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The Spin-Pair Compositions as Local Indicators of the Nature of the Bonding

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The spin-pair compositions at a given point of the position space are defined as the following ratios: that of the parallel spin-pair concentration to the antiparallel spin-pair concentration $D_{\mathrm{anti}}(\mathbf{r})$, to the total spin-pair concentration $D_{\mathrm{tot}}(\mathbf{r})$, and to the single spin-pair concentration $D_{\mathrm{s}}(\mathbf{r})$. The spin-pair concentrations are calculated by the integration of the pair functions $\pi^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)$, $\pi^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)$, $\pi^{\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2)$, and $\pi^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)$ over an arbitrary volume $V(\mathbf{r})$ around the reference point $\mathbf{r}$. Because the numbers of spin pairs are not proportional to the sampling volume, the dependence of the $D(\mathbf{r})$ functions upon the sample size $V(\mathbf{r})$ has been studied. It is shown that all $D(\mathbf{r})$ functions depend on the population $\bar{N}(\mathbf{r})$ of the sample. For $\bar{N}((\mathbf{r}) \leq 10^{-3}$, all $D(\mathbf{r})$ functions behave as $\bar{N}^{2/3}(\mathbf{r})$; therefore, size-independent spin-pair composition functions are defined as $c_\pi(\mathbf{r}) = \bar{N}^{2/3}(\mathbf{r})D(\mathbf{r})$. Approximate expressions of the $c_\pi(\mathbf{r})$ functions are proposed, which enable the recovery of the electron localization function of Becke and Edgecombe.

1. Introduction

The central concept in the chemical bond theory is that of the electron pair, which was introduced by G. N. Lewis,[1] 19 years after the discovery of the electron. This concept is very fruitful since it explains the stoichiometry of the most stable molecules (with the help of the octet rule and that of the Lewis structures) as well as their geometries, with the help of the VSEPR model.[2,3] In chemistry, an electron pair involves two electrons of opposite spin. In this short communication, I propose a simplified representation of the electrons in a molecule in terms of two scalar fields, namely, the density $\rho(\mathbf{r})$ and the spin-pair composition $c_\pi(\mathbf{r})$ that I will define later.

2. The Spin-Pair Composition

The electrons of an atom or of a molecule can be considered as belonging to an inhomogeneous continuum (electron gas) in the same manner a molecule of dioxygen belongs to the atmospheric air. This inhomogeneous electron gas is characterized in each point of the position space of coordinates $\mathbf{r}$ by its density $\rho(\mathbf{r})$ and by a dimensionless number, for example, $c_\pi(\mathbf{r})$, which accounts for its local composition in terms of electron pairs and is expected to reveal the inhomogeneity. This representation relies on the statistical interpretation of quantum mechanics, and therefore, both $\rho(\mathbf{r})$ and $c_\pi(\mathbf{r})$ must be derived from density functions.

The definition of the electron density $\rho(\mathbf{r})$ is straightforward: it is the probability of finding any electron at the position $\mathbf{r}$ and is given by

$$\rho(\mathbf{r}) = N\int\Psi(x, x_2, ..., x_N)\Psi^*(x, x_2, ..., x_N)\,\mathrm{d}x'\,\mathrm{d}\sigma \qquad (1)$$

in which x_i denotes the set of positions $\mathbf{r}_i$ and spin σ_i coordinates of the electron labeled by i, and the integration is performed over the spin coordinates of all the electrons and over the position coordinates of all the electrons except one. It can be alternatively expressed as the expectation value of the density operator $\hat{\rho}(\mathbf{r})$:

$$\rho(\mathbf{r}) = \langle\Psi|\hat{\rho}(\mathbf{r})|\Psi\rangle \qquad (2)$$

with

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N}\delta(\mathbf{r}_i - \mathbf{r}) \qquad (3)$$

The electron density can be written as the sum of two contributions arising from the α and β spin electrons, i.e.,

$$\rho(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) + \rho^{\beta}(\mathbf{r}) \qquad (4)$$

The electron density contains most of the physical information; knowing this information enables the determination of the energy of a N-electron system in its ground state with the necessary aid of the Hohenberg and Kohn theorem[4] and the determination of many linear response properties by making use of the Hellmann−Feynman theorem.[5,6] In the framework of the conceptual density functional theory, the chemical properties are related to other local functions, such as the hardness, the softness, the Fukui function, and their local versions,[7−12] which appear to be energy second derivatives which cannot be computed from the density itself. Paradoxically, none of these reactivity indicators depends on the local spin pairing. However, the concepts of spinphilicity and donicity have recently been proposed as global reactivity indicators for spin-catalyzed reactions.[13]

To get some insight onto the local pairing, it is useless to consider the spin contributions $\rho^{\alpha}(\mathbf{r})$ and $\rho^{\beta}(\mathbf{r})$ to the total density as being local descriptors, because in closed-shell singlets (which are the ground electronic states of a huge majority of chemical systems), these two quantities are identically equal. Therefore, the information on the pairing has to be extracted from the spin components of the two-particle density distribution:

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$$\pi(\mathbf{r},\mathbf{r}') = \int\int \Psi(x, x', x_3, ..., x_N)\Psi^* (x, x', x_3, ..., x_N)\, \mathrm{d}x''\, \mathrm{d}\sigma\, \mathrm{d}\sigma' \quad (5)$$

$$= \langle\Psi|\hat{\pi}(\mathbf{r},\mathbf{r}')|\Psi\rangle \quad (6)$$

$$= \pi^{\alpha\alpha}(\mathbf{r},\mathbf{r}') + \pi^{\alpha\beta}(\mathbf{r},\mathbf{r}') + \pi^{\beta\alpha}(\mathbf{r},\mathbf{r}') + \pi^{\beta\beta}(\mathbf{r},\mathbf{r}') \quad (7)$$

In eq 5, $\mathrm{d}x''$ indicates that the integration is performed over the coordinates of all the electrons but two. The two-particle density operator appearing in eq 6 is

$$\hat{\pi}(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N}\sum_{j\neq i}^{N}\delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}') \quad (8)$$

Finally, in eq 7, $\pi^{\sigma\sigma}(\mathbf{r},\mathbf{r}')$ represents the probability of finding one electron of spin σ at $\mathbf{r}$ and another at $\mathbf{r}'$ and $\pi^{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$ represents the probability of finding an electron of spin σ at $\mathbf{r}$ and and another of spin σ' at $\mathbf{r}'$.[14] It is worth noting that the Pauli principle prescribes $\pi^{\sigma\sigma}(\mathbf{r},\mathbf{r}) = 0$, whereas $\pi^{\sigma\sigma'}(\mathbf{r},\mathbf{r})$ is usually greater than zero. Unfortunately, these functions are functions of the coordinates of two points, and it is therefore necessary to lower this number to 1. This is done in the spirit of Dobson's interpretation of the Fermi hole curvature in terms of "other" electrons found in a small neighborhood near a given electron.[15] This number is calculated by integrating the conditional pair probabilities over a sphere of radius R centered on the reference electron.

In the present work, I consider the pair densities rather than the conditional probabilities. The integrated pair density for parallel spin electrons within a given finite sampling volume $V(\mathbf{r})$ surrounding the reference point $\mathbf{r}$ is

$$\bar{N}_{||}(\mathbf{r}) = \int_V\int_V \pi^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 + \int_V\int_V \pi^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \quad (9)$$

and that of antiparallel spin pairs is

$$\bar{N}_{\perp}(\mathbf{r}) = \int_V\int_V \pi^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 + \int_V\int_V \pi^{\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \quad (10)$$

and the sample population $\bar{N}(\mathbf{r})$ is

$$\bar{N}(\mathbf{r}) = \int_V \rho(\mathbf{r}_1)\, \mathrm{d}\mathbf{r}_1 \quad (11)$$

In the limit of noninteracting electrons in a singlet state, the number of antiparallel pairs is

$$\bar{N}^0_{\perp}(\mathbf{r}) = \frac{1}{2}\int_V \rho(\mathbf{r}_1)\, \mathrm{d}\mathbf{r}_1 \int_V \rho(\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_2 = \frac{1}{2}\bar{N}^2(\mathbf{r}) \quad (12)$$

The three functions

$$D_{\mathrm{anti}}(\mathbf{r}) = \frac{\bar{N}_{||}(\mathbf{r})}{\bar{N}_{\perp}(\mathbf{r})} \quad (13)$$

$$D_{\mathrm{tot}}(\mathbf{r}) = \frac{\bar{N}_{||}(\mathbf{r})}{\bar{N}_{\perp}(\mathbf{r}) + \bar{N}_{||}(\mathbf{r})} \quad (14)$$

$$D_{\mathrm{s}}(\mathbf{r}) = 2\frac{\bar{N}_{||}(\mathbf{r})}{\bar{N}(\mathbf{r})^2} \quad (15)$$

are dimensionless numbers which tend to zero in the region of the perfect antiparallel pairing. They can be viewed as the ratios of the parallel spin-pair concentration to the actual antiparallel spin-pair concentration $D_{\mathrm{anti}}(\mathbf{r})$, the actual total spin-pair concentration $D_{\mathrm{tot}}(\mathbf{r})$, and the pair concentration of a single pair $D_{\mathrm{s}}(\mathbf{r})$. There is therefore a conceptual analogy with solution chemistry, and the calculation of $\bar{N}_{||}(\mathbf{r})$ and $\bar{N}_{\perp}(\mathbf{r})$ can be viewed as a numerical titration. The definition of the $D(\mathbf{r})$ functions is independent of electronic state of the system, of the nature of the wave function, and of the way the calculation of this latter function has been carried out. These functions are defined for both exact and approximate wave functions, for both ground and excited states, as well as for stationary or time-dependent descriptions.

However, neither $\bar{N}_{\perp}(\mathbf{r})$ nor $\bar{N}_{||}(\mathbf{r})$ are proportional to the sampling volume, and therefore, the actual values of the $D(\mathbf{r})$ functions depend on the sampling which is an epistemologically uncomfortable position. In the independent-particle model, the probability of finding two parallel spin electrons at a small separation behaves as the square of the interparticle distance, the interparticle distance being $|\mathbf{r}_2 - \mathbf{r}_1|$, whereas the antiparallel spin probability is independent of this separation. Therefore, within small volumes, the $D(\mathbf{r})$ functions are expected to scale as $V^{3/2}(\mathbf{r})$. Instead of the volume itself, the sample population $\bar{N}(\mathbf{r})$ can be considered for the scaling since

$$V(\mathbf{r}) = \frac{\bar{N}(\mathbf{r})}{\bar{\rho}(\mathbf{r})} \quad (16)$$

where $\bar{\rho}(\mathbf{r})$ is the average density within $V(\mathbf{r})$.

To verify this power law, $D_{\mathrm{tot}}(\mathbf{r})$ and $D_{\mathrm{s}}(\mathbf{r})$ have been calculated with single determinental wave functions for representative samples of points and for a selection of atoms and molecules (for singlets $D_{\mathrm{anti}}(\mathbf{r}) = D_{\mathrm{s}}(\mathbf{r})$ with such wave functions). For each point, the calculations are carried out for 15 trial populations q_i belonging to the range $(10^{-10}-10^{-3})$ which determines the edge $a_i = (q_i/\rho(\mathbf{r}))^{1/3}$ of a cubic box centered at $\mathbf{r}$. Then, the exact population $\bar{N}(\mathbf{r};q_i)$ and the spin-pair compositions $D_{\mathrm{tot}}(\mathbf{r};q_i)$ and $D_{\mathrm{s}}(\mathbf{r};q_i)$ are calculated. The exponents of $\bar{N}(\mathbf{r};q_i)$ in the power law are determined by a least-squares fit of

$$D(\mathbf{r};q_i) = \bar{N}^{\alpha}(\mathbf{r};q_i)c_{\pi}(\mathbf{r}) \quad (17)$$

where $c_{\pi}(\mathbf{r})$ is the size-independent spin composition. The exponent α is always close to its expectation $^2/_3$, and the regression coefficient r^2 is always close to 1 (typically, $r^2 \sim 0.99$). Table 1 displays the $c_{\pi}(\mathbf{r})$, the exponents α, and the regression coefficients r^2 for D_{tot} and D_{s}; the systems considered are Ne (^{1}S), Ar (^{1}S), Kr (^{1}S), and Cr (^{7}S, $M_{\mathrm{S}} = 0, \pm 3$).

The numbers reported in Table 1 are not interesting by themselves, but they should be considered as being the results of numerical experiments demonstrating the reliability of eq 17, at least in chemically significant regions. For all closed-shell atoms and for the $M_{\mathrm{S}} = 0$ component of the septuplet, the $\alpha = {}^2/_3$ law is verified for densities $\rho(\mathbf{r})$ greater than 10^{-4} au. The noticeable deviations occur at lower densities because the size of the sampling volume becomes too large and therefore hampers the requirement of homogeneity of the sample. For closed-shell systems the $c_{\pi}(\mathbf{r})$ functions calculated from $D_{\mathrm{tot}}(\mathbf{r})$ and $D_{\mathrm{s}}(\mathbf{r})$ have values very close together. In the case of the chromium atom as expected from the definitions of $D_{\mathrm{tot}}(\mathbf{r})$ and $D_{\mathrm{s}}(\mathbf{r})$ the values of the corresponding $c_{\pi}(\mathbf{r})$'s are very close for $M_{\mathrm{S}} = 0$ and significantly different for $M_{\mathrm{S}} = \pm 3$ in the regions

TABLE 1: Distance from the Nucleus r (bohr), Electron Density $\rho(\mathbf{r})$, Size-Independent Spin-Pair Compositions $c_\pi(\mathbf{r})$, Exponents α, and Regression Coefficients r^2 of $D_{\mathrm{tot}}(\mathbf{r};q_i)$ and $D_{\mathrm{s}}(\mathbf{r};q_i)$

		$D_{\mathrm{tot}}(\mathbf{r})$			$D_{\mathrm{s}}(\mathbf{r})$		
r	$\rho(\mathbf{r})$	$c_\pi(\mathbf{r})$	α	r^2	$c_\pi(\mathbf{r})$	α	r^2
Ne							
0.00	590.4918273	0.003	0.6710	1.0000	0.003	0.6710	1.0000
0.20	14.5166518	0.813	0.6655	1.0000	0.816	0.6657	1.0000
0.50	2.2925161	0.692	0.6666	1.0000	0.696	0.6669	1.0000
0.60	1.7429237	0.485	0.6663	1.0000	0.486	0.6665	1.0000
0.70	1.2766312	0.413	0.6664	1.0000	0.414	0.6666	1.0000
1.40	0.1128045	0.582	0.6666	1.0000	0.584	0.6667	1.0000
2.10	0.0125334	1.245	0.6661	1.0000	1.252	0.6664	1.0000
2.70	0.0018051	2.762	0.6637	1.0000	2.799	0.6644	1.0000
3.10	0.0003666	5.135	0.6540	0.9996	5.290	0.6556	0.9997
3.50	0.0000565	10.500	0.6387	0.9987	10.911	0.6407	0.9989
4.20	0.0000011	16.156	0.5474	0.9870	17.830	0.5524	0.9885
Ar							
0.00	3724.3711905	0.008	0.6723	0.9999	0.008	0.6723	0.9999
0.20	34.4140960	0.997	0.6662	1.0000	1.001	0.6665	1.0000
0.50	3.5739246	0.657	0.6662	1.0000	0.659	0.6664	1.0000
0.60	1.5374822	1.509	0.6651	1.0000	1.519	0.6655	1.0000
0.70	0.7980277	2.729	0.6648	1.0000	2.762	0.6655	1.0000
1.40	0.2236378	0.356	0.6665	1.0000	0.357	0.6667	1.0000
2.10	0.0460064	0.509	0.6670	1.0000	0.510	0.6672	1.0000
2.70	0.0111683	0.841	0.6663	1.0000	0.844	0.6665	1.0000
3.10	0.0043356	1.256	0.6657	1.0000	1.263	0.6660	1.0000
3.50	0.0017207	1.939	0.6646	1.0000	1.956	0.6651	1.0000
4.20	0.0003592	3.863	0.6613	0.9999	3.935	0.6623	0.9999
5.00	0.0000534	8.639	0.6585	0.9999	8.824	0.6597	0.9999
Kr							
0.00	31257.2889808	0.013	0.6721	0.9999	0.013	0.6721	0.9999
0.20	78.4345150	0.890	0.6660	1.0000	0.894	0.6662	1.0000
0.50	11.2514215	0.508	0.6666	1.0000	0.510	0.6668	1.0000
0.60	6.0812935	0.556	0.6661	1.0000	0.557	0.6663	1.0000
0.70	3.1320538	0.757	0.6660	1.0000	0.759	0.6662	1.0000
1.40	0.2316985	0.736	0.6663	1.0000	0.740	0.6666	1.0000
2.10	0.0620067	0.429	0.6666	1.0000	0.430	0.6667	1.0000
2.70	0.0176109	0.625	0.6664	1.0000	0.627	0.6666	1.0000
3.10	0.0074308	0.864	0.6662	1.0000	0.867	0.6664	1.0000
3.50	0.0031278	1.242	0.6657	1.0000	1.249	0.6660	1.0000
4.20	0.0007179	2.418	0.6638	1.0000	2.445	0.6644	1.0000
5.00	0.0001356	4.810	0.6590	0.9998	4.930	0.6604	0.9996
Cr (^{7}S, $M_{\mathrm{S}} = 0$)							
0.00	9108.2991425	0.011	0.6726	0.9999	0.011	0.6726	0.9999
0.20	62.1574972	0.482	0.6663	1.0000	0.484	0.6665	1.0000
0.50	3.2938033	2.169	0.6656	1.0000	2.190	0.6661	1.0000
0.60	2.5464580	1.196	0.6665	1.0000	1.202	0.6668	1.0000
0.70	2.1224464	0.693	0.6668	1.0000	0.696	0.6671	1.0000
1.40	0.2307632	0.940	0.6663	1.0000	0.943	0.6665	1.0000
2.10	0.0309829	2.294	0.6656	1.0000	2.318	0.6661	1.0000
2.70	0.0090011	2.970	0.6654	1.0000	3.009	0.6662	1.0000
3.10	0.0043535	3.531	0.6645	1.0000	3.586	0.6654	1.0000
3.50	0.0022916	3.727	0.6640	1.0000	3.789	0.6649	1.0000
4.20	0.0009586	1.572	0.6682	1.0000	1.583	0.6686	1.0000
5.00	0.0004007	0.171	0.6785	0.9996	0.171	0.6785	0.9996
Cr (^{7}S, $M_{\mathrm{S}} = \pm 3$)							
0.00	9108.2991425	0.011	0.6726	0.9999	0.011	0.6726	0.9999
0.20	62.1574972	0.482	0.6663	1.0000	0.484	0.6665	1.0000
0.50	3.2938033	2.377	0.6655	1.0000	2.280	0.6661	1.0000
0.60	2.5464580	1.382	0.6665	1.0000	1.299	0.6668	1.0000
0.70	2.1224464	0.826	0.6667	1.0000	0.776	0.6670	1.0000
1.40	0.2307632	1.491	0.6661	1.0000	1.215	0.6665	1.0000
2.10	0.0309829	9.400	0.6630	1.0000	3.703	0.6660	1.0000
2.70	0.0090011	43.642	0.6515	0.9994	5.434	0.6661	1.0000
3.10	0.0043535	111.736	0.6204	0.9952	6.835	0.6653	1.0000
3.50	0.0022916	149.773	0.5504	0.9759	7.435	0.6648	1.0000
4.20	0.0009586	112.082	0.4747	0.9441	3.155	0.6686	1.0000
5.00	0.0004007	133.231	0.5080	0.9595	0.337	0.6787	0.9996

of the M and N shells. For instance, the N shell structure is not accounted for by $D_{\mathrm{tot}}(\mathbf{r})$.

3. Approximate Expressions and Electron Localization Function

Approximate expressions of the different $c_\pi(\mathbf{r})$'s would be useful for practical applications. The sampling volume is chosen as a cube of edge a centered at $\mathbf{r}$. Within the sampling volume, I assume that all the necessary quantities, namely, $\bar{N}(\mathbf{r})$, $\bar{N}^{\alpha\alpha}$, $\bar{N}^{\alpha\beta}$, $\bar{N}^{\beta\alpha}$, and $\bar{N}^{\beta\beta}$, can be evaluated by their Taylor expansions around the reference position $\mathbf{r}$ limited to the first nonzero term, i.e.,

$$\rho^\sigma(\mathbf{r}_1) = \rho^\sigma(\mathbf{r}) \tag{18}$$

$$\pi^{\sigma\sigma'}(\mathbf{r}_1,\mathbf{r}_2) = \rho^\sigma(\mathbf{r})\rho^{\sigma'}(\mathbf{r}) \tag{19}$$

$$\pi^{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\rho^\sigma(\mathbf{r}_1)\left(\frac{\partial^2 P^{\sigma\sigma}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)}{\partial x_2^2}\bigg|_{x_2=x_1=x}(x_2-x_1)^2 + \frac{\partial^2 P^{\sigma\sigma}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)}{\partial y_2^2}\bigg|_{y_2=y_1=y}(y_2-y_1)^2 + \frac{\partial^2 P^{\sigma\sigma}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)}{\partial z_2^2}\bigg|_{z_2=z_1=z}(z_2-z_1)^2\right) \tag{20}$$

where $P^{\sigma\sigma}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)$ is the conditional probability density

$$P^{\sigma\sigma}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{\pi^{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)}{\rho^\sigma(\mathbf{r}_1)} \tag{21}$$

With these assumptions, one obtains

$$\bar{N}(\mathbf{r}) \approx \rho(\mathbf{r})a^3 \tag{22}$$

$$\bar{N}^\sigma(\mathbf{r}) \approx \rho^\sigma(\mathbf{r})a^3 \tag{23}$$

$$\bar{N}_\perp \approx 2\bar{N}^{\alpha\beta} = 2\bar{N}^\alpha(\mathbf{r})\bar{N}^\beta(\mathbf{r}) = 2\rho^\alpha(\mathbf{r})\rho^\beta(\mathbf{r})a^6 \tag{24}$$

$$\bar{N}_{||} \approx \frac{1}{24}[\rho^\alpha(\mathbf{r})\nabla^2 P^{\alpha\alpha}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)|_{\mathrm{r}_1=\mathrm{r}_2=\mathrm{r}} + \rho^\beta(\mathbf{r})\nabla^2 P^{\beta\beta}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}}]a^8 \tag{25}$$

replacing a by $(\bar{N}(\mathbf{r})/\rho(\mathbf{r}))^{1/3}$ enables the $D_{\mathrm{anti}}(\mathbf{r})$ and $D_{\mathrm{s}}(\mathbf{r})$ functions to be expressed as

$$D_{\mathrm{anti}}(\mathbf{r}) \approx \frac{\bar{N}^{2/3}(\mathbf{r})(\rho^\alpha(\mathbf{r})\nabla^2 P^{\alpha\alpha}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)+\rho^\beta(\mathbf{r})\nabla^2 P^{\beta\beta}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2))}{12\rho^{2/3}(\mathbf{r})\rho^\alpha(\mathbf{r})\rho^\beta(\mathbf{r})} \tag{26}$$

$$D_{\mathrm{s}}(\mathbf{r}) \approx \frac{\bar{N}^{2/3}(\mathbf{r})(\rho^\alpha(\mathbf{r})\nabla^2 P^{\alpha\alpha}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)+\rho^\beta(\mathbf{r})\nabla^2 P^{\beta\beta}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2))}{3\rho^{8/3}(\mathbf{r})} \tag{27}$$

Since $\bar{N}_\perp$ and $\bar{N}_{||}$ are in a^6 and a^8, respectively, the approximate expressions of D_{anti} and D_{tot} are identical. It is worth noting that the $\bar{N}(\mathbf{r})^{2/3}$ factor explicitly appears in theses approximate expressions. In the absence of spin polarization ($M_{\mathrm{S}} = 0$), $\rho^\alpha(\mathbf{r}) = \rho^\beta(\mathbf{r}) = {}^1/_2\rho(\mathbf{r})$ as well as the two conditional probabilities are equal; therefore, D_{anti}, D_{tot}, and D_{s} have a unique approximate expression which yields for $c_\pi(\mathbf{r})$

$$c_\pi(\mathbf{r}) \approx \frac{\nabla^2 P^{\alpha\alpha}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)}{3\rho^{5/3}(\mathbf{r})} \tag{28}$$

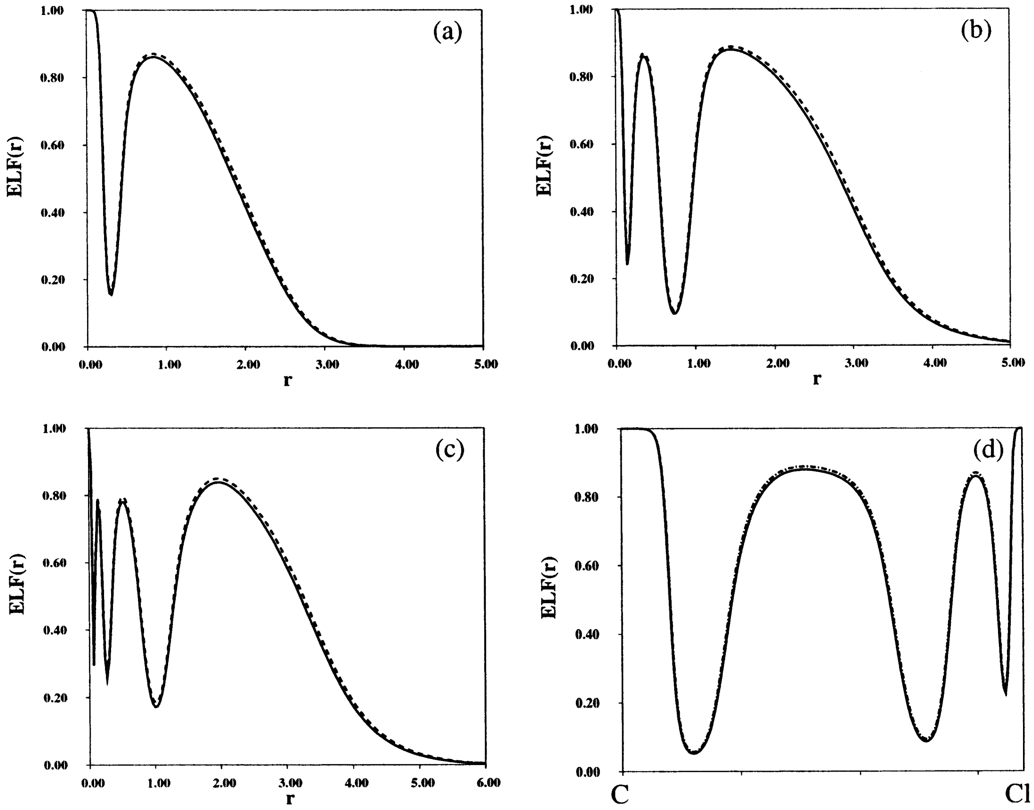

Figure 1. Localization function profiles of (a) Ne, (b) Ar, (c) Kr, and (d) CH_3Cl calculated with (full line) ELF and (dashed line) $c_\pi(\mathbf{r})$. For CH_3Cl, the functions are plotted along the C−Cl bond.

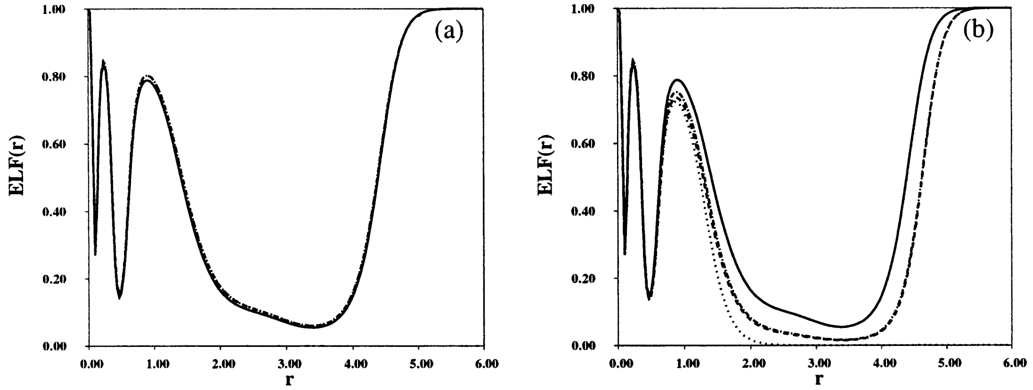

Figure 2. Localization function profiles of (a) Cr (^{7}S) $M_S = 0$ and (b) $M_S = \pm 3$ calculated with the (full line) standard ELF function, the modified ELF function derived from (dashed−dotted line) eq 27, the (dotted line) $c_\pi(\mathbf{r})$ function calculated from D_{tot}, and (dashed line) $c_\pi(\mathbf{r})$ calculated from D_s.

This approximate expression of $c_\pi(\mathbf{r})$ is within a constant identical to the D_σ/D_σ° quantity of the electron localization function (ELF) of Becke and Edgecombe.[16] Moreover, an interpretation of the ELF in terms of the integrated conditional probability has already been given by Dobson.[15,17]

Figure 1 compares the profiles obtained for the Ne, Ar, and Kr atoms and the methyl chloride molecule with ELF and with $1/(1 + c_\pi^2(\mathbf{r}))$. The function $c_\pi(\mathbf{r})$ has been calculated as the average of $\bar{N}^{-2/3}(\mathbf{r};q_i) \times D_s(\mathbf{r};q_i)$ determined with the 15 trial populations already used in the previous section, provided the sampling volume population is less than 0.001*e*:

$$c_\pi(\mathbf{r}) = \frac{1}{n}\sum_{i=1}^{n}\bar{N}^{-2/3}(\mathbf{r};q_i)D_s(\mathbf{r};q_i) \qquad (29)$$

The two curves almost coincide for the four systems. Figure 2 displays the profiles calculated with the ELF, an open-shell alternative of ELF deduced from eq 27, i.e., with

$$\frac{D_\sigma}{D_\sigma^\circ} = \frac{\rho^\alpha(\mathbf{r})\nabla^2 P^{\alpha\alpha}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2) + \rho^\beta(\mathbf{r})\nabla^2 P^{\beta\beta}_{\mathrm{cond}}(\mathbf{r}_1,\mathbf{r}_2)}{3\rho^{8/3}(\mathbf{r})} \qquad (30)$$

and the c_π functions corresponding to D_{tot} and D_s. As expected, for $M_S = 0$, the four curves coincide; for $M_S = \pm 3$, the c_π function of D_{tot} does not show the singly occupied valence shell, whereas the other c_π and the modified ELF are in excellent agreement. It is important to mention that the boundary of the *M* and *N* shells is found at 3.4 au for both components of the multiplet, and therefore, at least for the present example, the shell population is independent of the actual value of M_S.

4. Conclusions

The size-independent spin-pair composition function has a clear meaning as a local indicator of chemical bonding. This function relies on a chemical approach of the nature of the electron cloud in terms of parallel and antiparallel spin-pair concentrations. It can be safely evaluated within the chemically relevant regions of the molecular space, i.e., where the electron density is large enough to avoid numerical noise ($\rho(\mathbf{r}) > 10^{-3}$). The ELF function which is closely related to $c_\pi(\mathbf{r})$ is much easier to evaluate and to differentiate, because it has a compact analytical form in terms of the molecular orbitals, whereas $c_\pi(\mathbf{r})$ requires the performance of six-dimensional integrations over the sampling volume V. In all practical applications, it is therefore worthwhile to use ELF instead of $c_\pi(\mathbf{r})$. As shown for the Cr atom, eq 30 enables the derivation of a localization function, which is the ELF when the spin density is zero.

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