Atomic orbitals in molecules: general electronegativity and improvement of Mulliken population analysis

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An approach of atomic orbitals in molecules (AOIM) has been developed to study the atomic properties in molecules, in which the molecular orbitals are expressed in terms of the optimized minimal atomic orbitals. The atomic electronegativities are calculated using Pauling's electronegativity of free atom and are employed to find the electronegativity equilibrium in molecules and to describe the amphoteric properties of the transition metals from the groups 4 to 10. AOIM can also improve the numerical stability and accuracy of the original Mulliken population analysis.

1. Introduction

Although the molecular orbital (MO) theory has achieved great success, it can hardly replace the chemical bond (CB) theory completely in interpreting the electronic structure properties, such as the atomic charge, electronegativity,[1] ionic character of bond, bonds in transition metal complexes. MO theory based on the variation of total energy is adept in the delocalized properties of molecules, while CB theory established on the electronic varieties of atoms in molecules concerns with the local properties, in particular with the electron distribution and transfer among the atoms. The task to combine them is to express the molecular wave functions in terms of a set of suitable atomic orbitals (AO).

In the natural population analysis,[2] the AOs in a molecule are divided into the "minimal" set and the "Rydberg" set by their occupancy. The "minimal" set corresponds to all the occupied atomic orbitals in the ground state, and the "Rydberg" set consists of the remaining (formal unoccupied) orbitals. Liu and Li applied this method to improve the Mulliken population analysis,[3,4] and had obtained the reasonable populations on the minimal basis set. Their work confirmed that the calculated populations were fairly independent of the choice of the basis sets, and thus concluded that the minimal basis set was the key element in analyzing the properties of atoms in molecules. Our approach of atomic orbitals in molecules (AOIM) is to express MOs in terms of minimal basis set characterized by the variable ζ's, *i.e.* the exponents of the corresponding AOs that may be determined by the molecular wave functions posteriorly.

Our work is organized as follows. In section 2, after the principle and implement of AOIM are discussed, our program AOIM1.0[5] is outlined, and the resulted optimized-ζ's of valence shells of free atoms are compared with those from the energy optimization. In section 3, we generalize and apply the concept of the atomic electronegativity to atoms in any chemical systems based on the optimized exponents of Slater-type orbitals, and the behaviors and applications of the general electronegativity are discussed briefly. In section 4, we compare the Mulliken population analysis within the frame of AOIM to the original Mulliken population analysis, popular natural population analysis, and the experimental values. Finally our conclusions are summarized in section 5.

2. Atomic orbitals in molecules

In MO theory, the accurate expression of the molecular wave function needs large basis set including the additional basis sets such as polarizations. As a consequence, however, these additional basis sets may not have clear physical meaning directly associated with the original atoms because of their high energy levels and/or large sizes. Therefore, it is difficult to express the atomic properties properly by such extended basis sets. The key to interpret and predict atomic properties in molecules is to find a suitable basis set to clarify the nature and variety of atoms in molecules.

In CB theory, a molecule is described by a group of bonded atoms such that MOs can be expressed in terms of the linear combinations of AOs. Such AOs, usually described by certain atomic basis sets, should inherit the basic atomic nature from free atoms. In a free atom, the simplest atomic basis sets are hydrogen-like orbitals with the principle quantum number n, the angular-momentum quantum number l, and the magnetic quantum number m_z.

On the other hand, compared to the AOs in free atoms, the radial parts of AOs in molecules contract or expand and the degeneracy of AOs in the same subshells may be lifted as the spherical symmetry of atom is broken. The anisotropies of the potential and electron distribution in molecules lead further to the directionalities of covalence bonds. These variances of radial functions and directionalities of AOs denote the varieties of atoms in molecules.

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In our method, the highest occupied subshells have been set as 1s for H–He, 2s for Li–Be, 2p for B–Ne, 3s for Na–Mg, 3p for Al–Ar, 4s for K–Ca, 3d for Sc–Zn, 4p for Ga–Kr. We believe that the additions of AOs with higher quantum numbers are unnecessary for analysis of atomic properties.

Then, the preferable basis set should be the set of single-ζ hydrogen-like orbitals of atoms (the minimal basis set) with different radial functions and directionalities for analyzing the atomic properties of atoms in molecules.

However, employing the polynomials as the pre-exponential factors of radial parts of hydrogen-like AOs usually makes the computations complicated. Therefore, we replaced these AOs by the corresponding Slater-type orbitals (STO) $\chi_{nlm} = N_s R_n(\zeta,r) Y_{lm}(\theta, \phi)$, where N_s is the normalization factor, $Y_{lm}(\theta, \phi)$ the spherical harmonics, $R_{nl}(\zeta,r) = r^{n-1}e^{-\zeta r}$ the radial function, and ζ the parameter of n, l, and m_z in molecules. As the linear combinations of STOs, the single-ζ AOs are equivalent to the single-ζ STOs in expressing wave functions. Hereafter we would use the single-ζ STOs to analyze the properties of atoms in molecules and the term "minimal basis set" for the basis set of single-ζ STOs.

Now, following the procedure of Sanchez-Portal et al.,[6] we may transform the basis sets employed in the calculations into the minimal sets for expressing the MOs. Suppose n singly occupied MOs ψ_i ($i = 1, n$) can be written as linear combinations of the basis set $\{\phi_\mu\}$:

$$\psi_i = \sum_\mu C_{i\mu} \phi_\mu, \qquad (1)$$

and the wave function Ψ is expressed by a Slater determinant in terms of ψ_i

$$\Psi = |\psi_1 \ldots \psi_n|. \qquad (2)$$

By Löwdin orthogonalization,[7] ψ_i can also be written as a linear combination of the orthonormal basis set $\{\phi'_\mu\}$ as

$$\psi_i = \sum_\mu C'_{i\mu} \phi'_\mu, \qquad (3)$$

and

$$\phi'_\mu = \sum_\nu (S^{-1/2})_{\nu\mu} \phi_\nu, \qquad (4)$$

in which $S^{-1/2}$ is the square root of the inverse overlap matrix of ϕ_μ's and $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$. On the other hand, one may try the minimal basis sets $\{\chi_\sigma\}$ for all the atoms, and the new overlap matrix S^m is defined by $S^m_{\sigma\tau} = \langle \chi_\sigma | \chi_\tau \rangle$. The orthonormal STOs χ'_σ's are also obtained from the Löwdin orthogonalization

$$\chi'_\sigma = \sum_\tau [(S^m)^{-1/2}]_{\tau\sigma} \chi_\tau. \qquad (5)$$

The basis sets $\{\chi'_\sigma\}$ and $\{\phi'_\mu\}$ are connected by the coefficients $C'^m_{i\sigma}$:

$$C'^m_{i\sigma} = \sum_\nu \langle \chi'_\sigma | \phi'_\nu \rangle C'_{i\nu}. \qquad (6)$$

Then the projected MO ψ_i^m can be expressed as

$$\psi_i^m = \sum_\sigma C'^m_{i\sigma} \chi'_\sigma \qquad (7)$$

Among the commonly used basis sets, namely the single-ζ (i.e. the minimal), double-ζ, and double-ζ with polarization, the minimal basis set is the least basis set, and the double-ζ with polarization is the most and usually employed in accurate calculations. Because of less completeness of the minimal basis set, some electrons must be spilled if projecting large-basis-set space to the minimal-basis-set space. The electron spilling may arise from three origins: (1) the radial parts of STOs contract or expand inevitably in the molecules compared to those in the free atoms and the directions of p and d valence orbitals should be reoriented in the molecules; (2) one radial function cannot exactly replace a linear combination of two or more radial functions; and (3) the minimal basis set for higher quantum number is not well-defined.

The first type of the electron spilling is a consequence of intrinsic difference between the free atoms and the atoms in molecules such that the quality of projection may be evaluated by the value of the incompleteness Δ, namely, the spilling parameter of electrons:

$$\Delta = \sum_i^{occ} \delta_i = \sum_i^{occ} [1 - \sum_\sigma (C'^m_{i\sigma})^2], \qquad (8)$$

where δ_i is the number of the spilling electrons on the i-th MO. This spilling parameter is a function of all the exponents ζ_i's of STOs and the reorientation of atoms in the molecule. By minimizing the incompleteness for all the occupied MOs, one may obtain a new set of AOs in the molecule. After the incompleteness Δ is optimized to a minimum, the ζ-optimized STOs would mainly represent varieties of atoms in the molecule. From our calculation of free atoms, the δ_i's of s and p orbitals are less than 0.03 and those of d orbitals less than 0.06, which shows that the main component of molecular wave function has been retained.

The second type of the electron spilling would have some transferability between free atoms and atoms in molecules and the third type of electron spilling should be relatively small and can be ignored. Then we could impose to normalize each MO in the minimal optimized basis set for an intact total population, and the corrected MO is

$$\psi_i^{norm} = \sum_\sigma C^{norm}_{i\sigma} \chi_\sigma, \qquad (9)$$

where

$$C^{norm}_{i\sigma} = \sum_\tau \frac{C^{opt}_{i\tau}}{(1 - \delta_i)^{1/2}} [(S^{opt})^{-1/2}]_{\tau\sigma}, \qquad (10)$$

where $C_{i\tau}^{opt}$ is the coefficient of MO in the optimized minimal basis set and $(S^{opt})^{-1/2}$ is the square root of the inverse overlap matrix of the optimized STOs. All atomic properties of AOIM are based on this projected molecular wave function Ψ^m:

$$\Psi^m = |\psi_1^{norm} \ldots \psi_n^{norm}|. \qquad (11)$$

By such correction, the accurate orbital populations (<2.003) appear in free atoms H–Kr, which implies the reasonability of the correction of normalization.

Implement of AOIM

We have developed the program AOIM1.0 to calculate the optimized minimal basis set of molecules based on the

"formcheck" file of Gaussian03.[8] The procedure of the calculation of the projection is simple because only the overlap integrals and the Löwdin orthogonalization of STOs are needed. To simplify the overlap integral, the STO-6G[9] functions are used instead of STOs. The L-BFGS-B (i.e. the limited-memory quasi-Newton code for large-scale bound-constrained or unconstrained optimization) procedure[10] is used to optimize the exponents and the spherical azimuths of STOs. Because there is no analytical relation between the incompleteness Δ and the parameters of STOs, the partial derivatives of Δ with respect to ζ_i's and the spherical azimuths must be calculated numerically and consequently the calculations of the second partial derivatives are time-consuming. The L-BFGS-B procedure requires only the computations of the function value and its derivatives, which improves efficiency of the optimization.

The criterions of minimizing Δ are that (1) the change of Δ is sufficiently small ($<10^{-5}$), or (2) the projected gradients of Δ with respect to ζ_i's and spherical azimuths are sufficiently small ($<10^{-3}$) as in principle they should equal zero at the local minimum of Δ.

By default all wave functions were obtained using 6-31G** basis set at Hatree-Fock (HF) level in the geometric optimum by Gaussian03 program. The ζ's of STOs were optimized by the program AOIM1.0. The natural population analysis and the original Mulliken population analysis were implemented by Gaussian03, while the AOIM Mulliken population analysis and all Mayer bond order[11] analysis by AOIM1.0. The orbital populations in section 3 were calculated from the AOIM Mulliken population analysis.

Verification of AOIM

To verify the results of AOIM, the optimized-ζ's were calculated by AOIM1.0 and compared with those obtained from the energy optimization calculations[12] for valence shells of free atoms H–Kr (see Table 1). The exponents of the s orbitals (ζ_s's) from both optimizations are remarkably close and the ζ_p's of p orbitals and the ζ_d's of d orbitals from AOIM calculations are about 0.12(7%) and 0.45(12%) less than those from the energy optimization. The deviations of the p and d orbitals maybe come from the incompleteness of 6-31G** basis sets used in the calculations of the wave functions. But it does not change the conclusion that ζ's from the wave function optimization are consistent with those from energy optimization.

3. General electronegativity

The electronegativity is the measurement of the power of an atom in a molecule to attract electrons.[1] The traditional Pauling's definition of electronegativity is thermochemical, and the difference of the electronegativities between the atoms X and Y is defined (in units of $eV^{1/2}$) as $\chi_X - \chi_Y = [E_{XY} - (E_{XX} - E_{YY})^{1/2}]^{1/2}$, where E_{XX}, E_{YY} and E_{XY} are bonding energies of the X-X, Y-Y, and X-Y type molecules, respectively. There are also other scales of the electronegativity, for example, the Mulliken scale from the ionization energies and the affinity energies of atoms,[15] the Allred and Rochow scale

Table 1 The exponents of STOs in the valence shells and the electronegativities (Pauling units) of elements H–Kr

Atom	C&R[a]		AOIM		$\chi_P{}^{b}$	$\chi_{spec}{}^{c}$	χ_ζ	$\chi_{\zeta(d)}$
	ζ_s	ζ_p/ζ_d	ζ_s	ζ_p/ζ_d				
H	1.00		1.02		2.20	2.30	2.31	
He	1.69		1.62			4.16	3.83	
Li	0.64		0.67		0.98	0.91	0.93	
Be	0.96		1.00		1.57	1.58	1.52	
B	1.29	1.21	1.32	1.19	2.04	2.05	2.02	
C	1.61	1.57	1.61	1.49	2.55	2.54	2.51	
N	1.92	1.92	1.90	1.79	3.04	3.07	3.02	
O	2.25	2.23	2.23	2.06	3.44	3.61	3.51	
F	2.56	2.55	2.55	2.34	3.98	4.19	4.03	
Ne	2.88	2.88	2.86	2.68		4.79	4.58	
Na	0.84		0.88		0.93	0.87	1.01	
Mg	1.10		1.09		1.31	1.29	1.33	
Al	1.37	1.36	1.37	1.04	1.61	1.61	1.57	
Si	1.63	1.43	1.62	1.29	1.90	1.92	1.86	
P	1.88	1.63	1.86	1.53	2.19	2.25	2.16	
S	2.12	1.83	2.09	1.72	2.58	2.59	2.43	
Cl	2.36	2.04	2.32	1.93	3.16	2.87	2.72	
Ar	2.59	2.26	2.56	2.15		3.24	3.02	
K	0.87		0.86		0.82	0.73	0.83	
Ca	1.10		1.08		1.00	1.03	1.10	
Ga	1.77	1.56	1.82	1.35	1.81	1.76	1.84	
Ge	2.01	1.70	2.04	1.60	2.01	1.99	2.04	
As	2.24	1.86	2.24	1.82	2.18	2.21	2.25	
Se	2.44	2.07	2.44	1.99	2.55	2.42	2.44	
Br	2.64	2.26	2.63	2.17	2.96	2.68	2.65	
Kr	2.83	2.44	2.81	2.36		2.97	2.86	
Sc	1.16	2.37	1.15	1.65	1.36	1.15	1.18	2.14
Ti	1.20	2.71	1.20	2.46	1.54	1.28	1.25	3.32
V	1.24	2.99	1.26	2.72	1.63	1.42	1.33	3.70
Cr	1.28	3.25	1.18	2.75	1.66	1.57	1.22	3.75
Mn	1.32	3.51	1.19	2.97	1.55	1.74	1.24	4.11
Fe	1.36	3.73	1.38	3.37	1.83	1.79	1.48	4.70
Co	1.39	3.95	1.42	3.56	1.88	1.82	1.53	4.99
Ni	1.43	4.18	1.46	3.76	1.91	1.80	1.59	5.31
Cu	1.46	4.40	1.50	3.95	1.90	1.74	1.64	5.46
Zn	1.49	4.63	1.54	4.15	1.65	1.60	1.68	

[a] Clementi and Raimondi, ref. 12. [b] Pauling, data from ref. 13. [c] Allen, ref. 14.

from the electrostatic force exerted on the valence electrons,[16] the Allen's spectroscopic electronegativity[14] and the Nagle scale from the atomic polarizability.[17] Allen defined the electronegativity as the average one-electron energy of valence-shell electrons in ground free atoms. Then by the Aufbau Principle, the subshells are specified by the number of s and p electrons and thus the electronegativity may be expressed in terms of a per-electron (or one-electron energy) basis as

$$\chi_{spec} = (m\varepsilon_s + n\varepsilon_p)/(m + n), \qquad (12)$$

where m and n are the number of s and p valence electrons, respectively.[14] The ε_s and ε_p, usually referred to as single-electron orbital energies, are the change of the total energy when a single electron of the orbital is removed from the atom. In other ways, Hinze and Jaffe proposed the orbital electronegativity on the Mulliken scale,[18] and Sanderson postulated the principle of equalization of electronegativity,[19] and Parr et al. defined the absolute electronegativity as the negative value of the electronic chemical potential from density functional theory and gave a proof of the electronegativity equalization theorem.[20]
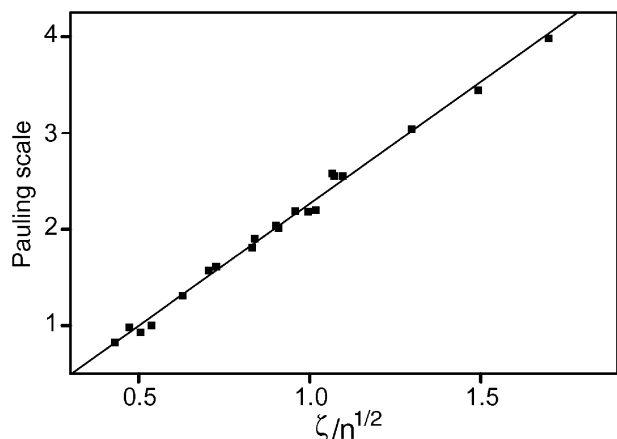
Fig. 1 Correlation between $\zeta_{sp}/n^{1/2}$ and Pauling electronegativity.

Fig. 2 General electronegativity χ_ζ vs. rows (dash line) and atomic charges (solid line) for some main group elements.

Because the energy ε of the atomic orbital is approximately equal to $-\zeta^2$ (in units of Rydbergs) in free atoms, ζ should be a crucial parameter to represent the properties of atomic orbitals as well as atoms. As the difference is very small between ζ_s and ζ_p, the average energy of single s or p valence electron ε_{sp} is

$$-\varepsilon_{sp} = \frac{-(n_s\zeta_s^2 + n_p\zeta_p^2)}{n_s + n_p}$$
$$\approx \left(\frac{n_s\zeta_s + n_p\zeta_p}{n_s + n_p}\right)^2 = \zeta_{sp}^2, \tag{13}$$

where ζ_{sp} is the average exponent and n_s and n_p are populations of s and p orbitals, respectively. The $\zeta_{sp}/n^{1/2}$ [in units of Rydberg$^{1/2}$, n is the principle quantum number of sp shell] vs. conventional electronegativity values on Pauling's scale[13] is plotted in Fig. 1 for the main group elements of the first four periods (except Cl, Br, and the noble gases), and the correlation coefficient between the two sets of values is 0.997 with the standard error 0.07. A linear least-squares fit of the data can be given as

$$\chi_\zeta = 2.526\zeta_{sp}/n^{1/2} - 0.262, \tag{14}$$

where χ_ζ is the electronegativity in the Pauling units derived from the optimized-ζ's. The χ_ζ's calculated from eqn (14) along with electronegativity values from other sources are also tabulated in Table 1.

Once the wave function is known, the optimized-ζ's of AOs can be calculated by AOIM, and the electronegativities of atomic orbitals and atoms are evaluated from eqn (14). This electronegativity, called the general electronegativity, is the measurement of the power of an atom in molecular environments to attract electrons.

Electronegativity of ion

The electronegativities of ions were calculated and plotted in Fig. 2. It clearly shows that: (1) electronegativities rise as the number of electrons decreases and *vice versa*; (2) the electronegativities of all the main group elements change approximately as linear functions of the atomic charges; and (3) the amplitude of electronegativities is no more than 0.5 on the Pauling's scale for gaining or losing one electron in their valence shells. These conclusions are all consistent with the common sense.
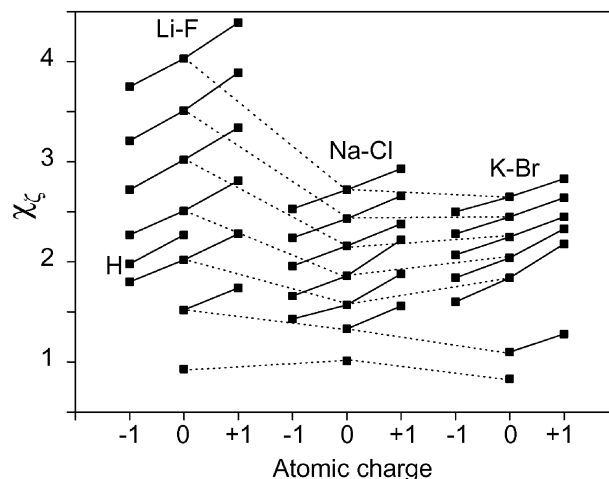
Electronegativity in homonuclear molecule

The electronegativities were also calculated for the atoms in simple homonuclear molecules such as $H_2(2.73)$, $N_2(3.15)$, $O_2(3.60)$, $F_2(4.08)$, $Cl_2(2.75)$, and $Br_2(2.68)$. Because there is no electron transfer between atoms, their atomic charges are zero and the increments of electronegativities only come from orbital overlaps in covalent bonds. The order of the increments is $H_2(0.42) \gg N_2(0.13) > O_2(0.09) > F_2(0.05) > Cl_2(0.03) \approx Br_2(0.03)$.

Electronegativity equilibrium in molecules

The principle of electronegativity equalization proposed by Sanderson[19] is that when two or more atoms with different electronegativity combine, they become adjusted to the same intermediate electronegativity within the compound. In a bond between two unlike atoms, the bonding electrons are preferentially and partially transferred from the less electronegative to the more electronegative atom.

In AOIM, the electronegativity rises as the number of electrons decreases in sp orbitals and the orbital overlaps raise the electronegativity only. When the atoms form a molecule, the electrons transfer from the less electronegative to the more electronegative atom, so that the difference of the electronegativities $\Delta\chi_m$ between the bonded atoms in a molecule is less than $\Delta\chi_a$ between the free atoms. For example, $\Delta\chi_m = 0.56$ in HF is less than $\Delta\chi_a = 1.72$ between atomic fluorin and hydrogen.

Our results are in agreement with Sanderson's postulation of the principle of electronegativity equalization ($\Delta\chi_m = 0$). Nevertheless, no theory proves general electronegativities to be equal in a molecule. On the other hand, because the projected gradients of incompleteness with respect to the optimized ζ_i's and hence χ_ζ's should equal zero in principle, we conclude that atoms would become adjusted to electronegativity equilibrium in a molecule.

Electronegativity of transition metal

The electronegativity of a transition metal is usually determined by the s and d orbitals in the valence shell. We propose two electronegativities for transition metals: s and d electronegativity. Our results in Table 1 indicate that the electronegativities of s orbitals are always less than 2.0 so that the s orbitals could be treated as metal orbitals as usual and the d electronegativities are larger than 3.0 (except 2.14 for Sc) so that these d orbitals should be treated as non-metal-like orbitals. Now the transition metals of group 4 to 10 can be taken as amphoteric elements whose s orbitals are electron donors and unfilled d orbitals are electron acceptors.

Bonds between amphoteric species

Based on the amphoteric character of some transition metals, the Lewis acid and base theory can be generalized to metal clusters and metal carbonyl complexes.

Because the electronegativities of amphoteric elements are either less than 2.0 or larger than 3.0, the metal atoms could be bonded in the type of ionic bond A_{ns}–$B_{(n-1)d}$, covalent bond A_{ns}–B_{ns} or $A_{(n-1)d}$–$B_{(n-1)d}$. For example, in $Fe_2(S = 9)$, both irons are neutral while the orbital charges are $3d^{-0.50}4s^{+0.50}$, indicating two ionic bonds in Fe_2, i.e. $A_{ns} \rightarrow B_{(n-1)d}$ and $B_{ns} \rightarrow A_{(n-1)d}$. The total Mayer bond order[11] of Fe–Fe is 2.0, in which the components of 4s–4s, $3d_{z^2}$–$3d_{z^2}$, $3d_{xz}$–$3d_{xz}$, $3d_{yz}$–$3d_{yz}$ are all about 0.5.

The ligand of metal carbonyl complex is monoxide carbon. The orbital electronegativities of the carbon atom are 2.53 for 2s and 2.59 for $2p_x$ and $2p_y$ in CO, which lie between two electronegativities of amphoteric elements while its electron configuration is $2s^{1.752}2p_x^{0.58}2p_y^{0.58}$. These indicate that the 2s orbital could be the electron donor and the $2p_x$ and $2p_y$ are electron acceptors. When CO interacts with the atom of amphoteric elements, there are usually two types of bonds, $C_{2s} \rightarrow M_{(n-1)d}$ σ bond and $M_{ns} \rightarrow$ CO π back-donating bond. For example, in $FeCO(S = 5)$, the orbital charges are Fe: $3d^{-0.24}4s^{+0.91}$ and C: $2s^{+0.182}2p_x^{-0.34}2p_y^{-0.34}$ compared with Fe and CO, respectively. The same behavior can also be observed for the isoelectronic compounds N_2 and CN^- of monoxide carbon. In addition, because the 3d electronegativity of scandium ($\chi_{\zeta(d)} = 2.14$) is too weak to gain electrons from CO, it is predicted that there is no usual metal carbonyl complex for scandium.

4. Population analysis

Assuming the overlap population between two basis functions of the different atoms is shared equally by the atomic orbitals, Mulliken population analysis (MPA)[4] provides a simple qualitative picture for chemists and is effective for small basis sets. However, because the extended basis sets for accurate calculations can not represent the true electronic capability of atoms, the results of the original MPA could be unreasonable and sensitive to the choice of basis sets,[2] in particular when the diffuse and polarization functions are added to basis sets.

In AOIM, these drawbacks can be mostly overcome by improving the basis sets. First, we use the minimal basis set in MPA to remove all the effects of the diffuse functions and the polarization functions. So MPA on this basis set is always reasonable. Secondly, the minimal basis set in MPA is optimized by either accurate or calculated wave functions, in which the incompleteness is minimized so that such ζ-optimized AOs are in equilibrium state in molecules. The equilibrium state of AOs provides a unified criterion intrinsically to determine the basis set in MPA so that the numerical stability of MPA is improved. As a consequence, Mulliken population analysis would be improved by the optimized minimal basis set and the MPA of AOIM would give more reliable and stable results than the original MPA.

An alternative method to the conventional Mulliken population analysis is the natural population analysis (NPA),[2] which is less dependent on the basis sets than the original MPA. However, the assigned atomic orbitals are obtained as eigenfunctions of the first-order atomic density matrix so that they are orthogonalized and multicentered, and consequently some atomic features of orbitals are missing.

The approach of the atoms in molecules (AIM) is a much less basis-set-dependent method based on analyzing the total electron density,[21] however the AIM fails to give any information of atomic orbitals. Because AIM is intrinsically different from MPA and NPA, we do not discuss it any further.

A reasonable population analysis requires numerical stability and accuracy. We will compare AOIM with NPA and the original MPA in these two respects.

Numerical stability

To illustrate the basis-set dependence of AOIM with NPA and the original MPA, we have carried out the calculations with the different basis sets 6-31G, 6-31++G, and 6-31G** on the acetic acid, which includes some typical covalent bonds: C–H, C–C, C–O, C=O, O–H, and the typical ionic compounds LiF and NaCl. Table 2 compares the atomic charges calculated from AOIM, NPA, and the original MPA as well as their differences between different basis sets.

As a posterior analysis of the molecular wave function, atomic charges must be related with wave functions so that the numerical values of atomic charges may change slightly as the wave function changes definitely. But if the wave functions have no definite change in different basis sets, there should be no obvious difference in the atomic charges. The difference of HF energies using different basis sets is used and fit to denote the difference of wave functions in a series of basis sets. From the differences of HF energies of acetic acid, LiF, and NaCl between 6-31++G and 6-31G (0.008 a.u., 0.016 a.u. and 0.003 a.u., respectively) and between 6-31G** and 6-31G (0.124 a.u., 0.013 a.u. and 0.008 a.u., respectively), it is concluded that the wave functions of each molecule are approximate to each other for these different basis sets, except that of acetic acid using 6-31G**.

Less difference between the atomic charges from approximate calculated wave functions means more numerical stability in population analysis. Table 2 shows that the average (maximum) differences between the atomic charges from the above approximate calculated wave functions are 0.01(0.03), 0.02(0.06), 0.06(0.16) for AOIM, NPA, and the original MPA, respectively. Therefore the AOIM and NPA are less basis-set

Table 2 Atomic charges and their differences in CH_3COOH, LiF, and NaCl

	Basis set	$C_1{}^a$	C_3	O_4	O_5	H_2	H_6	LiF	NaCl
AOIM	6-31G	0.38	0.87	0.63	0.59	0.12	0.38	0.96	0.89
	6-31++G	0.38	0.90	0.64	0.61	0.12	0.39	0.97	0.89
	Δ^{++b}	0	3	1	2	0	1	1	0
	6-31G**	0.34	0.96	0.67	0.63	0.10	0.39	0.96	0.89
	Δ^{**}	4	9	4	4	2	1	0	0
NPA	6-31G	0.78	0.93	0.67	0.78	0.26	0.51	0.92	0.94
	6-31++G	0.73	0.90	0.67	0.78	0.25	0.52	0.98	0.96
	Δ^{++}	5	3	0	0	1	1	6	4
	6-31G**	0.76	0.99	0.70	0.79	0.25	0.52	0.92	0.94
	Δ^{**}	2	6	3	1	1	1	0	0
MPA	6-31G	0.51	0.69	0.53	0.70	0.21	0.43	0.74	0.78
	6-31++G	0.67	0.60	0.55	0.59	0.24	0.51	0.76	0.76
	Δ^{++}	16	9	22	1	3	8	2	2
	6-31G**	0.41	0.72	0.56	0.59	0.16	0.36	0.66	0.67
	Δ^{**}	10	3	3	11	5	7	8	11

^{a} X_n is the nth atom in molecular formula CH_3COOH. ^{b} Δ^{++} (Δ^{**}) is 100 times absolute difference of the atomic charge between 6-31++G (6-31G**) and 6-31G.

dependent than the original MPA. It was also seen that the atomic charges changed slightly (0.04, 0.02 and 0.07 for AOIM, NPA and original MPA, respectively) after the calculated wave functions changed definitely.

The bond order is another important parameter in the chemical bond theory. The Mayer bond order[11] is equal to the experiential chemical bond order for the bonds such as H–H(1.0), O=O(2.0), C–H(1.0). The original Mayer bond order depends on basis sets. Table 3 compares Mayer bond orders of acetic acid, from which we conclude that Mayer bond orders of AOIM are independent of basis sets (with max. error 0.02), and those from other methods are basis-set-dependent (with max. error 0.19).

Therefore, the Mulliken population analysis of AOIM has similar numerical stability with the popular NPA and is more numerically stable than the original MPA. The Mayer bond order of AOIM has more numerical stability than those on basis sets for calculation.

Numerical accuracy

The accuracy of population analysis can be verified by the experimental dipole moments[22] of simple molecules. Because MPA has less numerical stability, only the results of NPA and AOIM are compared with the experimental values.

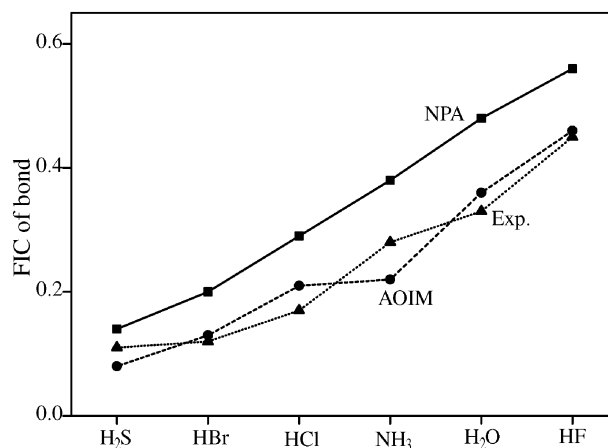The ionic character of the bond can be calculated from the atomic charges or experimental dipole moments for simple molecules consisting of single bonds such as hydrides and ionic halides. The fraction of ionic character (FIC) of bond is FIC $= \mu/(ZR)$, where μ is the dipole moment, Z is the formal atomic charge and R is the bond distance between two atoms. For NH_3, H_2S, and H_2O, the total dipole moments can be decomposed as the vectors in different directions to calculate the dipole moments of bonds. The calculated values of FIC of hydrides (ionic halides) from molecular wave functions are just the atomic charges of hydrogen (halogen) in molecules.

Fig. 3 describes the experimental and calculated FICs of bonds in some hydrides, in which the FICs from AOIM are closer to experimental values than those from NPA. The calculated FICs of H_2S and NH_3 are smaller than experimental values because the experimental values have increments of lone pair(s) on nitrogen and sulfur atom. Therefore the populations of hydrides in AOIM are more reasonable than those in NPA.

Fig. 4 describes the atomic charges of some typical alkali metal halides, in which the tendency of AOIM is consistent with that of electronegativities of halides (F > Cl > Br), while

Table 3 Mayer bond orders and maximum of differences between different basis sets in CH_3COOH

	Basis set	C–C	C–O	C=O	C–H	O–H
AOIM	6-31G	0.99	0.98	1.71	0.98	0.82
	6-31++G	1.00	0.97	1.70	0.98	0.81
	6-31G**	0.99	0.96	1.69	0.98	0.81
	$\Delta_{max} \times 100$	1	2	2	0	1
MPA	6-31G	0.89	0.90	1.84	0.94	0.76
	6-31++G	0.77	0.96	1.89	0.93	0.69
	6-31G**	0.96	1.00	1.87	0.96	0.85
	$\Delta_{max} \times 100$	19	10	5	3	16

Fig. 3 Comparisons of experimental values with NPA and AOIM in fractions of ionic character of bonds in some hydrides.
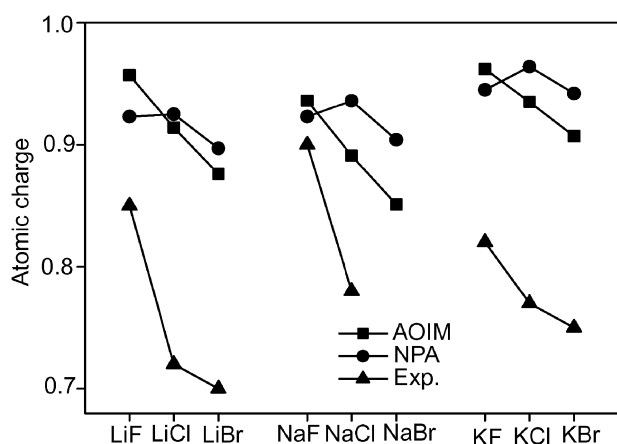
Fig. 4 Comparisons of experimental atomic charges with NPA and AOIM in alkali metal halides.

some abnormalities of tendency between F and Cl are observed in NPA. Thus the population analysis of halide ionic compound of AOIM is more reasonable than that of NPA.

Such comparisons in these typical simple molecules demonstrate that the AOIM may provide very reliable atomic charges in molecules.

5. Conclusion

To analyze the properties of atoms from molecular wave functions, we have developed an approach of the atomic orbitals in molecules based on the optimized minimal basis set. The optimized-ζ's were used to calculate Pauling's electronegativities of atoms in molecules, from which the electronegativity equilibrium in molecules is introduced, and the transition metals from the groups 4 to 10 are treated as amphoteric elements. The optimized minimal basis sets also provide reasonable basis sets for Mulliken population analysis such that the calculated atomic charges of hydrides are in good agreement with the experimental data. In summary, AOIM is powerful in studying the properties of atoms in molecules and could give some quantitative information of classical chemical bond theory, such as the electronegativity, atomic charge, and bond order.

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