ (X = C, Si, Ge, Sn, Pb, Uuq (the recently synthesized eka-Pb, element 114[46]); Y = CH_3, H, F, Cl, Br, I, At) functional groups on the basis of nonempirically and uniformly evaluated quantities such as ionization energy (I), electron affinity (A), electronegativity (χ), chemical hardness (η), global softness (S), and electrophilicity index (ω). It is tempting to follow the same line for a group of elements for which irregularities in periodicity, as occurring in group 14 elements are (nearly) absent, namely the halogens, i.e., the group 17 elements. Second, the influence of relativistic effects on the selected properties will be discussed as, in general, relativity gets more and more important when going down in the periodic table. Two directions can be followed in this discussion depending on whether spin−orbit effects are included or not. The former approach only takes into account the mass velocity and Darwin terms, whereas the latter has the advantage of including the spin−orbit effects accounting for a majority of the relativistic effects.[47] It may be tempting, to gain insight into periodicity, to include heavier congeners as Pb, but also Uuq, and At providing a more complete view on the periodic variation of atomic or functional group properties. Third, it might be plausible to delineate the contributions of independent atoms to a functional group property and to tackle, e.g., the importance of the central atom X in a functional group XY_3 property. Such a possibility could be realized due to the availability of nonempirical values, obtained at uniform level, of atomic as well as functional group properties. Finally, this study enables us to explore the status of Mulliken's original definition of electronegativity as a universally applicable model. As stated above, as a special case of eq 2, Mulliken's expression allows a nonempirical evaluation of this quantity, affording to check the influence, e.g., of the surroundings on the electronegativity of a given species (bonded atoms, solvent). In this sense, this apparent contradiction between the "isolated system" approach in Mulliken and the atoms-in-molecule approach present in many other scales (e.g., in Pauling's original one) could be lifted. Throughout its 70 years of existence, the Mulliken definition of electronegativity has acclaimed various reactions. The fact that within conceptual DFT its expression is regained as a special case of the more general expression (eq 1) certainly incited more support for the Mulliken expression although the debate continued in the early 1990s if the electronic chemical potential may really be identified with electronegativity.[13,48,49] In the present contribution, eq 2 will be the starting point enabling the evaluation of the isolated atoms and group electronegativities, hardness, and softness on equal footing. This approach has proved its quality in many papers, which appeared since the early 1990s.[4d,e] It should moreover be remarked that the Mulliken−Jaffé scale has been deemed to be synonymous with Mulliken's original scale. One should bear in mind that it is an important refinement to the Mulliken scale by considering the valence state of atoms to describe an atom in a molecule. Therefore, both scales may differ significantly and should not be used as synonymous to each other.

Computational Methods. All calculations were performed using the Amsterdam density functional (ADF) program.[50] Equilibrium structures of $H-XY_3$ were optimized using analytical gradient techniques.[51] Geometries and energies were calculated at the BP86 level of the generalized gradient approximation (GGA): exchange is described by Slater's Xα functional[52] with self-consistent nonlocal correlations due to Becke;[53] correlation is treated in the Vosko−Wilk−Nusair (VWN5) parametrization[54] with nonlocal corrections due to Perdew[55] added self-consistently (BP86).[56] This method is purely nonrelativistic (abbreviated as NR). Since relativistic effects might influence the results for the heavier elements, theoretical methods that include such effects must be considered to obtain reliable results. The ideal way is to perform four component fully relativistic calculations. However, this is an expensive and difficult approach. For a comprehensive study of the size envisaged in the paper, it is not feasible yet to use such methods. An alternative is to look for approximate methods. A prominent position among such methods is taken by the two-component approaches using the Pauli hamiltonian[57] or the zeroth-order regular approximation (ZORA)[58−62] Hamiltonian as available in ADF. The disadvantage of the Pauli hamiltonian stems from its singularity and it is better called a perturbative method yielding relativistic effects as a correction.[63] On the other hand, the ZORA Hamiltonian is variationally stable and has been widely used. This two-component ZORA approach to the full relativistic Hamiltonian has been chosen for treating the relativistic effects in the present study. The Hamiltonian then takes the form

$$H^{\mathrm{ZORA}} = V + \boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{2c^2 - V}\boldsymbol{\sigma}\cdot\mathbf{p} \tag{7}$$

where V is the potential, $V = V_{\mathrm{N}} + V_{\mathrm{coul}} + V_{\mathrm{xc}}$, V_{N}, V_{coul}, and V_{xc} are the nuclear attractive potential, the electron Coulomb repulsive potential, and the exchange-correlation potential, c is the velocity of light, and $\boldsymbol{\sigma}$ and $\mathbf{p}$ are the vectors of the Pauli spin matrices and the momentum operator, respectively. This expression already contains the necessary terms for relativity such as the mass-velocity-Darwin (MVD) terms as well as spin−orbit coupling. Therefore, we abbreviate it as SO in the discussion. The scalar ZORA Hamiltonian without the spin−orbit coupling term in ZORA is abbreviated as SR throughout. SR could be used for gradients with an accuracy of 0.001 Å. However, gradient calculations with SO are not possible and only single-point calculations may be performed.

The MOs were expanded in uncontracted sets of Slater type orbitals (STOs) containing diffuse functions: QZ4P.[64] It can be described as core triple-ζ, valence quadruple-ζ sets, with four sets of polarization functions. This very large basis set is the best STO basis available for accurate energetics. Although it could be used for nonrelativistic (NR) calculations, these all-electron basis sets were optimized for ZORA calculations, which means that nonrelativistic calculations might not always give the expected accuracy. In view of the size of the problem to be tackled (systematic study of XY_3 systems with X = C, Si, Ge, Sn, Pb, Uuq and Y = H, Me, F, Cl, Br, I, At), the combination of the selected Hamiltonians and the large basis set promotes this approach to a state-of-the-art study enabling us to give reliable answers to the problems outlined above.

Results and Discussion

The presentation of results is given in the following order. We first analyze the molecular geometry of the calculated $H-XY_3$ molecules at nonrelativistic and relativistic levels followed by a discussion of various functional group properties: ionization energy and electron affinity, electronegativity, hardness and softness, and electrophilicity.

Geometries of $H-XY_3$ Molecules. The geometries used as starting point for the evaluation of the group properties in the present study were fully optimized at both the NR and SR BP86/QZ4P levels within the symmetry point group restrictions of T_d for XH_4 and C_{3v} for HXY_3. All geometries were characterized as minima on the corresponding potential energy surface by performing numerical frequency calculations. The results for H−X bond distance are listed in Table 2. A complete list of geometry parameters is given in Figure S1 (Supporting Information). As could be expected the NR and SR geometries do not show any significant difference for the lighter molecules while the importance of relativistic effects is evident for heavier molecules. In these cases, the calculated H−X distances decrease when passing from NR to SR. For molecules containing C, Si, and Ge as a central atom, the X−H bond distances are not affected by scalar relativistic effects even for Y = At. The situation is different for molecules containing Sn, Pb, and Uuq as the central atom. These observations are in agreement with the conventional expectations. However, a remark should be made concerning the stabilization of electronic configuration of atoms due to spin−orbit splitting. For halogens, a formal ns^2np^5 configuration becomes a $ns_{1/2}{}^2np_{1/2}{}^2np_{3/2}{}^3$ configuration. For heavier elements such as At, it has been found that the valence $np_{1/2}$ orbital (spinor) is stabilized and the $np_{3/2}$ orbitals (spinors) are destabilized compared to the ns^2np^5 configuration.[65] On the other hand, the valence $ns_{1/2}{}^2np_{1/2}{}^2np_{3/2}{}^0$ configuration is overall stabilizing for the heavier group 14 elements because of the unfilled $np_{3/2}$ orbitals (spinors). The consequence of this interaction on the properties of heavier elements will be discussed in the following sections. In the next step, the geometries of the XY_3 fragment in the $H-XY_3$ molecules are used in the calculation of group properties, an obvious choice to mimic the geometry of the functional groups in a molecule. The fragment geometries of NR are used for NR calculations of the functional group properties, whereas SR geometries are used for the evaluation of both SR and SO properties.

Functional Group Properties. As can be seen from eqs 2 and 4, the two crucial quantities in the practical evaluation of the functional group properties are the vertical ionization energy and the electron affinity. Attention will therefore be first devoted to the discussion of these quantities.

Ionization Energy (*I*) and Electron Affinity (*A*). To check the reliability and efficiency of the methods in calculating I, the experimental values for the atoms C−Pb and F−At (Table 3)[66] are compared with the results from the three methods outlined above (Table 4). Even though a reasonable correlation for NR and SR values is obtained for the lighter elements, the heavier elements clearly need the inclusion of spin−orbit coupling to reproduce the experimental order. For group 14 elements, NR and SR values show a regular decrease on moving down the group. However, the correct order is not such a uniform decrease, but with Pb having a higher I value than Sn. For the halogens, SO underestimates I for At, which is still closer to the experimental value, compared to NR and SR. It can however be concluded that (Table 5) an excellent correlation of calculated and experimental values has been obtained at the SO level, confirming that the splitting of valence orbital energies due to spin−orbit interaction has energetic consequences in predicting I for heavier atoms. One can now have confidence in the calculated value for Uuq, which is found to have an unexpectedly high I (8.58 eV), the second highest in the group after carbon atom. In the absence of an experimental value for this element, a value of 8.54 eV from the highly accurate relativistic coupled cluster method is available for comparison.[67] As the approach where the BP86/QZ4P is combined with the ZORA relativistic Hamiltonian turns out to be reasonable, it could be used with confidence in the calculation of I for functional groups. Figure 1 depicts the evolution of the calculated NR, SR, and SO ionization energy. Numerical values can be found in Table 4. Most importantly, it is clearly seen that the order for atoms X is not transferred into the functional groups XY_3 having X as the central atom (Table 5). Although it is an expected behavior, the formation of atoms in molecules differentiates the isolated atom from the atom in a functional group. For XH_3 and XMe_3, I decreases when moving down the group from C to Uuq, the only exception being $UuqH_3$ having a higher I than PbH_3. For the halogens I varies in the order Uuq > Pb > Ge > Sn > C > Si except for CF_3 having a higher I than GeF_3, SnF_3, and SiF_3. This result indicates that sp^3 hybridized Pb and Uuq tend to keep electrons tightly with it. The halogens tend to increase I in the order F > Cl > Br > I > At. Even though the H always increases I to a larger extent than Me in a functional group, XH_3 groups have a smaller I value than XF_3 ones.

Turning now to the electron affinity (A), every atom considered in the present work has an experimentally known electron affinity except Uuq.[68] When going down in the group, A was found to decrease with the exception of F, which has a lower electron affinity than Cl. Comparison of NR, SR, and SO values (Table 4) for the atoms C−Uuq indicate that scalar

TABLE 2: Nonrelativistic (NR) and Scalar Relativistic (SR) H−X Bond Distances (in Å) in $H-XY_3$ (X = C, Si, Ge, Sn, Pb; Y = H, F, Cl, Br, I) at the BP86/QZ4P Level

	NR							SR						
	Me	H	F	Cl	Br	I	At	Me	H	F	Cl	Br	I	At
C	1.105	1.095	1.098	1.089	1.087	1.087	1.089	1.105	1.095	1.098	1.089	1.087	1.087	1.089
Si	1.497	1.487	1.468	1.471	1.474	1.479	1.485	1.496	1.487	1.467	1.471	1.474	1.479	1.486
Ge	1.547	1.540	1.525	1.532	1.533	1.541	1.544	1.544	1.537	1.518	1.522	1.531	1.538	1.542
Sn	1.750	1.733	1.719	1.726	1.729	1.733	1.736	1.727	1.715	1.699	1.708	1.715	1.719	1.724
Pb	1.835	1.819	1.805	1.809	1.816	1.817	1.822	1.799	1.768	1.730	1.767	1.780	1.787	1.793
Uuq	1.979	1.961	1.937	1.949	1.953	1.957	1.959	1.961	1.890	1.847	1.912	1.921	1.937	1.947

TABLE 3: Experimental Properties of Atoms C−Pb, H, and F−At[a]

	C	Si	Ge	Sn	Pb	H	F	Cl	Br	I	At
I	11.26	8.15	7.90	7.34	7.42	13.60	17.42	12.97	11.81	10.45	9.54
A	1.59	1.38	1.23	1.11	0.36	0.75	3.40	3.62	3.36	3.06	2.80
χ	6.43	4.77	4.57	4.23	3.89	7.18	10.41	8.30	7.59	6.76	6.17
η	4.84	3.39	3.34	3.12	3.53	6.43	7.01	4.68	4.23	3.70	3.37
S	0.1033	0.1475	0.1497	0.1603	0.1416	0.0778	0.0713	0.1068	0.1182	0.1351	0.1484
ω	4.27	3.36	3.13	2.87	2.14	4.01	7.73	7.36	6.81	6.18	5.65

[a] Values for χ (in eV), η (in eV), S (in eV^{-1}), and ω (in eV) are calculated from the experimental I (in eV)[66] and A (in eV)[68] values.

relativistic effects predict a correct order but more important is the inclusion of spin−orbit interaction in reproducing the experimental values (Table 3). For halogens, both the NR and SR levels reproduce the correct experimental order. However, the BP86/QZ4P level (SO) is shown to be fair for calculating A, despite a minor discrepancy noticed for F and Cl. Hence, this approach can be used for the discussion of functional groups, even though NR and SR were also computed for comparison. Again, it is interesting to see that, for the functional groups, the order Uuq > Pb > Sn > Ge > Si > C found for each Y is exactly the opposite of the order observed for atoms (Figure 2). An irregular variation is observed for halogens with C, Si, and Ge. Sn, Pb, and Uuq functional groups form a block with a sequence F > Cl > Br > I > At > H > Me. These results for the electron affinities are useful in discussing properties such as the electrophilicity index, which was shown previously to correlate with A (vide infra).

Electronegativity (χ). For atoms, experimental χ values obtained by averaging the experimental I and A values, are compared with the calculated ones. As can be seen, the calculated SO χ decreases from C (6.73 eV) to Pb (3.85 eV) and then increases again for Uuq (4.11 eV). This is verified in the experimental trends for C−Pb. Note that NR and SR quantities show a regular decrease from C to Uuq. However, the magnitudes of the C−Pb values are best reproduced by SO, especially for Sn and Pb illustrating the importance of spin−orbit coupling in heavy atoms. For C and Si the differences between three methods are insignificant. For Ge, the SO value (4.71 eV) is closer to the experimental value (4.57 eV) than NR (4.82 eV) and SR (4.79 eV) values. For H and the halogens, it can be seen that the experimental order F > Cl > Br > H > I > At is reproduced by NR, SR, and SO methods. However, again the experimental values for the heavier halogens Br, I, and At are best reproduced by SO. Figure 3 gives a detailed comparison between NR, SR, and SO for group 14 atoms (X) and functional groups (XY_3). Since the spin−orbit coupling as well as scalar effects are important for heavier elements, the SO result is used for discussion.

Moving on to functional groups, it can be seen that atoms and groups differ in that the order observed for X is no longer holding for XY_3 (Figure 3). For cases where hydrogen atoms or methyl groups are attached to the central, group 14 atom, the electronegativity order is C > Uuq > Pb > Sn > Ge > Si. Thus, for H and Me, CMe_3 is the most electronegative group and, for Si−Uuq, an increase of χ is found when going down in the periodic table with PbH_3 and SnH_3 being almost equally electronegative. When Y is a halogen, this ordering is changed to Uuq > Pb > Sn > Ge > C > Si essentially differing from the previous ordering in the position of C. This order is also holding for the heavier halogens I and At except that CI_3 and SiI_3 are equally electronegative, whereas CAt_3 is less electronegative than $SiAt_3$. An important point to note here is the highest electronegativity occurring for $UuqY_3$ with halogens, followed by the PbY_3 groups. Also noteworthy is the electronegativity order for Si and Ge. In all of the calculated functional groups, Ge is more electronegative than Si. Considering that this was a point of discussion on the quality of electronegativity scales,[69] the present results clearly illustrate that when passing from an isolated atom to a functional group the electronegativity (sequence) can change dramatically. This point may be of fundamental importance when discussing differences between the various electronegativity scales. The χ value of carbon is another point of consideration. We have found that CY_3 with Y = Me, H is more electronegative than other XY_3 (Y = Me, H) groups. Note that in the gas phase, alkyl groups, in general, were shown to exhibit similar electronic properties in the decreasing order on increasing functional group size, i.e., Me > ethyl > *n*-propyl > i-propyl > *n*-butyl > *tert*-butyl.[70] Combined with the halogen cases, these results indicate that the role of the central atom is not always dominant. This is also in agreement with previous studies on reactivities of fluoro compounds in organic and organometallic complexes.[71] However, for each of the XH_3 and XMe_3 series, the difference in magnitude of χ values between successive XY_3 groups is very small. Now we have to consider the variations in H, Me, and halogens for each of C−Uuq. Halogen containing groups retain the same order as found for the halogens themselves with XF_3 always being the most electronegative group, followed by XCl_3. These results correlate with the earlier suggestions in NMR studies of compounds with a MR_4 backbone (with R = aryl and M = Si, Ge, Sn, and Pb).[72] It also confirms the electronegativity effects on the stabilization of Pb compounds.[73] An exception is observed for X = C where CH_3 ($\chi = 5.72$ eV) is more electronegative than CCl_3 ($\chi = 5.62$ eV). This might be due to the energy changes upon the variation in geometry of the CH_3 group depending on the host to which it is attached. For example, the experimental adiabatic ionization energy (here the geometries for CH_3 and CH_3^+ ion are planar) is 9.84 eV,

TABLE 4: Nonrelativistic (NR) and Relativistic (Scalar (SR) and Spin−Orbit (SO)) Group Properties for XY_3 (X = C, Si, Ge, Sn, Pb, Uuq; Y = Me, H, F, Cl, Br, I, At) at the BP86/QZ4P Level[a]

	I			*A*			χ			η			*S*			ω		
	NR	SR	SO	NR	SR	SO	NR	SR	SO	NR	SR	SO	NR	SR	SO	NR	SR	SO
C	11.79	11.78	11.78	1.69	1.69	1.69	6.74	6.74	6.73	5.05	5.05	5.05	0.0991	0.0991	0.0991	4.50	4.50	4.49
Si	8.36	8.35	8.33	1.61	1.60	1.59	4.98	4.97	4.96	3.38	3.37	3.37	0.1481	0.1482	0.1483	3.68	3.67	3.65
Ge	8.10	8.07	7.97	1.54	1.51	1.45	4.82	4.79	4.71	3.28	3.28	3.26	0.1525	0.1525	0.1533	3.54	3.50	3.40
Sn	7.51	7.45	7.23	1.59	1.52	1.38	4.55	4.49	4.31	2.96	2.96	2.92	0.1691	0.1687	0.1710	3.50	3.40	3.17
Pb	7.26	7.14	7.31	1.60	1.43	0.39	4.43	4.29	3.85	2.83	2.86	3.46	0.1765	0.1751	0.1444	3.47	3.22	2.14
Uuq	6.90	6.63	8.58	1.61	1.30	−0.36	4.26	3.97	4.11	2.65	2.67	4.47	0.1888	0.1874	0.1119	3.42	2.95	1.89
H	13.61	13.61	13.61	0.91	0.91	0.91	7.26	7.26	7.26	6.35	6.35	6.35	0.0788	0.0788	0.0788	4.15	4.15	4.15
F	17.93	17.92	17.89	3.81	3.80	3.78	10.87	10.86	10.84	7.06	7.06	7.05	0.0709	0.0709	0.0709	8.37	8.36	8.33
Cl	13.15	13.13	13.08	3.83	3.82	3.77	8.49	8.47	8.43	4.66	4.66	4.65	0.1073	0.1074	0.1075	7.73	7.71	7.63
Br	11.99	11.96	11.75	3.63	3.59	3.43	7.81	7.77	7.59	4.18	4.18	4.16	0.1196	0.1195	0.1202	7.29	7.22	6.93
I	10.71	10.67	10.26	3.46	3.39	3.08	7.08	7.03	6.67	3.62	3.64	3.59	0.1380	0.1374	0.1393	6.92	6.79	6.21
At	10.15	10.07	9.04	3.35	3.19	2.45	6.75	6.63	5.74	3.40	3.44	3.29	0.1471	0.1453	0.1518	6.70	6.39	5.00
CMe_3	8.11	8.11	8.11	0.19	0.19	0.19	4.15	4.15	4.15	3.96	3.96	3.96	0.1262	0.1263	0.1263	2.17	2.17	2.17
$SiMe_3$	7.29	7.28	7.28	0.32	0.32	0.32	3.80	3.80	3.80	3.48	3.48	3.48	0.1435	0.1437	0.1437	2.08	2.08	2.08
$GeMe_3$	7.20	7.19	7.19	0.51	0.52	0.52	3.86	3.85	3.85	3.35	3.33	3.33	0.1494	0.1500	0.1500	2.22	2.23	2.23
$SnMe_3$	7.11	7.05	7.05	0.86	0.85	0.85	3.98	3.95	3.95	3.13	3.10	3.10	0.1600	0.1613	0.1614	2.54	2.52	2.52
$PbMe_3$	7.03	6.98	6.94	1.00	1.16	1.15	4.01	4.07	4.04	3.02	2.91	2.90	0.1657	0.1718	0.1726	2.67	2.84	2.82
$UuqMe_3$	6.88	6.93	6.83	1.16	1.56	1.44	4.02	4.24	4.13	2.86	2.68	2.70	0.1749	0.1864	0.1855	2.82	3.36	3.17
CH_3	10.99	10.99	10.99	0.44	0.44	0.44	5.72	5.72	5.72	5.28	5.28	5.28	0.0948	0.0948	0.0948	3.10	3.10	3.10
SiH_3	9.14	9.13	9.13	1.08	1.08	1.08	5.11	5.10	5.10	4.03	4.03	4.03	0.1240	0.1241	0.1241	3.24	3.24	3.24
GeH_3	8.99	8.98	8.98	1.24	1.25	1.25	5.12	5.12	5.12	3.87	3.87	3.87	0.1291	0.1294	0.1294	3.38	3.39	3.39
SnH_3	8.48	8.49	8.49	1.41	1.44	1.44	4.95	4.96	4.96	3.54	3.53	3.52	0.1414	0.1418	0.1419	3.46	3.49	3.49
PbH_3	8.29	8.35	8.31	1.50	1.63	1.61	4.89	4.99	4.96	3.39	3.36	3.35	0.1474	0.1487	0.1492	3.53	3.70	3.68
$UuqH_3$	7.96	8.52	8.44	1.55	2.17	2.05	4.76	5.35	5.25	3.20	3.18	3.20	0.1562	0.1574	0.1565	3.53	4.50	4.31
CF_3	11.54	11.53	11.53	1.02	1.02	1.02	6.28	6.28	6.28	5.26	5.25	5.25	0.0951	0.0952	0.0952	3.75	3.75	3.75
SiF_3	10.51	10.51	10.51	1.56	1.57	1.57	6.03	6.04	6.04	4.47	4.47	4.47	0.1118	0.1119	0.1119	4.07	4.08	4.08
GeF_3	11.19	11.28	11.28	2.87	2.98	2.98	7.03	7.13	7.13	4.16	4.15	4.15	0.1202	0.1205	0.1205	5.94	6.12	6.12
SnF_3	10.79	11.05	11.05	3.22	3.51	3.51	7.01	7.28	7.28	3.79	3.77	3.77	0.1321	0.1326	0.1325	6.48	7.03	7.03
PbF_3	10.71	11.74	11.75	3.49	4.45	4.45	7.10	8.09	8.10	3.61	3.65	3.65	0.1385	0.1372	0.1370	6.97	8.98	8.99
$UuqF_3$	10.25	12.67	12.84	3.43	5.18	5.36	6.84	8.92	9.10	3.41	3.74	3.74	0.1467	0.1336	0.1338	6.86	10.64	11.08
CCl_3	9.44	9.43	9.43	1.82	1.82	1.82	5.63	5.63	5.62	3.81	3.80	3.80	0.1313	0.1314	0.1314	4.17	4.16	4.16
$SiCl_3$	9.05	9.04	9.04	1.93	1.94	1.94	5.49	5.49	5.49	3.56	3.55	3.55	0.1404	0.1408	0.1408	4.23	4.25	4.25
$GeCl_3$	9.43	9.50	9.49	2.87	3.00	2.99	6.15	6.25	6.24	3.28	3.25	3.25	0.1524	0.1538	0.1539	5.77	6.00	6.00
$SnCl_3$	9.31	9.48	9.47	3.08	3.37	3.36	6.19	6.42	6.42	3.11	3.06	3.06	0.1607	0.1637	0.1637	6.17	6.75	6.74
$PbCl_3$	9.33	9.97	9.97	3.33	4.16	4.15	6.33	7.07	7.06	3.00	2.91	2.91	0.1667	0.1721	0.1720	6.68	8.59	8.57
$UuqCl_3$	9.11	10.67	10.66	3.30	4.94	4.98	6.20	7.80	7.82	2.90	2.87	2.84	0.1723	0.1744	0.1761	6.63	10.62	10.78
CBr_3	8.90	8.87	8.83	2.09	2.08	2.06	5.49	5.47	5.45	3.40	3.40	3.38	0.1469	0.1472	0.1477	4.43	4.41	4.39
$SiBr_3$	8.59	8.57	8.55	2.15	2.18	2.17	5.37	5.38	5.36	3.22	3.20	3.19	0.1554	0.1564	0.1568	4.49	4.52	4.51
$GeBr_3$	8.90	8.94	8.90	2.95	3.06	3.05	5.92	6.00	5.97	2.97	2.94	2.93	0.1683	0.1702	0.1709	5.91	6.12	6.09
$SnBr_3$	8.82	8.94	8.89	3.12	3.35	3.33	5.97	6.14	6.11	2.85	2.80	2.78	0.1753	0.1789	0.1797	6.24	6.75	6.71
$PbBr_3$	8.80	9.36	9.28	3.26	4.01	3.97	6.03	6.69	6.62	2.77	2.68	2.65	0.1807	0.1869	0.1884	6.57	8.36	8.26
$UuqBr_3$	8.67	9.99	9.76	3.28	4.71	4.64	5.97	7.35	7.20	2.70	2.64	2.56	0.1854	0.1896	0.1953	6.62	10.24	10.13
CI_3	8.23	8.18	8.04	2.43	2.39	2.33	5.33	5.29	5.18	2.90	2.89	2.85	0.1724	0.1728	0.1753	4.89	4.83	4.71
SiI_3	8.05	8.02	7.90	2.50	2.51	2.46	5.27	5.26	5.18	2.78	2.76	2.72	0.1802	0.1814	0.1841	5.01	5.03	4.94
GeI_3	8.30	8.31	8.14	3.13	3.18	3.10	5.71	5.74	5.62	2.59	2.57	2.52	0.1932	0.1949	0.1985	6.31	6.43	6.27
SnI_3	8.19	8.30	8.12	3.12	3.34	3.25	5.65	5.82	5.69	2.54	2.48	2.43	0.1971	0.2016	0.2054	6.30	6.82	6.64
PbI_3	8.20	8.64	8.38	3.25	3.86	3.71	5.73	6.25	6.04	2.48	2.39	2.34	0.2020	0.2091	0.2141	6.62	8.17	7.82
$UuqI_3$	8.10	9.39	8.71	3.23	4.44	4.18	5.66	6.92	6.44	2.44	2.48	2.27	0.2053	0.2018	0.2207	6.58	9.66	9.16
CAt_3	7.91	7.81	7.14	2.55	2.46	2.07	5.23	5.13	4.61	2.68	2.68	2.54	0.1863	0.1869	0.1972	5.10	4.93	4.19
$SiAt_3$	7.79	7.70	7.10	2.64	2.59	2.28	5.22	5.15	4.69	2.57	2.55	2.41	0.1945	0.1959	0.2078	5.29	5.19	4.57
$GeAt_3$	7.99	7.95	7.25	3.15	3.14	2.70	5.57	5.55	4.98	2.42	2.41	2.28	0.2068	0.2079	0.2195	6.42	6.39	5.43
$SnAt_3$	7.91	7.94	7.25	3.14	3.26	2.82	5.52	5.60	5.04	2.38	2.34	2.22	0.2100	0.2138	0.2256	6.41	6.70	5.72
$PbAt_3$	7.92	8.26	7.44	3.26	3.72	3.12	5.59	5.99	5.28	2.33	2.27	2.16	0.2143	0.2200	0.2317	6.69	7.89	6.45
$UuqAt_3$	7.82	8.71	7.68	3.20	4.21	3.44	5.51	6.46	5.56	2.31	2.25	2.12	0.2167	0.2226	0.2358	6.58	9.29	7.30

[a] *I*, *A*, χ, η, and ω are given in eV, whereas *S* is in eV^{-1}.

whereas the calculated value (for pyramidal CH_3 and CH_3^+ ion) is 10.99 eV. Similarly, the *A* values are 0.08 and 0.44 eV, respectively. This amounts to a combined difference of 0.76 eV, which shows up as an increase in electronegativity. Therefore, it is also possible that CH_3 might be less electronegative than CCl_3 and CBr_3 in line with chemical intution. Other XH_3 groups are expected to show this behavior to a lesser extent (Table 5). XMe_3 is always the least electronegative of all of the functional groups considered.

When a comparison is made with other scales of electronegativty, many have not followed the sequences predicted by the present study. It is interesting to note that in the latest of the group electronegativity scales, a method based on the electrostatic potential by Suresh and Koga,[30] the authors made

TABLE 5: Summary of Comparison of Trends between Atomic and Group Properties

Vertical Ionization Energy (*I*)	
atoms: C > Si > Ge >Pb > Sn (experimental)	**atoms**: F > H > Cl> Br > I > At (experimental)
atoms: C > Uuq > Si > Ge > Pb > Sn (calculated)	**Atoms**: F > H > Cl> Br > I > At (calculated)
Me: C > Si > Ge > Sn > Pb > Uuq	**C**: F > H > Cl > Br > Me > I > At
H: C > Si > Ge > Sn > Uuq > Pb	**Si**: F > H > Cl > Br > I > Me > At
F: Uuq > Pb > C > Ge > Sn > Si	**Ge**: F > Cl > H > Br > I > At > Me
Cl: Uuq > Pb > Ge > Sn > C > Si	**Sn**: F > Cl > Br > H > I > At > Me
Br: Uuq > Pb > Ge > Sn > C > Si	**Pb**: F > Cl > Br > I > H > At > Me
I: Uuq > Pb > Ge > Sn > C > Si	**Uuq**: F > Cl > Br > I > H > At > Me
At: Uuq > Pb > Ge ∼ Sn > C > Si	
Vertical Electron Affinity (*A*)	
atoms: C > Si > Ge > Sn > Pb (experimental)	**atoms**: Cl > F > Br > I > At > H (experimental)
atoms: C > Si > Ge > Sn > Pb > Uuq (calculated)	**atoms**: F > Cl > Br > I > At > H (calculated)
Me: Uuq > Pb > Sn > Ge > Si > C	**C**: I > At > Br > Cl > F > H > Me
H: Uuq > Pb > Sn > Ge > Si > C	**Si**: I > At > Br > Cl > F > H > Me
F: Uuq > Pb > Sn > Ge > Si > C	**Ge**: I > Br > Cl > F > At > H > Me
Cl: Uuq > Pb > Sn > Ge > Si > C	**Sn**: F > Cl > Br > I > At > H > Me
Br: Uuq > Pb > Sn > Ge > Si > C	**Pb**: F > Cl > Br > I > At > H > Me
I: Uuq > Pb > Sn > Ge > Si > C	**Uuq**: F > Cl > Br > I > At > H > Me
At: Uuq > Pb > Sn > Ge > Si > C	
Electronegativity (*χ*)	
atoms: C > Si > Ge > Sn > Pb (experimental)	**atoms**: F > Cl > Br > H > I > At (experimental)
atoms: C > Si > Ge > Sn > Uuq > Pb (calculated)	**atoms**: F > Cl > Br > H > I > At (calculated)
Me: C > Uuq > Pb > Sn > Ge > Si	**C**: F > H > Cl > Br > I > At > Me
H: C > Uuq > Pb ∼ Sn > Ge > Si	**Si**: F > Cl> Br > I > H > At > Me
F: Uuq > Pb > Sn > Ge > C > Si	**Ge**: F > Cl > Br > I > H > At > Me
Cl: Uuq > Pb > Sn > Ge > C > Si	**Sn**: F > Cl > Br > I > At > H > Me
Br: Uuq > Pb > Sn > Ge > C > Si	**Pb**: F > Cl > Br > I > At > H > Me
I: Uuq > Pb > Sn > Ge > C ∼ Si	**Uuq**: F > Cl > Br > I > At > H > Me
At: Uuq > Pb > Sn > Ge > Si > C	
Chemical Hardness (*η*)	
atoms: C > Pb > Si > Ge > Sn (experimental)	**atoms**: F > H > Cl > Br > I > At (experimental)
atoms: C > Uuq > Pb > Si > Ge > Sn (calculated)	**atoms**: F > H > Cl > Br > I > At (calculated)
Me: C > Si > Ge > Sn > Pb > Uuq	**C**: H > F > Me > Cl > Br > I > At
H: C > Si > Ge > Sn > Pb > Uuq	**Si**: F > H > Cl > Me > Br > I > At
F: C > Si > Ge > Sn > Uuq > Pb	**Ge**: F > H > Me > Cl > Br > I > At
Cl: C > Si > Ge > Sn > Pb > Uuq	**Sn**: F > H > Me > Cl > Br > I > At
Br: C > Si > Ge > Sn > Pb > Uuq	**Pb**: F > H > Cl > Me > Br > I > At
I: C > Si > Ge > Sn > Pb > Uuq	**Uuq**: F > H > Cl > Me > Br > I > At
At: C > Si > Ge > Sn > Pb > Uuq	
Global Softness (*S*)	
Inverse Order of Hardness (*η*)	
Electrophilicity (*ω*)	
atoms: C > Si > Ge > Sn > Pb (experimental)	**atoms**: F > Cl> Br > I > At > H (experimental)
atoms: C > Si > Ge > Sn > Pb > Uuq (calculated)	**atoms**: F > Cl> Br > I > At > H (calculated)
Me: Uuq > Pb > Sn > Ge > C > Si	**C**: I > Br > At > Cl > F > H > Me
H: Uuq > Pb > Sn > Ge > Si > C	**Si**: I > At > Br > Cl > F > H > Me
F: Uuq > Pb > Sn > Ge > Si > C	**Ge**: I > Br > F > Cl > At > H > Me
Cl: Uuq > Pb > Sn > Ge > Si > C	**Sn**: F > Cl > Br > I > At > H > Me
Br: Uuq > Pb > Sn > Ge > Si > C	**Pb**: F > Cl > Br > I > At > H > Me
I: Uuq > Pb > Sn > Ge > Si > C	**Uuq**: F > Cl > Br > I > At > H > Me
At: Uuq > Pb > Sn > Ge > Si > C	

a contentious point: "In general, if the E atom of H_3C-EXYZ has a high electronegativity, the −EXYZ group will also show a high electronegativity". The authors' prediction of the dependency of group electronegativity on the central atom, i.e., X of −XY_3 group, is however not confirmed. According to their scale, e.g., the XH_3 series varies as C > Ge > Si > Sn > Pb. On the other hand, the present investigation predicts a different order: C > Pb > Sn > Ge > Si. A similar order is also found for Y = Me. Information available based on experimental NMR studies is clearly in favor of the present investigation.[72] Considering various factors including electronic and relativistic effects (scalar and spin−orbit coupling), it may be inferred that the electronegativity is a complex phenomenon, which does not depend on a single factor or a moiety of the functional group.

Chemical Hardness (*η*) and Softness (*S*). Similarly to χ, experimental chemical hardness (η) and softness (S) values for atoms were obtained from experimental atomic I and A values. On moving down group 14, it is seen that η varies in the order C > Pb > Si > Ge > Sn. NR and SR results do not follow this trend. Only at the SO level the experimental data are reproduced both in magnitude and trend (Table 4). Notice the dramatic effect of the spin−orbit coupling on the hardness values of Pb and Uuq, which are harder than Si, Ge, and Sn. In conclusion, the group 14 atomic hardness trends show a decrease followed by an increase on moving down the group. On the other hand, for H and the halogens, all three methods give the calculated experimental order of F > H > Cl > Br > I > At, the sequence thus being unaffected by relativistic effects. This might be due

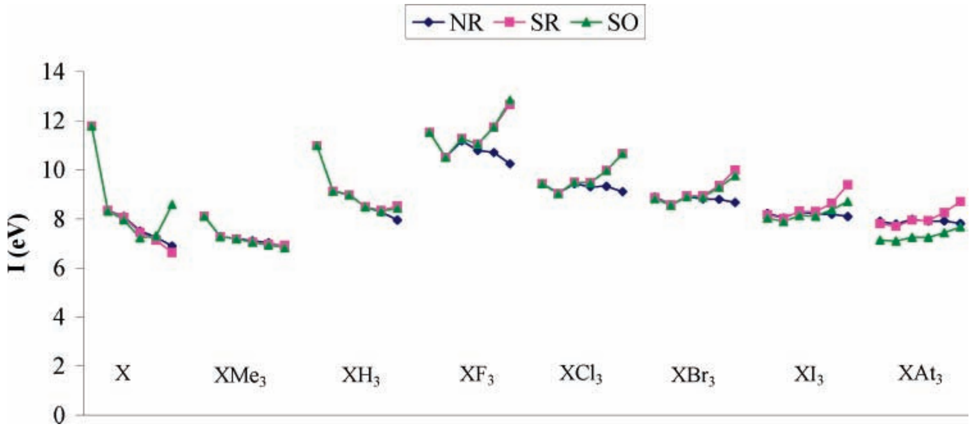

Figure 1. Nonrelativistic (NR) and relativistic (scalar (SR) and spin−orbit (SO)) vertical ionization energies (*I*, eV) for atoms (X = C, Si, Ge, Sn, Pb, Uuq) and groups XY_3 (X = C, Si, Ge, Sn, Pb, Uuq; Y = Me, H, F, Cl, Br, I, At), respectively, at the BP86/QZ4P level.

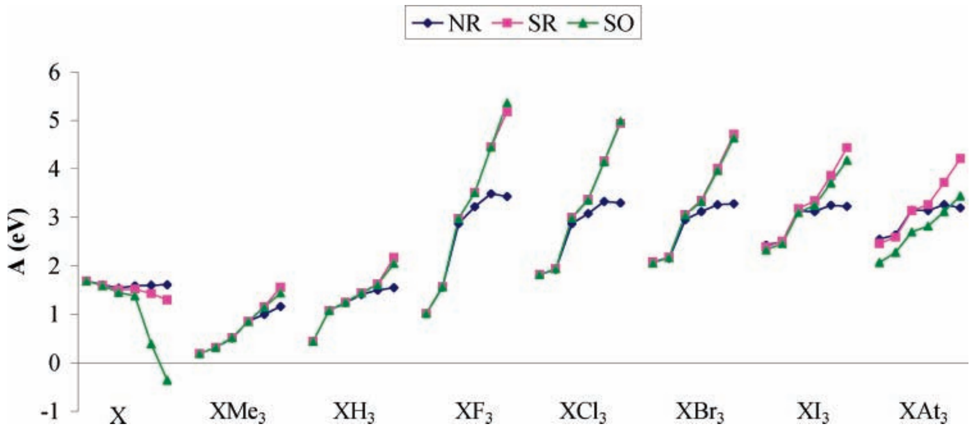

Figure 2. Nonrelativistic (NR) and relativistic (scalar (SR) and spin−orbit (SO)) vertical electron affinities (*A*, eV) for atoms (X = C, Si, Ge, Sn, Pb, Uuq) and groups XY_3 (X = C, Si, Ge, Sn, Pb, Uuq; Y = Me, H, F, Cl, Br, I, At), respectively, at the BP86/QZ4P level.

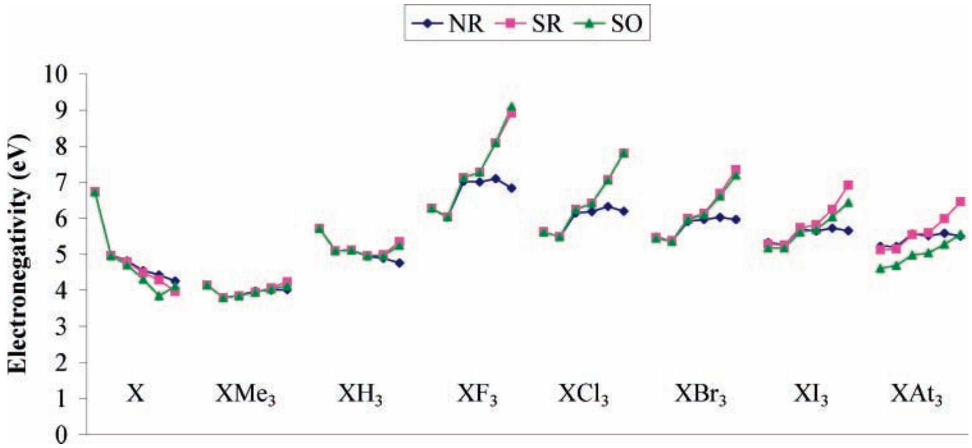

Figure 3. Nonrelativistic (NR) and relativistic (scalar (SR) and spin−orbit (SO)) electronegativities (χ, eV) for atoms (X = C, Si, Ge, Sn, Pb, Uuq) and groups XY_3 (X = C, Si, Ge, Sn, Pb, Uuq; Y = Me, H, F, Cl, Br, I, At), respectively, at the BP86/QZ4P level.

to the fact that a difference of energies is taken to calculate η, which may cancel out the contributions due to relativity. However, considering the dramatic effect shown by Pb and Uuq due to spin−orbit interaction, such an effect may be expected for At. As remarked previously, it is not observed perhaps due to the substantially filled valence orbitals in halogens than in Pb or Uuq. These results point out that straightforward generalization of the idea of decreasing hardness and increasing softness along the columns of the periodic table should always be looked upon carefully. Moving on to the functional groups and concentrating upon the hardness variations (the trends for softness being obviously the inverse ones), comparison between the NR, SR, and SO results is provided in Figure 4 (see Figure 5 for global softness comparisons). All three methods follow the order C > Si > Ge > Sn > Pb > Uuq except for $UuqF_3$, which is harder than PbF_3. This observation is distinct from the isolated atom results. Although halogens follow the atomic order in molecules as well for each X, the positions of H and Me are irregular with H > Me always.

Electrophilicity (ω). This is a relatively new index in the attempt to explain the effect of functional groups on the molecular charge distribution and molecular reactivity. Experimental values for atoms show a monotonically decreasing trend when going down the group for C−Uuq and the halogens. H

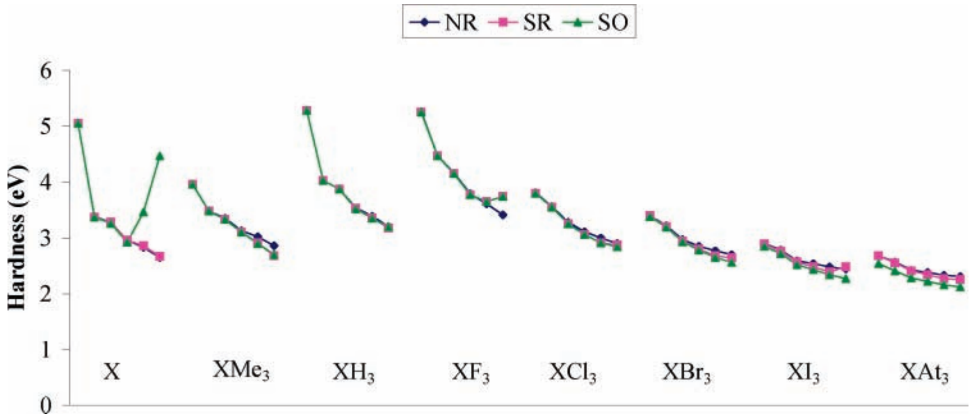

Figure 4. Nonrelativistic (NR) and relativistic (scalar (SR) and spin−orbit (SO)) chemical hardness values (η, eV) for atoms (X = C, Si, Ge, Sn, Pb, Uuq) and groups XY$_3$ (X = C, Si, Ge, Sn, Pb, Uuq; Y = Me, H, F, Cl, Br, I, At), respectively, at the BP86/QZ4P level.

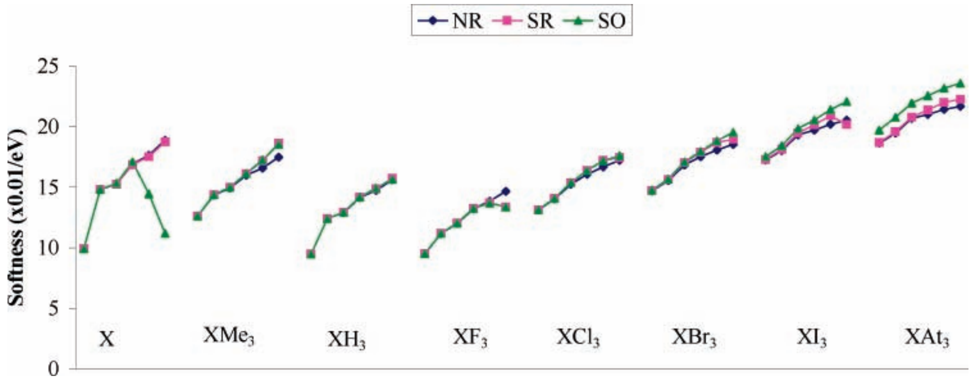

Figure 5. Nonrelativistic (NR) and relativistic (scalar (SR) and spin−orbit (SO)) global softness values (S, eV^{-1}) for atoms (X = C, Si, Ge, Sn, Pb, Uuq) and groups XY$_3$ (X = C, Si, Ge, Sn, Pb, Uuq; Y = Me, H, F, Cl, Br, I, At), respectively, at the BP86/QZ4P level.

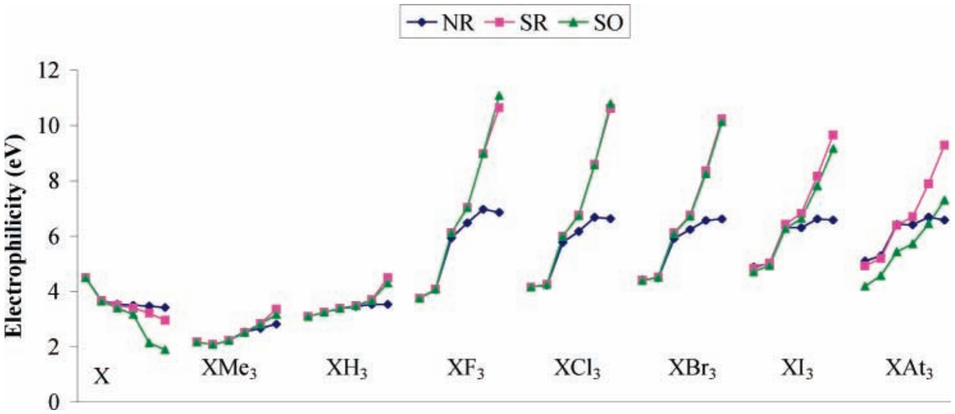

Figure 6. Nonrelativistic (NR) and relativistic (scalar (SR) and spin−orbit (SO)) electrophilicity indices (ω, eV) for atoms (X = C, Si, Ge, Sn, Pb, Uuq) and groups XY$_3$ (X = C, Si, Ge, Sn, Pb, Uuq; Y = Me, H, F, Cl, Br, I, At), respectively, at the BP86/QZ4P level.

has a lower value than At. The results of NR, SR, and SO all follow the experimental trend (Tables 3−5). However again, numerical values are reproduced only excellently by SO for heavier elements such as Br, I, At, Sn, and Pb. Even though scalar relativistic effects are seen to improve the numerical results over nonrelativistic results, spin−orbit interaction is evidently not negligible for heavier elements. On this basis (cf. Figure 6), the SO results are used for the discussion of the functional group results. Effects of X and Y in XY$_3$ may be analyzed as follows (Table 5). For a given Y, the ordering Uuq > Pb > Sn > Ge > Si > C is obtained, except for CMe$_3$ which is more electrophilic than SiMe$_3$. This result is a complete reversal of the evolution found for atoms. When the variation of Y for each X is considered, the lowest electrophilic power is obtained for XMe$_3$, followed by XH$_3$. For SnY$_3$, PbY$_3$, and UuqY$_3$ a uniform pattern of decreasing order F > Cl > Br > I > At > H > Me is found. For CY$_3$, SiY$_3$, and GeY$_3$, the most electrophilic functional group turns out to be XI$_3$, whereas the other halogens show a more irregular variation. These results clearly point to the interplay of X and Y in determining the electrophilic nature of commonly used functional groups. In the literature, some studies were reported on the similarity/difference of ω with intuitively related quantities such as electronegativity and electron affinity. The large number of data available, calculated at a uniform level, incited us to investigate these correlations for X and XY$_3$.

Figures 7 and 8 show the correlation between the calculated electrophilicity index (ω) and the electronegativity (χ) and electron affinity (A), respectively. A reasonable correlation with R^2 value of 0.738 is obtained between ω and χ, showing that

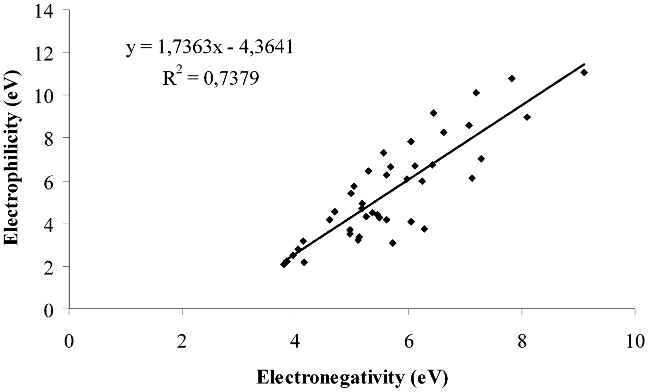

Figure 7. Correlation between calculated group electronegativities and electrophilicity indices.

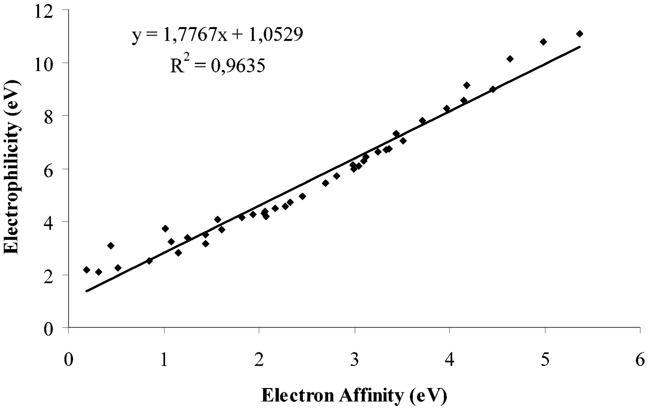

Figure 8. Correlation between calculated group electron affinities and electrophilicity indices.

the χ^2 term in the numerator of ω is not totally unaffected by the denominator η but that it can be expected that the periodic trends for χ might also be found for ω. The results as summarized in Table 5 show that this is true especially for atoms and functional groups involving heavier elements. At the same time, such a correlation is not well established for functional groups with lighter elements. As discussed in the Introduction, the electrophilicity index was previously shown to be related to the electron affinity.[43] This is confirmed with an R^2 of 0.964 indicating a nearly linear correlation between ω and A as illustrated in Figure 8. It can be concluded that electrophilicity, although different from electronegativity and the electron affinity, nevertheless is highly correlated with electron affinity, much more than with the electronegativity.

Does such nearly linear correlation mean that there exists a one-to-one relationship between the pair of properties on going from atoms to molecules? To obtain a general picture including all of the properties studied in this paper, a regression analysis is presented as follows.

Regression Analysis. Since the calculated property values are available for both atoms and functional groups, it is possible to analyze the general nature of the correlation between central atomic and functional group properties in the case of XY_3 groups shedding further light on the difference in trends between isolated atoms and functional groups. Thus, for XY_3, an equation could be written in three variables

$$P(XY_3) = \alpha^*\mathrm{P}(X) + \beta^*\mathrm{P}(Y) + \gamma \quad (8)$$

where P is the calculated property and α, β, and γ are constants. This three-dimensional linear regression equation estimates a dependent variable $P(XY_3)$ from the independent variables $P(X)$ and $P(Y)$. Clearly, this equation is based on the additivity of the contributions, which, as far as we know, was only theoretically supoorted for the softness.[74] We thought it would be tempting to investigate additivity also for the other properties. If XY_3 properties for Y = H, F, Cl, Br, I, At are considered, there is a set of 36 points and the constants α, β, and γ can be determined by solving simultaneously the equations

TABLE 6: Results of Regression Analysis for the Equation of Group Property *P*, i.e., $P(XY_3) = \alpha^*P(X) + \beta^*P(Y) + \gamma^a$

	constants			calculated v/s	simulated
property	α	β	γ	$y = m^*x + k$	R^2
I	0.08	0.44	2.87	1.0101*x − 0.0595	0.8047
A	−1.04	0.65	1.96	1.0044*x − 0.0004	0.7728
χ	−0.37	0.46	4.22	0.9957*x − 0.0296	0.6421
η	0.24	0.48	−0.06	1.0048*x − 0.0163	0.7585
S	0.20	1.17	0.94	0.9985*x + 0.0101	0.8234
ω	−1.79	0.71	7.07	0.9978*x + 0.0096	0.7522

[a] Equation $y = m^*x + k$ gives linear correlation between calculated XY_3 properties and the simulated values from regression analysis.

$$\Sigma P(XY_3) = \alpha^*\Sigma P(X) + \beta^*\Sigma P(Y) + \gamma^*36 \quad (9)$$

$$\Sigma P(XY_3)^*P(X) = \alpha^*\Sigma P(X)^2 + \beta^*\Sigma \mathrm{P}(X)^*P(Y) + \gamma^*P(X) \quad (10)$$

$$\Sigma P(XY_3)^*P(Y) = \alpha^*\Sigma P(X)^*P(Y) + \beta^*\Sigma P(Y)^2 + \gamma^*P(Y) \quad (11)$$

The results of the regression analysis and a linear correlation between the calculated XY_3 properties and the predicted values from the regression analysis are given in the Table 6. It is seen that the correlation coefficient between calculated and simulated values is by far the highest for the softness with α and β positive (similarly for hardness) rigorously confirming earlier observations.[75] In the case of electronegativity, α and β show opposite signs indicating that the relation between the group electronegativity and the central atom value is not clear-cut. It clearly points out that discussing group electronegativities is a more delicate problem than group softness. In the latter case, the various subunits (atoms) are working unidirectional, whereas in the former case, opposing factors may be at work. This way, the regression results show fair agreement with the results summarized in Table 5 for electronegativity. The situation for the electrophilicity, the product of S and χ^2 may be expected to be intermediate. This turns out to be the case, the correlation factor being intermediate between that of S and χ. Thus, the regression analysis reveals the fundamental differences between the set of properties, with the correlation coefficients varying from 0.642 to 0.823.

Conclusions

In this paper, a series of important atomic and functional group properties are computed and studied using high level density functional theory calculations including relativistic effects. Three models, namely NR (nonrelativistic), SR (scalar ZORA), and SO (ZORA), at all electron BP86/QZ4P level are utilized. Although each of the three models are giving similar results for functional groups involving lighter elements, scalar as well as spin−orbit coupling effects are important for functional groups involving heavier elements. A complete analysis of the complete groups 14 (C−Uuq) and 17 (F−At) is provided both for the isolated atoms and for the functional groups of formula, XY_3 (X being an element of group 14 and Y of group 17) mainly incited by the anomalous behavior and the differences in order in various scales of the group 14 elements (e.g., in electronegativity) both as elements and involved in functional groups as compared to the monotonic evolution of the group 17 elements omnipresent in the scales presented hitherto. Comparison of the present work and available experimental results shows that they are in agreement provided the spin−orbit effects are incorporated in the methods for calculating the properties. Mulliken's expression for the electronegativity as a special case of the $(\partial E/\partial N)_v$ identification of the electronic chemical potential turns out to be easily implemented, permitting the evaluation of its companion quantities (hardness, softness, electrophilicity) at a uniform high level and affording direct comparison with "experiment" through the ionization energy and electron affinity. For the group 14 elements, the atomic electronegativities show a uniform decrease from C to Pb increasing to Uuq as verified in the experimental data for C−Pb but at variance with several other scales. The theoretical hardness sequence C > Uuq > Pb > Si > Ge > Sn in agreement with experimental values for C−Pb is opposed to the trends of decreasing hardness on going down the periodic table as is found in the halogen group. The behavior of the XY_3 groups however follows the "normal" C > Si > Ge > Sn > Pb sequence for the hardness. Regression analyses using the atomic and functional group properties have shown the presence or absence of additivity of X and Y in the functional group, $-XY_3$. Thus, a more electronegative central atom might also lead to decreased functional group electronegativity. Additionally, it reveals the fundamental differences between the set of properties.

All in all, based on its conceptual and computational robustness, the methodology presented in this paper might be of great use in discussing trends in a variety of DFT-based reactivity descriptors for atoms and functional groups involving from the lightest to the heaviest elements and contribute to the understanding of the evolution of atomic, group and molecular properties throughout the periodic table.

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Supporting Information Available: Equilibrium geometries of H-XY_3 molecules (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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