Shape of the geometrically active atomic states of carbon*

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We have developed a computer code for *ab initio* the variational configuration interaction calculation of the electronic structure of atoms via variationally optimized Lagurre type orbitals, treating the orbital effective charges as variational parameters. Excited states of the same symmetry, in order to avoid the inherent restrictions of the standard method of Hylleraas–Unheim and MacDonald, are computed variationally by minimizing the recently developed minimization functionals for excited states. By computing, at the minimum, the one-electron density and the probability distribution of the two-electron angle, and the most probable two-electron angle, we investigate the atomic states of the carbon atom. We show that, without resorting to the (admittedly unproven) concept of hybridization, as an intrinsic property of the atomic wave function, the most probable value of the two-electron angle is around the known angles of carbon bonding, i.e. either 109° or 120° or 180°, depending on each low-lying state of the bare carbon atom.

Keywords: carbon, hybridization, excited states, variational principle

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1. Introduction

In the early ages of theoretical physical chemistry, Mulliken noticed the ongoing tendency that "the more accurate the calculations become, the more the concepts tend to vanish into thin air". Indeed, with the advent of modern methods, algorithms, computer software, and hardware helping the theory of bonding, the thesaurus of qualitative ideas like hybridization, hypervalence, etc., became of rather secondary significance for the theoretical physical chemistry itself. Such concepts changed their status from the initial *a priori* explanatory virtues, expressing the active causal agents, to the rather passive role as subject of the eventual *a posteriori* recovery from the bare output of the electronic structure methods. The first principles are now perceived as incorporated in the *ab initio* methods themselves, most often the qualitative ideas appeared superfluous with respect to the ways and tasks of computational physical chemistry.

Nicolaides and Komninos[2] have presented a theory of molecular formation, according to which the shape of polyhedral or coordination compounds is fixed, to a very good approximation, by the shape of a particular state or states of the central atom, which is activated by spin and spatial coupling of optimal strength between this state, called the geometrically active atomic state (GAAS) and the state of the ligands. The concept of the shape of atomic states is defined and computed quantum mechanically from the probability distribution of the angular two-electron density $\rho(\cos\theta_{1,2})$ of the angle $\theta_{1,2}$ formed by the position vectors of two electrons in the given atomic state. Specifically, it is deduced from the distribution's maximum which provides the most probable value of $\theta_{1,2}$. Nicolaides and Komninos have demonstrated their theory by explaining the shape of BeH_2, BH_2, CH_4, SiH_4, H_2O, H_2S, NH_3, PH_3, SF_6, and TiH_4 in terms of the shapes of the following GAAS. Be: $2s2p\ ^3P^o$, B: $2s2p^2\ ^4P^e$, C: $2s2p^3\ ^5S^o$, Si: $3s3p^3\ ^5S^o$, O: $2s2p^5\ ^3P^o$, S: $3s^23p^33d\ ^3P^o$, N: $2s^2p^4\ ^4P^e$, P: $3s3p^33d\ ^4P^o$, S: $3s3p^33d^2\ ^7F^o$, and Ti: $3d^24s4p\ ^5G^o$, all of the highest spin. In this work we investigate the extension of the GAAS concept to excited atomic states of lower spin, choosing the carbon atom, which exhibits all kinds of "hybridization", and which occurs at the usual angle of either 109°, or 120° or 180°. We show that the two-electron angular separation of these angles is an intrinsic property of the wave function of the low-lying excited states of the C atom: $^5S^o$, $^3D^o$ and $^3P^o$ respectively.

We have developed a computer code for *ab ini-*

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tio variational configuration interaction calculation of electronic structure of atoms via variationally optimized Lagurre-type orbitals (VLTO):[3,4] Taking example from the hydrogen atom whose orbitals are, one could say, essentially Slater-type orbitals (STO) with (Lagurre) polynomial coefficients, rather than the usual STO monomials, we also used variationally optimised polynomial coefficients for each exponent. The result is that the atom is described by only a few analytic orbitals (VLTOs) tailored to the problem (as few as the corresponding mostly accurate numerical orbitals — contrary to large numbers of STOs, or even larger number of Gaussian-type orbitals), while the accuracy reached is comparable to the most accurate numerical results.[5] Analytic VLTOs resemble numerical orbitals both in shape (and in conciseness) and in accuracy.[3,4] Yet, being analytic, in practice they are immediately applicable, without the need of approximating interpolations in large tables of numerical values.

For excited states of the same symmetry, the standard method of Hylleraas–Unheim and MacDonald (higher roots of the secular equation) has several inherent restrictions preventing the approach to any desired accuracy, if the lowest state is not determined exactly.[6] In order to avoid the inherent restrictions, such states are computed variationally by minimizing the recently developed minimization functionals for excited states (cf. arXiv:0801.3673).[6]

In this paper, we will use our code, by calculating the one-electron and the angular two-electron density, to study the shape of GAAS for the carbon atom in the low-lying states.

2. Theory and method

Given the atom with nuclear charge $Z_{\rm nuc}$ and N electrons, as well as the symmetry and the electron occupancy, the desired N-electron normalized wave function, consisting of $N_{\rm c}$ (predetermined) configurations, is

$$\Psi(r_1 s_1, \ldots, r_N s_N) = \sum_{p=1}^{N_c} c_p \Gamma_p(r_1 s_1, \ldots, r_N s_N),$$
$$|\Psi|^2 = 1, \quad \Gamma_p = \sum_{i=1}^{N_d} f_{ip} D_i, \tag{1}$$

where the linear parameters c_p are determined from a desired (usually the lowest) root of the secular equation

$$\det |H_{p,q} - S_{p,q} E| = 0, \tag{2}$$

which is solved by the strategy on p. 455 of Ref. [7]. Here E is the total energy, $S_{p,q} = \sum_{i,j=1}^{N_d} f_{ip} f_{jq} \langle D_i | D_j \rangle$ is the overlap matrix; the Hamiltonian matrix elements

$$H_{p,q} = \sum_{i,j=1}^{N_d} f_{ip} f_{jq} \langle D_i | H | D_j \rangle \tag{3}$$

are calculated by the method on p. 66 of Ref. [8], where

$$H = -\sum_{i=1}^{N} \left(\frac{1}{2} \nabla_i^2 + \frac{Z_{\rm nuc}}{r_i} \right) + \sum_{i>j}^{N} \frac{1}{|r_i - r_j|} \equiv \sum_{i=1}^{N} h(i) + \sum_{i>j}^{N} g(i,j). \tag{4}$$

The D_i are all (N_d), consistent with the desired electronic state, Slater determinants formed out of predetermined orbitals (VLTOs), to be optimised, and f_{ip} are all $(N_d \times N_c)$ consistent corresponding coefficients, which we determine by implementing the method described in Ref. [9].

$$\langle D_a | \sum_{i=1}^{N} h(i) | D_b \rangle = (D_{aa} D_{bb})^{-1/2} \sum_{i,j=1}^{N} \langle a_i | h | b_j \rangle D_{ab}(a_i b_j). \tag{5}$$

Here $D_{ab} = \det |\langle a_1 | b_1 \rangle \langle a_2 | b_2 \rangle \cdots \langle a_n | b_n \rangle|$, $D_{ab}(a_i b_j)$ denotes the usual cofactor of the element $\langle a_i | b_i \rangle$ in the determinant D_{ab}; D_{aa} and D_{bb} are similar normalization factors; a_i and b_j are the spin-orbitals.

$$\langle D_a | \sum_{i>j}^{N} g(i,j) | D_b \rangle = (D_{aa} D_{bb})^{-1/2} \sum_{i>t}^{N} \sum_{j>l}^{N} \langle a_i a_t | g | b_j b_l \rangle D_{ab}(a_i a_t b_j b_l), \tag{6}$$

where $D_{ab}(a_i a_t b_j b_l)$ is the cofactor of D_{ab} defined by deleting the rows and columns containing $\langle a_i | b_i \rangle$ and $\langle a_k | b_l \rangle$ and attaching a factor $(-1)^{i+j+t+l}$ to the resultant minor.

In our code, in order to avoid evaluating a minor on the right-hand side of Eqs. (5) and (6) for every term, to speed up the program, whenever the overlap integrals matrix $S_{ab} = \langle D_a | D_b \rangle$ is non-singular, we use Jacobi's

ratio theorem (Archbold, 1961).[10] Thus we have

$$D_{ab}(a_i b_j) = (S^{-1}_{ab})_{ji} D_{ab} \tag{7}$$

(the standard definition of the inverse matrix elements), and

$$D_{ab}(a_i a_t b_j b_l) = [(S^{-1}_{ab})_{ji}(S^{-1}_{ab})_{lk} - (S^{-1}_{ab})_{li}(S^{-1}_{ab})_{jk}] D_{ab}, \tag{8}$$

where S^{-1}_{ab} is its inverse. If S_{ab} happens to be singular, we artificially make it non-singular by adding to each of its elements a physically negligible random error O (10^{-10}).

The spin-orbitals a_i and b_j are constructed by our proposed VLTO[3] of the form $R_{n,l}(\{g\}, r, z_{n,l}, b_{n,l}, q_{n,l})$ $\mathrm{Y}_{l,m}(\theta,\phi)\chi(s)$, where $\mathrm{Y}_{l,m}(\theta,\phi)$ are spherical harmonics and $\chi(s)$ are spin functions. We treat the angular and spin part of the matrix elements of Eqs. (5) and (6) according to the methods of Chapter 6 of Refs. [11]. After integrating over the angular and spin parts, we have

$$\langle a_i | \, h \, | b_j \rangle = \langle R_{n_i l_i} | \, h \, | R_{n_j l_j} \rangle \, \delta(l^i, l^j) \delta(m^i_l, m^j_l) \delta(m^i_s, m^j_s), \tag{9}$$

and

$$\begin{aligned} \langle a_i a_t | g | b_j b_l \rangle = & \sum_{k=0}^{\infty} d_k(i,j) d_k(t,l) G^k(i,t,j,l) \delta(m^i_s, m^j_s) \delta(m^t_s, m^l_s) \\ & \times \delta(m^i_l + m^t_l, m^j_l + m^l_l), \end{aligned} \tag{10}$$

where d_k can be expressed in terms of Winger $3j$ coefficients $A^{j_1,j_2,j_3}_{m_1,m_2,m_3}$ (cf. p. 175 of Ref. [11])

$$d_k(l m_l, l' m'_l) = \sqrt{\frac{2l'+1}{2l+1}} A^{k,l',l}_{0,0,0} A^{k,l',l}_{m_l - m'_l, m'_l, m_l}. \tag{11}$$

Here i, t, j, and l are orbital indices, which refer to all necessary quantum numbers. $G^k(i,t,j,l)$ are radial integrals.

The parameters $z_{n,l}$, $b_{n,l}$, and $q_{n,l}$ are determined from the optimization, i.e., (non-linear variational) minimization of the lowest root of Eq. (2) for the lowest state of each symmetry, or of the functional Ω_n, mentioned below, for the excited states of the same symmetry. The excited state energy expressed as

$$E[\phi_n] = E_n - \sum_{i<n} (E_n - E_i) \langle i | \phi_n \rangle^2 + \sum_{i>n} (E_i - E_n) \langle i | \phi_n \rangle^2 \equiv E_n - P_L + P_H \tag{12}$$

is evidently a saddle point; and, since the standard method of Hylleraas–Undheim and MacDonald (i.e. higher roots of the secular equation) is inherently restricted not to be able to approach the excited states, if the lowest is not determined exactly,[6] the excited states should be computed independently, variationally, by minimizing the functional[6]

$$\Omega_n[\phi_0, \phi_1, \ldots; \phi_n] \equiv E[\phi_n] + 2 \left[\sum_{i<n} \frac{(E[\phi_n] \langle \phi_i | \phi_n \rangle - \langle \phi_i | H | \phi_n \rangle)^2}{E[\phi_n] - E[\phi_i]} \right] \Bigg/ \left[1 - \sum_{i<n} \langle \phi_i | \phi_n \rangle^2 \right], \tag{13}$$

which has a minimum at $|\phi_n\rangle \to |n\rangle$ for a wide range of inaccuracy in ϕ_n (unvaried), $i < n$, and allows $|\phi_n\rangle$ to approach the exact excited state $|n\rangle$ to any desired precision, without improving the lower lying approximants $|\phi_i\rangle$.

Once the orbitals are optimized, the optimized wave function of Eq. (1) is determined and ready to calculate the one-electron density and the angular two-electron density.

The one-electron density $\rho(\boldsymbol{r}_1)$ and the angular two-electron density $\rho(\cos\theta_{1,2})$, i.e. the probability for the position vectors of any two electrons to form an angle $\theta_{1,2}$, are calculated as follows.

For the N-electron atom, the one-electron density is defined as

$$\rho(\boldsymbol{r}_1) \equiv \int \psi^*(\boldsymbol{r}_1 \boldsymbol{s}_1, \boldsymbol{r}_2 \boldsymbol{s}_2, \ldots, \boldsymbol{r}_N \boldsymbol{s}_N) \psi(\boldsymbol{r}_1 \boldsymbol{s}_1, \boldsymbol{r}_2 \boldsymbol{s}_2, \ldots, \boldsymbol{r}_N \boldsymbol{s}_N) \mathrm{d}\boldsymbol{r}_2, \ldots, \mathrm{d}\boldsymbol{r}_N \mathrm{d}\boldsymbol{s}_1 \mathrm{d}\boldsymbol{s}_2 \ldots \mathrm{d}\boldsymbol{s}_N. \tag{14}$$

It provides directly an intuitive physical picture of the electron distribution in an atomic state.

By using Eq. (1), we have

$$\rho(\boldsymbol{r}_1) = \sum_{p,q}^{N_c}\sum_{i,j}^{N_d} c_p c_q f_{p,i} f_{q,j} D^1_{i,j}, \tag{15}$$

where $D^1_{i,j} = \sum_{k,l}^{N} a_k(\boldsymbol{r}) a_l(\boldsymbol{r})$. Comparing with Eqs. (5) and (9), one can see that if we make the substitution $\langle R_{n_i l_i}|h|R_{n_j l_j}\rangle \to \langle R_{n_i,l_i}(r_1)\mathrm{Y}_{l_i,m_i}(\theta_1,\phi_1)|R_{n_j,l_j}(r_1)Y_{l_j,m_j}(\theta_1,\phi_1)\rangle$, our code can readily calculate $\rho(\boldsymbol{r}_1)$.

As for the angular two-electron density, it is defined as

$$\rho(\cos\theta_{1,2}) = \int_{\theta_{1,2}=\mathrm{const}} \pi(\boldsymbol{r}_1,\boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2, \tag{16}$$

where $\pi(r_1, r_2)$ is the two-electron density

$$\pi(\boldsymbol{r}_1,\boldsymbol{r}_2) \equiv \int \psi^*(\boldsymbol{r}_1\boldsymbol{s}_1,\boldsymbol{r}_2\boldsymbol{s}_2,\ldots,\boldsymbol{r}_n\boldsymbol{s}_n)\psi(\boldsymbol{r}_1\boldsymbol{s}_1,\boldsymbol{r}_2\boldsymbol{s}_2,\ldots,\boldsymbol{r}_n\boldsymbol{s}_n)\mathrm{d}\boldsymbol{r}_3,\ldots,\mathrm{d}\boldsymbol{r}_n\mathrm{d}\boldsymbol{s}_1,\ldots,\mathrm{d}\boldsymbol{s}_n. \tag{17}$$

By using Eq. (1), we have

$$\pi(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_{p,q}^{N_c}\sum_{n,m}^{N_d} c_p c_q f_{p,n} f_{q,m} D^2_{n,m}, \tag{18}$$

where

$$D^2_{n,m} = \sum_{i,t,j,l}^{N} u_i(\boldsymbol{r}_1)u_t(\boldsymbol{r}_2)u_j(\boldsymbol{r}_1)u_l(\boldsymbol{r}_2) \equiv \sum_{i,t,j,l}^{N} \Pi_{itjl}(\boldsymbol{r}_1,\boldsymbol{r}_2). \tag{19}$$

Therefore, substituting Eqs. (17)–(19) into Eq. (16), we obtain

$$\rho(\cos\theta_{1,2}) = \sum_{p,q}^{N_c}\sum_{n,m}^{N_d}\sum_{i,t,j,l}^{N} c_p c_q f_{p,n} f_{q,m} f_{itjl}(\cos\theta_{1,2}), \tag{20}$$

where

$$f_{itjl}(\cos\theta_{1,2}) = \int_{\theta_{1,2}=\mathrm{const}} \Pi_{itjl}(\boldsymbol{r}_1,\boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2. \tag{21}$$

First we expand $f_{itjl}(\cos\theta_{1,2})$ in terms of orthogonal Legendre polynomials (cf. Ref. [11])

$$f_{ijtl}(\cos\theta_{1,2}) = \sum_{k=0}^{\infty} a_k \mathrm{P}_k(\cos\theta_{1,2}). \tag{22}$$

Then, according to the methods of Chapter 6 in Ref. [11], after integrating over the angular and spin parts, we have

$$\begin{aligned} f_{itjl}(\cos\theta_{1,2}) = &\sum_{k=0}^{\infty} d_k(i,j)d_k(t,l)\Pi^k(i,t,j,l) \\ &\times \delta(m_s^i, m_s^j)\delta(m_s^t, m_s^l) \\ &\times \delta(m_l^i + m_l^t, m_l^j + m_l^l), \end{aligned} \tag{23}$$

where

$$\Pi^k(i,t,j,l) = \langle R_i|R_j\rangle\langle R_t|R_l\rangle \frac{2k+1}{2}\mathrm{P}_k(\cos\theta_{1,2}). \tag{24}$$

Thus, by replacing, $G^k(i,t,j,l)$ in Eq. (10) with $\langle R_i|R_j\rangle\langle R_t|R_l\rangle\frac{2k+1}{2}\mathrm{P}_k(\cos\theta_{1,2})$, our code readily calculates $\rho(\cos\theta_{1,2})$ (normalized by $N(N-1)/2$).

3. Results and discussion

We systematically study the carbon atom in $1s^2 2s 2p^3$ configuration in the lowest lying states $^3\mathrm{P}^\mathrm{e}$, $^1\mathrm{D}^\mathrm{e}$, $^1\mathrm{S}^\mathrm{e}$, $^5\mathrm{S}^\mathrm{o}$, $^3\mathrm{D}^\mathrm{o}$ and $^3\mathrm{P}^\mathrm{o}$. The results are shown in Fig. 1 and Table 1.

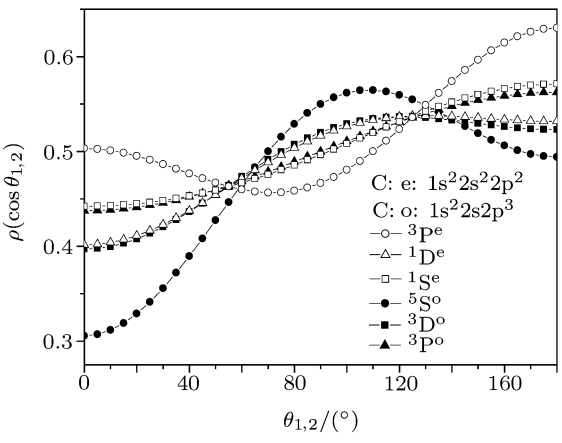


Fig. 1. The two-electron angle probability distribution as a function of two-electron angle in the computed low-lying states of C atom. All probability maxima occur at either 109° or 120° or 180°, the known angles of C-bonding.

We compute the energy using three variationally optimized Laguerre-type orbitals (VLTOs) 1s, 2s and 2p, which we improve by correlation with two more VLTOs, 3s and 3p (in full configuration interaction of these five orbitals). The resulting five VLTOs, being tailored to the problem, provide a very concise, clearly intuitive and quite accurate picture of the states: Although the energy needs, of course, further improvement by higher order orbitals, the main configuration, given in Table 1, immediately allows one to determine the remaining unoccupied orbitals available to bonding (also indicated in Table 1). To complete the last column, $\theta_{1,2}^{\max}$ of Table 1, we show in Fig. 1 the probability distribution of the two-electron density $\rho(\cos\theta_{1,2})$. Apart from details, in all the lowest lying states $\rho(\cos\theta_{1,2})$ has maximum at either 120° or 180° or 109°, i.e., the main picture revealed is that in all the lowest lying states, depending on the excited state, the carbon atom disposes electrons separated mainly by either 120° or 180° or 109°. Via the main VLTOs, the above picture is justified:

Table 1. Low-lying states of C atom computed by configuration interaction using variationally optimized Laguerre-type orbitals, in two approximations (without and with 3s, 3p correlation). The main configuration of occupied and the remaining unoccupied orbitals are shown, along with the most probable two-electron angle within the free atom (cf. Fig. 1). A and B indicate the spin functions.

state	E/(a.u.) 1s, 2s, 2p	E/(a.u.) 1s,2s,2p+3s,3p	occupied	unoccupied	$\theta_{1,2}^{\max}/(^\circ)$
^{3}P^e	–37.547	–37.717	0.95 $2s^2$ $2p_0A$ $2p_1A$	$2p^2_{-1}$ $2p_0B$ $2p_1B$	130
^{1}D^e	–37.483	–37.661	0.93 $2s^2$ $2p_1^2$	$2p_0^2$ $2p^2_{-1}$	180
^{1}S^e	–37.388	–37.628	0.63 $2s^2$ $[2p_0^2 + 2p_{-1}2p_1(AB\text{-}BA)]$	$2p^2_{-1}$ $2p_1^2$	180
^{3}P^o	–37.328	–37.394	0.99 $2s^2$ $2p_1A$ $3sA$		180
^{5}S^o	–37.497	–37.614	0.97 $2sA$ $2p_{-1}A2p_0A2p_1A$	$2sB$ $2p_{-1}B2p_0B2p_1B$	109
^{3}D^o	–37.270	–37.414	$2sA$ $2p_0A2p_1A(0.92$ $2p_1B + 0.2$ $3p_1B)$	$2sB$ $2p_0B2p^2_{-1}$	120
^{3}P^o	–37.205	–37.350	0.58 $2sA$ $2p_1A$ $[2p_0A$ $2p_0B+2p_1B$ $2p_{-1}A]$		
			$+0.18$ $2sB$ $2p_1A$ $[2p_0A$ $3p_0A-2p_{-1}A3p_1A]$		
			-0.16 $2sA$ $2p_1A$ $[2p_0A$ $3p_0B-3p_1B$ $2p_{-1}A]$	$2sB$ $[2p_1B2p^2_{-1}$ or $2p_{-1}B2p_0^2]$	180

In a closer look at Table 1, the ground state (^{3}P^e) configuration is $2s^2$ $2p_0A$ $2p_1A$ (A and B indicate the spin functions). One electron circulates on (near) the xy plane and the other is on the $2p_0$ orbital, perpendicular to the xy plane. Their repulsion justifies the deviation from 90°. The unoccupied orbitals, available to bonding, $2p^2_{-1}$ $2p_0B$ $2p_1B$, have the same "geometry". The 1st excited state, ^{1}D^e has main configuration $2s^2$ $2p_1^2$, where two electrons circulate "on" the xy plane, separated by 180° and the unoccupied orbitals are $2p_0^2$ $2p^2_{-1}$, whose electrons would also be separated by 180°. The main configuration of the 2nd excited state, ^{1}S^e, is $2s^2$ $[2p_0^2 + 2p_{-1}2p_1(AB - BA)]$, with the two-electrons separated by 180°. The electrons in the unoccupied orbitals, $2p^2_{-1}$ $2p_1^2$, would also be separated by 180°. The 4th excited state, ^{5}S^o, main configuration is 2 sA $2p_{-1}A2p_0A2p_1A$, with the four electrons tetrahedrally dispersed. The unoccupied orbitals (the same with spin down) would also be tetrahedrally dispersed. The 5th excited state involving 2s, 2p and ^{3}D^o has the main configuration 2 sA $2p_0A$ $2p_1^2$, where one electron is in a spherically symmetric orbital and the other on the z-axis, with a two-electron angular separation of 120°, which is again justified by their repulsion. The unoccupied orbitals are $2sB2p_0B2p^2_{-1}$, of similar angular separation, but $2p_1$ is closed, and the next most significant configuration is $0.2(2sA$ $2p_0A$ $2p_1A$ $3p_1B)$. Although energetically allowed (cf. below), if this state forms a double bond, CH_2=CH_2, then the impression revealed is that two electrons circulate on (near) the xy plane and two electrons stick above or below the plane, like antennas, separated by 120°, so that the double-bond is formed by the circulating electrons. However, it is unclear whether the double-bond is formed by excitation to this state, or by some deformation of the ^{5}S^o tetrahedral orbitals. Finally, the 6th excited state involving 2s, 2p and ^{3}P^o has the main configuration 0.6 $2sA$ $2p_1A[2p_0A$ $2p_0B+2p_1B$ $2p_{-1}A]$, where $2sA$ is spherical and $2p_1A$ is in a "cycle" on the xy plane, while its electron repels the electron in the spherical 2s orbital. Thus, the electron in the spherical 2s orbital tends to be opposite to the electron which is confined to circulating mainly on the xy cycle, staying as far as possible, i.e. also near the xy plane mainly, and oppositely, showing angular separation of 180°. In the first configuration, $2p_0$ is partially closed (or emptied), however, by the next most significant configurations, 0.18 $2sB$ $2p_1A$ $(2p_0A$ $3p_0A-2p_{-1}A3p_1A)$ -0.16 $2sA$ $2p_1A$ $(2p_0A$ $3p_0B-3p_1B$ $2p_{-1}A)$, which is correlated with a $3p_0$-type correlation orbital; both perpendicular to the xy plane, and $2p_1$with a $3p_1$-type correlation orbital, on the xy plane. This state is quite excited, although still energetically favorable (cf. below) for a triple bond. However, according to the above "shape" revealed, a triple bond would more probably consist

partially of two σ-bonds, rather than two π-bonds. Therefore, we conclude that this excited state should not form a triple bond. A simple rotation of the tetrahedral $^5S^o$ atom (by simultaneous bonding of the three equivalent "legs") seems more probable.

It should be noticed that this state is the 1st excited state of $^3P^o$ symmetry (its energy is a saddle point). Since it cannot be calculated by the standard method of Hylleraas–Undheim and MacDonald (i.e. the 2nd root of the secular equation) which is inherently restricted not to be able to approach the 1st excited state if the lowest is not determined exactly,[6] it was computed independently, variationally, by minimizing the functional Ω_n (cf. Eq. (13)),[6] without the need of improving the lowest state of $^3P^o$ symmetry. As shown in Table 1, the latter has main configuration 0.99 $2s^2$ $2p_1A$ $3sA$, where 2s is closed, and the electrons of $2p_1A$ and $3sA$ are separated by 180°.

We should notice that, by computing the one-electron density ($\rho \boldsymbol{r}_1$), all odd excited states are spherically symmetric.

Concerning a potential bonding, in the three lowest states (of even parity) 2s is closed. In the next three states (of high spin and odd parity) 2s is amenable to bonding. The lowest of these, $^5S^o$ ($\theta_{1,2}^{\max} = 109°$), has tetrahedral "shape" and evidently can form compounds of tetrahedral symmetry. It lies 96.4 kcal/mol[12] higher than the ground state; indicatively, the C–H bond dissociation energy (BDE) cf. Ref. [13] in CH_4 is 105.0 kcal/mol (total gain = $105.0 \times 4 - 96.4 = 323.6$ kcal/mol), and the $CH_3{-}CH_3$ BDE is 90.2 kcal/mol, while in general the C–H BDE of tetrahedrally coordinated C in various organic compounds is about 100 kcal/mol. The next higher state, $^3D^o$ ($\theta_{1,2}^{\max} = 120°$), lies 183.2 kcal/mol[12] higher than the ground state; indicatively, the C–H BDE in $CH_2{=}CH{-}H$, or in $CH_3CH{=}CH{-}H$, is 111.2 kcal/mol, while the double bond BDE of $CH_2{=}CH_2$ is 174.1 kcal/mol (gain = $111.2 \times 4 + 174.1 - 183.2 \times 2 = 252$ kcal/mol). Finally, the higher lying state, $^3P^o$ ($\theta_{1,2}^{\max} = 180°$), is 215.1 kcal/mol above the ground state; indicatively, the triple-bond BDE of CH≡CH is 229.5 kcal/mol, while the C–H BDE in CH≡C–H is 132.8 kcal/mol, in $CH_3C{\equiv}C{-}H$ it is 130.2 kcal/mol and the C–C BDE in $CH_3{-}C{\equiv}CH$ is 126.0 kcal/mol (gain = $229.5+132.8\times 2 - 215.1 \times 2 = 64.9$ kcal/mol).

4. Conclusions

The configuration interaction computation reveals a shape of GAAS which can be calculated by $\theta_{1,2}^{\max}$, verifying the GAAS theory of Nicolaides and Komninos,[2] applied not only to the largest spin state but also to various low-lying states of the carbon atom. Clearly, the atomic "shape" is an intrinsic property of the atomic wave function, as a compromise of "space quantization" (angular momentum) and of dynamic electron repulsion within the atom. If the bonding occurs through the above states, there is no need to refer to the concept of hybridization; the inherent "shape" predicts the same results as obtaining through the hybridization hypothesis. Therefore, as Mulliken noticed, the more accurate the calculations become, the more qualitative ideas, like hybridization, hypervalence, etc., became of rather secondary significance for the theoretical physical chemistry itself.

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