Theor Chem Acc (2011) 128:223–229
DOI 10.1007/s00214-010-0835-2

REGULAR ARTICLE

On the efficient calculation of the quantum properties (dipolar moments) of the molecular heteroatomic (nitrogen) polycyclic aromatic hydrocarbons

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Received: 12 May 2010 / Accepted: 6 October 2010 / Published online: 26 October 2010

Abstract In this work, we have developed an efficient (very fast) theoretical methodology able to calculate the quantum properties of any molecular heteroatomic PAH. If all the heteroatoms are Nitrogens, we can obtain these results directly from its chemical formula. We have obtained and analyzed the electric dipolar moment of 43 small Nitrogen PAHs (NPAHs). We have obtained the atomic spin densities of several large (5,000 atoms) molecular Nitrogen Graphene Nanoribbons (GNRs), which have the Nitrogen atoms in the same zig-zag edge. According to our computational results, this kind of molecular Nitrogen GNRs should have significant ferroelectric and ferromagnetic properties.

Keywords Hatree–Fock · Nitrogen PAHs · Dipolar moment · Graphene nanoribbons · Ferromagnetic · Ferroelectric

1 Introduction

The calculation of the quantum properties of the molecules is a topic of a great interest for the chemical community [1, 2]. Several journals have been devoted to the study of the heterocyclic compounds [3–5]. Even for the very specialized case of polycyclic aromatic hydrocarbons (PAHs), it is easy to find review works of medical [6], astronomical [7], or technical interest [8, 9]. We are using the term PAH in its broader sense, which includes infinite (periodic is more correct) systems. Thus, a graphene sheet might be seen as a 2D-infinite PAH, formed only by Carbon atoms. A graphene nanoribbon (GNR) may be defined as a PAH having a rectangular shape with regular edges, saturated with hydrogen atoms. The GNR term has been used in the bibliography for denoting both 1D-infinite (periodic) systems and (graphene) molecular (finite) nanoribbons. Several theoretical works have been devoted to describing the quantum structure of small irregular molecular PAHs [10–13] and GNRs [14–22].

We have recently presented a methodology [23–25] able to obtain a very fast reasonable quantum description of any PAH. In the case of a molecular PAH, we can obtain [25] this description directly from its chemical formula. Our present interest is to extend this methodology to the case of PAHs having heteroatoms. In Sects. 2 and 3, this extension is performed at a theoretical level. In Sect. 2, we briefly review the general theory, and in Sect. 3, we explain the methodological details specific to the molecular heteroatomic PAH case.

The correctness and quality of our computational results are analyzed in Sect. 4. We have focused our interest on Nitrogen (or aza) PAHs (NPAHs) because there are many theoretical studies [26–35] dealing with them. This subject has some technical interest since the Nitrogen-doped graphene structures have been used in fuel cells [36] and as electrochemical biosensors [37]. Our analysis has established that it is possible to obtain a reasonable very fast quantum description of any molecular NPAH, directly from its chemical formula.

In Sect. 5, we have focused our interest on the calculation of molecular Nitrogen GNRs that have all their C–H

Electronic supplementary material The online version of this article (doi:10.1007/s00214-010-0835-2) contains supplementary material, which is available to authorized users.

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uppermost units replaced by Nitrogen atoms. We suspected that these same zig-zag edge nitrogen (SZEN) GNRs should have interesting electronic properties. We have found significantly large values of the dipolar electric and (spin) magnetic moments in these compounds. These large values would imply, supposing that our analysis is realistic enough, that these N-GNRs have significant ferroelectric and ferromagnetic properties. To our knowledge, there is no study describing simultaneously the ferroelectric and the ferromagnetic properties of large molecular N-GNRs.

2 Review of the Hückel–Hubbard restricted frozen Hartree–Fock (FHF) method

The FHF theory has been justified several times [23–25]. This (self-consistent field) method finds, for a molecule having N_e electrons, the best N_e spin molecular orbitals (SMOs) to be filled from a given set of $2N_b$ SMOs φ_m (or m). This optimal selection is performed by minimizing the generalized one-determinant Energy expression $E_{N_e}^{\mathrm{FHF}}$ given by

$$E_{N_e}^{\mathrm{FHF}} = \sum_m n_m \left(\varepsilon_m + \sum_{m'<m} n_{m'} V_{mm'} \right); \quad V_{mm'} > 0 \tag{1}$$

with respect to the occupation numbers n_m of the SMOs m, under the restrictions $n_m = \{0, 1\}$ and $\sum_m n_m = N_e$. Each ε_m term represents the one-electron kinetic-nuclear Energy of an SMO m, and the $V_{mm'}$ term represents the repulsive two-electron coulomb-exchange interaction between the SMOs m and m'.When the FHF theory is used to restricted level, the SMO set is expressed as $\{\varphi_m\} = \{\varphi_{s\sigma}\} = \{\mathbf{c}_s \otimes \boldsymbol{\sigma}\}$, where the $\boldsymbol{\sigma}$ spin set is formed by the usual spin functions α, β. Each one of the N_b column spatial vectors $\mathbf{c}_s$ is formed by N_b expansion coefficients c_{bs}. The N_b columns $\mathbf{c}_s$ can be collected in an $N_b \times N_b$ square matrix $\mathbf{C}$, $\mathbf{C} = \oplus\, \mathbf{c}_s$.

The present version of our code works to semi-empirical Hückel–Hubbard level. Each one of the N_a atoms a is represented by one atomic basis b and one electron, which is equivalent to imposing $N_b = N_e = N_a$.

The $\mathbf{C}$ matrix is obtained by solving a one-electron extended Hückel matrix eigen-problem, $\mathbf{HC = SC\varepsilon}$. The one-electron Energy set, $\{\varepsilon_m\}$, is obtained from the diagonal elements of the eigen-value matrix ε, ε_{ss}, according to $\{\varepsilon_m\} = \{\varepsilon_{s\sigma}\} = \{\varepsilon_{s\alpha}\} \oplus \{\varepsilon_{s\beta}\}$, with $\{\varepsilon_{s\alpha}\} = \{\varepsilon_{s\beta}\} = \{\varepsilon_{ss}\}$. The elements of the $\mathbf{H}$ and $\mathbf{S}$ matrices are given as $H_{aa} = -\alpha_a$, $H_{aa'} = -\beta_{aa'} B_{aa'}$, $S_{aa} = 1$, and $S_{aa'} = \mathrm{s}_{aa'} B_{aa'}$, with $a' \neq a$. The symbols α_a, $\beta_{aa'}$, and $\mathrm{s}_{aa'}$ represent semi-empirical positive (Hückel) parameters to be specified. The elements $B_{aa'}$ of the bonding binary matrix $\mathbf{B}$ are nonzero only if the atoms a and a' are directly bonded, and in this case $B_{aa'} = 1$. The eigenvectors $\mathbf{c}_s$ have been normalized with respect to the unit matrix, that is $\mathbf{c}_s^t \mathbf{c}_s = 1$.

Inside the Hubbard approximation, the $V_{mm'}$ terms are calculated by considering only the two-electron one-center atomic integrals. With this approximation, the term $V_{mm'}$ is zero when the SMOs m and m' have the same spin functions, because the one-center exchange atomic integral nulls the coulombic one. When m and m' have different spin, then $V_{mm'}$ is calculated according to

$$V_{ss'} = \sum_{a=1}^{a=N_a} \gamma_a c_{as}^2 c_{as'}^2, \tag{2}$$

γ_a being positive (Hubbard) semi-empirical atomic parameters. The symbols s and s', which can be equal, represent the spatial part of m and m', respectively.The quantum properties of the molecule can be obtained from the $\{\mathbf{c}_m\}$, $\{\varepsilon_m\}$, and $\{n_m\}$ sets. The two electronic atomic spin densities d_a^σ of an atom a are calculated according to $d_a^\sigma = \sum_s n_{s\sigma} c_{as}^2$ The atomic spin excess of each atom, d_a, is calculated as the difference between its two densities, $d_a = d_a^\alpha - d_a^\beta$. The numerical value of the (spin) magnetic dipolar moment μ_m of the molecule is given (in Bohr's magnetons, μ_b) by the sum of its d_a values, $\mu_m = \sum_{a=1}^{a=N_a} d_a$. The Mulliken charges q_a (in a. u.) are calculated according to $q_a = 1 - d_a^\alpha - d_a^\beta$.

The rightward horizontal μ_x and the upward vertical μ_y components of the electric dipolar moment, $\vec{\mu}_e$, are calculated in Debyes, as $\mu_x = 4.8 \sum_a x_a q_a$ and $\mu_y = 4.8 \sum_a y_a q_a$, where the atomic coordinates, x_a and y_a, are given in Å. The modulus of the $\vec{\mu}_e$ vector is represented by μ_e, $\mu_e = |\vec{\mu}_e|$.

The values of the μ_x and μ_y components do not depend on the origin of coordinates. We have adopted the (advantageous) convention $\sum_a x_a = \sum_a y_a = 0$.

3 The specific theory of the heteroatomic PAHs

The structure of any molecular PAH can be formed by linking (downward) N_y horizontal rows, made of several aromatic rings (not necessarily chained), each row being represented by a string $\mathbf{r}_w$. This structure can be formulated as $(\mathbf{r}_1; \mathbf{r}_2; \ldots \mathbf{r}_w \ldots \mathbf{r}_{N_y})$ where any string $\mathbf{r}_w$ is formed by integer numbers m_i according to the structure $\mathbf{r}_w \equiv m_0, m_1, m_2, m_3 \ldots$ When $m_0 > 0$, the row is made (from left to right) of m_0 rings, m_1 vacancies, m_2 rings, m_3 vacancies, and so on. When $m_0 < 0$, the row is made of m_0 vacancies, m_1 rings, m_2 vacancies, m_3 rings, and so on. The one-row PAHs (oligoacenes, [32]), formed by N_x chained rings, are formulated simply as (N_x). This graphene-PAH (or gPAH) nomenclature is general, systematic, compact and provides an automatic numbering (row-wise) of the Carbon atoms, as well as some information on the molecular plane orientation.

The heteroatoms (or not-Carbon elements) T, U, V … can be allocated by using the information included in a further string $\mathbf{r}_T$, explained as follows. Place yourself in the first atom and start reading $\mathbf{r}_T$. Any time you find the string “$>m_i$” jump $m_i + 1$ Carbon atoms. Any time you find the string “Tm_i” replace the next $m_i + 1$ Carbon atoms by heteroatoms T. For example, if the string $\mathbf{r}_T$ has the structure $\mathbf{r}_T \equiv Tm_0 > m_1\, Um_2\ldots$, the first $m_0 + 1$ atoms are of type T, the next $m_1 + 1$ atoms are Carbons, the next $m_2 + 1$ atoms are of type U…, and so on. This $\mathbf{r}_T$ convention is particularly advantageous when there are many heteroatoms. For example, if all the Carbon atoms are changed into T ones, the $\mathbf{r}_T$ string is simply $TN_a - 1$. Any heteroatomic PAH can be represented by its ghPAH formula $(\mathbf{r}_1;\ \mathbf{r}_2;\ \ldots \mathbf{r}_w \ldots \mathbf{r}_{N_y}\mathbf{r}_T)$.

This ghPAH nomenclature is totally general and provides some information on the orientation of the molecule with respect to the horizontal rightward x axes. Thus, for example, the pyridine molecule can be formulated as $(1 > N)$, or as $(1 > 3N)$. In the first case, the Nitrogen is placed at the uppermost atomic position of the molecule. In the second case, the Nitrogen is placed at the lowest position. In Fig. 1, the ghPAH nomenclature is applied to formulating the SZEN-pentacene and the 1,10-phenanthroline molecules.

Our analysis discards the hydrogen atoms and assumes that the PAH has a regular honeycomb (graphene) structure with parametric equal inter-nuclear equilibrium distance ρ. The quantum properties of any (up to 16,000 atoms) molecular heteroatomic PAH can be calculated from the input made up of the binary matrix $\mathbf{B}$, the x_a, y_a nuclear coordinates, and the atomic Hückel–Hubbard (HH) parameters α_a, $\beta_{aa'}$, $s_{aa'}$, γ_a. The matrix $\mathbf{B}$ and the x_a, y_a nuclear coordinates can be automatically generated from the gPAH string, $(\mathbf{r}_1;\ \mathbf{r}_2;\ \ldots \mathbf{r}_w \ldots \mathbf{r}_{N_y})$, and from the ρ value. The HH parameters can automatically be generated (up to three different heteroatoms) from the ghPAH formula and from the element parameters α_E, $\beta_{EE'}$, $s_{EE'}$, γ_E $(E = C, T, U, V)$.

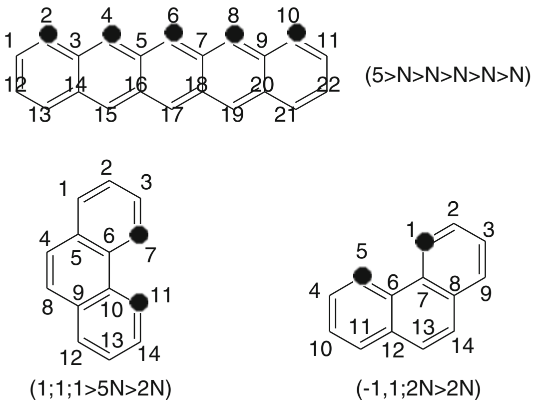

Fig. 1 Geometrical structure, gPAH formula, and Carbon–Nitrogen numbering of the SZEN-pentacene (*up*) and of the 1,10-phenanthroline (*down*). The Nitrogen atoms are represented by *black filled circles*. The term SZEN indicates that the Nitrogen atoms are placed at the same zig-zag (*horizontal up*) edge of the pentacene (or 5-oligoacene). The ghPAH formula and numbering of the 1,10-phenanthroline (probably 3,4-diazaphenanthrene) depends on its orientation. The vertical dipolar component, μ_y, of the $(1;\ 1;\ 1 > 5\ \mathrm{N} > 2\ \mathrm{N})$ orientation is null by symmetry

The main drawback of this approach lies in its low (chemical) accuracy. In order to improve this accuracy, it is convenient to perform an optimization of the element parameters. We have made this optimization only for the Carbon and Nitrogen atoms.

The Carbon–Nitrogen optimal parameter set has been obtained by (basically) fitting the “best” theoretical (experimental if available) μ_e values of 27 polar NPAHs, reported by other authors [26–35]. The quality of the fitting depends mainly on the $\beta_{EE'}$ parameters. We are using the (theoretically unjustified) values $\beta_{\mathrm{CN}} = \beta_{\mathrm{NN'}} = 4.5$ eV and $\beta_{\mathrm{CC'}} = 3.8$ eV. This last value differs slightly from the one, $\beta_{\mathrm{CC'}} = 3.6$ eV, obtained by fitting [25] the (optical) experimental energy gaps (E_g) of 123 PAHs.

We are using $\alpha_{\mathrm{C}} = 0$ and $\alpha_{\mathrm{N}} = 3.274$ eV. This last α_{N} value is the difference between the atomic ionization energies, $\alpha_{\mathrm{N}} = I_{\mathrm{N}} - I_{\mathrm{C}}$. We have previously proposed several energetic estimations of the value of the dimensionless Hubbard parameter γ, $\gamma = \gamma_{\mathrm{C}}/\beta_{\mathrm{CC'}} = \gamma_{\mathrm{N}}/\beta_{\mathrm{NN'}}$. In [23], we used a one-electron argument and arrived to $\gamma \approx 2$. In the PAH optical fitting [25], we used an N_e-electron argument and arrived to $0 < \gamma < 6$, with $\gamma = 3$ the optimal value. Here, we are using this γ value, which is equivalent to taking $\gamma_{\mathrm{C}} = 3\ \beta_{\mathrm{CC'}}$ and $\gamma_{\mathrm{N}} = 3\ \beta_{\mathrm{NN'}}$.

We have found that the quality of both fittings (dipolar and optical) does not improve (significantly) by introducing overlap parameters $s_{aa'}$. Thus, we have discarded them ($s_{\mathrm{aa'}} = 0$). The μ_e values depend linearly on ρ. We are using the value $\rho = 1.40$ Å, very close to the ones by Li et al. [35], who take $R_{\mathrm{CC'}} = 1.41$ Å, $R_{\mathrm{CN}} = 1.38$ Å, and $R_{\mathrm{NN'}} = 1.39$ Å.

The fitting of the dipolar moments can be improved by increasing the number of parameters whose numerical values are not justified.

The conclusions of the Nitrogen analysis have been extended to the Boron and Oxygen elements. We are using $\alpha_T = I_T - I_{\mathrm{C}}$ and $\gamma_T = 3\ \beta_{TT'}$, with $T = B$ or O. The β parameters have been calculated using the approximation $H_{aa'} \approx (H_{aa} + H_{a'a'}) \times 0.5$, which leads to $\beta_{TE} = \beta_{\mathrm{CC'}} + 0.5 \times (\alpha_T + \alpha_E)$, with $E = C, N, B, O$.

4 Results for the R_6 (six aromatic rings at the most) molecular irregular NPAHs

We can not expect reliable results from a semi-empirical one-determinant minimal-basis calculation performed without any geometry optimization. In spite of these limitations, the agreement of our E_g results [25] with the experimental values, for 123 molecular PAHs, is reasonable. This agreement is similar to the one obtained by using the intermediate neglect differential overlap spectroscopic (INDO/S) approach, to configuration interaction level, with geometry optimization. However, we found sporadic significant anomalies in the optical results. We tried to relate these anomalies with factors such as shape, symmetry, or percentage of hydrogen, but we failed in finding any definite pattern. The present work is devoted, mainly, to studying the capabilities of the FHF in calculating the dipolar moments of the NPAHs. We have found that the FHF provides a reasonable description of these moments, although we have again found significant sporadic random deviations.

For all the mentioned reasons, we have performed the optical analysis only for the (SZEN) oligoacenes. There is a reasonable agreement (see Fig. 2) of our E_g results with the (Koopmans-DFT) ones by Winkler and Houk [32]. These authors recognize that “Koopmans’ theorem is not strictly valid in DFT”. There is a symmetry problem inherent to the HF (or DFT) methodology. The mono-electron Energy of the HO (LU) SMO considers the (repulsive) interaction of one electron with an electronic field formed by $N_e - 1$ (N_e) electrons. Obviously, the acronym HO (LU) refers to the highest occupied (lowest unoccupied) SMO. The FHF approach does not have this HO–LU asymmetry problem because it considers only the two-electron (repulsive) interactions between SMOs having different spins. The electron of the HO FHF α SMO experiments the same repulsive field, described by the β electrons, than the electron of the LU one. Thus, the FHF E_g values should be, in general, smaller than the HF ones.

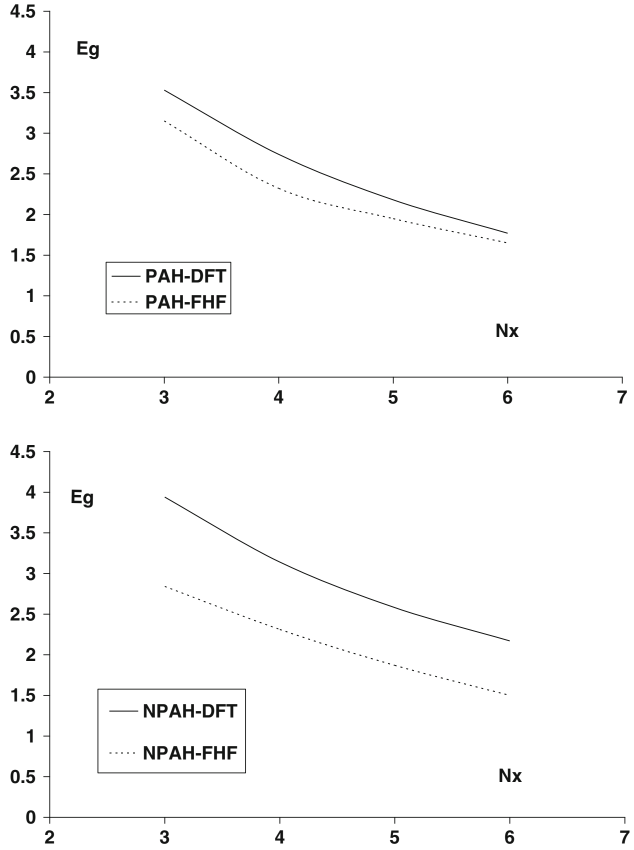

Fig. 2 Dependence of the DFT [32] and FHF Energy gaps E_g, in eV, of the oligoacenes (or PAHs) and of the SZEN-oligoacenes (or NPAHs), on the number of their aromatic rings, N_x. The results of the PAHs are shown in the *up panel*, and obviously, the PANH ones are given in the *down panel*. The authors of Ref. [32] provide the μ_e value only for the SEN hexaacene, $\mu_e^{\text{DFT}} = 12.82$ D, being $\mu_e^{\text{FHF}} = 11.84$ D

We have established the qualitative correctness of the calculated moments $\vec{\mu}_e$ by analyzing their μ_x and μ_y components for 43 R_6 NPAHs. The qualitative, both electrostatic and symmetric, correctness of these (vector) dipolar results provides a strong support to the reliability of the code. According to our definition, the vector $\vec{\mu}_e$ points out from (negative) Nitrogen atoms to (positive) Carbon ones. The achieved mean value $\bar{e}$ of the percentage relative μ_e errors of the polar molecules ($\bar{e} = \sum_{i=1}^{i=27} e_i/27, e_i = 100 \times \left|\mu_e^{\text{exct}} - \mu_e^{\text{appr}}\right|/\mu_e^{\text{exct}}$) is 20%.

The numerical accuracy of the components μ_x and μ_y has been checked by comparing (see Table 1) our values with the ones published by Brown et al. for some azaphenantrenes and azaanthracenes [33, 34]. These authors are, probably, the only ones who provide numerical (absolute) values of μ_x and μ_y. We have assumed that their axes a_μ, b_μ are very close to our x, y ones. For the quinoline, our results show an excellent (fortuitous) agreement with the experimental values, $e_{\text{quin}} = 5\%$. However, the large deviations ($\sim 50\%$) observed in some of these molecules remind us that we cannot expect high accuracy results because of the rough approximations used. The strength of our approach lies on its tremendous computational efficiency (fastness). The calculation of a NPAH with $N_a \approx 100$ can be done in a fraction of a PC second, whereas an NPAH with $N_a \approx 5{,}000$ needs a few PC hours.

We give (see Table 2) preliminary (rough) results for the remaining azaphenantrenes and azaanthracenes and for the polar naphthyridines. We have been able to find in the existing literature the μ_e value for only one of these molecules.

The interested reader can find the whole results in the supplementary Table s1.

5 The ferroelectric and ferromagnetic properties of the molecular SZEN-GNRs

The geometric (C, N) structure of the molecular SZEN-GNRs is formed by first linking N_y parallel oligoacenes

Table 1 Comparison of our μ_x, μ_y values, in Debyes, with the ones published by Brown et al. [33, 34]

IUPAC	Common	Present work	Met.	μ_x	μ_y
Azanaphthalene	Quinoline	$2 > N$	FHF	−0.19	−1.98
			DFT	−0.22	−2.08
			EXP	−0.14	−2.01
2-Azanaphthalene	Isoquinoline	$2N$	FHF	1.85	−0.16
			DFT	2.45	−0.94
			EXP	2.36	−0.90
9-Azaanthracene	Acridine	$3 > 2N$	FHF	0	−2.99
			DFT	0	−1.95
10-Azaphenanthrene	Phenanthridine	$1;\ 1;\ 1 > 2N$	FHF	1.17	−2.20
			DFT	1.40	−1.90
4,5-Diaza phenanthrene	1,10-phenanthroline	$1;\ 1;\ 1 > 5N\ > 2N$	FHF	−2.79	0
			DFT	−3.29	0

Table 2 Preliminary results for the μ_x, μ_y components, in Debyes, of the remaining azaanthracenes and azaphenantrenes, and of the polar naphthyridines

Anth.	μ_x	μ_y	Phen.	μ_x	μ_y	Napht.	μ_x	μ_y
$3N$	2.09	0.16	$1;\ 1;\ 1N$	1.55	−1.18	$2N > 1N$	2.09	−2.19
$3 > N$	−0.28	−2.26	$1;\ 1;\ 1 > N$	−0.41	−1.79	$2N > 2N$	0	−0.32
			$1;\ 1;\ 1 > 1N$	−1.27	−1.57	$2N > 6N$	2.04	1.82
			$1;\ 1;\ 1 > 5N$	−1.38	0.75	$2 > N > N$	0	−3.91

The experimental μ_e value of the 1,8-diazanaphtyridine (or $2 > N\ > N$ PANH) seems to be [27] 4.10 D

having N_x, $N_x + 1$, N_x, $N_x + 1\ldots$ aromatic rings, and then replacing the uppermost N_x Carbon atoms by Nitrogen ones. The significant (large) results corresponding to $N_y = N_x = 7$ are shown in Fig. 3. Most of the atomic negative charge concentrates at the Nitrogen atoms, placed at the up edge. The Mulliken atomic charges, q_a, of these Nitrogen edge atoms are represented by the q_e symbol. On the other hand, a significant amount of the positive charge is spread (or un-localized) over all the Carbon atoms. This un-localization of the positive charge distribution implies a large μ_e value. Most of the excess spin density concentrates at the down-edge Carbon atoms. The atomic excess density, d_a, of these Carbon edge atoms is represented by the d_e symbol. The values q_a and d_a remain unchanged (up to four figures) under the left–right reflection of the vertical plane (normal to the figure) that crosses the two edge central atoms c and c''. Due to this symmetry, we have $\mu_x = 0$.

The interested reader can find the whole atomic results in the supplementary Tables s2 and s3.

The increase of the electronic density at the Nitrogen atoms implies a higher occupation of the empty lowest beta SMOs, located in these atoms. This effect reduces the Nitrogen d_e values significantly. The symmetric antiferromagnetic coupling between the opposite zig-zag edges is

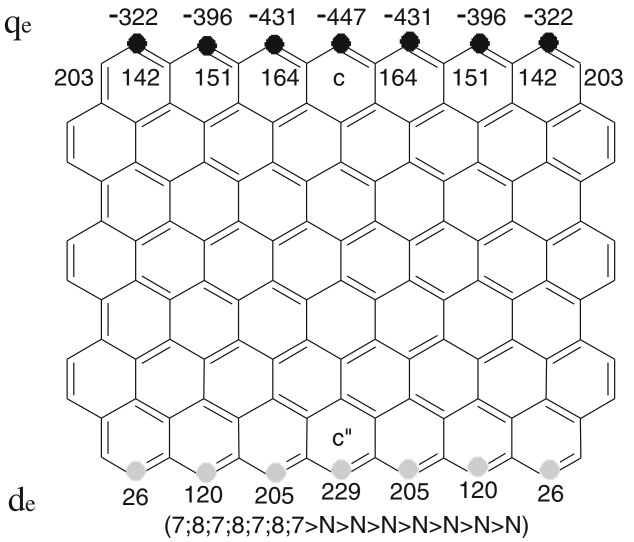

Fig. 3 Geometrical structure and ghPAH formula (*down*) of an SZEN-GNR having $N_y = N_x = 7$. The *black filled circles* represent the Nitrogen atoms of the horizontal up edge, and the *gray filled circles* represent the Carbon atoms of the horizontal down edge. The up-edge Nitrogen negative charges and the down-edge Carbon (excess) densities are represented by q_e and d_e, respectively. All the atomic results have been multiplied by 1,000. The central c and c'' atoms are symmetry invariant

Table 3 Dependence of the mean atomic electric moment μ_a on the number of rows, N_y, and rings (of the shortest oligoacene), N_x, of the SZEN-GNRs

$N_y \backslash N_x$	7	15	23	31	39	47
7	526	597	583	681	659	650
15	492	618	674	641	682	648
23	479	613	664	686	701	712
31	473	610	659	659	645	680
39	469	608	568	611	689	660
47	466	493	691	655	717	723

These μ_a results are given in mDebyes/atom

Table 4 Dependence of the spin (excess), d_e^c, in $m\mu_B$, of the central edge carbon, c'' atom, on the number of rows, N_y, and rings, N_x, of the SZEN-GNRs

$N_y \backslash N_x$	7	15	23	31	39	47
7	229	231	220	186	193	190
15	229	223	211	209	208	206
23	229	220	211	210	207	207
31	229	219	211	210	207	206
39	229	218	213	209	208	208
47	229	216	213	210	209	208

then not possible. This fact implies a larger μ_m value. These conclusions agree with the ones of Li et al. [35]. These authors have theoretically studied several periodic ($N_x \approx \infty$) thin ($N_y = 9$) Nitrogen-doped zig-zag GNRs. In one of these GNRs, they replaced a C–H unit of the upper zig-zag edge by a Nitrogen atom. Their conclusion was: the spin polarization of this "doped" edge is suppressed, whereas the "un-doped" lower edge has an atomic magnetization of 0.19 $\mu_{B.}$.

We have performed a systematic study of the dependence of the dipolar moments of large molecular SZEN-GNRs on their thickness (N_y) and length (N_x). The conclusions obtained for the 36 SZEN-GNRs with N_y, $N_x = 7, 15, 23, 31, 39, 47$ are similar to one another.

In Table 3, we show the dependence of their mean atomic electric moment μ_a, defined as $\mu_a = \mu_e / N_a$, on N_y and N_x. The existing convergence irregularities are due to the numerical approximations of our approach. The numerical errors of the charges q_a (or of the atomic spin densities d_a^σ) are amplified by the large x_a values. In fact, we found significant symmetry losses ($\mu_x \neq 0$) when larger GNRs were calculated. The μ_a moment should tend to a large value close to 0.7 D. These results extend the conclusions of Hudgins et al. [31], who found large μ_e values for the cations of small circum coronenes and ovalenes. These large values of μ_a suggest that the SZEN-GNRs should have significant ferroelectric properties.

In Table 4, we show the dependence of the spin (excess), d_e^c, of the central Carbon edge atom c'', on the number of rows (thickness) N_y and (shortest) oligoacene length N_x of the studied SZEN-GNRs. The convergence of the d_e^c values is more regular than the one of the μ_a ones, since they are obtained as differences between the atomic spin densities d_a^σ. The limit of d_e^c (N_y, N_x), for N_y, $N_x \to \infty$, should be very close to 0.208 μ_B. The atomic magnetization value (0.19 μ_B, $N_y = 9$, $N_x \approx \infty$) by Li et al. [35], mentioned before, agrees up to two figures with the result of our most alike molecular GNR (0.190 μ_B, $N_y = 7$, $N_x = 47$). The large values of d_e^c suggest that the (molecular) SZEN-GNRs should have significant ferromagnetic properties.

Finally, we have replaced, for the 36 N-GNRs considered, the lowest (gray) Carbon atoms (which concentrate most of the spin) by Borons. It seems there is some interest [38–43] on the theoretical study of GNRs which have simultaneously Nitrogen and Boron (BN-GNRs). We have arrived to the expected conclusions. The rejecting of electrons by the Boron significantly increases (decreases) the electric (magnetic) molecular moment. The μ_a values are multiplied by a factor of about 2, and the BN-GNRs become nearly diamagnetic.

6 Conclusions

Our improvements over the existing scientific bibliography are the following.

We have designed a methodology that is able to obtain a very fast reasonable quantum description of any molecular heteroatomic PAH. The quantum description of any NPAH can directly be obtained from its (ghPAH) chemical formula. We present novel values of the electric dipolar moments $\vec{\mu}_e$ for several small NPAHs. We have obtained the atomic spin densities for large (2,500 rings) SZEN-GNRs. These densities respect the spatial symmetry. According to our theoretical results, the molecular SZEN-GNRs should have significant ferroelectric and ferromagnetic properties.

Acknowledgments We would like to acknowledge the long-lived (1967–2008) contribution (to the field of the theoretical study of the nitrogen PAHs) by Prof. Ronald Brown, who passed away in November 2008. This project was financially supported by the CICYT, Spain, through the grant CTQ2008-06839-C03-03/PP. Special thanks are due to Dr. I. Rodriguez Ramos and Dr. A. Guerrero Ruiz for their helpful advice.

References

1. Nobel Prizes in (Theoretical) Chemistry: Pauling LC (1954), Mulliken RS (1966), Fukui K et Hoffman RS (1981), Kohn W et Pople JA (1998)

2. Lipkowitz KB, Boyd DB (eds) (1990–2010) Reviews in computational chemistry, vol. 1–27. Wiley Online Library
3. Fukumoto K (ed) (1973–2010) Heterocycles, vol 1–82
4. Castle L (ed) (1964–2010) J Heterocycl Chem, vol 1–47
5. Kalvinsh I (ed) (1965–2010) Chem Heterocycl compd, vol 1–46
6. Mumtaz M, George J (1995) Toxicological profile for polycyclic aromatic hydrocarbons. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta
7. Tielens AGGM (2008) Annual review of astronomy and astrophysics space sciences division. NASA 46:289
8. Wu J, Pisula W, Müllen K (2007) Chem Rev 107:718
9. Allen MJ, Tung VC, Kaner RB (2010) Chem Rev 110:132
10. Nakayama N, Nagashima U (2003) J Mol Struct (Theochem) 640:25
11. Radovic LR, Bockrath B (2005) J Am Chem Soc 127:5917
12. Hata T, Murakami T, Shibuya H, Ono Y (2006) Chem Pharm Bull 54:646
13. Khavryuchenko VD, Tarasenko YA, Strelko VV, Khavryuchenko OV, Lisnyak VV (2007) Int J Mod Phys B 21:4507
14. Huang YC, Chang CP, Lin MF (2007) Nanotechnology 18:495401
15. Pisani L, Chan JA, Montanari B, Harrison NM (2007) Phys Rev B 75:64418
16. Yang L, Park CH, Son YW, Cohen ML, Louie SG (2007) Phys Rev Lett 99:186801
17. Hod O, Barone V, Scuseria GE (2008) Phys Rev B 77:35411
18. Raza H, Kan EC (2008) J Comput Electron 7:372
19. Li Y, Zhou Z, Shen P, Chen Z (2009) J Phys Chem C 113:15043
20. Zhou J, Wang Q, Sun Q, Chen XS, Kawazoe Y, Jena P (2009) Nano Lett 9:3867
21. Pollet R, Amara H (2009) J Chem Theory Comput 5:1719
22. Xiang H, Kan E, Wei SH, Whangbo MH, Yang J (2009) Nano Lett 9:4025
23. Alvarez-Collado JR (2008) Int J Quantum Chem 108:257
24. Alvarez-Collado JR (2008) J Chem Phys 129:154703
25. Alvarez-Collado JR (2010) Int J Mod Phys B (accepted)
26. Brown RD, Coller BAW (1967) Theoret Chim Acta 7:259
27. Markgraf JH, Skinner JF, Marshall GT (1988) J Chem Eng Data 33:9
28. Doerksen RJ, Thakkar AJ (1996) Int J Quantum Chem 30:1633
29. Palmer MH, McNab H, Walker IC, Guest MF, McDonald M, Siggel MRF (1998) Chem Phys 228:39
30. Mattioda AL, Hudgins DM, Bauschlicher CW, Rosi M, Allamandola LJ (2003) J Chem Phys A 107:1486
31. Hudgins DM, Bauschlicher CW, Allamandola LJ (2005) Astrophys J 632:316
32. Winkler M, Houk KN (2007) J Am Chem Soc 129:1805
33. McNaughton D, Godfrey PD, Brown RD, Thorwirth S (2007) Phys Chem Chem Phys 9:591
34. McNaughton D, Godfrey PD, Brown RD, Thorwirth S, Grabow JU (2008) Atrophys J 678:309
35. Li Y, Zhou Z, Shen P, Chen Z (2009) ACS Nano 3:1952
36. Qu L, Liu Y, Baek JB, Dai L (2010) ACS Nano 4:1321
37. Wang Y, Shao Y, Matson DW, Li J, Lin Y (2010) ACS Nano 4(4):1790
38. Barone V, Peralta JE (2008) Nano Lett 8:2210
39. Du A, Chen Y, Zhu Z, Amal R, Lu GQ, Smith SC (2009) J Am Chem Soc 131:17354
40. Chen W, Li Y, Yu G, Zhou Z, Chen Z (2009) J Chem Theory Comput 5:3088
41. Lai L, Lu J, Wang L, Luo G, Zhou J, Qin R, Gao Z, Mei WN (2009) J Phys Chem C 113:2273
42. Zheng XH, Wang XL, Abtew TA, Zeng Z (2010) J Phys Chem C 114:4190
43. Chen W, Li Y, Yu G, Li CZ, Zhang SB, Zhou Z, Chen Z (2010) J Am Chem Soc 132:1699