Relationship between chemical shift and atomic charge

By i_was_a_baby
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NMR(Nuclear Magnetic Resonance) is a physical phenomenon in which nuclei in a strong static magnetic field are perturbed by a weak oscillating magnetic field (in the near field and therefore not involving electromagnetic waves) and respond by producing an electromagnetic signal with a frequency characteristic of the magnetic field at the nucleus. In NMR spectroscopy, the chemical shift is the resonant frequency of a nucleus relative to a standard in a magnetic field. Often the position and number of chemical shifts are diagnostic of the structure of a molecule. Chemical shifts are also used to describe signals in other forms of spectroscopy such as photoemission spectroscopy. In quantum chemistry, when the atom is in different chemical environment, the degree of screen electrons to nuclear is variable, and the chemical shifts can be different. So, in order to study the relationship with NMR and electron structure, several types of atomic charges can be employed in this article, such as ADCH, Hirshfeld, Mulliken, NPA, MK and RESP charges. As examples, Borane-derived complexes have been researched.

Geometry and Frequency: M06-2X/6-31G* (Gaussian 09 version D 01)
NMR: M06-2X/def2-TZVP (Gaussian 09 version D 01)
Atomic charge: M06-2X/6-31G*
NPA: NBO 3.1 (inside Gaussian 09 version D 01)
Mulliken: Gaussian 09 version D 01
ADCH and Hirshfeld: Multiwfn 3.6(dev)
MK and RESP: Multiwfn 3.6(dev) with cubegen module of Gaussian 09 version D 01

Well, Let's begin!

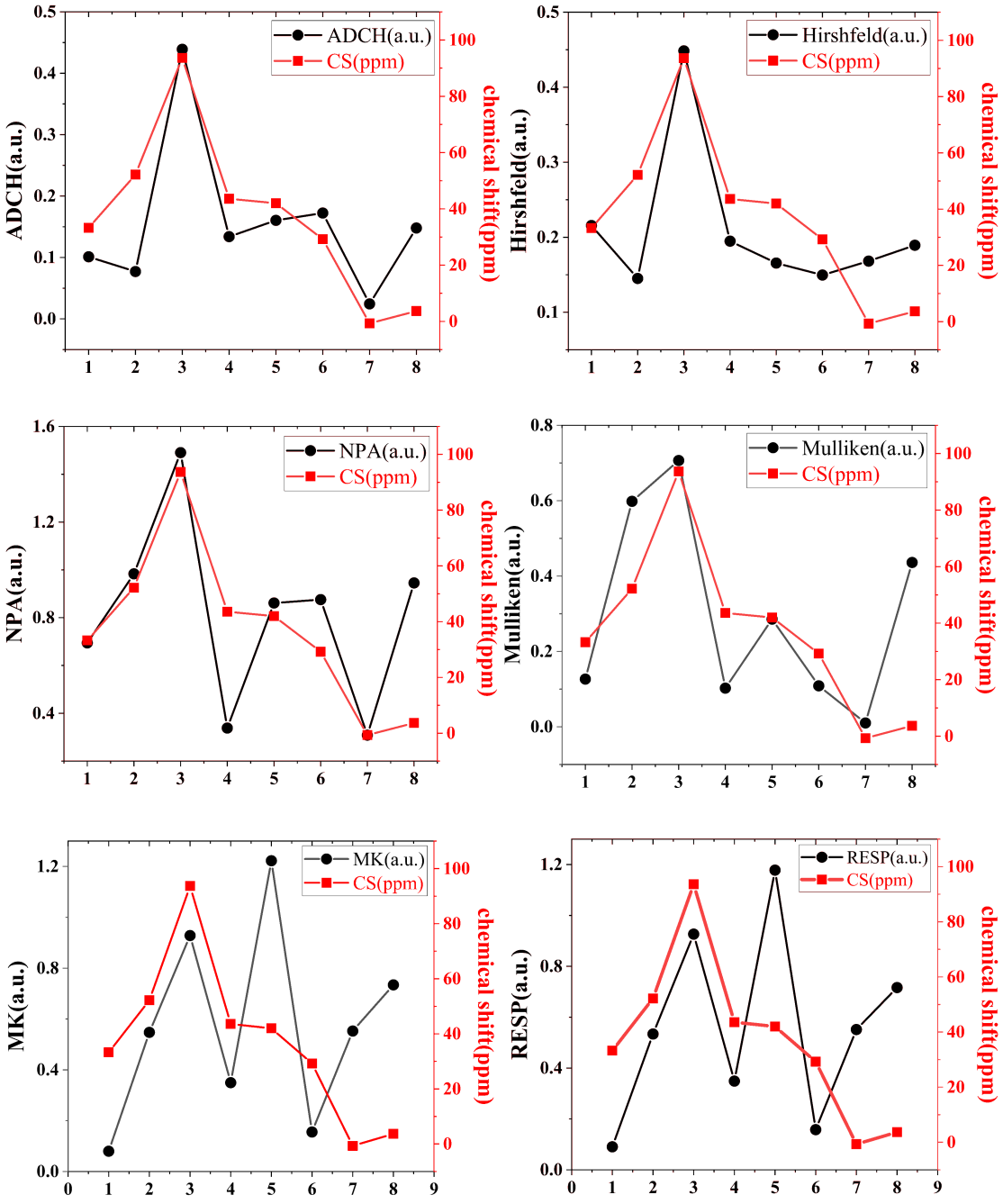
Table the value of each type of atomic charge and chemical shifts

	$B(CF_3)_3$	$B(CCl_3)_3$	BF_3	BCl_3	$B(C_6F_5)_3$	BPh_3	BH_3	BMe_3
ADCH	0.101	0.077	0.439	0.134	0.160	0.172	0.024	0.148
Hirshfeld	0.216	0.145	0.448	0.195	0.166	0.150	0.168	0.189
NPA	0.695	0.984	1.490	0.338	0.862	0.876	0.309	0.945
Mulliken	0.126	0.598	0.707	0.103	0.286	0.109	0.010	0.436
MK	0.080	0.548	0.928	0.350	1.223	0.156	0.553	0.734
RESP	0.090	0.534	0.926	0.349	1.178	0.158	0.551	0.716
CS*	33.266	52.185	93.662	43.597	41.995	29.235	-0.674	3.674

*CS=chemical shifts

Figure curve line plots of each type of atomic charge and chemical shifts. The

number 1~8 mean the molecules of $B(CF_3)_3$, $B(CCl_3)_3$, BF_3, BCl_3, $B(C_6F_5)_3$, BPh_3, BH_3, and BMe_3, respectively.



*CS=chemical shifts

By overview, the change law of **ADCH** charge is similar to the change law of CS. The atomic charge of Hirshfeld can be accepted in some cases. Others, as you see, are unnecessary to be considered.