

## Fullerenes as polyradicals

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**Abstract:** We present the investigation of the electronic structure of  $X_{60}$  molecules ( $X=C, Si$ ), containing 60 odd electrons with spin-dependent interaction between them. Conditions for the electrons to be excluded from the covalent pairing are discussed. A computational spin-polarized quantum-chemical scheme is suggested to evaluate four parameters – energy of radicalization, exchange integral, atom spin density, and squared spin – to characterize the effect quantitatively. A polyradical character of the species, weak for  $C_{60}$  and strong for  $Si_{60}$ , is established.

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### 1 Introduction

It cannot be said that fullerenes suffer from lack of theoretical interest. Both the basic molecule  $C_{60}$  and its homologues  $C_{70}$ ,  $C_{84}$ , etc. as well as analogues  $Si_{60}$ ,  $Ge_{60}$  have been repeatedly and thoroughly studied [see 1-7 and references therein]. In some sense, the molecule turned out to be a proving ground for testing different computational techniques, from the simplest to the most sophisticated. Constantly justifying the molecule's stability, several attempts at theoretical calculations have concentrated mainly on the reliability of reproducing the molecular structure and its possible distortion. There have been no doubts concerning the covalent bonding of atoms in the molecules. It has been taken for granted that all valence electrons participate in covalent pairing. That was the reason for the closed shell approximation to be exploited independently of whichever computational method has been used. The first examination of the validity of the approach has been made in a comparative study of the  $C_{60}$  and  $Si_{60}$  molecules [8–10], which has shown a

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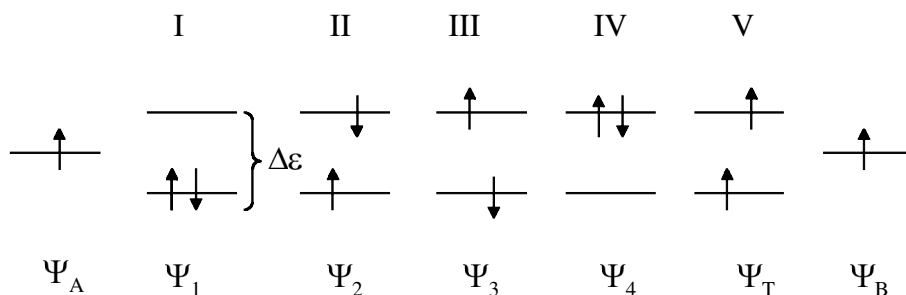
strange feature in the high-spin states behavior of the molecules. A sequence of spin-varying states, singlet (RHF)-triplet-quintet formed a progressively growing series by energy for the  $C_{60}$  molecule while for the  $Si_{60}$  molecule the energy of the triplet and quintet states turned out to drop drastically with respect to the RHF singlet. Obviously, this peculiarity has clearly demonstrated the difference in the electronic structure of both molecules. However, the observation is highly significant since it concerns the basic properties of odd electron behavior in fullerenic structures. The current paper is devoted to the phenomenon which is based on the extraction of odd electrons from covalent coupling. The paper is arranged as follows. Section 2 is devoted to conceptual grounds of the computational experiment that has been carried out. Section 3 concerns exchange integrals as the main energetic characteristics of the electron coupling. Section 4 presents the results for lone pairs of odd electrons as well as for a set of pairs incorporated in the  $C_{60}$  and  $Si_{60}$  structures. Essential features of the study are discussed in Section 5.

## 2 Basic Concepts

Fullerenes are typical species with odd electrons which is the reason for including the concept of aromaticity for them since the moment of their discovery [11]. However further examinations have revealed that in spite of extreme conjugation, fullerenes behave chemically and physically as electron-deficient alkenes rather than electron-rich aromatic systems [12], [13] so that the electron pairing seems to be the main dominant of electronic structure. Conceptually, the problem of an electron pair is closely connected with a fundamental problem in the quantum theory of the hydrogen molecule. According to the Heitler-London theory [14], two hydrogen atoms (electrons) retain their individuality (atomic orbitals, involving spin), and look like two individual radicals with spin  $S=1/2$  when they are far from each other (weak interaction). When the distance approaches the interatomic chemical bond (strong interaction), the electrons, as well as their spins, become delocalized over both atoms, their properties are described by a generalized molecular function (molecular orbital) and spins are aligned antiparallel to provide tight covalent bonding between the atoms. As shown below [15], a continuous transition in the electron behavior from free radical-like to tightly coupled covalent bonding is indeed observed when the distance between the atoms changes from infinity to the chemical bond length. In other words, the covalent bonding fades away when the electron interaction is weakening.

In the context of the current investigation, two problems should be pointed out when this fundamental finding happens to be of crucial importance. The first concerns diradicals in organic chemistry [16–23]. The phenomenon is caused by a pair of odd electrons connected with either C-C or C-N and N-N atom pairs and is common for species largely varying by composition. Generalizing its main aspects, the phenomenon is essentially caused by a fading away of the covalent atomic coupling, as stated above, in the part connected with odd electrons. The illustration in Figure 1 explains the main points of the diradical problem. Initially the doubly degenerate atomic levels  $\Psi_A$ , and  $\Psi_B$  are split due

to electron interaction with the energy difference  $\Delta\varepsilon$ . Two spins of the relevant electrons can be distributed over the split levels in five different ways. Configurations I, II, III, and IV are related to the singlet state while the only configuration V describes the triplet one. The latter is identical to the one with both spins directed down. As a result, the triplet state is spin-pure at any  $\Delta\varepsilon$ , while the singlet state is either purely covalent (configuration I) and, consequently, spin-pure at large  $\Delta\varepsilon$ , or is a mixture of configurations I-IV and becomes spin-mixed at lower  $\Delta\varepsilon$ . The energy difference  $\Delta\varepsilon$  turns out to be the main criterion for attributing the species to either covalently bonded or diradical species and the analysis of carbenes [19], [23] can be considered as the best example of this kind.



**Fig. 1** Diagram of the energy level and spin configurations of a lone electron pair.

The other problem is related to molecular magnets presented by dimers composed of two transition metal atoms surrounded by extended molecular ligands [24–26]. Two odd electrons are associated with metal atoms and their interaction is *a priori* weak. As previously noted, the triplet state is spin-pure while the singlet state is spin-mixed and is described by a combination of functions  $\Psi_1$ ,  $\Psi_2$ , and  $\Psi_3$  [27]. First attempts at an analysis of the electron interaction have been based on the direct consideration of configuration interaction [24, 25]. However, as pointed in [26], it is more natural to consider the electron interaction within the SCF approximation by using different MOs for electrons with different spins [28–30]. The method is indeed equivalent to that involving configuration interaction that was exemplified in the case of conjugated molecules [30]. Later, Noodleman [31] explicitly elaborated the technique, called the *broken symmetry approach* [32], making it a practically feasible computational scheme based on quantum-chemical spin-polarized technique.

Following these general concepts, the two fullerenes  $C_{60}$  and  $Si_{60}$  are the subject of the current study. The analysis has been done employing an extended computational experiment based on the framework of spin-polarised Hartree-Fock calculations which highlight the main characteristics that are responsible for the molecule's peculiar behavior.

### 3 Exchange Integrals

As shown for both diradicals [19], [20] and molecular magnets [25], the criterion based on the quantity  $\Delta\varepsilon$  forms the basis of a qualitative analysis of the phenomenon, important in tracing the behavior of the odd electrons, say, when changing the structural parameters

of the species. At the same time, as shown in the previous Section, the peculiarities of the odd electron pair behavior are caused by spin-mixing related to the singlet state of the pair. Therefore, the spin-dependent energy should be a more appropriate quantitative characteristic of the phenomenon. Actually, as mentioned earlier, the value of this energy gradually decreases when weakening the electron interaction as shown for the hydrogen molecule [15]. In its turn, decreasing the value under controlled conditions will indicate a larger deviation of the electron coupling from the covalent bonding. Therefore, the correct estimation of the value of this energy is important.

Let us consider two limiting cases of strong and weak electron interaction. Obviously, diatomic molecules cover the former case. According to the Heitler-London theory [14], the energy of states of spin multiplicity  $2S+1$ , where  $S$  is full spin of two atoms with spins  $S_A$  and  $S_B$  each, ranging from 0 to  $S_A + S_B$ , can be expressed as

$$E^{2S+1} = E(0) - 4S_A S_B J_{AB} \sim E'(0) + S(S-1)J_{AB}. \quad (1)$$

Here  $E(0)$  and/or  $E'(0)$  is the energy of the singlet state formed by covalently coupled electron pairs,  $S_A$  and  $S_B$  denote remained free spin of atoms  $A$  and  $B$ , integral  $J_{AB}$  describes the electron exchange. In case of homonuclear molecules,  $S_A^{\max} = S_B^{\max} = n/2$ , where  $n$  determines the number of unpaired electrons. The expression was inspired by the Heisenberg theory of ferromagnetism [33] and is quite useful in practice, in describing high-spin states of diatomic molecules [14]. The exchange integral is negative for the majority of molecules with only rare exceptions such as the oxygen molecule and a few others. That the high-spin states are spin-pure is implied by the appearance of the spin-dependent part in Eq.(1) in the form  $S(S-1)J_{AB}$  where the factor  $S(S-1)$  corresponds to the eigen value of operator  $\hat{S}^2$ . Applying to the general problem of odd electrons, Eq.(1) suggests the integral  $J_{AB}$  to be the main energy criterion of the electron behavior in the limit of strong interaction. In what follows, the expression will be used in the form

$$J = \frac{E^{2S_{\max}+1} - E^0}{S_{\max}(S_{\max} - 1)}, \quad (2)$$

where  $E^{2S_{\max}+1}$  and  $E^0$  are related to the states of the highest and the lowest multiplicities, respectively. A practical utility of the expression is due to the fact that both needed energies can be quite accurately determined by using modern quantum-chemical tools. The value  $E^0$ , related to covalently bound singlet state, is well determined by a closed-shell version of a selected technique while the  $E^{2S_{\max}+1}$  value, which corresponds to the ferromagnetic alignment of all spins, is given by an open-shell version of the technique. The ferromagnetic spin configuration is unique under any conditions (see Figure 1) so that the relevant solution is always true and the corresponding eigenfunctions satisfy both the Hamiltonian and the  $\hat{S}^2$  operator equations. We shall use a Hartree-Fock technique for the values determination so that Eq. (2) can be rewritten in the following way

$$J = \frac{E^{UHF}(S_{\max}) - E^{RHF}(0)}{S_{\max}(S_{\max} - 1)}. \quad (3)$$

Unlike the covalently bound, unique, one-determinant singlet state in the limit of strong interaction, the state becomes broken by both space and spin symmetry [34] when odd electron interaction weakens. As suggested in [31], the one-determinant singlet wave function in this case can be expressed as [35]:

$$|\Psi_B\rangle = (N!)^{-1/2} M^{-1/2} \det [(a_1 + cb_1)\alpha, a_2\alpha \dots a_n\alpha | (b_1 + ca_1)\beta, b_2\beta \dots b_n\beta] \\ \approx M^{-1/2} (\phi_1 + c\phi_2 + c\phi_3). \quad (4)$$

The principal determinant  $\phi_1$  describes pure covalent coupling of  $n$  odd electrons while small amounts of the charge transfer determinants  $\phi_2$  and  $\phi_3$ , corresponding to  $A^- - B^+$  and  $A^+ - B^-$  configurations (see II and III in Fig.1) are mixed in due to non-orthogonality of atomic orbitals  $\overline{a_1} = a_1 + cb_1$  and  $\overline{b_1} = b_1 + ca_1$ . The open shell manner for the function  $|\psi_B\rangle$  is just appropriate to distinguish electron spins of atoms  $A$  and  $B$ . The function corresponds to the antiferromagnetic (AF) alignment of spins of odd electrons.

As shown in [31], the energy of the above AF state is a specific weighted average of the energies of the pure spin multiplets. On the other hand, according to Eq. (4) it can be expressed as

$$E_B \equiv E_{AF}^{UHF} = E_{cov} - E_{rad} \quad , \quad (5)$$

where the last term on the right hand side is due to the ionic contributions and is an independent *measure* of the extraction of odd electrons from the covalent coupling. The term may be called as the *energy* of either *radicalization*, or *spin-mixing*, or *non-covalence* depending on which aspect is to be emphasized. In what follows we shall prefer to call it radicalization. Since both energies  $E_{AF}^{UHF}$  and  $E_{cov} = E_{AF}^{RHF}$  can be calculated within the same QCh approach by using the corresponding open shell and closed shell versions, the  $E_{rad}$  energy can be readily evaluated as the difference  $E_{rad} = E_{AF}^{RHF} - E_{AF}^{UHF}$ . Since ionic energies are always negative,  $E_{rad} \geq 0$ .

When odd electrons are covalently coupled,  $E_{AF}^{UHF} = E_{AF}^{RHF}$  and, consequently,  $E_{rad} = 0$ . The corresponding exchange integral  $J$  which provides the high-spin series of the electron energies has to be determined by Eq.(3). In its turn,  $E_{rad} \neq 0$  is an unambiguous indication that the odd electron coupling deviates from the covalent one. As suggested in [31], the  $J$  values can be determined from the following expressions:

$$E_{AF}^{UHF} = E_F^{UHF} + S_{\max}^2 J, \quad (6)$$

and

$$J = \frac{E_{AF}^{UHF} - E_F^{UHF}}{S_{\max}^2}, \quad (7)$$

where  $E_{AF}^{UHF}$  and  $E_F^{UHF}$  correspond to the lowest ( $S=0$ ) and highest ( $S = S_{\max}$ ) multiplicity of the  $n$  electron system and are determined by one of the spin-polarized UHF techniques. As has been already mentioned, the ferromagnetic state always corresponds to a true solution of the relevant QCh equations. According to [31], energies of the series of high-spin-pure states are described by

$$E(S) = E_{AF}(0) - \frac{S(S+1)}{S_{\max}^2} (E_{AF}^{UHF} - E_F^{UHF}) = E_{AF}(0) - S(S+1)J, \quad (8)$$

where the pure singlet state has the form

$$E_{AF}(0) = E_F^{UHF} + S_{\max}(S_{\max} + 1)J = E_{AF}^{UHF} + S_{\max}J. \quad (9)$$

It is important to note that Eqs. (3), (6)-(9) are valid not only for lone pair of odd electrons. They retain their form in the case of  $n$  identical pairs with the difference that the exchange integral  $J$  is substituted by  $\sim J/n$ . In the weak interaction limit it is derived from the explicit expressions for the integral [31]. In the limit of strong interaction it was proved by a comparative study of the  $H_2$  and  $H_6$  systems [15, 36].

Eqs. (3), (7) and (8) form the basis of the carried computational experiment which is aimed at the analysis of the odd electron properties of two fullerene molecules  $C_{60}$  and  $Si_{60}$ . The computations have been performed by using semiempirical spin-polarized CLUSTER-Z1 sequential codes [37] in the version which is adequate for the AM1 technique [38]. In addition, two other quantities were calculated, namely, eigenvalues of the  $\hat{S}^2$  operator [29], [39]

$$(S^{**2})^{UHF} = 1/4(N_{\alpha} - N_{\beta})^2 + 1/2|N_{\alpha} - N_{\beta}| - Sp(P^{\alpha} S P^{\beta} S) \quad (10)$$

and spin density at atom  $A$

$$D_{sp,A} = \sum_{i \in A} P_{ii}^{\alpha} - P_{ii}^{\beta}. \quad (11)$$

Here  $N_{\alpha}$  and  $N_{\beta}$  ( $N_{\alpha} \geq N_{\beta}$ ,  $N_{\alpha} + N_{\beta} = N$ ,) are the numbers of electron with spin up and down, respectively,  $N$  is the total number of electrons while  $P^{\alpha}$  and  $P^{\beta}$  denote the relevant density matrices. A comparison of the  $(S^{**2})^{UHF}$  values [40] with the exact  $(S^{**2}) = S(S - 1)$  makes possible an analysis of the purity of the considered spin states [41].

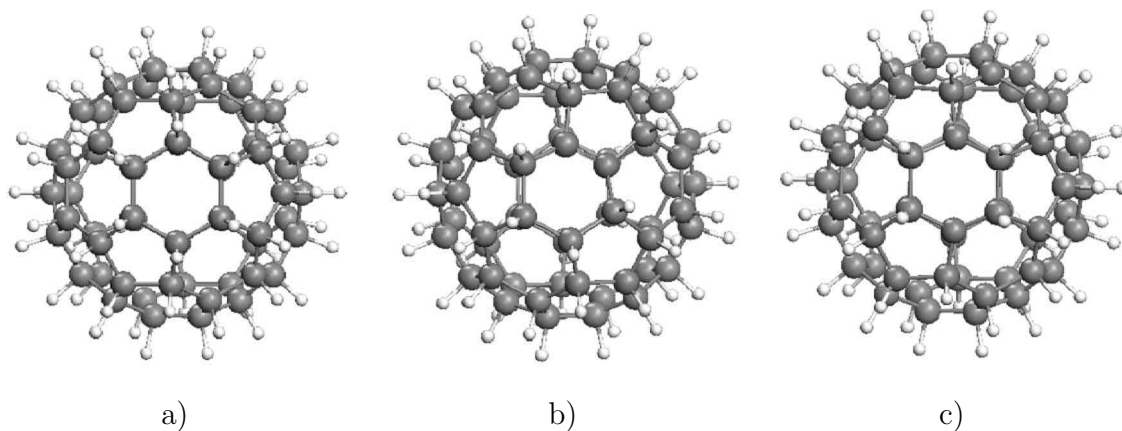
## 4 Results

### 4.1 One Electron Pair in the $X_{60}$ Structure

In both organic and silicon chemistry the atom composition of pairs with odd electrons is rather variable (see, for example, [16], [20]). In what follows, we shall restrict ourselves to the pairs of the  $>C-C<$  and  $>Si-Si<$  (and later  $>X-X<$ ) type only, where each atom is connected with three neighbors and which are characteristic of fullerenes  $X_{60}$ . Individual pairs in the fullerene structure can be formed by a virtual dehydrogenation of the  $X_{60}H_{60}$  molecules, as shown in Figure 2. Both basic molecules are tightly bonded covalently with  $E_{rad} = 0$  (see Table 1). Similar hexagon fragments were selected within the molecule structure which were then partially dehydrogenated that resulted in the formation of 1,2- and 1,4- pairs of odd electrons. The calculated values  $E^{RHF}$ ,  $E_{AF}^{UHF}$ , and  $E_F^{UHF}(S_{\max} = 1)$  are listed in Table 1 [44]. Eq. (3) was used when determining exchange parameter  $J$  for pairs with  $E_{rad} = 0$  while Eq. (7) was applied to determine  $J$  for pairs with  $E_{rad} > 0$ .

According to Hoffman's classification [19], the first of the above mentioned pairs is related to *via space* pair while the other to *via bond* pair. As seen from the table, the

formation of the 1,2-pair in the  $C_{60}H_{58}$  molecule does not disturb the covalent bonding since, as previously,  $E_{rad} = 0$  so that  $E_{AF}^{UHF}$  and  $E_F^{UHF}$  describe spin-pure states with spin density at atoms equal either to zero or to one in the singlet and triplet states, respectively.



**Fig. 2** Molecules  $X_{60}H_{60}$  (a) and  $X_{60}H_{58}$  with 1,2- (b) and 1,4- (c) pairs of odd electrons.

Exchange parameter  $J$  is rather large and similar to that of the ethylene molecule (see Table 1). The other pair of the  $C_{60}H_{58}$  molecule is characterized by a significant energy  $E_{rad}$ , small exchange parameter  $J$  and noticeable deviation of the calculated values  $(S^{**2})^{UHF}$  from the exact ones. Taken together, the features undoubtedly show the deviation from the covalent coupling in the pair hence compelling us to take it as a diradical as conventionally accepted.

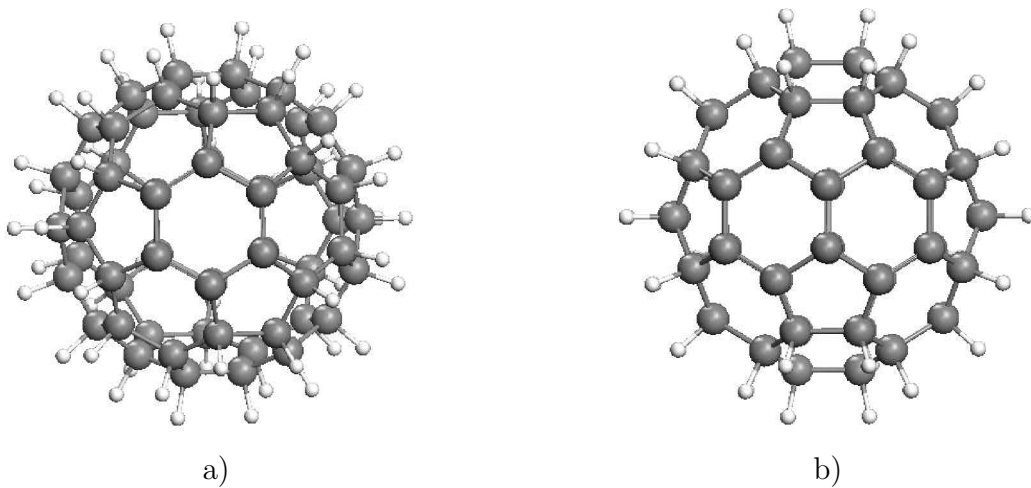
Contrary to the carbon species, the formation of any pair in the  $Si_{60}H_{58}$  molecule is followed by obvious diradical effects. Thus, energy  $E_{rad} > 0$  for both pairs; the values of  $(S^{**2})^{UHF}$  differ from the exact ones; atomic spin density  $D_{sp,A}$  at the pair atoms is large in the spin-mixed singlet state and considerably exceeds 1 in the triplet. As stated earlier, the 1,2-pair and 1,4- pair differ rather drastically. The diradical character of both pairs is quite obvious. The characteristics of the  $Si_{60}H_{58}$  molecule pairs discussed here are similar to those of silicoethylene (see Table 1). As is well-known [45], the latter does not exist in the gaseous state and is mentioned with respect to silicoethylene polymer that might be explained by its evidently diradical character.

## 4.2 Set of Odd Electron Pairs in the $X_{60}$ Structures

While lone odd electron pairs have been studied at least qualitatively and semi-quantitatively [19], [20], [23], the only study of a cyclic  $H_6$  cluster [15], [36] can be attributed to the examination of the pair sets. At the same time sets of pairs  $>C-C<$  and  $>Si-Si<$  are not a rarity for both organic and silicon chemistry. It suffices to mention the extensive class of aromatic compounds.

Since hexagon motive  $X_6$  is deeply inherent in fullerene structures, its exploitation as a model set of odd electron pairs seems quite natural. Additionally,  $X_{10}$  configuration

demands attention since there are strong arguments to consider perdehydronaphthalene  $C_{10}$  as a building stone of the  $C_{60}$  molecule [46–48]. The corresponding two fragments studied in the current paper are shown in Figure 3 in the form of  $X_{60}H_{54}$  and  $X_{60}H_{50}$  molecules. As stated earlier, those are formed by a virtual dehydrogenation of the basic  $X_{60}H_{60}$  species. Two molecular species  $X_6H_6$  and  $X_{10}H_8$  are added to provide a more complete picture of the pair sets.  $X_{60}$  molecules complete the study. The calculated characteristics are given in Tables 2 and 3.



**Fig. 3** Molecules  $X_{60}H_{54}$  (a) and  $X_{60}H_{50}$  (b) with  $X_6$  and  $X_{10}$  fragments, respectively.

**$X_6H_6$  and  $X_6$  fragment** There are three electron pairs in the molecular structures,  $S_{\max} = 3$ , and the relevant state of the ferromagnetic aligning of six spins corresponds to a septet. As seen from Table 2, the  $C_6H_6$  molecule is tightly bound covalently,  $E_{rad} = 0$ . Both singlet and septet states are spin-pure, however, the singlet state spin density is slightly different from zero and is regularly distributed over atoms of the molecule with values shown in the table. The exchange parameter  $J$  is still large, yet lower compared to that of ethylene molecule. The benzene fragment  $C_6$  of the  $C_{60}H_{54}$  molecule behaves in a fully similar manner so that its formation does not affect the covalent bonding. As in the case of the  $C_6H_6$  molecule, singlet state spin density on the benzene fragment atoms is also nonzero and larger than previously.

An alternative picture (see Table 3) can be seen for the  $Si_6H_6$  molecule while both the molecule itself and its  $Si_6$  analogue in the  $Si_{60}H_{54}$  species behave quite similarly. Those are characterized by large values of  $E_{rad}$ , a small parameter  $J$  and similar values of atomic spin densities, in both singlet and septet state. The latter is sufficiently spin-pure while the singlet state is evidently spin-mixed since the obtained  $(S^{**2})^{UHF}$  value differs significantly from zero. The discussed features lead to the compelling conclusion that both silicobenzene molecule and its analogue in the  $Si_{60}H_{54}$  molecule should be attributed to *polyradicals*.

**$X_{10}H_8$  and  $X_{10}$  fragment** There are five odd electron pairs in the molecular species,  $S_{\max} = 5$ , and the multiplicity of the ferromagnetic state is 11. Analyzing data given in



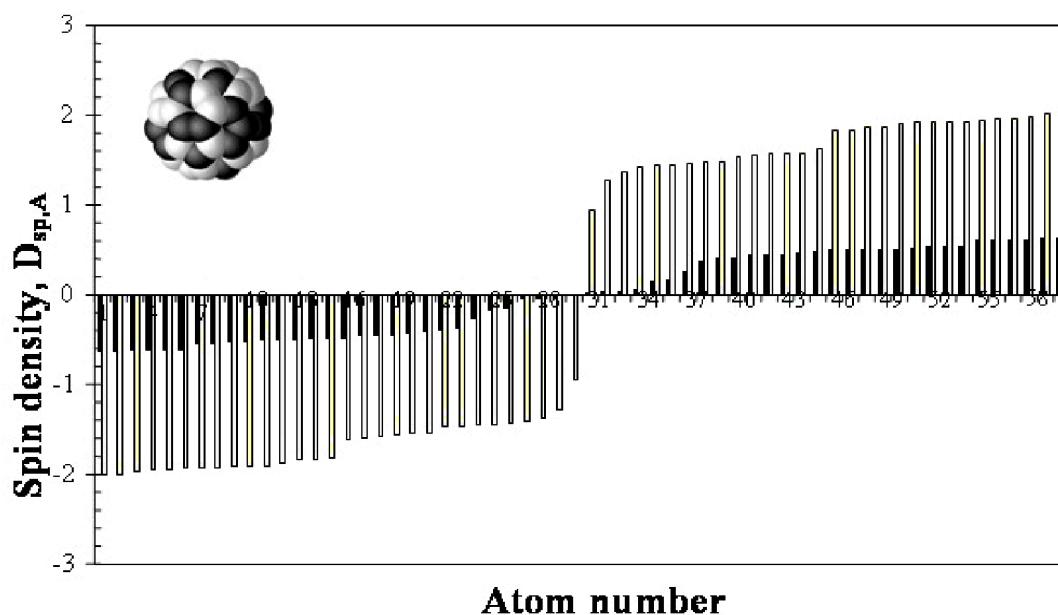
Table 2, an unexpected discovery can be made concerning the violation of the molecule covalent bonding in the naphthalene  $C_{10}H_8$ . To the best of our knowledge, the stability of the covalent bound singlet state of the molecule has never been in doubt. However, calculations show that not only  $E_{rad}$  noticeably differs from zero, but  $(S^{**2})^{UHF}$  is non-zero as well, showing spin-mixed character of the singlet state. High values of atomic spin density are also remarkable. The findings show convincingly a polyradical behavior of the molecule, though not too strong. As seen from Table 2, this tendency is not only kept, but even strengthened for the  $C_{10}$  fragment in the  $C_{60}H_{50}$  molecule. Assuming the fragment to be a building stone of the  $C_{60}$  molecule [39–41], its properties may genetically forecast a possible polyradical character of  $C_{60}$  [49].

The data in Table 3 related to siliconathtalene and  $Si_{10}$  fragment of the  $Si_{60}H_{50}$  molecule leave no doubts concerning the polyradical character of both molecules. Evidently, the effect is much bigger compared to that of the carbon species. For both silicon species  $E_{rad}$  are large,  $(S^{**2})^{UHF}$  drastically differs from zero for singlet states and even in the ferromagnetic states the  $(S^{**2})^{UHF}$  values do not coincide with the exact ones. The latter is followed by a non-regular distribution of the atomic spin density over atoms.

**Fullerenes  $C_{60}$  and  $Si_{60}$**  There are 30 odd electron pairs in each molecule,  $S_{max} = 30$ , and the multiplicity of the states with ferromagnetic alignment of all 60 spins is 61. As seen from Tables 2 and 3,  $E_{rad} > 0$  for both molecules, for the  $Si_{60}$  just drastically. The UHF singlet states are spin-mixed, and again, the mixing for silicon species is enormously large as seen from the deviation of the  $(S^{**2})^{UHF}$  values from zero. In both cases the atomic spin density is quite large and is distributed over atoms in a rather complicated manner. Figure 4 presents the spin density distribution in such a manner that the determined value gradually grows from the left to the right while the sums over the values in both cases are zero. White-and-black image of the  $X_{60}$  molecule shown in the figure insert highlights the space distribution of positive and negative spin density over atoms. Taken together, the presented data make a polyradical character of the odd electron bonding in both molecules fully evident.

## 5 Discussion

The above analysis has convincingly shown that  $X_{60}$  fullerene composition of atoms with odd electrons results in weakening the covalent bonding that is just drastic in the case of silicon species. To describe the phenomenon concisely, the term *polyradicalization* has been suggested in order to emphasize the fact that a rather peculiar chemical behavior should be expected from the species. As shown in the study, four parameters can be proposed to describe the effect quantitatively. The main parameter  $E_{rad} = E^{RHF} - E_{AF}^{UHF}$  indicates in a straightforward manner the weakening of the bonding, when it is non-zero. Three other parameters, namely, exchange parameter  $J$ ,  $(S^{**2})^{UHF}$ , and  $D_{sp,A}$ , describe quantitatively the conditions under which the weakening occurs. Taken together, they provide a complete picture of the phenomenon discussed. Additionally,



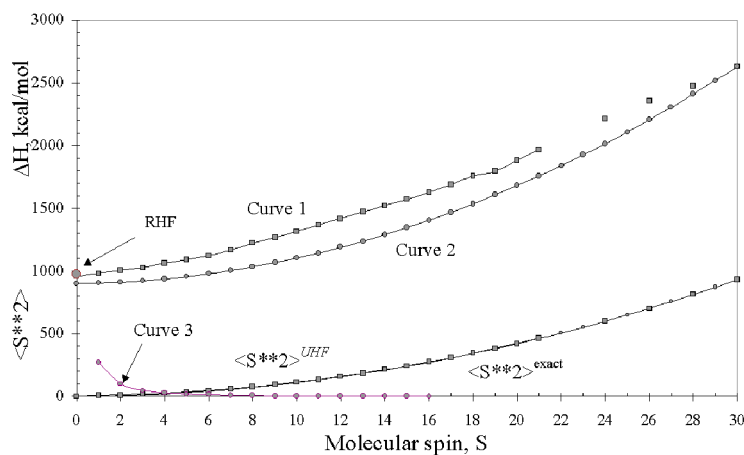
**Fig. 4** Spin density distribution over atoms of molecule  $C_{60}$  (dense black bars) and  $Si_{60}$  (contour bars) in the UHF singlet state. Insert: space distribution of the density for the  $Si_{60}$  molecule.

the computational approach employed makes it possible to determine the energy of high-spin states of the studied compounds. Figure 5 presents the data related to  $E(S)$  and  $(S^{**2})^{UHF}$  calculated in accordance with Eqs. (8) and (10) for both  $C_{60}$  and  $Si_{60}$  species. The series of the  $E^{UHF}(S)$  energies of spin-mixed states, calculated in a straightforward manner by using the applied tool, are included for comparison. As seen from the figure, the difference between the series of spin-pure and spin-mixed states is not too large as might be expected. This is much more surprising since the calculated  $E^{UHF}(S)$  relate to the optimized structures which are different for different spin states, sometimes rather significantly, while the  $E(S)$  series is related to the same structure. It may be concluded that the applied spin-polarized QCh tool provides a quite reliable presentation of high-spin states. Curves 3 in the figure plots the ratio

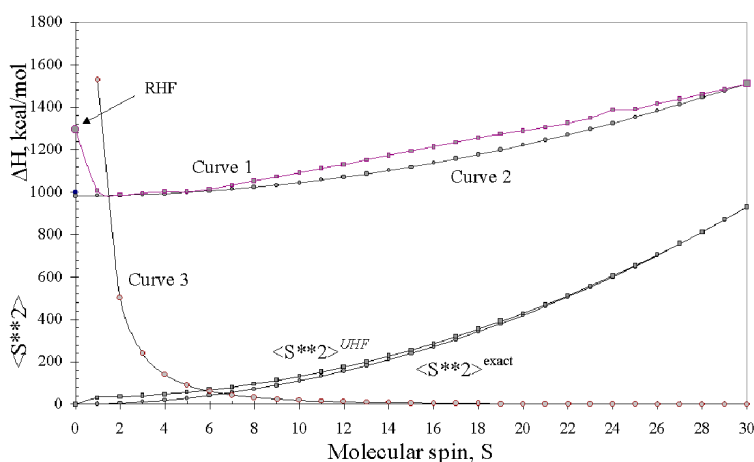
$$\zeta(\%) = \frac{(S^{**2})^{UHF} - S(S-1)}{S(S-1)},$$

which characterizes spin purity of the states. As seen from the figure, in the case of  $C_{60}$ , the high-spin states become spin-pure at rather low spin values while only at high spins the similar is observed for the  $Si_{60}$  molecule.

Even in the earliest studies of diradicals, Hoffman [17–19] and other authors [20] have tried to exhibit the criterion of the transition from covalent pairing to odd electron pair radicalization. However, only the energy difference  $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$  between the energies of two orbitals of the pair was suggested that was not enough to formalize the criterion. A considerable extension of the number of quantitative parameters, readily accessible by the modern spin-polarized QCh techniques, makes it now possible to suggest a formal criterion



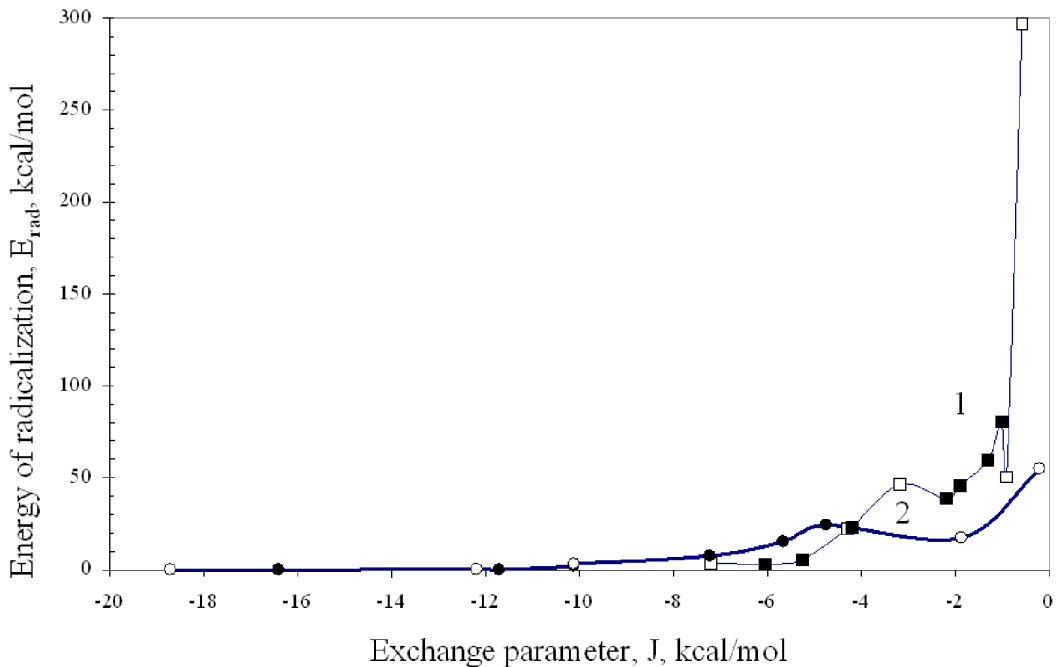
a)



b)

**Fig. 5** Heat of formation of the UHF- (curves 1) and pure- (curves 2) spin states of the molecules  $C_{60}$  (a) and  $Si_{60}$  (b); RHF singlet states are shown by arrows; curves 3 present  $\zeta$  values (see text).

for the transition. Figure 6 illustrates the behavior of  $E_{rad}$  versus exchange parameter  $J$  on the basis of the data summarized in Table 4. It is seen that the dependence for both carbon and silicon species is quite similar and clearly exhibits a quasi-threshold character. One may conclude that for the studied species the transition starts when  $J$  reaches  $\sim 10$  kcal/mol. The behavior of  $E_{rad}(J)$ , or more precisely, the steepness of the curves after transition, truly formalizes the difference in the polyradicalization of different species. As seen in the figure, the steepness is a few times more for the silicon species in comparison with carbon molecules. The obvious preference shown by silicon atoms towards polyradicalization instead of double bond formation is well supported by high values of atomic spin densities (see Tables 1 and 2). The latter quantity, in turn, is provided by electrons taken out of chemical bonding [50]. Actually, Figure 7 presents absolute values of the atom spin density  $|D_{sp,A}|$  multiplied by an electron spin, and atom



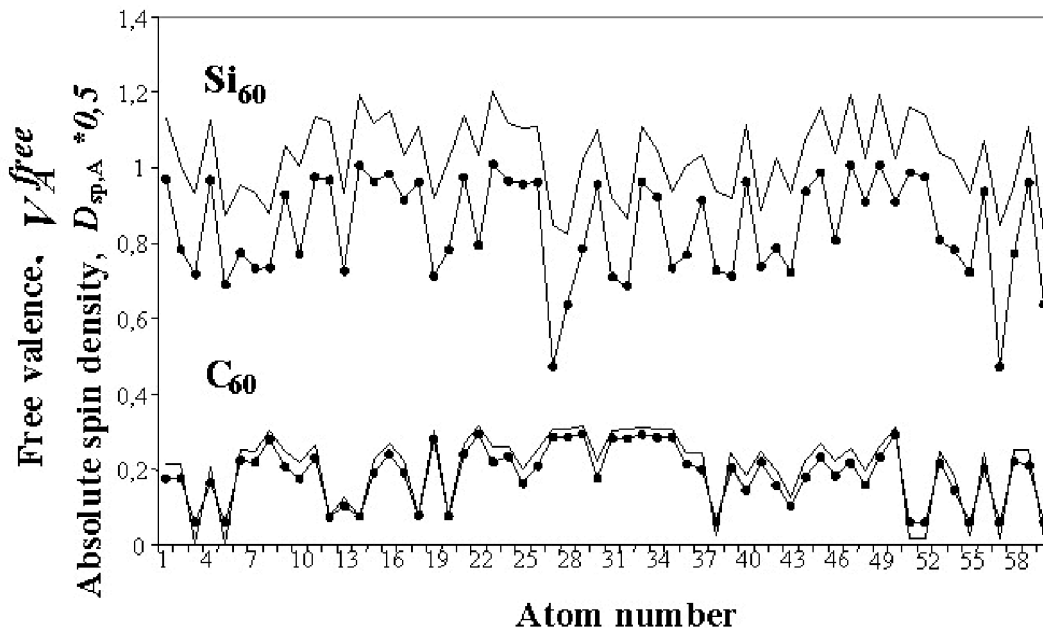
**Fig. 6** Energy of polyradicalization versus exchange parameter  $J$  for odd electron pairs  $>Si-Si<$  (1) and  $>C-C<$  (2). Empty and filled points correspond to fullerene and “aromatic B structures”, respectively

free valence  $V_A^{free}$  distributed over the molecules atoms. The latter is determined as:

$$V_A^{free} = N_{val}^A - \sum_{B \neq A} K_{AB}, \quad (12)$$

where  $N_{val}^A$  is the number of valence electrons of atom  $A$  while  $\sum_{B \neq A} K_{AB}$  presents a generalized bond index [51], summarized over all atoms excluding atom  $A$ . A close similarity should be noted between the two values, which are calculated independently. Taken together, the data present a quantitative explanation of the difference in bonding carbon and silicon atoms, showing how much every odd electron is free of bonding. Therefore, silicon fullerene is, on average, made of  $\sim 100\%$  polyradical while its carbon counterpart is only of  $\sim 20\%$  polyradical. This observation explains why silicon atoms “dislike”  $sp_2$  hybridization [9,10]. On the other hand, this can be described as follows. While carbon atom interaction leads the odd electron to participate in the action thus strengthening it, silicon atoms prefer to leave the odd electrons free in a form of spin density, while the atom interaction is kept at much weaker level. As a result, the electronic structure of carbon atom happens to be quite labile or soft while that of silicon atom is much more rigid. The difference could be naturally explained in terms of the difference in the length of C-C and Si-Si bonds that differ by about 0.1 nm. As shown by the example of ‘via space’ and ‘via bond’ lone C-C pairs in Section 3.1, changing the intra-pair distance from 0.134 to 0.267 nm indeed results in a drastic strengthening of the radical character of the pair. However, in the case of silicon species, the difference is still large so that some other silicon individual characteristics are important. The obtained findings throw light

as well on why "A comparison of the chemistry of tetravalent carbon and silicon reveals such gross differences that the pitfalls of casual analogies should be apparent" [54].



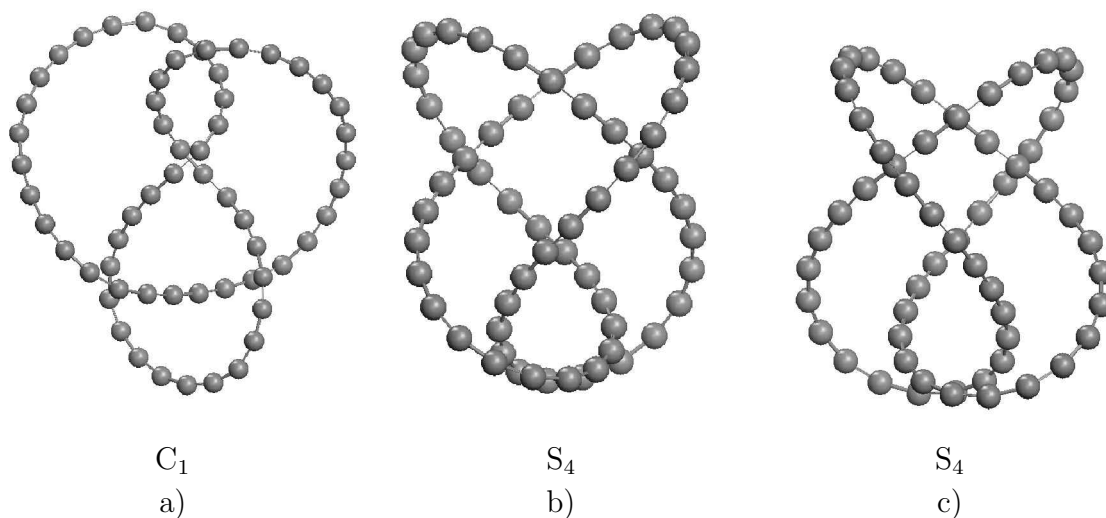
**Fig. 7** Free valence (solid curves) and absolute spin density (dotted curves) distributed over atoms of  $C_{60}$  and  $Si_{60}$  molecules.

Thus the disclosed polyradical character of the basic fullerene molecule  $C_{60}$  is indeed consistent with extreme diversity of its properties which sometimes seem to be somewhat contradictory. It suffices to mention, for example, the diamagnetism of a free molecule and pristine  $C_{60}$  crystals [55, 56] and a ferromagnetic behavior of either carpet-like polymerized crystalline species [57] or TDAE-  $C_{60}$  charge complex [58], [59]. However, even Salem and Rowland have already stated [20] that diradical electronic structure is readily amenable to any external effects caused by either intramolecular chemical substitution or by intermolecular interaction. Actually, our recent studies have shown that the above mentioned peculiarities in the magnetic behavior are closely connected with changing the main polyradical characteristics  $E_{rad}$ ,  $J$ , and  $D_{sp,A}$ .

A peculiar influence of the molecular structure when keeping the chemical composition can be demonstrated for the  $C_{60}$  molecule in the shape of 4<sub>1</sub> knot [60]. Figure 8 shows a starting and two equilibrated structures related to the RHF and UHF singlet states while Table 5 presents main characteristic of the electronic state.

As seen from the figure and the table, both computational schemes result in quite similar molecular structures of  $S_4$  symmetry with constant length C-C bonds, shorter in the case of the UHF approach. As a result, the radical character of the molecule is clearly evident. The energy of radicalization is large and constitutes 286.51 kcal/mol; similarly large is the UHF squared spin value. Spin density at atoms of  $\sim \pm 1$  is quite uniformly distributed over atoms, pointing to  $\sim 50\%$ - radicalization of the molecule.

Another example of “strange” or anomalous behavior of the  $C_{60}$  admixtures such as effective inhibition of radical destruction of polystyrene [61] as well as sensitization of penetration through cell membranes [62] should be obviously analyzed from this viewpoint.



**Fig. 8** Starting (a) and equilibrated structures of the  $C_{60}4_1$  knot composition in the singlet RHF (b) and UHF (c) state.

The polyradical character of the  $Si_{60}$  molecule is supported experimentally even more clearly. The first consequence provided by the phenomenon may be formulated as a prohibition of the existence of particular chemical entities and even whole classes such as alkenes, alkynes, aromatic compounds, and fullerenes, typical for its carbon analogue. Only polyradicalization suppression can provide chemical stability that in the latter case may be realized in the form of  $Si_{60}H_{60}$  and  $Si_{60}C_{60}$  species [9], [10]. The very high susceptibility of silicon atoms to polyradicalization provides the reason for the magnetism of its crystal surfaces [63] that has already become a physical reality in contrast to the absence of similar effects for diamond crystal.

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Molecular species	Quantity	RHF	UHF (S=0)	UHF (S <sub>max</sub> )	<i>E<sub>rad</sub></i>
C <sub>60</sub> H <sub>60</sub>	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup>	334.161	334.161 0		0
C <sub>60</sub> H <sub>58</sub> 1,2-pair	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup> <i>D<sub>sp,A</sub></i> <i>J</i> , kcal/mol	316.319	316.315 0 0/0	352.457 2.021 1/1	0.004
C <sub>60</sub> H <sub>58</sub> 1,4-pair	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup> <i>D<sub>sp,A</sub></i> <i>J</i> , kcal/mol	389.304	334.422 1.031 -1.03/+1.03	334.623 2.027 +1.02/+1.02	54.88
Ethylene	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup> <i>D<sub>sp,A</sub></i> <i>J</i> , kcal/mol	16.449	16.449 0 0/0	49.241 2.008 +1.02/+1.02	0
Si <sub>60</sub> H <sub>60</sub>	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup>	441.599	441.597 0		0.002
Si <sub>60</sub> H <sub>58</sub> 1,2-pair	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup> <i>D<sub>sp,A</sub></i> <i>J</i> , kcal/mol	461.070	457.430 1.050 -1.5/+1.5	464.639 2.148 +1.31/+1.31	3.64
Si <sub>60</sub> H <sub>58</sub> 1,4-pair	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup> <i>D<sub>sp,A</sub></i> <i>J</i> , kcal/mol	504.097	453.606 1.383 -1.63/+1.63	454.510 2.269 +1.55/+1.55	50.49
Silicoethylene	$\Delta H$ , kcal/mol (S <sup>**2</sup> ) <sup>UHF</sup> <i>D<sub>sp,A</sub></i> <i>J</i> , kcal/mol	54.502	48.934 0.899 -1.33/+1.33	54.185 2.017 +1.17/+1.17	5.57

<sup>1</sup> Ethylene and silicoethylene are calculated in the current study.

**Table 1** Energetic characteristics of a lone pair of odd electrons in the X<sub>60</sub> structures<sup>1</sup>.

Molecular species	Quantity	RHF	UHF (S=0)	UHF (S <sub>max</sub> )	<i>E<sub>rad</sub></i>
C <sub>6</sub> H <sub>6</sub>	ΔH, kcal/mol	21.954	21.952	162.350	0.002
	(S * *2) <sup>UHF</sup>	0	0	12.016	
	<i>D<sub>sp,A</sub></i>	0	-0.15/+0.15	1.01	
	<i>J</i> , kcal/mol		-11.70		
C <sub>6</sub> fragment in C <sub>60</sub> H <sub>54</sub>	ΔH, kcal/mol	330.476	330.292	484.045	0.18
	(S * *2) <sup>UHF</sup>	0	0.207	12.027	
	<i>D<sub>sp,A</sub></i>	0	-0.29/+0.29	1.09	
	<i>J</i> , kcal/mol		-12.80		
C <sub>10</sub> H <sub>8</sub>	ΔH, kcal/mol	40.466	38.619	291.512	1.85
	(S * *2) <sup>UHF</sup>	0	0.743	30.025	
	<i>D<sub>sp,A</sub></i>	0	-(0.41–0.47)/ +(0.41–0.47)	(0.97–1.09)	
	<i>J</i> , kcal/mol		-10.12		
C <sub>10</sub> fragment in C <sub>60</sub> H <sub>50</sub>	ΔH, kcal/mol	363.146	360.027	612.829	3.12
	(S * *2) <sup>UHF</sup>	0	1.009	30.035	
	<i>D<sub>sp,A</sub></i>	0	-(0.50–0.52)/ +(0.50–0.52)	(0.96–0.97)	
	<i>J</i> , kcal/mol		-10.11		
C <sub>60</sub>	ΔH, kcal/mol	972.697	955.380	2629.790	17.32
	(S * *2) <sup>UHF</sup>	0	4.937	930.386	
	<i>D<sub>sp,A</sub></i>	0	±(0.61 – 0)	1.0–0.8	
	<i>J</i> , kcal/mol		-1.86		

<sup>1</sup> Data dispersion is given in brackets.

**Table 2** Energetic characteristics of sets of odd electrons pairs in the C<sub>60</sub> structures<sup>1</sup>.

Molecular species	Quantity	RHF	UHF (S=0)	UHF (S <sub>max</sub> )	<i>E<sub>rad</sub></i>
Si <sub>6</sub> H <sub>6</sub>	ΔH, kcal/mol	144.509	121.246	158.973	23.26
	(S**2) <sup>UHF</sup>	0	2.678	12.029	
	<i>D<sub>sp,A</sub></i>	0	-1.51/+1.51	1.09	
	<i>J</i> , kcal/mol			-4.19	
Si <sub>6</sub> fragment in Si <sub>60</sub> H <sub>54</sub>	ΔH, kcal/mol	511.168	488.902	527.641	22.27
	(S**2) <sup>UHF</sup>		3.174	12.164	
	<i>D<sub>sp,A</sub></i>		-1.67/+1/67	1.14-1.09	
	<i>J</i> , kcal/mol			-4.30	
Si <sub>10</sub> H <sub>8</sub>	ΔH, kcal/mol	226.706	188.134	242.668	38.57
	(S**2) <sup>UHF</sup>	0	4.609	30.457	
	<i>D<sub>sp,A</sub></i>	0	-(1.53–1.71)/ + (1.53–1.71)	complicated distribution	
	<i>J</i> , kcal/mol			-2.18	
Si <sub>10</sub> fragment in Si <sub>60</sub> H <sub>50</sub>	ΔH, kcal/mol	566.321	519.85	599.43	46.47
	(S**2) <sup>UHF</sup>	0	5.585	31.347	
	<i>D<sub>sp,A</sub></i>	0	-(1.68–1.93)/ + (1.68–1.93)	complicated distribution	
	<i>J</i> , kcal/mol			-3.18	
Si <sub>60</sub>	ΔH, kcal/mol	1295.988	999.215	1513.208	296.77
	(S**2) <sup>UHF</sup>	0	31.764	930.576	
	<i>D<sub>sp,A</sub></i>	0		(0.98–1.01)	
	<i>J</i> , kcal/mol			-0.57	

<sup>1</sup> Data dispersion is given in brackets.

**Table 3** Energetic characteristics of sets of odd electrons pairs in the Si<sub>60</sub> structures<sup>1</sup>.

Molecular species	Carbon		Silicon	
	$E_{rad}$	J	$E_{rad}$	J
X <sub>2</sub> H <sub>4</sub>	0.00	-16.40	5.57	-5.25
1,2 pair X <sub>60</sub> H <sub>58</sub>	0.004	-18.07	3.64	-7.21
1,4 pair X <sub>60</sub> H <sub>58</sub>	54.88	-0.20	50.49	-0.90
X <sub>6</sub> H <sub>6</sub>	0.002	-11.70	23.26	-4.19
X <sub>6</sub> fragment of X <sub>60</sub> H <sub>54</sub>	0.18	-12.80	22.27	-4.30
X <sub>10</sub> H <sub>8</sub>	1.85	-10.12	38.57	-2.18
X <sub>10</sub> fragment of X <sub>60</sub> H <sub>50</sub>	3.12	-10.11	46.47	-3.18
X <sub>14</sub> H <sub>10</sub>	7.45	-7.22	45.97	-1.90
X <sub>18</sub> H <sub>12</sub>	15.32	-5.66	59.53	-1.29
X <sub>22</sub> H <sub>14</sub>	24.23	-4.74	80.22	-1.01
X <sub>60</sub>	17.32	-1.86	296.77	-0.57

**Table 4** Fundamental energetic parameters of >X-X< odd electron pairs, kcal/mol.

Quantity	RHF	UHF(S=0)
$\Delta H$ , kcal/mol	1961.45	1674.94
$\langle C-C \rangle$ , Å	1.273	1.282
Bond order	1.825	1.633
( $S^{**2}$ )	0	18.13
$D_{sp,A}$	0	+1.13/-1.13

**Table 5** Electronic characteristics of the  $C_{60}$  4<sub>1</sub> knot in the singlet state.