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Spin Magnetism of Finite Length Carbon Nanotubes

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Спиновый магнетизм углеродных нанотрубок конечной длины

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Спіновий магнетизм вуглецевих нанотрубок кінцевої довжини

We apply the calculation model, which is based on the Hartree-Fock-Racah theory of the averaged quasi-spin multiplet degenerate open shell, to demonstrate that finite zigzag CN hyperbolic levels give rise to a lot of spectroscopic terms with the nonzero total spin and the energy, very close to that of the ground state. Hence, a very small external influence can produce parallel orientation of CN spins, which does not disappear immediately and results in the observable remanence.
Key Words: zigzag carbon nanotubes, Hartree-Fock-Racah calculation model, configuration interaction, spin magnetism.

Мы применяем модель расчета, основанную на теории Хартри-Фока-Рака для усредненного квазиспинового мультиплета вырожденной открытой оболочки, чтобы продемонстрировать, что гиперболические уровни у конечных зигзаг CN расщепляются в большое количество спектроскопических состояний с ненулевым суммарным спином и энергией, очень близкой к основному состоянию. Поэтому очень небольшое внешнее воздействие может привести к параллельной ориентации спинов CN, которая может не исчезнуть сразу и привести к наблюдаемой остаточной намагниченности.
Ключевые слова: углеродные зигзаг нанотрубки, Хартри-Фока-Рака расчетная модель, конфигурационное взаимодействие, спиновый магнетизм.

Ми застосовуємо модель розрахунку, засновану на теорії Хартрі-Фока-Рака для усередненого квазі-спінового мультиплета виродженої відкритої оболонки, щоб продемонструвати, що гіперболічні рівні в кінцевих зигзаг CN розщеплюються у велику кількість спектроскопічних станів з ненульовим сумарним спіном і енергією, дуже близькою до основного стану. Тому дуже невелика зовнішня дія може привести до паралельної орієнтації спінів CN, яка може не зникнути відразу і призвести до спостережуваної залишкової намагніченості.
Ключові слова: вуглецеві зігзаг нанотрубки, Хартрі-Фока-Рака розрахункова модель, конфігураційна взаємодія, спіновий магнетизм.

1 Introduction

The spin magnetism of carbon nanotubes (CN) has been observed recently by detecting of the inhomogeneous magnetic field of CN when it placed on a uniformly magnetized ferromagnetic film [1]. The authors of Ref. [1] estimate value of found magnetic moment as 0.001 μ_B per carbon atom and interpret it as brought by each electron from the bond with ferromagnetic film when chemical potentials of the latter and CN are aligned [2].

Almost simultaneously, it was theoretically proved that finite zigzag CN possess a specific set of one-electron levels, half-filled and situated in the close vicinity of the Fermi level [3], [4] (in contrast to armchair CN). These hyperbolic levels (in terms of [4]) and the ground state degeneracy of finite zigzag CN with even number of teeth were found in tight binding approximation (TBA) and by means of a technique, based on the special version of Hartree-Fock-Racah theory for the averaged quasi-spin multiplet [5]. This approach has already allowed explaining a lot of fullerene properties [6], [7].

The same scheme is used to demonstrate directly that hyperbolic levels give rise to a lot of spectroscopic terms with the nonzero total spin. The highest spin value is approximately proportional to the number of hyperbolic states, calculated in TBA. It is found that for the large enough length of CN and diameter of order 0.5 nm, the energy of the state with the highest spin is the lowest. Hence, a very small influence (in particular, of the external magnetic field) can produce parallel orientation of CN spins, which does not disappear immediately and results in the observable remanence. The longer CN is the greater the number of hyperbolic levels and magnetic states and the narrower the conduction band. Approximately 0,2% of all pi-electrons are shown (in TBA) to belong to the hyperbolic levels for CN with 10^5 atoms C [4].

2 Calculation model

To include the electron interaction we use the Hamiltonian for the open shell averaged quasi-spin multiplet [5]:

$$\mathbf{F} = \mathbf{F}^{(1)} - [\mathbf{Y}, \mathbf{F}^{(2)}]_+, \quad \mathbf{F}^{(1)} = \mathbf{H} + G(\mathbf{I} + \mathbf{Y}) + (2f - 1)G(\mathbf{I} - \mathbf{Y}^2),$$
$$\mathbf{F}^{(2)} = (2f - 1)(\mathbf{H} + G(\mathbf{I} + \mathbf{Y})) + \zeta J(\mathbf{I} - \mathbf{Y}^2) + \eta K(\mathbf{I} - \mathbf{Y}^2) \tag{1}$$

Here, $\mathbf{I} + \mathbf{Y}$ is the charge and bond-order density matrix, $\mathbf{I} - \mathbf{Y}^2$ is the same for the open shell, $\mathbf{F}$ is the Fock operator, $\mathbf{H}$ is the nuclear core energy matrix, J and K are linear matrix operations, describing Coulomb and exchange interactions and acting on the charge distribution, indicated in brackets, and $G = J + K$. The optimal orbitals (or matrix $\mathbf{Y}$) and energy $E_{\xi\eta}$, characterizing the averaged quasi-spin multiplet, can be found from the matrix conditions:

$$\mathbf{FY} = \mathbf{YF}, \quad \mathbf{Y}^3 = \mathbf{Y}, \quad E_{\xi\eta} = \mathrm{Tr}[(\mathbf{I} + \mathbf{Y})(\mathbf{F}^{(1)} + \mathbf{H}) + (\mathbf{I} - \mathbf{Y})(\mathbf{F}^{(2)} + (2f - 1)\mathbf{H})] / 2. \tag{2}$$

Numerical constants f, ζ, and η depend on the number of electron pairs n (n can be half-integer) in the open shell, the degeneration degree (or the number of one-electronic levels included in the open shell) m, the spin s, and the seniority number v, $v = s, s + 1, \ldots, n$.

$$f = n / m,$$
$$\zeta = 1 - 4f(m - n)/(m - 1) + 2[s(s + 1) + v(m + 1 - v)] / m(m - 1)(m + 2), \tag{3}$$
$$\eta = 1 - 8f(m - n)/(m - 1) + 4[s(s + 1) + v(m + 1 - v)]/(m - 1)(m + 2).$$

In the present case, $n = m/2$, and the highest geminals occupation number $(n+1)/2$ corresponds to a mixed state with $v = s = 0$ [5]. It should be mentioned that the above

equations describe the Hartree-Fock open shell with the highest possible spin ($n = v = s$) as well as the most correlated (condensed) state of electronic pairs ($s = v = 0$ for maximal possible n) [5].

3 Results and discussions

The results of numerical calculations are shown in the Table 1. It demonstrates that in all case the state with maximal possible spin for each n is the lower one. Thus, for zigzag CN the first possibility is realized: the higher spin terms have a lower energy in accordance with the Hund rule. It is also clear that the longer CN is the more orbitals (corresponding to the hyperbolic levels) may be included in the open shell, and the appropriate state has the energy lower or comparable to that of the proposed ground state with lower spin (see the highlighted data). The states with the higher spin prevail for the longer finite CN. These states as well as hyperbolic levels originate from the finite length of CN [4]. However, for the larger number of open shell orbitals, the calculation demonstrates the penetration of the spin density deeper inside CN. Nevertheless, the state with the spin density concentrated at the tube ends remains the lower one for any given spin. The average calculated magnetic moment per "surface" (i.e. belonging to the CN teeth) carbon atom is $0.2 - 0.3$ μ_B.

Table 1 – Energy lowering of zigzag CN as compared to standard ground state

M	N	R**	L**	N	0/0, n=3	0/1*	1/1	2/3	3/3	SCF
CN with even number of teeth (n) and degenerate shell, (ground state s = v = 0, n = 1)										
5	8	3.17	9.10	80	-0.6871	0.9091	1.8240	0.4869	1.7909	1.0774
6	8	3.17	11.20	96	-0.0926	1.0139	2.0315	1.1187	2.4745	1.3758
4	10	3.92	7.0	80	-0.8270	0.6364	1.2777	0.3907	1.7142	0.8058
5	10	3.92	9.10	100	-0.0663	0.7578	1.5206	1.2089	2.6062	0.9894
4	12	4.68	7.0	96	-0.5459	0.5381	1.0797	0.7140	2.0637	0.7683
					0/0, n=5	0/1	1/1	3/3	5/5	SCF
7	12	4.68	13.3	168	-2.1709	0.8002	1.6022	3.9956	2.5285	1.3003
8	12	4.68	15.40	192	-5.6576	0.8548	1.7106	4.3561	3.0829	1.4809
7	14	5.45	13.3	196	-1.1498	0.7005	1.4025	3.9084	3.8375	1.0232
CN with odd number of teeth (n), (ground state s = 0, n = v = 2)										
					0/0, n=4	1/2	2/2	¾	4/4	SCF
6	5	2.06	11.20	60	-7.3796	0.5204	1.7353	-5.7030	-4.5094	0.2553
5	9	3.54	9.10	90	-3.7618	0.5699	1.7912	-1.7677	-0.3267	-0.0538
6	9	3.54	11.20	108	-3.2746	0.6190	1.9344	-1.2852	0.1575	-0.1930
4	11	4.30	7.0	88	-3.1654	0.5058	1.5765	-1.0551	0.4557	0.4131
5	11	4.30	9.10	110	-2.4433	0.5584	1.7334	-0.3259	1.2058	-0.0246
3	13	5.07	4.90	78	-3.4057	0.4408	1.3623	-1.2234	0.3090	0.6234
4	13	5.07	7.0	104	-2.3611	0.4929	1.5218	-0.1801	1.3725	0.5157
					1/2	2/2	3/4	4/4	6/6	SCF
6	15	5.83	11.2	180	0.5530	1.6888	1.6094	3.2852	1.5771	0.1067
5	17	6.60	9.10	170	0.4969	1.5144	1.3715	3.0031	1.9627	0.1190

* The values of s/v, n=v. ** In A°.

The finite zigzag CN give a rare example of a system with naturally separated set of orbitals, corresponding to the set of levels with very narrow gaps. The well-known method of configuration interaction (CI) is very suitable just for such case. Another conclusion form the table (see cases $m = 5$, $n = 9$; $m = 5$, $n = 10$; $m = 5$, $n = 11$) is that the present particular version of CI technique, which admits consideration of mixed states, allows

sometimes to build states with lower energy than that of the Hartree-Fock state with the same spin. It should be mentioned that the most important for the above conclusions states are pure: those with maximal spin ($n = v = s$) and states of the degenerate open upper shell of zigzag CN with even number of teeth ($n = 1$, $v = 1$, $s = 0$, $s = 1$ and $v = 0$, $s = 0$). In the latter case the triplet state is the lower and singlet states separated from each other and from the triplet by equal energy intervals. The table also demonstrates that the correlated state (maximal n, $s = 0$) in zigzag CN lies much higher than the Hartree-Fock states.

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