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Comparison of ab Initio Hartree−Fock and Kohn−Sham Orbitals in the Calculation of Atomic Charge, Bond Index, and Valence

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Atomic charges, bond indices (two-center and three-center), and valences have been calculated for a number of closed-shell molecules using ab initio Hartree−Fock (HF) and Kohn−Sham (KS) orbitals. In a few molecules we have also studied the variation of molecular valence, orbital energy and orbital valence with bond angle. Several basis sets and population analysis schemes have been employed in the present calculations. It is observed that, compared to the HF orbitals, the KS orbitals predict a slightly enhanced covalency. Otherwise, at least on the basis of bond index and related concepts, no appreciable difference is noticed between their performance in the theoretical study of bonding.

I. Introduction

The Kohn−Sham (KS) version[1] of the density functional theory (DFT)[2−7] has, in recent years, made a tremendous impact in the development of quantum chemistry. In the KS method a set of one-electron eigenequations are solved iteratively to obtain eigenfunctions (orbitals) and eigenvalues (orbital energies). In this respect it is similar to Hartree and Hartree−Fock (HF) methods. The exchange potential term, $K(r)$ in the Fock operator is replaced by the exchange−correlation potential term, $v_{xc}(r)$ in the one-electron KS operator. Unlike $K(r)$, $\upsilon_{xc}(r)$ cannot be determined exactly. It is evaluated via the relation

$$\upsilon_{xc}(r) = \frac{\delta E_{ex}[\rho(r)]}{\delta \rho(r)} \quad (1)$$

where $E_{xc}[\rho(r)]$ is the exchange−correlation functional and $\rho(r)$ is the electron density at r. A number of approximate expressions are available for this functional. Their relative performance has recently been assessed by Cohen and Handy.[8] Of these functionals, the one designated by the acronym, B3LYP (Becke[9] three-parameter nonlocal exchange functional with the nonlocal correlation functional of Lee, Yang, and Parr[10]) is most widely used[8] in the calculation of molecular electronic structure and energetics.

In the early days of KS/DFT, not much significance was attached to the KS orbitals; they were regarded as auxiliary functions which could be used only to calculate the total electron density. The situation, however, changed considerably in the past 15 years or so. A number of papers elucidating the nature of KS orbitals and highlighting their importance in chemistry, have been published in 1990s.[11−22] Very recently, it has been shown by Stowasser and Hoffmann[21] that the shape and symmetry of the KS orbitals are quite similar to those of the HF orbitals which chemists are so familiar with. They found a linear relation between $|e_i(\text{KS}) - e_i(\text{HF})|$ and $e_i(\text{HF})$ for the occupied as well as for the unoccupied orbital energies (e_i). The similarity between HF and KS orbitals was noted by Kar and Sannigrahi[22] in the calculation of condensed Fukui functions,[23] atomic spin populations[24] and free valences[25,26] of open-shell molecules.

The aim of the present investigation is to assess the performance of KS orbitals vis-à-vis that of HF orbitals in the study of chemical bonding using the quantified concepts of bond index and valence.[25−31] For this purpose we have chosen a number of closed-shell molecules and calculated their atomic charges, two-center (2c) and three-center (3c) bond indices and atomic valences using HF and KS orbitals, and different schemes of population analysis. We have also compared the orbital energy and orbital valence correlation diagrams[32−34] and studied the variation of molecular valence[33−36] with bond angle in some triatomic linear and nonlinear molecules. We hope that a study of most of the important aspects of chemical bonding, as expressed by the bond index and valence, allows us to demonstrate the equivalence of the HF and KS orbitals in this respect.

II. Method of Calculation

The calculations have been performed at the experimental geometry[37] of the molecules, whenever it was available; otherwise we have used the HF/6-31G* optimized geometry. The KS orbitals have been determined using the B3LYP[9,10] method. For the calculation of atomic charges we have employed Mulliken population analysis (MPA),[38] the population analysis

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TABLE 1: Comparison of Atomic Charges (q_A) Calculated from ab Initio HF and KS Orbitals[a]

		charge						charge			
		6-31G*		6-311+G**				6-31G*		6-311+G**	
molecule	atom	HF	KS	HF	KS	molecule	atom	HF	KS	HF	KS
CH_4	H	0.169	0.157	0.108	0.127	H_2S	H	0.011	0.118	0.056	0.072
		0.129	0.131	0.033	0.044			0.101	0.112	−0.046	−0.031
		0.216	0.227	0.180	0.203			0.131	0.150	0.122	0.135
		−0.004	0.017	−0.030	0.002			0.013	0.023	−0.323	−0.051
NH_3	H	0.339	0.300	0.228	0.225	HCl	H	0.245	0.227	0.163	0.165
		0.233	0.224	0.071	0.077			0.199	0.196	0.008	0.014
		0.371	0.369	0.342	0.349			0.278	0.280	0.248	0.255
		0.363	0.350	0.354	0.328			0.272	0.259	0.280	70.258
H_2O	H	0.449	0.399	0.258	0.251	CO	C	0.293	0.149	0.098	0.010
		0.326	0.308	0.098	0.098			0.068	−0.013	0.168	0.101
		0.478	0.466	0.460	0.458			0.612	0.494	0.591	0.483
		0.583	0.550	0.601	0.550			1.399	1.247	1.327	1.144
HF	H	0.544	0.488	0.296	0.285	CS	C	−0.025	−0.089	−0.052	−0.244
		0.406	0.380	0.134	0.126			−0.130	−0.199	−0.292	−0.358
		0.557	0.534	0.557	0.550			−0.070	−0.163	−0.074	−0.176
		0.723	0.676	0.748	0.700			−0.821	−0.793	−0.836	−0.730
SiH_4	H	−0.137	−0.059	−0.188	−0.123	HNC	H	0.438	0.362	0.306	0.270
		−0.068	−0.032	−0.138	−0.106			0.294	0.265	0.111	0.103
		−0.213	−0.160	−0.202	−0.148			0.465	0.443	0.452	0.434
		−0.719	−0.669	−0.741	−0.671			0.571	0.526	0.565	0.503
CO_2	C	0.926	0.634	0.635	0.464		N	−0.610	−0.398	−0.290	−0.143
		0.357	0.196	0.224	0.088			−0.270	−0.193	−0.180	−0.129
		1.271	1.034	1.211	0.996			−0.831	−0.726	−0.816	−0.713
		2.729	2.379	2.549	2.148			−1.786	−1.593	−1.705	−1.444
CS_2	C	−0.032	−0.031	0.728	0.531		C	0.172	0.035	−0.016	−0.127
		−0.182	−0.272	−0.521	−0.613			−0.025	−0.075	0.068	0.026
		−0.298	−0.428	−0.271	−0.421			0.366	0.283	0.364	0.280
		−1.323	−1.296	−1.316	−1.191			1.215	1.067	1.139	0.940
HCN	H	0.316	0.244	0.225	0.196	LiH	Li	0.169	0.118	0.358	0.296
		0.189	0.172	0.074	0.070			0.286	0.063	0.236	0.214
		0.235	0.229	0.223	0.220			0.732	0.669	0.815	0.771
		0.244	0.222	0.218	0.198			0.899	0.886	0.903	0.887
	C	0.028	0.018	0.013	0.039	LiF	Li	0.692	0.542	0.692	0.621
		−0.097	−0.113	0.027	0.005			0.352	0.242	0.458	0.403
		0.118	0.082	0.122	0.090			0.924	0.858	0.975	0.961
		1.206	1.058	1.089	0.876			0.946	0.932	0.938	0.917
	N	−0.344	−0.263	−0.238	0.235	LiCl	Li	0.485	0.391	0.465	0.401
		−0.092	−0.059	−0.101	−0.075			0.168	0.125	0.237	0.213
		−0.353	−0.311	−0.345	−0.310			0.933	0.905	0.941	0.927
		−1.450	−1.280	−1.307	−1.074			0.939	0.930	0.931	0.915
NaF	Na	0.728	0.563	0.837	0.757	NaH	Na	0.261	0.206	0.418	0.341
		0.502	0.367	0.697	0.646			0.121	0.086	0.273	0.231
		0.925	0.827	0.988	0.969			0.663	0.544	0.777	0.662
		0.932	0.865	0.942	0.904			0.809	0.729	0.809	0.714
PH_3	H	−0.013	0.031	−0.042	−0.001	NaCl	Na	0.663	0.559	0.626	0.538
		0.007	0.031	−0.112	−0.086			0.384	0.328	0.502	0.473
		−0.042	−0.006	−0.048	−0.007			0.937	0.883	0.959	0.929
		−0.521	−0.446	−0.612	−0.505			0.917	0.879	0.914	0.875

[a] The four values of q_A from top to bottom against each atom correspond to MPA, LPA, NPA, and AIM, respectively.

performed in the Löwdin-orthogonalized[39] basis of atomic orbitals (LPA), natural population analysis (NPA),[40] as well as the Atoms-in-Molecules (AIM) method.[41] The extended versions of the same PA achemes (MPA,[26,29] LPA,[29,42] NPA,[40,43] and AIM[44]) have been used to calculate 2c and 3c bond indices. For the calculation of molecular valence, orbital valence and orbital bond index only MPA has been used. The working expressions for various quantities are given in the Appendix. The Gaussian 94 program[45] has been employed in MPA, LPA, and NPA calculations. MPA and NPA atomic charges are standard outputs of this program. Additional subroutines have been written to calculate all other quantities except the NPA bond indices for which the NBO program of Glendening et al.,[43] integrated in the Gaussian program, has been used. AIM calculations were performed using Gaussian 92[46] and Gaussian 94.[45] The PROAIM program of Bader and co-workers[47] was used to generate the atomic overlap matrices, which served as input for the calculation of 2c and 3c bond indices.

The effect of basis sets on various calculated quantities has been studied using STO-3G, 6-31G* and 6-311+G** basis sets.

III. Results and Discussion

Atomic charges, 2c bond indices, and valences have been calculated for 20 simple molecules with varying bond ionicity. These results are presented in subsection A. Three-center bond indices are calculated for three types of molecules, such as those with nonclassical structure, hypervalent molecules, and molecules with cumulated double bonds. These results are described in subsection B. Subsection C includes those aspects of the study of bond index and valence which are aimed at finding a structure-property type of correlation (e.g., valence correlation diagrams).

A. Atomic Charges, Two-center Bond Indices, and Valences. Calculated values of atomic charges (q_A) are summarized in Table 1. There are 16 values for each q_A (DFT and Hartree−Fock with two basis sets and four different partitioning schemes), which in most cases are scattered over a wide range. It is well-known that we cannot speak about a unique definition of the atomic charge, as we can in the case of a usual quantum mechanical observable. In fact, the “goodness” of a given atomic

TABLE 2: Comparison of Two-Center Bond Indices (I_{AB}) Calculated from ab Initio HF and KS Orbitals

		bond index			
		6-31G*		6-311+G**	
molecule	bond	HF	KS	HF	KS
CH_4	CH	0.958	0.964	0.982	0.977
		0.980	0.980	0.984	0.983
		0.953	0.947	0.968	0.958
		0.983	0.984	0.982	0.983
NH_3	NH	0.857	0.879	0.949	0.958
		0.951	0.955	1.058	1.058
		0.863	0.864	0.884	0.880
		0.874	0.884	0.889	0.911
H_2O	OH	0.770	0.807	0.964	0.966
		0.906	0.916	1.149	1.152
		0.772	0.785	0.791	0.793
		0.667	0.706	0.650	0.716
HF	FH	0.683	0.737	0.979	0.984
		0.857	0.876	1.232	1.244
		0.690	0.716	0.693	0.702
		0.482	0.549	0.448	0.522
SiH_4	SiH	0.953	0.958	0.924	0.938
		0.994	0.996	0.984	0.992
		0.938	0.957	0.941	0.959
		0.479	0.538	0.453	0.539
CO_2	CO	1.933	2.028	1.897	1.939
		2.400	2.435	2.518	2.545
		1.820	1.886	1.840	1.899
		1.074	1.291	1.192	1.425
CS_2	CS	1.874	1.893	1.105	1.217
		2.219	2.231	2.460	2.456
		1.976	1.986	2.001	2.001
		2.065	2.078	2.081	2.089
HCN	HC	0.863	0.891	0.937	0.947
		0.916	0.914	0.926	0.925
		0.930	0.931	0.936	0.935
		0.898	0.905	0.915	0.922
	CN	2.973	3.003	2.785	2.695
		3.321	3.337	3.389	3.409
		2.976	2.987	2.981	2.991
		2.264	2.394	2.377	2.540
HNC	HN	0.765	0.809	0.888	0.894
		0.856	0.862	0.983	0.979
		0.797	0.762	0.775	0.774
		0.666	0.708	0.675	0.736
	NC	2.378	2.450	2.245	2.203
		3.004	3.066	3.175	3.232
		2.382	2.470	2.384	2.471
		1.682	1.861	1.763	1.983
PH_3	PH	0.968	0.965	0.940	0.945
		1.012	1.012	1.035	1.044
		0.993	0.996	0.991	0.995
		0.857	0.910	0.803	0.888
H_2S	SH	0.948	0.951	0.957	0.968
		1.007	1.005	1.105	1.110
		0.981	0.976	0.986	0.982
		1.077	1.077	1.133	1.120
HCl	ClH	0.903	0.914	0.972	0.980
		0.985	0.986	1.180	1.185
		0.923	0.922	0.943	0.940
		0.980	0.990	0.993	1.015
CO	CO	2.288	2.419	2.210	2.211
		2.965	3.067	3.297	3.395
		2.131	2.260	2.152	2.271
		1.506	1.711	1.584	1.816
CS	CS	2.539	2.483	2.370	2.508
		3.059	2.961	3.376	3.285
		2.585	2.684	2.621	2.718
		2.668	2.763	2.692	2.788
LiH	LiH	0.971	0.986	0.871	0.912
		1.000	1.004	0.951	0.962
		0.464	0.553	0.298	0.356
		0.206	0.233	0.197	0.227
LiF	LiF	0.582	0.852	0.601	0.754
		1.203	1.391	1.089	1.197
		0.149	0.277	0.049	0.079
		0.169	0.202	0.181	0.225
LiCl	LiCl	0.915	1.064	0.918	0.985
		1.441	1.519	1.340	1.389
		0.133	0.187	0.116	0.144
		0.159	0.180	0.175	0.207
NaH	NaH	0.931	0.956	0.825	0.883
		0.992	0.999	0.933	0.955
		0.560	0.704	0.317	0.469
		0.392	0.512	0.389	0.534
NaF	NaF	0.515	0.815	0.330	0.467
		0.938	1.178	0.676	0.797
		0.785	0.148	0.336	0.023
		0.220	0.353	0.194	0.278
NaCl	NaCl	0.623	0.798	0.642	0.759
		1.105	1.204	0.945	1.000
		0.123	0.225	0.080	0.139
		0.226	0.300	0.228	0.311

charge definition is not an inherent quality; it is strongly dependent on its use. For example, the best charges to describe the charge transfer between atoms are not necessarily appropriate to describe the molecular electrostatic potential occurring in intermolecular forces or the set of charges which can successfully model the core electron binding energy shifts may fail to reproduce dipole moment derivatives obtained from IR intensities. Some recent MP2 and DFT calculations[48−50] of atomic charges demonstrated that the charges derived from the generalized atomic polar tensors (GAPT)[51] possess some attracting features. They are relatively insensitive to the basis set (unlike the MPA or LPA charges): they provide a good description of the experimental dipole moment derivatives and correlate well with core electron binding energies. Obviously, neither the more-or-less sophisticated partitioning schemes in the atomic orbital space (MPA, LPA, or NPA) nor the physically well-founded space partitioning method (AIM) are able to compete with the GAPT charges in these respects. Nevertheless, despite their limitations, the population analysis schemes used in the present study are relatively well-adapted to characterize interatomic charge-transfer phenomena, which are essential for the understanding of chemical bonding.

Among the KS/DFT methods B3LYP seems to be most appropriate for the calculation of atomic charge.[48]

Atomic charges given in Table 1 exhibit certain useful qualitative trends. Independent of basis sets and population analysis (PA) schemes, the HF charges are slightly higher than the KS charges. A similar observation was made by Geerlings et al.[48] who compared AIM and APT charges of a number of molecules obtained using HF, post-HF, and several versions (the XC potentials are different) of KS/DFT methods.[69] The nature of the difference between HF and KS charges indicates that the latter orbitals are somewhat less polarized than their HF counterparts. Barring a few sporadic exceptions the magnitude of charge separation varies in the order, LPA < MPA < NPA < AIM. That the AIM scheme leads to a more polar charge distribution than NPA, was noted also by Jansen et al.[17] In the predominantly ionic molecules (Li and Na compounds) considered here the order of NPA and AIM charges is often reversed. The atomic charges of hydrogen in the first-row and second-row hydrides follow the orders, $CH_4 < NH_3 < H_2O <$ HF and $SiH_4 < PH_3 < H_2S <$ HCl, in agreement with the variation of electronegativity of elements in a period. In the ionic molecules, only the KS/6-311+G** charges vary in the

TABLE 3: Comparison of Atomic Valences (V_A) Calculated from ab Initio HF and KS Orbitals[a]

		atomic valence						atomic valence			
		6-31G*		6-311+G**				6-31G*		6-311+G**	
molecule	atom	HF	KS	HF	KS	molecule	atom	HF	KS	HF	KS
CH_4	C	3.834	3.856	3.927	3.908	SiH_4	Si	3.813	3.832	3.697	3.757
		3.921	3.918	3.938	3.932			3.977	3.985	3.937	3.969
		3.812	3.790	3.870	3.833			3.753	3.827	3.762	3.836
		3.932	3.935	3.928	3.934			1.921	2.160	1.813	2.161
	H	0.931	0.936	0.957	0.960		H	0.960	0.976	0.912	0.944
		1.002	1.001	1.090	1.091			1.008	1.013	1.020	1.034
		0.954	0.949	0.968	0.959			0.956	0.975	0.961	0.980
		1.094	1.086	1.110	1.108			0.824	0.895	0.802	0.886
NH_3	N	2.571	2.636	2.848	2.875	PH_3	P	2.904	2.895	2.820	2.836
		2.854	2.866	3.175	3.174			3.035	3.035	3.106	3.132
		2.589	2.593	2.653	2.639			2.979	2.987	2.973	2.986
		2.623	2.652	2.667	2.733			2.570	2.729	2.406	2.662
	H	0.844	0.864	0.941	0.952		H	0.963	0.963	0.923	0.936
		0.965	0.969	1.154	1.154			1.019	1.018	1.075	1.085
		0.864	0.866	0.885	0.880			1.000	1.002	1.001	1.004
		0.905	0.915	0.925	0.952			1.084	1.110	1.077	1.121
H_2O	O	1.539	1.613	1.928	1.933	CO_2	C	3.866	4.055	3.794	3.878
		1.813	1.832	2.298	2.305			4.800	4.871	5.036	5.091
		1.544	1.569	1.583	1.586			3.641	3.771	3.681	3.798
		1.333	1.412	1.300	1.432			2.149	2.583	2.383	2.850
	H	0.765	0.801	0.975	0.977		O	2.096	2.294	1.924	2.061
		0.914	0.923	1.209	1.212			2.657	2.788	2.805	2.912
		0.773	0.785	0.792	0.794			2.053	2.206	2.075	2.214
		0.673	0.714	0.657	0.726			1.446	1.731	1.518	1.809
H_2	S	1.896	1.902	1.914	1.937	CS_2	C	3.748	3.786	2.210	2.434
		2.013	2.010	2.209	2.219			4.437	4.461	4.920	4.912
		1.962	1.953	1.972	1.964			3.952	3.972	4.002	4.003
		2.155	2.152	2.267	2.241			4.129	4.156	4.163	4.175
	H	0.945	0.948	0.954	0.968		S	2.202	2.313	1.180	1.402
		1.011	1.009	1.132	1.138			2.664	2.768	2.983	3.078
		0.984	0.978	0.990	0.985			2.466	2.570	2.517	2.621
		1.109	1.107	1.218	1.164			2.456	2.562	2.466	2.580
HCl	Cl	0.903	0.914	0.972	0.980	HCN	H	0.875	0.906	0.953	0.969
		0.985	0.986	1.180	1.185			0.979	0.985	1.068	1.076
		0.923	0.922	0.943	0.940			0.945	0.949	0.952	0.954
		0.980	0.990	0.993	1.015			0.973	0.988	1.000	1.015
CO	C	2.288	2.419	2.210	2.211		C	3.836	3.894	3.722	3.642
		2.965	3.067	3.297	3.395			4.237	4.252	4.315	4.334
		2.131	2.260	2.152	2.271			3.906	3.918	3.917	3.925
		1.506	1.711	1.584	1.816			3.162	3.300	3.292	3.462
CS	C	2.539	2.483	2.370	2.508		N	2.985	3.018	2.801	2.718
		3.059	2.961	3.376	3.285			3.384	3.408	3.530	3.560
		2.585	2.684	2.621	2.717			2.991	3.004	2.998	3.010
		2.668	2.763	2.692	2.788			2.339	2.478	2.462	2.633
HNC	H	0.791	0.842	0.926	0.953	LiF	Li	0.582	0.852	0.601	0.754
		0.931	0.946	1.126	1.133			1.203	1.391	1.089	1.197
		0.785	0.806	0.798	0.815			0.149	0.277	0.049	0.079
		0.682	0.739	0.700	0.773			0.169	0.202	0.181	0.225
	N	3.143	3.259	3.134	3.097	LiCI	Li	0.915	1.064	0.918	0.985
		3.860	3.927	4.157	4.211			1.441	1.519	1.340	1.389
		3.144	3.245	3.159	3.256			0.133	0.187	0.116	0.144
		2.347	2.570	2.437	2.719			0.159	0.180	0.175	0.207
	C	2.403	2.484	2.283	2.262	NaH	Na	0.931	0.956	0.825	0.883
		3.078	3.150	3.317	3.386			0.992	0.999	0.933	0.955
		2.405	2.501	2.408	2.501			0.560	0.704	0.317	0.469
		1.703	1.892	1.788	2.020			0.392	0.512	0.389	0.534
LiH	Li	0.971	0.986	0.871	0.912	NaF	Na	0.515	0.815	0.330	0.467
		1.000	1.004	0.951	0.962			0.938	1.178	0.676	0.797
		0.464	0.553	0.298	0.356			0.148	0.336	0.023	0.063
		0.206	0.233	0.197	0.227			0.220	0.353	0.194	0.278
HF	H	0.683	0.737	0.979	0.980	NaCI	Na	0.623	0.798	0.642	0.759
		0.857	0.876	1.232	1.244			1.105	1.204	0.945	1.000
		0.690	0.716	0.693	0.702			0.123	0.225	0.080	0.139
		0.482	0.549	0.448	0.522			0.226	0.300	0.228	0.311

[a] The four values of V_A from top to bottom against each atom correspond to MPA, LPA, NPA, and AIM, respectively.

expected order, namely, MH < MCl < MF, where M = Li and Na. AIM charges are grossly overestimated in some cases (q_C in CO, CO_2, CS and CS_2; q_C and q_N in HCN and HNC; q_H in SiH_4 and PH_3) with respect to all the other PA methods. It is interesting to note that in the same set of molecules the atomic dipole moments are exceptionally high (1.8 D for the C atom in the HNC molecule or 2.1 D for P in PH_3). One can also note that the NPA charges are often much closer to the AIM charges than the MPA or LPA ones. Basis sets generally have a strong influence on atomic charges. Of the four PA schemes, AIM is the least sensitive to basis sets, reflecting the fact that it is based on a space-partitioning of the equilibrium electron density. In contrast to the other three schemes, the variation of the AIM charges depends entirely on the change of the wave function

TABLE 4: Comparison of Three-Center Bond Indices (I_{ABC}) Calculated from ab Initio HF and KS Orbitals[a]

		I_{ABC}						I_{ABC}			
		6-31G*		6-311+G**				6-31G*		6-311+G**	
molecule	ABC	HF	KS	HF	KS	molecule	ABC	HF	KS	HF	KS
$C_3H_5^+$	CCC	0.211	0.263	0.191	0.238	Li_2H_2	LiHLi	0.181	0.206	0.120	0.144
		0.287	0.313	0.309	0.330			0.251	0.256	0.225	0.231
		0.219	0.249	0.219	0.250			0.028	0.036	0.016	0.019
		0.258	0.276	0.255	0.269			0.006	0.007	0.006	0.007
C_3	CCC	0.315	0.337	−0.328	0.112	Li_4	LiLiLi	0.253	0.237	0.230	0.235
		0.479	0.519	0.559	0.600			0.278	0.277	0.282	0.283
		0.308	0.365	0.295	0.347			0.153	0.154	0.154	0.155
		0.442	0.475	0.428	0.472			n.a.[b]	n.a.	n.a.	n.a.
B_2H_6	BHB	0.239	0.248	0.247	0.254	$(FHF)^-$	FHF	−0.070	−0.104	−0.164	−0.193
		0.280	0.282	0.278	0.278			−0.111	−0.122	−0.018	−0.014
		0.259	0.267	0.251	0.267			−0.064	−0.086	−0.065	−0.080
		0.046	0.065	0.039	0.064			−0.003	−0.011	−0.004	−0.010
						F_3^-	FFF	−0.209	−0.267	−0.209	−0.279
								−0.180	−0.231	−0.193	−0.246
								−0.218	−0.273	−0.205	−0.264
								−0.151	−0.204	−0.147	−0.204

		I_{ABC}						I_{ABC}			
		6-31G*		6-311+G**				6-31G*		6-311+G**	
molecule	ABC	HF	KS	HF	KS	molecule	ABC	HF	KS	HF	KS
CL_3^-	ClClCl	−0.251	−0.194	−0.234	−0.291	CO_2	OCO	−0.224	−0.315	−0.342	−0.420
		−0.291	−0.226	−0.191	−0.224			−0.148	−0.200	−0.053	−0.102
		−0.216	−0.254	−0.217	−0.251			−0.297	−0.380	−0.291	−0.370
		−0.124	−0.159	−0.123	−0.159			−0.035	−0.085	−0.059	−0.121
N_3	NNN	−0.531	−0.612	−0.772	−0.807	CS_2	SCS	−0.421	0.498	,−0.343	−0.430
		−0.261	−0.285	−0.303	−0.325			−0.317	−0.363	−0.259	−0.304
		−0.561	−0.588	−0.563	−0.588			−0.468	−0.523	−0.482	−0.539
		−0.254	−0.296	−0.260	−0.298			−0.215	−0.253	−0.203	−0.246

[a] The four values of I_{ABC} from top to bottom against each atom correspond to MPA, LPA, NPA, and AIM, respectively. [b] n.a. = not available.

TABLE 5: Comparison of ab Initio HF and KS Orbital Valences (V_i) and Orbital Bond Indices in Some Representative Molecules[a]

		I_{ABC}					
		6-31G*			6-311+G**		
molecule	MO	V_i	$(I_{AB})_i$[b]	$(I_{AC})_i$	V_i	$(I_{AB})_i$	$(I_{AC})_i$
Li_4	a_g	1.224	0.249	0.301	1.321	0.249	0.226
		1.256	0.243	0.361	1.276	0.246	0.298
	b_{1u}	1.183	0.231	0.130	1.323	0.248	0.289
		1.222	0.230	0.127	1.274	0.242	0.173
HF_2^{-c}	$2\sigma_g$	0.188	0.125	−0.063	0.086	0.059	−0.035
		0.229	0.153	−0.077	0.143	0.098	−0.059
	$2\sigma_u$	0.050	0.000	0.050	0.018	0.000	0.018
		0.061	0.000	0.061	0.033	0.000	0.034
	$3\sigma_g$	0.543	0.362	−0.181	0.359	0.247	−0.135
		0.519	0.346	−0.173	0.408	0.279	−0.151
	$3\sigma_u$	0.370	0.000	0.370	0.161	0.000	0.161
		0.411	0.000	0.411	0.209	0.000	0.209
CO_2	$3\sigma_g$	0.622	0.291	0.040	0.586	0.285	0.016
		0.642	0.298	0.045	0.642	0.302	0.037
	$2\sigma_u$	0.597	0.320	−0.043	0.528	0.268	−0.009
		0.643	0.345	−0.048	0.609	0.316	−0.024
	$4\sigma_g$	0.357	0.209	−0.062	0.334	0.183	−0.033
		0.328	0.199	−0.070	0.309	0.169	−0.030
	$1\pi_u$	0.738	0.492	−0.246	0.678	0.441	−0.204
		0.750	0.500	−0.250	0.728	0.479	−0.230
	$3\sigma_u$	0.418	0.169	0.080	0.411	0.189	0.033
		0.362	0.133	0.097	0.397	0.183	0.032
	$1\pi_g$	0.436	0.000	0.436	0.406	0.062	0.282
		0.492	0.000	0.493	0.456	0.051	0.355

[a] The upper and the lower entries against each MO (valence) correspond to HF and KS orbitals, respectively. [b] In all molecules $(I_{AB})_i = (I_{BC})_i$. The Li atoms along the longer diagonal in Li_4 are the central atoms in the 3c bonds. [c] The MO valences and bond indices of the doubly degenerate $1\pi_u$ and $1\pi_g$ orbitals in HF_2^- are zero and hence they are not tabulated.

quality with respect to the basis set. There is one glaring case of anomaly in atomic charges, where the Mulliken charge suggests a completely reversed order of strong polarity with respect to all the other PA schemes. This is the MPA/X/6-311+G** (X = HF and KS) value in CS_2, indicating an unusual behavior, probably related to the special structure of the overlap matrix for the "small" C atom between two "large" S atoms.

Calculated values of 2c bond indices (I_{AB}) are summarized in Table 2. Bond index is a measure of covalent multiplicity of a bond. It is therefore a purely theoretical quantity. The reliability of the calculated values of I_{AB} can be ascertained only with reference to the classical valence theory (as embodied in the Lewis model) and the concept of resonance. For a purely covalent single bond I_{AB} is 1.0, for a double bond I_{AB} is 2.0, and so on. Calculated bond indices generally deviate from these ideal values either due to the ionicity of the bond or due to delocalization of lone pair electrons or due to both. Basis sets, PA schemes, and the presence of multicenter bonding also have a strong influence[30] on 2c bond indices.

In the framework of the MO theory the most general expression for a 2c bond index is the correlation of fluctuations of the electron populations of the two atoms involved in the bonding:[52−55]

$$
\begin{aligned}
I_{AB} &= -2\langle(\hat{N}_A - \langle\hat{N}_A\rangle)(\hat{N}_B - \langle\hat{N}_B\rangle)\rangle \\
&= -2(\langle\hat{N}_A\rangle\,\langle\hat{N}_B\rangle - \langle\hat{N}_A\hat{N}_B\rangle) \qquad (2)
\end{aligned}
$$

where $\hat{N}_A$ is an atomic population operator, corresponding to one of the PA schemes.

In the case of single-determinant wave functions, constructed from Hartree−Fock or Kohn−Sham orbitals, the above general definition coincides with the earlier propositions which related a bond index to the exchange part of the two-particle density matrix.[27,30,41,52] Recently, Bader and co-workers[56] proposed to call the above interatomic correlation quantity as delocalization index. According to these authors, the term bond order should be reserved to the count of the Lewis-bonded pairs between

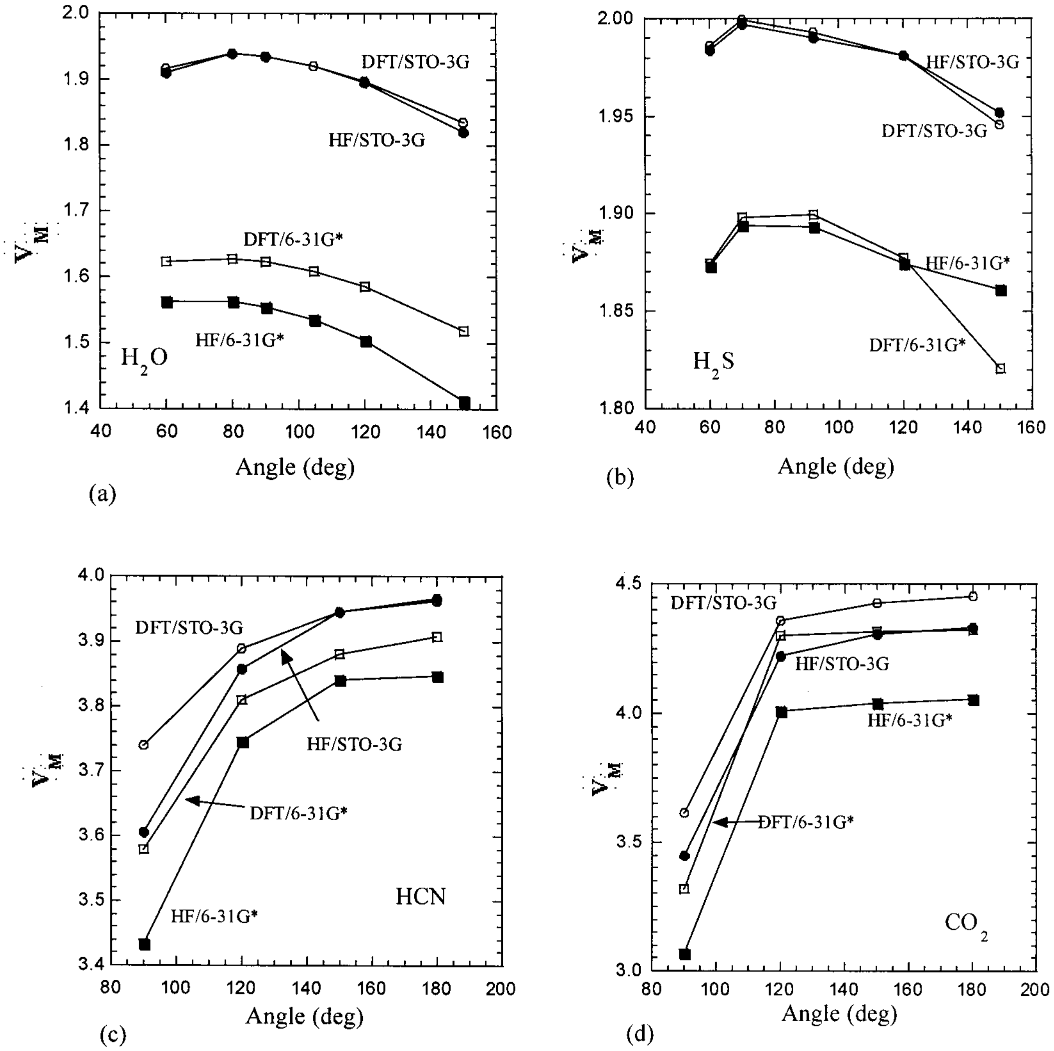

Figure 1. Variation of molecular valence (V_M) with bond angle in H_2O, H_2S, HCN and CO_2.

two atoms connected by a bond path determined from the equilibrium electron density. We, however, think that the term bond index used throughout this article is not going to lead to any confusion, although some more understanding is needed to have a consensual characterization of covalent, ionic, polar, and multicenter bonding in molecules. Like atomic charges, bond indices also follow certain general trends. As can be seen from Table 2, I_{AB}(KS) is slightly higher than I_{AB}(HF) in most of the molecules. The variation of 2c bond indices with respect to the PA schemes is more pronounced in the ionic molecules, where we observe the order I_{AB}(LPA) > I_{AB}(MPA) > I_{AB}(AIM) > I_{AB} (NPA). In other cases reversal of ordering often occurs between AIM and NPA and/or between NPA and MPA bond indices. With respect to the variation of basis sets, no general pattern emerges; the NPA and AIM bond indices are found to be somewhat stable in this regard. The XH bond indices in the first row hydrides follow the order $I_{CH} > I_{NH} > I_{OH} > I_{FH}$ which is consistent with the variation of electronegativity of X. No general trend seems to exist in the second-row hydrides. The CO bond indices are greatly overestimated by LPA and somewhat underestimated by AIM. The anomaly we observed in the MPA/6-311+G** atomic charges of CS_2 persists also in the bond indices. Quite unrealistic I_{AB} values are predicted for the Li compounds by MPA and LPA. The bonding in the Na compounds is described more satisfactorily. Only the bond indices corresponding to the larger basis set, reflect the electronegativity difference between F and Cl.

Table 3 summarizes the atomic valences (V_A) of the molecules. For closed-shell molecules V_A is equal to the sum of AX (X ≠ A) bond indices. Atomic valences should therefore obey the same trends as that of bond indices. Thus, we have V_A(KS) > V_A(HF), and V_A(LPA) > V_A(MPA) > V_A(NPA) > V_A(AIM). Of course, there are a number of exceptions to these general trends especially with regard to the ordering of NPA and AIM values. In the first-row hydrides V_H increases in the expected order, $CH_4 > NH_3 > H_2O >$ HF. The second-row hydrides do not follow any particular trend. Valences of Li and Na reflect the electronegativity difference of F and Cl only for the higher basis set.

In a diatomic molecule (AB) $V_A = V_B = I_{AB}$. However, in a polyatomic molecule the bond indices corresponding to the nonbonded interactions (say, $I_{HH'}$ in H_2O, $I_{OO'}$ in CO_2, etc.) also contribute to the valences of the terminal atoms. If the equality

$$\frac{1}{2}\sum_{A}\sum_{B} I_{AB} = N \tag{3}$$

where N is the total number of electrons in a molecule, is satisfied to a good accuracy by considering only the bonded and self-interaction (I_{AA}) terms, then the bonding is said to be classical. Otherwise, there is a possibility of the presence of 3c−2e and 3c−4e bonds. We shall discuss this point in further details in the next subsection.

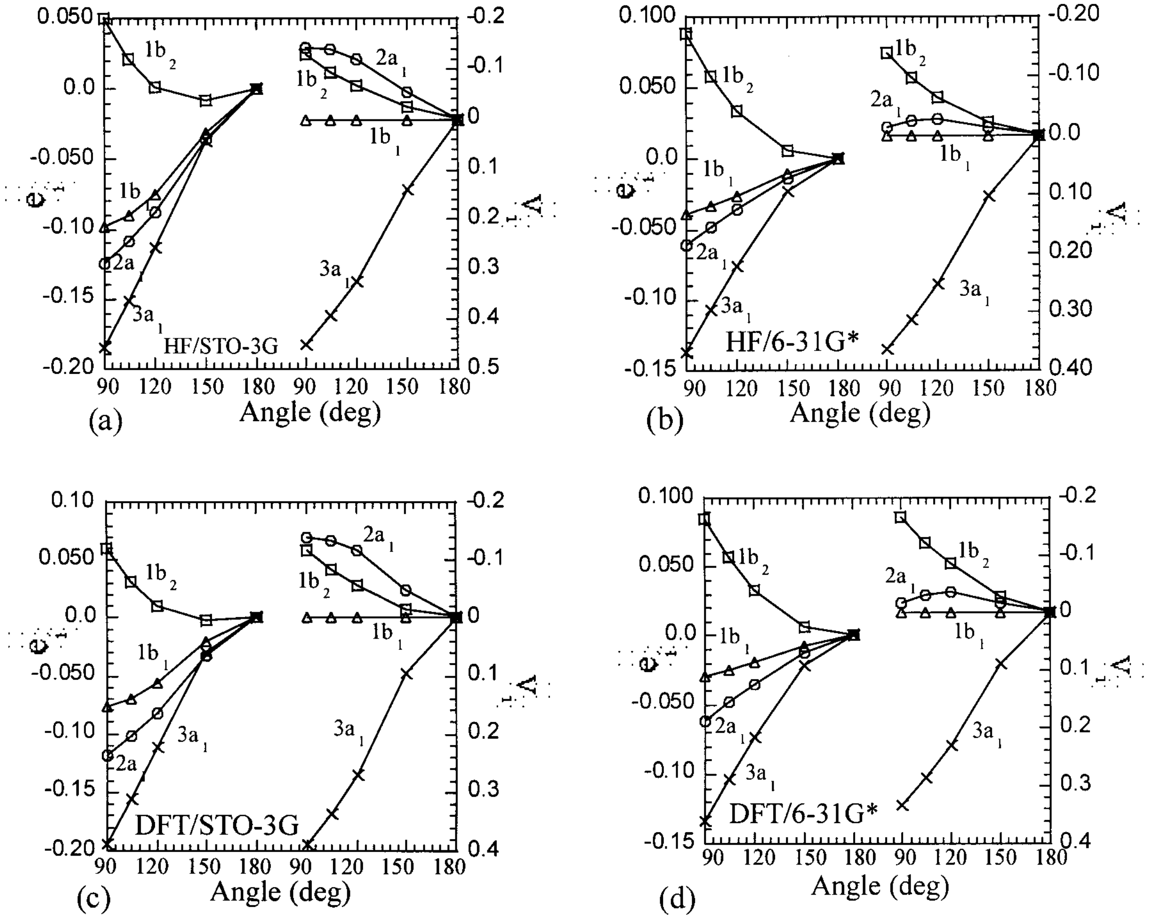

Figure 2. Orbital energy (e_i in au.) and valence (V_i) correlation diagrams of H_2O.

B. Three-Center Bond Indices. The expression for a 3c bond index (I_{ABC}) in terms of fluctuations of electron populations on the constituent atoms is given by[57,58]

$$I_{ABC} = 2\prod_{X=A}^{C}\langle(\hat{N}_X - \langle\hat{N}_X\rangle)\rangle \tag{4}$$

For a single-determinant wave function as has been used here, eq 4 takes the standard form.[28,29,31] Three-center bond indices of some closed-shell molecules are given in Table 4. As can be seen, $I_{ABC} > 0$ in $C_3H_5^+$, C_3, B_2H_6, Li_2H_2, and Li_4. These are nonclassical molecules with 3c−2e bonds.[29,31,59] The AIM values of BHB and NPA and AIM values of LiHLi bond indices are appreciably uunderestimated with respect to MPA and LPA ones. Otherwise the average value of I_{ABC} for 3c−2e bonds fall in the range of 0.20−0.25. In C_3, I_{ABC} is appreciably higher than this average value (MPA/6-311+G** values are abnormally underestimated). This has been attributed[60] to a new type of bonding, namely, multiple 3c bonding. The 3c−2e bond indices follow the same general trends as the 2c bond indices: I_{ABC} (KS) > I_{ABC} (HF) and I_{ABC} (MPA) < I_{ABC} (LPA). However, with respect to the other PA schemes and basis sets no general patterns are visible. The remaining six molecules in Table 4 have significantly high, but negative, values of I_{ABC}. Of these HF_2^-, F_3^-, and Cl_3^- are called hypervalent[61] molecules. They are characterized by 3c−4e bonds. The last three molecules, although they have $I_{ABC} < 0$, can be described by Lewis structures with consecutive double bonds (cumelene-type). In the molecules with negative 3c bond indices, we have $|I_{ABC}|_{KS} > |I_{ABC}|_{HF}$.

The relation analogous to eq 3 for 3c bond indices is given by

$$\frac{1}{4}\sum_{A}\sum_{B}\sum_{C} I_{ABC} = N \tag{5}$$

We may write (5) in the following alternative form:

$$\sum_{A} N_A^{(3)} + \sum_{A<B<C} N_{ABC}^{(3)} = N' + \sum_{A<B<C} N_{ABC}^{(3)} = N \tag{6}$$

where N_A, N_{AB}, etc., denote populations. Comparing (5) and (6), one can express[57] these populations in terms of bond indices. For systems with 3c−2e bonds ($I_{ABC} > 0$) and for those with negative 3c bond indices we have $N > N'$ and $N' > N$, respectively. In both cases the difference, $|N - N'|$ is significantly high.

A comparison of the AIM partition with the MPA, LPA, and NPA schemes reveals a similar behavior as that of the 2c bond indices: while for nonpolar molecules the approaches give quite similar results, the AIM bond index strongly decreases with the increasing polarity of the system. A qualitative different picture of the B_2H_6 molecule emerges from the AIM partition, as compared to the three others. While BHB 3c bond index is around 0.25 in MPA, LPA, and NPA, and the BB 2c bond index is relatively high (around 0.5), the AIM analysis yields an almost negligible 3c BHB (0.05) and 2c BB (0.06) bond index, and the H···H 2c bond index is around 0.2. The negligibly small values of the BHB and BB indices and a rather high value of the H···H index are due to the fact that the AIM analysis of

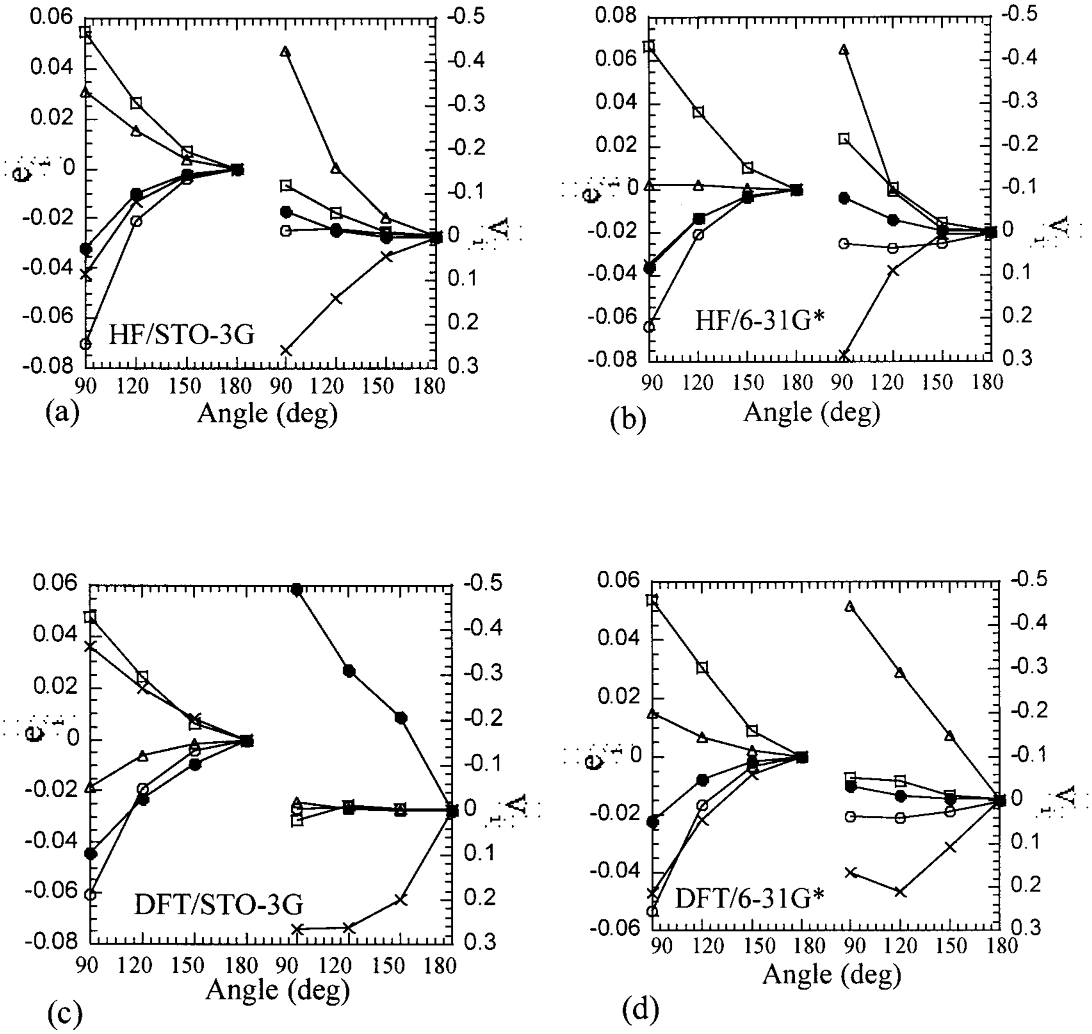

Figure 3. Orbital energy (e$_i$ in a.u.) and valence (V$_i$) correlation diagrams of HCN. The curves represented by −○−, −□−, −x−, −●−, and −△− refer to 3a′−3σ, 4a′−4α, 5a′−5α, 1a″−1π, and 6a′−1π MOs, respectively.

diborane predicts the B atoms to be highly electron-deficient ($q_B \approx +2.0$) and the bridging H atoms to be electron-rich ($q_H \approx -0.7$).

The origin of sign of I_{ABC} has been investigated analytically using three-center three-orbital models[31,62] with appropriate bonding topologies. It can also be understood using the concept of orbital bond index,[36] $(I_{AB})_i$ which was quantified by Kar and Marcos.[63] We have calculated these indices for three molecules choosing one from each class (nonclassical, hypervalent, and cumelene-type). These values are shown in Table 5. Also included in this table are the values of orbital valence[33] V_i, which is a measure of the degree of bonding of an MO. Only MPA has been used in these calculations. The orbital valences of the KS orbitals are generally somewhat greater than those of HF orbitals. The orbital bond indices, however, do not follow the same trend because the contribution of the self-interaction terms $(I_{AA})_i$ (not tabulated) to V_i outweighs that of the $(I_{AB})_i$ terms.

The V_i values of both a$_g$ and b$_{1u}$ MOs in Li_4 are quite high implying that these are strongly bonding MOs. As the $(I_{AB})_i$ values indicate, all three 2c bonds contribute almost to the same extent to V_i. These two bonding MOs together account for two 3c−2e bonds in Li_4. As the V_i values indicate the main contribution to bonding in HF_2^- comes from the two highest occupied MOs (3σ_g and 3σ_u) which are not as strongly bound as the corresponding MOs of Li_4. In the 3σ_g MO, $(I_{AB})_i$ lies between 0 and 1.0 and $(I_{AC})_i < 0$, while in the 3σ_u MO, $(I_{AB})_i = 0$ and $(I_{AC})_i > 0$. The net contribution of two MOs to I_{AB} and I_{AC} is positive. The 3σ_u MO in HF_2^- is localized on the terminal atoms. In CO_2 1π_u (HOMO-2) and 1π_g (HOMO) MOs play the same role as the 3σ_g and 3σ_u MOs in HF_2^-. In this molecule $I_{CO} > 1.0$ (in HF_2^-, $I_{HF} < 1.0$) due to the presence of a σ bond resulting from the contributions of the σ-type valence MOs. This analysis based on orbital bond index and orbital valence indicates that the presence of an occupied high-energy bonding MO (σ_g/π_u) and an occupied nonbonding or weakly bonding MO (σ_u/π_g) with no contribution from the central atom is responsible for the negative values of 3c bond indices in hypervalent and cumelene-type molecules.

C. Variation of Molecular Valence, Orbital Energy, and Orbital Valence with Bond Angle. The idea of using total valence (the sum of atomic valences) to compare the relatively stability of isomers was first proposed by Bhattacharjee and Sannigrahi.[35] To avoid double counting the bond indices, a factor of one-half was subsequently used[33,36] to define molecular valence (V_M), i.e.,

$$V_M = \frac{1}{2}\sum_A V_A \tag{7}$$

Gopinathan and co-workers[30] observed that V_M is maximum at or near the equilibrium bond angle of a molecule. This was further verified[34,64] and found to be qualitatively valid.

We have calculated, using HF and KS orbitals, the molecular valence of two nonlinear (H_2O and H_2S) and two linear (HCN and CO_2) molecules at different bond angles. Figure 1 shows the variation of V_M with bond angle. The STO-3G molecular valences are generally higher than the corresponding 6-31G* values, the difference being more pronounced in the nonlinear molecules. Since $V_A(KS) > V_A(HF)$, the $V_M(DFT)$ curves generally lie above the $V_M(HF)$ curves. In H_2O all the four curves show a maximum at $\angle HOH = 80°$, which does not compare favorably with the equilibrium bond angle of the molecule (104.5°). The STO-3G V_M curves in H_2S show a maximum at $\angle HSH = 70°$, while for the 6-31G* basis the molecular valence maximizes at an angle of 90° which is very close to the equilibrium bond angle (92°). In the linear molecules V_M is correctly predicted to be maximum at the bond angle of 180° by all the four curves. The results of these four molecules indicate that HF and KS orbitals yield comparable valences not only at or near the equilibrium bond angle but also at other angles.

The importance of Mulliken−Walsh[32] correlation diagrams (plots of valence orbital energy vs bond angle) in the theory of chemical bonding[65] and molecular spectroscopy[66] can hardly be deemphasized. It was shown[33] that orbital valence can serve as a qualitatively reliable ordinate in the Mulliken−Walsh diagrams. The resulting curves were called valence correlation diagrams. We have calculated HF and KS orbital energies and valences of H_2O and HCN at angles ranging from 90° to 180°. In the calculation of orbital valences MPA has been used. The variation of orbital energy and valence with bond angle is shown in Figure 2 for H_2O and in Figure 3 for HCN. The reduced ordinates[67] ($y_{red}(\theta) = y(180°) - y(\theta)$) are used in these plots, where θ is the bond angle.

As can be seen in Figure 2, the HF and KS (DFT) orbital energy diagrams are remarkably similar. The order of $2a_1$ and $1b_2$ orbital valences has been interchanged in the STO-3G and 6-31G* basis sets. However, for a given basis set the HF and KS (DFT) curves run parallel to each other. According to the energy diagrams the bent structure of H_2O is due to the stabilizing effect of $1b_1$, $2a_1$, and $3a_1$ MOs which more than compensates the destabilizing effect of the $1b_2$ MO. In the orbital valence diagrams the $1b_1$ MO behaves like a nonbonding orbital; now the bent structure of H_2O results from the stabilizing effect of the $3a_2$ MO which outweighs the combined destabilizing effect of $2a_1$ and $1b_2$ MOs.

In the case of HCN (Figure 3), the HF/STO-3G and DFT/STO-3G energy curves for 5a′ and 6a′ MOs exhibit opposite behavior. However, for the larger basis set the corresponding curves are quite similar. It is apparently not possible to account for the linearity of HCN on the basis of the energy correlation diagrams because there are three MOs which favor a bent structure, whereas there are only two MOs with an opposite tendency. For the orbital valence also the HF and DFT curves compare more favorably for the larger basis set. All the four valence correlation diagrams are adequate to account for the linear structure of HCN.

4. Concluding Remarks

The aim of the present investigation was to compare the performance of HF and KS orbitals in the study of chemical bonding on the basis of bond index and related concepts. Compared to HF orbitals, KS orbitals overemphasize covalency marginally. Otherwise, they are quite similar. The two types of orbitals predict comparable values of bond indices, valences and related quantities not only at the equilibrium geometry of the molecules but also at other geometries.

To verify whether the noted difference between HF and KS orbitals is due to any special feature of the B3LYP method, we tested the performance of another version of KS/DFT, namely, the B3PW91 method (Becke[9] three-parameter nonlocal exchange functional with the nonlocal correlation functional of Perdew and Wang[68]). This and B3LYP methods are known[8] to predict electronic structure and energetics in close correspondence. We observed the same trend in atomic charges, 2c bond indices and valences obtained by these two versions of KS/DFT.

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Appendix

The most general definition of atomic charge, 2c and 3c bond indices invokes the atomic population operator $\hat{N}$ corresponding to various population analysis (PA) schemes. Second operator quantization formalism allows us to write these operators in a particular compact form. In the case of the orthogonal Löwdin and NAO basis sets, we can express the electronic population operator of atom A as

$$\hat{N}(\mathrm{LPA,NPA}) = \sum_{i\in \mathrm{A}} \psi_i^{+}\, \psi_i^{-} \tag{8}$$

where ψ_i^+ and ψ_i^- are creation and annihilation operators for either the Löwdin or the NAO basis sets. The atomic Mulliken population operator is defined as

$$\hat{N}(\mathrm{MPA}) = \sum_{i\in \mathrm{A}} \chi_i^{+}\, \tilde{\chi}_i^{-} \tag{9}$$

where χ_i^+ and $\tilde{\chi}_i^-$ form a pair of anticommutating creation and annihilation operators, and the biorthogonal basis $\tilde{\chi}$ is related to the original nonortogonal AO basis set by the transformation $\tilde{\chi} = \chi S^{-1}$, where S is the AO overlap matrix. Finally, the second-quantized form of the AIM atomic population operator is

$$\hat{N}(\mathrm{AIM}) = \sum_{ij} \mathrm{S}_{ij}^{\mathrm{A}}\, \phi_i^{+}\, \phi_j^{-} \tag{10}$$

where ϕ_i are the molecular orbitals and $\mathrm{S}_{ij}^{\mathrm{A}}$ is the atomic overlap matrix.

For closed-shell molecules described by the single-determinant wave function, the working expressions for atomic charge (q_A), 2c bond index (I_{AB}), and 3c bond index (I_{ABC}) are given by

$$q_\mathrm{A} = Z_\mathrm{A} - \sum_a D_{aa}^{\mathrm{A}} \tag{11}$$

$$I_\mathrm{AB} = \sum_\mathrm{a}\sum_\mathrm{b} D_{ab}^{\mathrm{A}}\, D_{ba}^{\mathrm{B}} \tag{12}$$

$$I_\mathrm{ABC} = \sum_\mathrm{a}\sum_\mathrm{b}\sum_\mathrm{c} D_{ab}^{\mathrm{A}}\, D_{bc}^{\mathrm{B}}\, D_{ca}^{\mathrm{C}} \tag{13}$$

Here, Z_A is the atomic number of A and D_{ab}^{A} denotes a kind of generalized atomic density matrix, which satisfies

$$\sum_\mathrm{A} D_{ab}^{\mathrm{A}} = D_{ab} \tag{14}$$

and is specific to the PA scheme. For the different schemes we have

$$D^{\mathrm{A}}_{ab}(\mathrm{MPA}) = \begin{bmatrix} \sum_k P_{ak}S_{kb} & \text{if } a \in \mathrm{A} \\ 0 & \text{if } a \in \mathrm{A} \end{bmatrix} \tag{15}$$

$$D^{\mathrm{A}}_{ab}(LPA) = \begin{bmatrix} \tilde{P}_{ab} & \text{if } a \in \mathrm{A} \\ 0 & \text{if } a \in \mathrm{A} \end{bmatrix} \tag{16}$$

$$D^{\mathrm{A}}_{ab}(\mathrm{NPA}) = \begin{bmatrix} \tilde{\tilde{P}}_{ab} & \text{if } a \in \mathrm{A} \\ 0 & \text{if } a \in \mathrm{A} \end{bmatrix} \tag{17}$$

$$D^{\mathrm{A}}_{ab}(\mathrm{AIM}) = \sum_k P_{ak}S^{\mathrm{A}}_{kb} \tag{18}$$

where P is the AO density matrix, S is the overlap matrix, $\tilde{P} = S^{1/2}PS^{1/2}$ is the density matrix in the Löwdin orthogonalized AO basis, $\tilde{\tilde{P}}$ is the density matrix in the (orthogonal) natural atomic orbital (NAO) basis, and S^{A}_{ab} is the atomic overlap population matrix. In the case of $D^{\mathrm{A}}_{\mathrm{ab}}(\mathrm{AIM})$, usually the molecular orbital (MO) basis is used

$$D^{\mathrm{A}}_{ij} = n_i S^{\mathrm{A}}_{ij} \tag{19}$$

Orbital valence (V_i) and orbital bond index ($(I_{AB})_i$) are calculated using the expanded form of D matrix in eq 12 and the following relations.

$$\sum_i^{\mathrm{occ}} \mathrm{V}_i = V_{\mathrm{M}} = \frac{1}{2}\sum\nolimits_{\mathrm{A}} V_{\mathrm{A}} = \frac{1}{2}\sum_{\mathrm{A}}\sum_{\mathrm{B}\neq\mathrm{A}} I_{\mathrm{AB}} \tag{20}$$

$$I_{\mathrm{AB}} = \sum_i^{\mathrm{occ}} (I_{\mathrm{AB}})_i \tag{21}$$

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