Hyperfine Interactions in Graphene and Related Carbon Nanostructures

Oleg V. Yazyev
Ecole Polytechnique Fédérale de Lausanne (EPFL),
Institute of Chemical Sciences and Engineering, CH-1015 Lausanne, Switzerland
(Dated: August 30, 2018)

Hyperfine interactions, magnetic interactions between the spins of electrons and nuclei, in graphene and related carbon nanostructures are studied. By using a combination of accurate first principles calculations on graphene fragments and statistical analysis, I show that both isotropic and dipolar hyperfine interactions can be accurately described in terms of the local electron spin distribution and atomic structure. A complete set of parameters describing the hyperfine interactions of $^{13}$C and other nuclear spins at substitution impurities and edge terminations is determined.

PACS numbers: 71.70.Jp, 81.05.Uw, 85.75.-d, 03.67.Pp

Graphene and related carbon nanostructures are considered as potential building blocks of future electronics, including spintronics [1] and quantum information processing based on electron spins [2] or nuclear spins [3]. Carbon nanostructures are attractive for these applications because of the weak spin-orbit interaction in materials made of light elements [4, 5]. Promising results for the spin-polarized current lifetimes in carbon nanotubes [6, 7, 8] and graphene [9] unambiguously confirm the potential of these materials. A number of quantum dot devices, components of solid-state quantum computers, based on carbon nanostructures have been proposed recently [10, 11, 12, 13]. Hyperfine interactions (HFIs), the weak magnetic interactions between the spins of electrons and nuclei, become increasingly important on the nanoscale. In carbon nanostructures the interactions of electron spins with an ensemble of nuclear spins are expected to be the leading contribution to the electron spin decoherence [4, 7, 14]. Minimizing HFIs is thus necessary for achieving longer electron spin coherence times [15]. In some other instances the HFIs play an important role as a link between the spins of electrons and nuclei in the nanostructures [3, 10, 16, 17, 18] underlying the implementations of quantum information processing involving nuclear spins. Probing HFIs with magnetic resonance techniques also provides a wealth of information about structure and dynamics of carbon materials [19]. A common understanding and an ability to control the HFIs are thus necessary for engineering future electronic devices based on graphene and related nanostructures.

In this Letter, I study the hyperfine interactions in carbon nanostructures by using a combination of accurate first principles calculations on graphene fragments and statistical analysis. I show that the interaction of the conduction (low-energy) $\pi$ electron spins with nuclear spins can be described in terms of only the local (on-site and first-nearest-neighbor) $\pi$ electron spin distribution and the local atomic structure. The conduction electron spin distribution can be determined using simpler computational approaches (e.g. tight binding or analytical approximations [21, 21]) and tuned by tailoring nanosstructure dimensions and applying external fields [22, 23]. The effective spin-Hamiltonian of the HFI between the electron spin $S$ and the nuclear spin $I$ can be written as

$$\mathcal{H}_{\text{HFI}} = \frac{\rho_e(r)}{r} + \frac{\rho(r)}{\sqrt{2}} + \frac{\rho(c)}{\sqrt{3}}$$

where $\rho_e(r)$, $\rho(r)$, and $\rho(c)$ are the electron, total, and nuclei spin densities, respectively.

The all-electron density functional theory (DFT) calculations [24] were performed using a combination of the EPR-III Gaussian orbital basis set [25] specially tailored for the calculations of hyperfine couplings and the B3LYP exchange-correlation hybrid density functional [26]. This computational protocol (see Ref. [27] for details) can be applied to molecules of limited size and predicts hyperfine coupling constants (HFCCs) in excellent agreement with experimental results [27]. Spin-orbit and relativistic effects which are not important for the calculation of HFIs in light-element systems [28] have been neglected. For a set of representative experimentally measured $^{13}$C isotropic HFCCs of graphenic ion-radicals [29] our computations provide a mean absolute error of 1.1 MHz ($\approx\%2$ of the range of magnitudes), which justifies the use of calculated HFCCs as a reference.

The effective spin-Hamiltonian of the HFI between the electron spin $S$ and the nuclear spin $I$ can be written as

$$\mathcal{H}_{\text{HFI}} = \frac{\rho_e(r)}{r} + \frac{\rho(r)}{\sqrt{2}} + \frac{\rho(c)}{\sqrt{3}}$$

where $\rho_e(r)$, $\rho(r)$, and $\rho(c)$ are the electron, total, and nuclei spin densities, respectively.
\(\mathbf{H} = \mathbf{s} \cdot \mathbf{A} \cdot \mathbf{I},\) where the 3x3 HFI tensor \(\mathbf{A} = A_{\text{iso}} \mathbf{T} + A_{\text{dip}} \mathbf{T}^d\) is usually decomposed into the scalar HFCC \(A_{\text{iso}}\) and the traceless dipolar HFI tensor \(A_{\text{dip}} \mathbf{T}^d\). The HFI tensor \(\mathbf{A}\) reflects the distribution of the electron spin density \(\rho^s(\mathbf{r}) = \rho^s_1(\mathbf{r}) - \rho^s_2(\mathbf{r})\) viewed from the position of the nucleus \(I\). In carbon nanostructures the nuclear spins are those of the \(^{13}\text{C}\) isotope (\(\approx\)1.1\% natural abundance and can be artificially changed; the dominant \(^{12}\text{C}\) isotope has zero spin) and other elements originating from impurities and boundaries. The electron spin density \(\rho^s(\mathbf{r})\) can be further decomposed into the contribution of half-populated conduction electron states lying close to the Fermi level (or singly occupied molecular orbitals in the molecular context), \(\rho^s_1(\mathbf{r}) = \sum_n \rho^n(\mathbf{r})\) ≥ 0, and the contribution of the fully populated valence states perturbed by the exchange with spin-polarized conduction electrons, \(\rho^s_2(\mathbf{r}) = \sum_n |\psi_\uparrow(\mathbf{r})|^2 - |\psi_\downarrow(\mathbf{r})|^2\). The crucial role of the exchange-polarization effect is illustrated with a model electron-doped hydrogen-terminated graphene fragment in the doublet spin state (Fig. 1). While the projection of \(\rho^s_1(\mathbf{r})\) on the \(xy\) plane (Fig. 1a) is positive everywhere and reveals an enhancement at the zig-zag edges, the projection of the total spin-density \(\rho^s(\mathbf{r})\) (Fig. 1b) is negative where \(\rho^s_1(\mathbf{r})\) is close to zero. The isotropic (Fermi contact) HFCC is proportional to the total spin density at the position of nucleus \(I\), \(A_{\text{iso}} = (4\pi/3\beta_c)\beta_N g_I \mu_I \rho^s(\mathbf{r}_I)\), where \(\beta_c\) and \(\beta_N\) are the Bohr and nuclear magnetons, while \(g_I\) and \(\mu_I\) are the \(g\)-values of free electron and nucleus \(I\), respectively. \(S\) is the maximum value of the electron spin projection. For the ideal graphene and planar sp\(^2\) carbon nanostructures (all nuclei lie in the \(z=0\) plane) \(\rho^s(z=0) = 0\) due to the \(p_z\) symmetry of the conduction states. However, there is a contribution of the \(\sigma\) symmetry valence states \(\rho^s_\sigma(z=0) \neq 0\) due to the exchange-polarization effect. For the model graphene fragment \(\rho^s_\sigma(z=0)\) (Fig. 1c) shows an alternating pattern with a relative dominance of the negative spin density. Since the \(\sigma\) states are situated well above and well below the Fermi level in sp\(^2\) carbon nanostructures, the valence exchange-polarization phenomenon exhibits the property of locality. This property was exploited by Karpus and Fraenkel almost 50 years ago to describe the isotropic \(^{13}\text{C}\) HFCCs in conjugated organic radicals [31]. The main contribution to the hyperfine anisotropy originates from the total spin population \(n\) of the on-site \(p_z\) atomic orbital, which also incorporates the contribution of exchange-polarized valence states. Assuming a local axial symmetry, \(\mathbf{T}\) can be written as a diagonal matrix with elements \(T_{zz} = 2T_{xx} = -T_{yy} = A_{\text{dip}}\), where \(A_{\text{dip}} = [1/(5S)]\beta_c \beta_N g_I \mu_I (1/R^3_{2p})\) (\(R_{2p}\) is the distance of the carbon 2p electron to nucleus).

The HFIs were calculated for a set of 12 (~1 nm size) electron- and hole-doped planar hydrogen terminated graphene fragments (Fig. 2b) in the spin-doublet ground states. This provides overall statistics for 206 independent \(^{13}\text{C}\) HFCCs. The calculated \(A_{\text{iso}}\) and \(A_{\text{dip}}\) values are fitted to the extended form of the Karpus-Fraenkel expression

\[A = a_j (1 + \sum_{i \in NN} b_j \Delta r_i) n^c + c \sum_{i \in NN} (1 + d \Delta r_i) n^c_i,\]

where the two terms account for the contributions of the on-site and nearest neighbor (NN) conduction electron spin populations on unpaired electron, \(n^c\) and \(n^c_i\), respectively, calculated from first principles. The on-site coefficients \(a_j\) and \(b_j\) are distinguished for the cases of C atoms with 3 carbon NNs \((j=3)\) and the boundary atoms with 2 carbon NNs \((j=2)\). The C–C bond length effects are encountered through the coefficients \(b_j\) and \(d\) with \(\Delta r_i = r_i - r_0\) being the deviation of the bond length \(r_i\) from the value for the ideal graphene, \(r_0 = 1.42\) Å. Only statistically significant local properties were included in the linear expression [31]. The results of the regressions are summarized in Tab. II (1 MHz=4.136×10\(^{-3}\) μeV). Fig. 2b,c) shows the fitted (using expr. [31] and regression parameters) values \(A_{\text{iso}}\) (\(A_{\text{dip}}\)) versus the calculated \(A_{\text{iso}}\) (\(A_{\text{dip}}\) values. Regressions to the linear expression [31] provide accurate estimations (root-mean-square-errors are 1.7 MHz and 1.2 MHz for \(A_{\text{iso}}\) and \(A_{\text{dip}}\), respectively. The calculated isotropic HFCCs span about the same range of magnitudes (−16.7 MHz<\(A_{\text{iso}}<21.1\) MHz) as the dipolar HFCCs (−5.9 MHz<\(A_{\text{dip}}<22.7\) MHz). The

---

**TABLE I:** Parameters (in MHz) fitted to the results of calculations of a set of nanographite molecules.

|   | \(a_2\) | \(a_3\) | \(b_2\) | \(b_3\) | \(c\) | \(d\) |
|---|---|---|---|---|---|---|
| \(A_{\text{iso}}\) | 162 | 128 | 2.3 | 6.1 | -57.4 | -7.4 |
| \(A_{\text{dip}}\) | 155 | 131 | 2.7 | 3.6 | -19.4 | -12.8 |
HFCCs of boundary atoms tend to be larger due to the fact that low-energy states localize at the zigzag graphene edges [20]. The on-site and the NN exchange-polarization effects have competitive character ($a_3/c \approx -2$) in the case of isotropic HFCCs. Our calculations predict $\approx 50\%$ larger values for the parameters $a_2$, $a_3$ and $c$ for $A_{iso}$ compared to those obtained by Karplus and Fraenkel in their early studies of HFCCs in molecular radicals ($a_2=99.8$ MHz, $a_3=85.5$ MHz and $c=-39$ MHz) [31]. This difference can be explained by the incorporation of the electron correlation effects in our calculations and to the local atomic structure of the graphene lattice. Both $A_{iso}$ and $A_{dip}$ show a tendency to enhance the on-site and to weaken the NN contributions with the increase of $C$–$C$ bond lengths. The dipolar HFCC is mostly influenced by the on-site contribution of the half-populated conduction state and the NN exchange-polarization effect is weaker in this case ($a_3/c \approx -7$). When compared to typical solid state environments based on heavier elements, the $^{13}$C HFCCs in graphene and related nanostructures are weaker (e.g. $117$ MHz [31]) and with the calculated isotropic Knight shifts in graphite intercalates ($44$ MHz is small due to the partial compensation of the on-site and the NN exchange-polarization effects). This value is consistent with the values derived from the experimental $^{13}$C Knight shifts in graphene intercalates ($-25$ MHz < $A_{iso}$ < $-50$ MHz) [32] and with the calculated isotropic Knight shifts in metallic carbon nanotubes [34]. The nonferromagnetic case with the conduction state distributed over the atoms of only one sublattice (A) is physically realized at the zigzag edges [20] and around single-atom point defects in sublattice B [35]. Considerable alternating Fermi contact and dipolar HFCCs are predicted in this case. An antiferromagnetic pattern can be realized in the case of heavily disordered systems with localized defect and edge states in both sublattices [36]. The magnitudes of HFIs are minimized and maximized in the cases of ferromagnetic and antiferromagnetic electron spin distributions, respectively.

Many carbon nanostructures of reduced dimensionality (e.g. nanotubes and fullerenes) represent non-planar topologies. Local curvatures lead to the $sp^2$–$sp^3$ rehybridization of carbon atoms and enable a Fermi contact interaction involving the low-energy $\pi$ electron spins [19]. This results in a positive contribution of the $\pi$ states unless $n^e$ is close to zero: a contribution due to the NN exchange-polarization effect is negative in this case. The degree of rehybridization $m$ of the $\pi$ states (spin $s^m$) can be described using a local bond angles analysis [37]. For the case of large curvature radii the original expression for $m$ can be reformulated in a more convenient form, $m=d_{cc}^R/8(1/R_1 + 1/R_2)^2$, where $d_{cc}$ is the C–C distance, $R_1$ and $R_2$ are the principal curvature radii. The curvature-induced contribution to the Fermi contact $^{13}$C HFCC is then $A_{iso}^{curv}=(4\pi/3)b_\beta g_N g_I n m \phi_\beta(0)$, where $\phi_\beta(0)$ is the magnitude of the carbon atomic $2s$ wavefunction at the point of nucleus $(8\pi/3)b_\beta g_N g_I n m \phi_\beta^2(0)=3.5\times10^3$ MHz. The curvature-induced direct coupling becomes significant ($m>10^{-2}$) only in ultranarrow carbon nanotubes ($d<1$ nm) and fullerenes.

Since the natural abundance of the “HFII-active” $^{13}$C isotope is small ($\approx 1\%$), consideration of the nuclei of other elements is important for a complete description of HFIs in carbon nanostructures. The common substitution impurities are boron and nitrogen with all natural isotopes having nuclear spins. Graphene edges can be terminated by hydrogen and fluorine atoms with both $^1$H and $^{19}$F spin-1/2 nuclei ($99.9885\%$ and $100\%$ natural abundance, respectively) having high $g$-values (g($^1$H)/g($^{13}$C)$\approx$g($^{19}$F)/g($^{13}$C)$\approx$1). I consider HFIs in a reduced set of molecular fragments (only 3- and 4-ring structures included) with impurities and edge functionalizations in all possible positions. The calculated HFCCs have been fitted to the Karplus-Fraenkel relation, with no $\Delta t$ terms included (Tab. III). The variations of the local charge density of states in the vicinity of impurities does

| Nucleus | Position | $A_{iso}$ | $A_{dip}$ |
|--------|----------|-----------|-----------|
| $^{11}$B | subst. impurity | 43 | -31 |
| $^{13}$B | subst. impurity | 60 | 6 |
| $^{14}$N | subst. impurity | 150 | -22 |
| $^1$H | C$_{sp^2}$ edge | 131 | -58 |
| $^{19}$F | C$_{sp^2}$ edge | 240 | -40 |
| $^1$H | C$_{sp^3}$ edge | 350 |
| $^{19}$F | C$_{sp^3}$ edge | 750 |
| $^{13}$C | C$_{sp^3}$ edge | -68 |

TABLE II: Hyperfine coupling constants for three general cases of spin populations $n^e$ of the carbon atoms of A and B sublattices of graphene.

| $n^e_A=n^e_B>0$ | $n^e_A>0; n^e_B=0$ | $n^e_A=-n^e_B>0$ |
|---|---|---|
| $A_{iso}(A)/n^e$ | $A_{iso}(B)/n^e$ | $A_{dip}(A)/n^e$ | $A_{dip}(B)/n^e$ |
| 73 | -44 | -44 | 73 | 73 |
| 128 | -172 | 131 | 58 |
| 300 | -300 | 189 | -189 | -189 |

TABLE III: Parameters (in MHz) describing the HFIs of nuclei of substitutional impurities ($^{11}$B and $^{13}$N), monatomic functional groups ($^1$H and $^{19}$F) and rehybridized ($sp^3$) carbon atoms ($^{13}$C) at the edges.

Since the natural abundance of the “HFII-active” $^{13}$C isotope is small ($\approx 1\%$), consideration of the nuclei of other elements is important for a complete description of HFIs in carbon nanostructures. The common substitution impurities are boron and nitrogen with all natural isotopes having nuclear spins. Graphene edges can be terminated by hydrogen and fluorine atoms with both $^1$H and $^{19}$F spin-1/2 nuclei ($99.9885\%$ and $100\%$ natural abundance, respectively) having high $g$-values (g($^1$H)/g($^{13}$C)$\approx$g($^{19}$F)/g($^{13}$C)$\approx$1). I consider HFIs in a reduced set of molecular fragments (only 3- and 4-ring structures included) with impurities and edge functionalizations in all possible positions. The calculated HFCCs have been fitted to the Karplus-Fraenkel relation, with no $\Delta t$ terms included (Tab. III). The variations of the local charge density of states in the vicinity of impurities does
not have any significant influence on HFIs. Both Fermi contact and dipolar HFCCs of the impurity nuclear spins show a monotonic increase along the $^{13}\text{C}^{14}\text{N}$ series when compared to the results for $^{13}\text{C}$ HFCCs (Tab. 4). The NN relative exchange-polarization effects ($a/c$ ratio) on the Fermi contacts HFCCs tend to decrease along the series. While the HFIs of the nuclear spins in substitution impurities are highly anisotropic, the hyperfine couplings of the edge nuclei show small anisotropy due to the $sp^3$ character of bonding. When $^1\text{H}$ and $^{19}\text{F}$ edge nuclei are bound to the $c_2$ atoms, the isotopic HFCCs are of the same order of magnitude as those of the $^{13}\text{C}$ spins in the graphene lattice. The influence of the NN carbon atoms (second NNs to the terminating atom) is very similar for $^1\text{H}$ and $^{19}\text{F}$ nuclei and smaller than in the case of $^{13}\text{C}$ HFCCs ($a_\text{H}/c_\text{H}\approx a_\text{F}/c_\text{F}\approx-6$). The spin polarization effect on $^{19}\text{F}$ HFCCs is stronger and of opposite sign compared to that of protons ($a_\text{F}/a_\text{H}\approx c_\text{F}/c_\text{H}\approx-2$). When edge atoms are bound to the rehybridized $sp^3$ carbon atoms, $n^*$ is zero but the NN contribution is significantly enhanced. The NN contribution to the $^{13}\text{C}$ hyperfine coupling of the $sp^3$ edge carbon atom itself ($c=-68$ MHz) has a similar magnitude as that of the $sp^2$ edge atoms ($c=-57$ MHz). HFIs with the boundary spins (H-terminated edges are often obtained in experiments) have to be taken into account when designing carbon-based nanoscale devices for spintronics or quantum computing. A chemical modification of the graphene edges (e.g. substitution of the hydrogen atoms by alkyl-groups) can be suggested to reduce electron spin decoherence effects from the HFIs with boundary spins.

In conclusion, the results of first principles calculations show that the hyperfine interactions in graphene and related nanostructures are defined by the local distribution of the conduction electron spins and by the local atomic structure. A complete set of parameters describing the hyperfine interactions was determined for the $^{13}\text{C}$ and other common nuclear spins. These results will permit control of the magnetic interactions between the spins of electrons and nuclei by tailoring the chemical and isotopic compositions, local atomic structures, and strain fields in $sp^2$ carbon nanostructures. Some practical recipes for minimizing interactions with nuclear spins are given.

I acknowledge D. Loss and Yu. G. Semenov for motivating discussions, and S. Arey, D. Bulaev, L. Helm, V. G. Malkin, D. Stepanenko, and I. Tavernelli for comments on the manuscript. I also thank the Swiss NSF for financial support and CSCS Manno for computer time.

---

* Electronic address: oleg.yazyev@epfl.ch

1. I. Žutić, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. 76, 323 (2004).
2. D. Loss and D. P. DiVincenzo, Phys. Rev. A 57, 120 (1998).
3. B. E. Kane, Nature 393, 133 (1998).
4. Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, Nature 427, 821 (2004).
5. S. D. Bader, Rev. Mod. Phys. 78, 1 (2006).
6. K. Tsukagoshi, B. W. Alphenaar, and H. Ago, Nature 401, 572 (1999).
7. S. Sahoo, T. Kontos, C. Schönberger, and C. Sürgers, Appl. Phys. Lett. 86, 112109 (2005).
8. L. E. Hueso, J. M. Pruneda, V. Ferrari, G. Burnell, J. P. Valdés-Herrera, B. D. Simons, P. B. Littlewood, E. Arta-cho, A. Fort, and N. D. Mathur, Nature 445, 410 (2007).
9. E. W. Hill, A. K. Geim, K. Novoselov, F. Schedin, and P. Blake, IEEE Trans. Magn. 42, 2694 (2006).
10. M. Bockrath, W. Liang, D. Bozovic, J. H. Haenfer, C. M. Lieber, M. Tinkham, and H. Park, Science 291, 283 (2001).
11. M. R. Buitelaar, A. Bachtold, T. Nussbaumer, M. Iqbal, and C. Schönberger, Phys. Rev. Lett. 88, 156801 (2002).
12. B. Trauzettel, D. V. Bulaev, D. Loss, and G. Burkard, Nat. Phys. 3, 192 (2007).
13. P. G. Silvestrov and K. B. Efetov, Phys. Rev. Lett. 98, 016802 (2007).
14. Y. G. Semenov, K. W. Kim, and G. J. Iafrate, Phys. Rev. B 75, 045429 (2007).
15. A. V. Khatskii, D. Loss, and L. Glazman, Phys. Rev. Lett. 88, 186802 (2002).
16. J. M. Taylor, C. M. Marcus, and M. D. Lukin, Phys. Rev. Lett. 90, 206803 (2003).
17. R. J. Epstein, F. M. Mendoza, Y. K. Kato, and D. D. Awschalom, Nat. Phys. 1, 94 (2005).
18. L. Childress, M. V. G. Dutt, J. M. Taylor, A. S. Zibrov, F. Jelezko, J. Wrachtrup, P. R. Hamer, and M. D. Lukin, Science 314, 281 (2006).
19. C. H. Pennington and V. A. Stenger, Rev. Mod. Phys. 68, 855 (1996).
20. K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B 54, 17954 (1996).
21. V. M. Pereira, F. Guinea, J. M. B. Lopes dos Santos, N. M. R. Peres, and A. H. Castro Neto, Phys. Rev. Lett. 96, 036801 (2006).
22. I. Ţifrea and M. E. Flatté, Phys. Rev. Lett. 90, 237601 (2003).
23. M. Poggio, G. M. Steever, R. C. Myers, Y. Kato, A. C. Gossard, and D. D. Awschalom, Phys. Rev. Lett. 91, 207602 (2003).
24. The Gaussian03 code [M. J. Frisch et al., Gaussian03, Rev. C.02, Gaussian, Inc., Wallingford, CT, 2004] was used.
25. N. Rega, M. Cossi, and V. Barone, J. Chem. Phys. 105, 11060 (1996).
26. A. D. Becke, Phys. Rev. A 38, 3098 (1988); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988); A. D. Becke, J. Chem. Phys. 98, 5649 (1993).
27. L. Hermesilla, P. Calle, J. M. García de la Vega, and C. Sierio, J. Phys. Chem. A 109, 1114 (2005).
28. E. van Lenthe, A. van der Avoird, and P. E. S. Wormer, J. Chem. Phys. 108, 4783 (1998).
29. J. R. Bolton and G. K. Fraenkel, J. Chem. Phys. 40, 3307 (1964); D. J. M. Fassaert and E. de Boer, Recl. Trav. Chim. Pays-Bas 91, 273 (1972); R. F. Claridge, C. M. Kirk, and B. M. Peake, Aust. J. Chem. 26, 2055 (1973).
[30] M. Kaupp, M. Bühl, and V. G. Malkin, eds., *Calculation of NMR and EPR parameters: Theory and Applications* (Wiley-VCH: Weinheim, 2004).

[31] M. Karplus and G. K. Fraenkel, J. Chem. Phys. **35**, 1312 (1961).

[32] H. Overhof and U. Gerstmann, Phys. Rev. Lett. **92**, 087602 (2004).

[33] J. Conard, H. Estrade, P. Lauginie, H. Fuzellier, G. Furdin, and R. Vasse, Physica B **99**, 521 (1980).

[34] O. V. Yazyev and L. Helm, Phys. Rev. B **72**, 245416 (2005).

[35] K. Kelly and N. Halas, Surf. Sci. **416**, L1085 (1998).

[36] O. V. Yazyev and L. Helm, Phys. Rev. B **75**, 125408 (2007).

[37] R. C. Haddon, J. Am. Chem. Soc. **108**, 2837 (1986).

[38] Y. Kobayashi, K. I. Fukui, T. Enoki, and K. Kusakabe, Phys. Rev. B **73**, 125415 (2006).