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Effect of spin contamination in UHF wavefunctions on charge density-based local quantities

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Abstract

The effect of spin contamination in UHF wavefunctions on charge density-based local quantities has been investigated for 16 open-shell molecules. These quantities are found to be quite sensitive to spin contamination. When the $\langle \hat{S}^2 \rangle$-error in the UHF method is appreciable, the calculated local quantities deviate markedly from the classically expected values. The spin contamination can be totally eliminated either by the ROHF or by the SUHF (spin constrained UHF) method. In the latter the $\langle \hat{S}^2 \rangle$-error is constrained using a Lagrangian multiplier, λ. The SUHF solutions gradually converge to the ROHF solutions as $\lambda \to \infty$. However, most of the spin contamination is removed by using very small positive values of λ. The lowest value of λ for which the $\langle \hat{S}^2 \rangle$-error (calculated up to the fourth place of decimal) vanishes is referred to as the threshold λ, or λ_t. Using $\lambda = \lambda_t$ excellent agreement is obtained between the SUHF and ROHF values for various local quantities.

Keywords: Atomic charge; Free valency; Spin contamination; Spin population; SUHF wavefunction

1. Introduction

It is well known that the unrestricted HF (UHF) wavefunction [1] of a many-electron open-shell system is not in general an eigenfunction of the spin operator, $\hat{S}^2$. Thus it cannot describe a spectroscopic state with a given spin multiplicity. A UHF wavefunction is usually a mixture of states with spin multiplicity $2S + 1$, $2S + 3$, etc., where S is the spin quantum number of the state with the lowest multiplicity. This is referred to as spin

contamination. It raises the $\langle \hat{S}^2 \rangle$ value and lowers the energy of a UHF wavefunction compared to the corresponding values obtainable from the spin-correct restricted open-shell HF (ROHF) method [2]. The UHF wavefunction being a single determinant provides a good basis for estimating correlation energy via Møller–Plesset (MP) perturbation theory. However, the convergence in the unrestricted perturbation series (UMPn) becomes slower [3] with the increasing spin contamination in the reference UHF wavefunction.

Based on the spin projection operator of Löwdin [4], several methods have been proposed to project out the undesired spin components of a UHF wavefunction. These include the projected UHF (PUHF) [5], extended HF (EHF) [6,7], annihilated

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UHF (AUHF) [8,9] and half-projected HF (HPHF) [10,11] methods. The basic mathematical structures of these methods, along with their scope and limitations in relation to that of the ROHF method, have recently been highlighted by Andrews et al. [12]. In this context they proposed a very simple and elegant technique for the elimination of spin contamination in a UHF wavefunction by constraining its $\langle \hat{S}^2 \rangle$ value using a Lagrangian multiplier λ. The resulting procedure has been called the spin-constrained UHF (SUHF) method. Taking the CN radical as a test case they have shown that small values of λ can significantly reduce the $\langle \hat{S}^2 \rangle$-error while changing the energy only slightly, and as $\lambda \to \infty$ the SUHF solutions converge to the ROHF solutions. They also performed SUMPn calculations for the CN radical using large values of λ.

The charge density-based local quantities such as atomic charge, bond index, valency, free valency and unpaired spin population are currently in widespread use [13–15] for the study of bonding in molecules and intermolecular complexes. Most of these calculations have been carried out at the HF level using the RHF method for the closed-shell and the UHF method for the open-shell systems. However, due to spin contamination the UHF method may lead to physically unacceptable values for the bonding parameters. This aspect of the UHF method has never been addressed before. We have, therefore, examined the effect of spin contamination in UHF wavefunctions on the afore-mentioned charge density-based local quantities. For this purpose ab initio UHF, SUHF and ROHF calculations have been performed on 16 open-shell molecules with a spin multiplicity of 2 or 3. Some of the chosen molecules represent cases where the spin contamination is as high as about 50% of the exact value.

2. Method of calculation

We have used the Mulliken scheme of population analysis (MPA) [16] for the calculation of atomic charge (q_A), bond index (I_{AB}), valency (V_A), free valency (F_A) and unpaired spin population (S_A). For a UHF wavefunction these quantities are defined by the following relations [15]:

$$q_A = Z_A - Q_A = Z_A - \sum_a^A D_{aa} \tag{1}$$

$$I_{AB} = \sum_a^A \sum_n^B (D_{ab}D_{ba} + D_{ab}^s D_{ab}^s) \tag{2}$$

$$V_A = \sum_{B \neq A} I_{AB} \tag{3}$$

$$F_A = \sum_a^A \sum_b^A D_{ab}^s D_{ab}^s \tag{4}$$

$$S_A = \sum_a^A D_{aa}^s \tag{5}$$

where Z_A is the atomic number of A, Q_A is the total number of electrons on atom A, D is the first-order density matrix and D^s is the spin density matrix. These density matrices are defined as

$$D = D^\alpha + D^\beta = P^\alpha S + P^\beta S = C^\alpha \tilde{C}^\alpha S + C^\beta \tilde{C}^\beta S \tag{6}$$

$$D^s = D^\alpha - D^\beta \tag{7}$$

In Eq. (6) C^σ is the coefficient matrix of the occupied MOs with σ spin, $\tilde{C}^\sigma$ is its transpose, and S is the AO overlap matrix.

The expectation value of the $\hat{S}^2$ operator for a UHF wavefunction is given by [12]

$$\langle \hat{S}^2 \rangle = S_z(S_z + 1) + n_\beta - \mathrm{Tr}(SP^\beta SP^\alpha) \tag{8}$$

where $S_z = (n_\alpha - n_\beta)/2$ and n_α is the number of occupied spin orbitals with α spin. By constraining the last term in Eq. (8) to a particular constant chosen so that $\langle \hat{S}^2 \rangle$ is close to the exact value one obtains the modified UHF or the SUHF equations [12]:

$$(F^\alpha - 2\lambda SP^\beta S)C^\alpha = SC^\alpha \epsilon^\alpha \tag{9}$$

$$(F^\beta - 2\lambda SP^\alpha S)C^\beta = SC^\beta \epsilon^\beta \tag{10}$$

where F^σ is the standard UHF matrix and λ is the Lagrangian multiplier associated with the spin constraint. Eqs. (9) and (10) are solved for various

positive values of λ starting from $\lambda = 0$ which corresponds to the UHF solutions. Once the SUHF eigenvectors are obtained, various local quantities are calculated using the same relations as have been employed in the case of a UHF wavefunction.

The SUHF equations yield the ROHF solutions as $\lambda \rightarrow \infty$. We have, however, obtained the latter directly by solving the ROHF equations corresponding to the highest M_S value for a given spin state. Thus, like UHF and SUHF, ROHF wavefunctions are also given by a single Slater determinant. For such a wavefunction

$$D = D^C + D^O \tag{11}$$

$$D^2 = 2D^C + D^O = 2D - (D^O)^2 \tag{12}$$

where D^C and D^O refer respectively to the closed-shell and the open-shell part of the density matrix. In the UHF formalism expressions for I_{AB} and F_A are defined [15] using the relation

$$D^2 = 2D - (D^s)^2 \tag{13}$$

Eq. (12), therefore, implies that ROHF expressions for these quantities can be obtained from Eqs. (2) and (4) respectively by replacing D^S by D^O. The expression for S_A is obtained from Eq. (5) in the same manner.

All calculations have been performed using the 6-31G* or 6-31G** basis set at the equilibrium geometries [17,18] of the molecules optimized at the same level of theory. The parameter λ in Eqs. (9) and (10) is increased in very small steps until the error in $\langle \hat{S}^2 \rangle$ (these values are calculated up to the fourth place of decimal) is zero. This minimum value of λ is referred to as the threshold λ, or λ_t.

3. Results and discussion

The specific molecules chosen in the present investigation include BeH, OH, CH, NO, CN, NH, CH_2^+, NH_2, NO_2, OCN, C_2H, CH_2, NH_2^+, HNC, Li_2C and CH_3. Ground state UHF energies, spin contaminations, threshold λ (λ_t), the relative values of SUHF energies at λ_t with respect to UHF, and ROHF energies with respect to SUHF are given in Table 1. Of the selected molecules,

the spin contamination in the UHF wavefunction is minimum (0.24%) for BeH and maximum (58.3%) for C_2H. As can be seen from Table 1, there is no correlation between the extent of spin contamination and λ_t. For example, the $\langle \hat{S}^2 \rangle$-errors for NO_2 and C_2H are 2.2 and 58.3% and the corresponding λ_t values are 5.00 and 3.20 respectively. For a series of molecules with a given multiplicity ΔE_1 generally increases with increasing spin contamination in their UHF wavefunctions. No definite trend is, however, observed for ΔE_2.

The λ-dependence of ΔE_1, $\Delta \langle \hat{S}^2 \rangle$, F_A and S_A is shown in Figs. 1–4 for CN, C_2H, HNC and Li_2C where the UHF wavefunctions possess an appreciable degree of spin contamination. We first concentrate our attention on ΔE_1 and $\Delta \langle \hat{S}^2 \rangle$. It is seen that about 99% of spin contamination is eliminated by using very small values of λ (0.1 for CN, C_2H and HNC, and 0.02 for Li_2C). Under this situation the SUHF energies are lower than the corresponding ROHF values by only 3.0–6.0 mhartree. When λ is increased further by a small amount the error in $\langle \hat{S}^2 \rangle$ practically vanishes and ΔE_1 slowly approaches its value at λ_t. The ΔE_2 values given in Table 1 indicate that

Table 1
Calculated UHF energies (E_{UHF}, in hartree), spin contamination ($\Delta \langle \hat{S}^2 \rangle$), threshold λ (λ_t) and the relative energies ($\Delta E_1 = E_{SUHF} - E_{UHF}$ and $\Delta E_2 = E_{ROHF} - E_{SUHF}$, in mhartree) of some open-shell molecules

| Molecule	$-E_{UHF}$	$\Delta \langle \hat{S}^2 \rangle$	λ_t	ΔE_1	ΔE_2
BeH($^2\Sigma^+$)	15.14775	0.0018	0.50	0.229	0.101
OH($^2\Pi$)	75.38831	0.0049	4.00	3.035	0.825
CH($^2\Pi$)	38.26691	0.0057	3.50	2.838	0.680
NO($^2\Pi$)	129.24788	0.0125	5.00	5.826	0.714
CN($^2\Sigma^+$)	92.20483	0.3822	3.00	15.805	0.418
NH($^3\Sigma^-$)	54.96264	0.0133	5.00	6.058	0.881
$CH_2^+(C_{2v},^2A_1)$	38.570596	0.0042	3.00	1.862	0.520
$NH_2(C_{2v},^2B_1)$	55.56482	0.0071	4.00	3.455	0.738
$NO_2(C_{2v},^2B_1)$	204.03149	0.0162	5.00	7.227	0.745
OCN($C_{\infty v},^2\Sigma^-$)	167.12887	0.0830	4.00	9.835	0.530
$C_2H(C_{\infty v},^2\Sigma^-)$	76.15211	0.4375	3.20	17.657	0.177
$CH_2(C_{2v},^3B_1)$	38.92549	0.0145	3.50	4.459	0.629
$NH_2^+(C_{2v},^3B_1)$	55.21703	0.0204	5.00	8.171	0.966
HNC($C_s,^3A'$)	92.72648	0.3553	3.50	17.845	0.882
$Li_2C(D_{\infty h},^3\Sigma_g^-)$	52.62437	0.8014	4.50	20.245	0.547
$CH_3(D_{3h},^2A_2)$	39.56446	0.0111	3.50	3.575	0.608
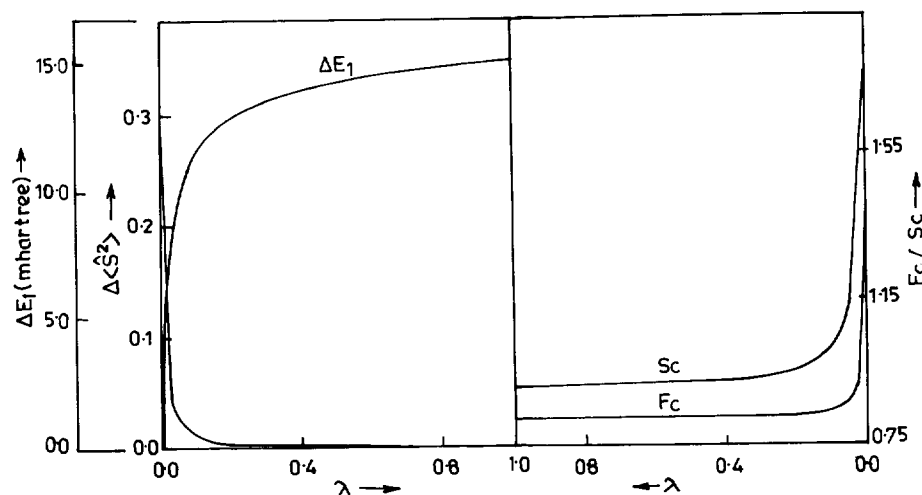
Fig. 1. Variation of $\Delta\langle \hat{S}^2 \rangle$, ΔE_1, F_C and S_C of CN with λ.

the SUHF energies at λ_t agree with the corresponding ROHF values within 1.0 mhartree.

Calculated values of atomic charges, bond indices, atomic valencies, free valencies and unpaired spin populations for the chosen molecules obtained by using UHF, SUHF (for λ_t) and ROHF wavefunctions are presented in Table 2. We have reported theses quantities only for the non-equivalent atoms (other than H) in the molecules. The V_H and I_{AH} (in C_2H and HNC) values were found to be close to 1.0 while F_H and S_H were negligibly small. Although not tabulated, the various local quantities were calculated in each

case using the SUHF density matrices by varying λ from 0 to λ_t.

Before discussing the results of Table 2 we refer back to Figs. 1–4 and focus our attention on the variation of F_A and S_A with λ. These local quantities have recently been successfully applied by Misra and Sannigrahi [19] to rationalize a number of reactions involving two identical or different open-shall molecules. As can be seen from the figures, both F_A and S_A decrease very sharply when λ is varied within a narrow range and thereafter slowly attain the SUHF value corresponding to $\lambda = \lambda_t$. A similar trend was also
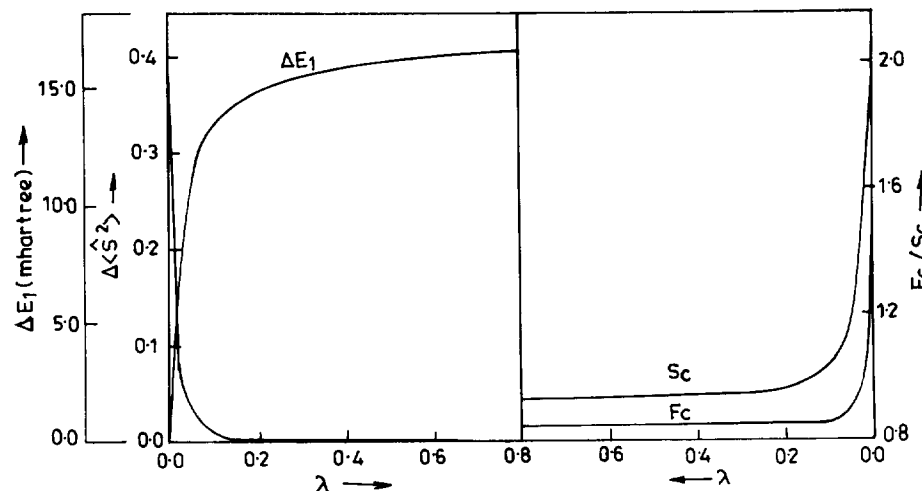
Fig. 2. Variation of $\Delta\langle \hat{S}^2 \rangle$, ΔE_1, F_C and S_C of C_2H with λ.
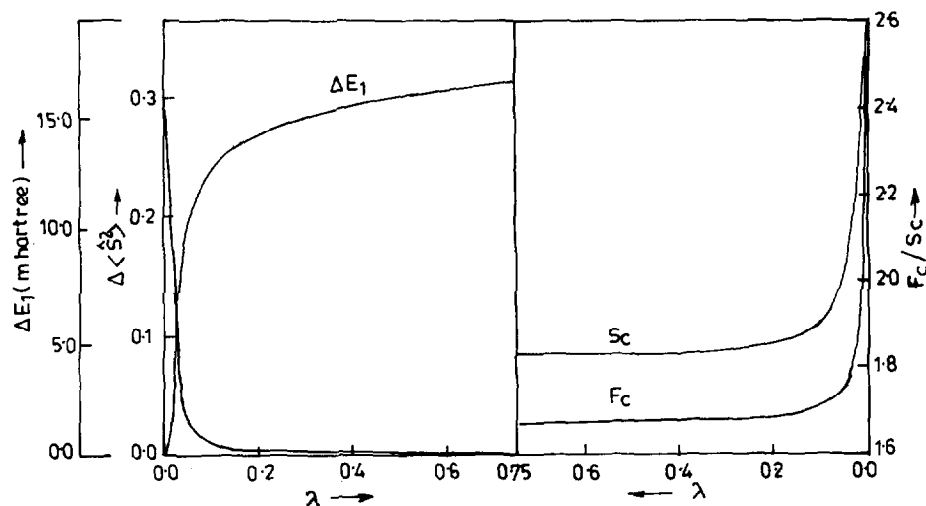
Fig. 3. Variation of $\Delta\langle\hat{S}^2\rangle$, ΔE_1, F_C and S_C of HNC with λ.

found in other molecules. It is interesting to note that F_A and S_A vary with λ almost in the same manner although there is no formal relation between them. The former is quadratic in both diagonal and off-diagonal elements (see Eq. (4)) of the spin density matrix (D^S or D^O), while the latter is linear only in diagonal elements (see Eq. (5)). A good correlation between F_A and S_A was also observed [20,21] earlier.

It can be seen from Table 2 that both positive and negative values of S_A are predicted (excepting BeH, NO and NO$_2$) by the UHF method. Negative

values of S_A correspond to the situation when the β spin density is higher than the α spin density. Such values are quite appreciable in the case of CN, OCN, C$_2$H, HNC and Li$_2$C. The negative spin population is an artefact of the UHF method. Although it is in accord with experiment in some cases [22], it is not possible to provide a rationale for the negative values in terms of classical valence theory. For example, if one obtains $S_A = 2.0$ and $S_B = -1.0$ in the diatomic molecule AB with a doublet spin state, one would interpret this as there being two unpaired electrons on A with α
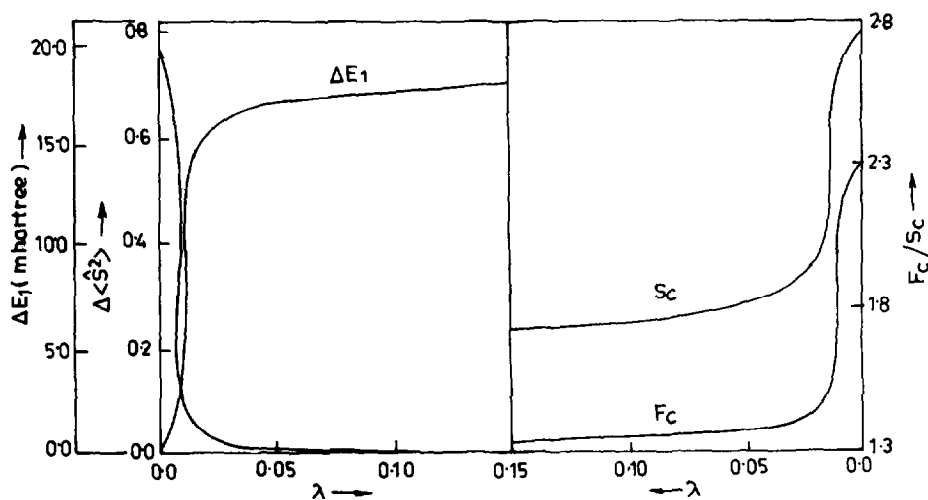

Fig. 4. Variation of $\Delta\langle\hat{S}^2\rangle$, ΔE_1, F_C and S_C of Li$_2$C with λ.

Table 2
Calculated[a] UHF, SUHF ($\lambda = \lambda_t$) and ROHF values of atomic charges (q_A), bond indices (I_{AB}), valencies (V_A), free valencies (F_A) and unpaired spin populations (S_A) of some open-shell molecules

Molecule	Atom	q_A	I_{AB}	V_A	F_A	S_A	Molecule	Atom	q_A	I_{AB}	V_A	F_A	S_A
BeH	Be	+0.151	0.974	0.974	0.960	0.906	OCN[b]	O	−0.344	1.866	2.002	0.191	0.465
		+0.152	0.981	0.981	0.958	0.971			−0.402	1.966	2.138	0.016	0.125
		+0.153	0.982	0.982	0.958	0.979			−0.404	1.968	2.140	0.014	0.119
OH	O	−0.352	0.863	0.863	1.000	1.047		C	+0.727	1.923	3.789	0.064	−0.388
		−0.358	0.862	0.862	0.991	0.998			+0.794	1.847	3.813	0.012	0.104
		−0.354	0.864	0.864	0.991	0.996			+0.795	1.845	3.813	0.012	0.108
CH	C	−0.082	0.933	0.933	1.005	1.066		N	−0.383		2.059	0.603	0.924
		−0.089	0.937	0.937	0.993	0.999			−0.397		2.015	0.599	0.771
		−0.086	0.936	0.936	0.993	0.997			−0.390		2.017	0.597	0.773
NO	N	+0.185	2.092	2.092	0.574	0.846	ClC2H[b]	Cl	−0.096	2.515	2.527	1.441	2.123
		+0.190	2.111	2.111	0.536	0.732			−0.084	3.095	3.108	0.849	0.920
		+0.188	2.115	2.115	0.539	0.734			−0.085	3.096	3.109	0.849	0.921
	O				0.115	0.154		C2	−0.128	0.911	3.425	0.554	−1.222
					0.078	0.268			−0.144	0.917	4.012	0.005	0.070
					0.071	0.266			−0.144	0.917	4.013	0.005	0.072
CN	C	+0.251	2.500	2.500	1.346	1.911	CH$_2$	C	−0.268	0.950	1.900	1.962	2.225
		+0.293	2.947	2.947	0.827	0.911			−0.272	0.963	1.925	1.923	1.967
		+0.290	2.949	2.949	0.830	0.924			−0.273	0.961	1.922	1.923	1.961
	N				0.435	−0.911	NH$_2^+$	N	+0.032	0.740	1.480	1.973	2.172
					0.009	0.089			+0.018	0.740	1.479	1.940	1.974
					0.008	0.076			+0.019	0.740	1.480	1.940	1.970
NH	N	−0.256	0.884	0.884	2.009	2.127	HNC	N	−0.456	1.641	2.512	0.392	−0.669
		−0.269	0.891	0.891	1.984	1.995			−0.516	2.014	2.888	0.015	0.138
		−0.265	0.891	0.891	1.984	1.985			−0.517	2.015	2.889	0.014	0.140
CH$_2^+$	C	+0.328	0.869	1.739	0.955	1.070		C	+0.174		1.645	2.144	2.555
		+0.324	0.870	1.739	0.948	0.976			+0.233		2.026	1.672	1.833
		+0.329	0.871	1.741	0.948	0.974			+0.231		2.027	1.671	1.826
NH$_2$	N	−0.522	0.903	1.805	0.999	1.121	CLi$_2$	C	−0.366	0.599	1.197	2.312	2.757
		−0.531	0.905	1.811	0.984	0.996			−0.463	1.093	2.190	1.328	1.620
		−0.527	0.905	1.811	0.984	0.992			−0.461	1.097	2.193	1.317	1.623
NO$_2$	N	+0.668	1.691	3.382	0.355	0.530		Li	+0.183		1.044	0.239	−0.379
		+0.672	1.707	3.414	0.343	0.581			+0.232		1.185	0.018	0.186
		+0.680	1.707	3.414	0.334	0.578			+0.230		1.186	0.018	0.188
	O	−0.334		1.906	0.079	0.235	CH$_3$	C	−0.384	0.964	2.890	1.015	1.280
		−0.336		1.930	0.045	0.210			−0.404	0.973	2.918	0.982	1.000
		−0.340		1.931	0.045	0.211			−0.392	0.973	2.920	0.982	0.991

[a] The three successive values for each quantity correspond to those obtained in the UHF, SUHF and ROHF calculations respectively.
[b] The two sets of bond indices refer to I_{AB} and I_{BC} respectively in the ABC molecule.

spin and one unpaired electron on B with β spin. The S_A values for all the three methods (see Table 2) are found to be higher than the corresponding F_A values, the difference being maximum at the UHF level. The SUHF ($\lambda = \lambda_t$) and ROHF values of both F_A and S_A differ very marginally.

The variation of atomic charge, bond index and valency with λ has not been shown. Atomic charges are used to calculate condensed fukui functions [23] which are useful local reactivity indices. Misra and

Sannigrahi [19] have observed that even though the UHF and ROHF atomic charges differ in some cases by a large margin, the calculated condensed fukui functions are remarkably stable with respect to spin contamination. From Table 2 we find that, barring a few cases like CN, OCN, HNC and Li$_2$C, atomic charges are generally insensitive to the spin contamination in the UHF wavefunction. In all cases the SUHF (for λ_t) and ROHF values are in very good agreement. The I_{AB} and V_A values in

Table 2 show the same trend. When the spin contamination is appreciable, the use of spin-corrected wavefunctions leads to a significant enhancement (SUHF or ROHF vs. UHF) in the corresponding bond indices and valencies ($I_{CN} = 2.95$ vs. 2.50, $V_C = 2.95$ vs. 2.50; $C1C2H$, $I_{C1C2} = 3.10$ vs. 2.52, $V_{C1} = 3.11$ vs. 2.53; HNC, $I_{NC} = 2.01$ vs. 1.64, $V_C = 2.03$ vs. 1.64; Li_2C, $I_{LiC} = 1.09$ vs. 0.60, $V_C = 2.19$ vs. 1.20). The spin-corrected values are found to be close to integers and are easily amenable to classical interpretation. Thus all the charge density-based local quantities obtained by the SUHF method (for λ_t) can be regarded as reliable substitutes for the corresponding ROHF values.

4. Concluding remarks

Taking a number of open-shell molecules as test cases it has been shown that the spin contamination in their UHF wavefunctions has a pronounced effect on the charge density-based local quantities which are used in the study of chemical bonding. The bonding parameters calculated by the UHF method are not at all reliable especially when the spin contamination is significant. In such cases the active valency of the molecules is underestimated and the free valency is overestimated. About 99% of the spin contamination can be removed by performing SUHF calculations using very small positive values (say, 0.1) of λ. The lowest value of λ which renders the SUHF method spin correct predicts various local quantities in very good agreement with the corresponding ROHF values. Under this situation the SUHF energy differs from the ROHF value by at most 1.0 mhartree. The present investigation shows that for the study of bonding in open-shell molecules one should use either the ROHF method or the spin-correct SUHF method.

Acknowledgement

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