NICOTINE ADSORPTION ON BN POROUS SHEETS: A DENSITY FUNCTIONAL THEORY STUDY

R. MAJIDI[1], A.R. KARAMI[2]

[1]*Deparment of Physics, Shahid Rajaee Teacher Training University, Lavizan, Tehran, Iran,*
E-mail: royamajidi@gmail.com, r.majidi@srttu.edu

[2]*Deparment of Chemistry, Shahid Rajaee Teacher Training University, Lavizan, Tehran, Iran,*
E-mail: arkaramigazafi@gmail.com

The usage of BN porous sheet as sensor for detection of nicotine molecule was investigated. The structural and electronic properties of three different BN porous sheets were calculated by density functional theory. The calculations show that nicotine molecule is physisorbed on BN porous sheets and charge is transferred from molecule to sheet. Adsorption of the donor molecule makes these BN porous structures with insulating properties, n-type semiconductors. The sensitivity of the electronic properties of BN porous sheets to the presence of nicotine molecule indicates the possibility of using these sheets as sensor for nicotine detection.

Key words: Density functional theory; Two-dimensional porous sheets; Nicotine; Electronic property; Sensor.

1. INTRODUCTION

Nicotine is highly toxic alkaloid that is present in tobacco leaves [1, 2]. Nicotine treatment had been shown to improve cognitive function including attention, concentration, learning and memory [3]. However, nicotine has beneficial therapeutic properties; its undesirable and addictive side effects have limited its therapeutic use [4]. It should be mentioned that nicotine overdose can cause insomnia, withdrawal symptoms, rapid breathing, heart palpitations and high blood pressure [5]. Therefore, fabrication of sensitive sensors and filters is essential for detection of nicotine molecule. The recent advances in nanotechnology have enabled researchers to design and fabricate sensors by using nanostructures. Many sensors based on fullerene, carbon nanotubes, graphene and graphyne sheets and tubes have been suggested for detection of different molecules [6-20]. Particularly, the use of fullerene and carbon nanotubes for nicotine detection was reported [16-20]. It was shown that carbon nanotubes can be used as nicotine sensors due to sensitivity of their electronic properties to the presence of nicotine [16, 17]. Recently, we have investigated the possibility of using pristine, defective and porous graphene sheets for nicotine detection [21]. The results indicate that the defective and porous graphene sheets and carbon nanotubes are more sensitive to the presence of nicotine molecule than the perfect graphene and nanotubes [16, 17, 21]. The carboxylated carbon nanotubes were also used as an additive in filter tips to increase and tar sorption [19]. Non-carbon based nanomaterials were also

attracted considerable attention because of their interesting properties. Recently, BN two-dimensional sheets have been successfully predicted and fabricated. For instance, novel structures of BN porous sheets were constructed by selectively substitution of C atoms by B and N atoms [22-26]. These BN porous sheets with the electronic properties distinct from the pristine and porous graphene sheets open new perspective to novel applications. In the present work, we have investigated nicotine adsorption on BN porous sheets to determine whether these materials are applicable for sensing nicotine molecule.

2. COMPUTATIONAL METHOD AND MODELS

The calculations were performed by OpenMX3.7 package [27], whose fundamental is density functional theory (DFT). The function of Perdew, Burke and Ernzerhof (PBE) [28] based on generalized gradient approximation (GGA) was used to describe the exchange and correlation potential. The cutoff energy was set to be 100 Ry. The number of k-points taken along each high symmetry lines in the Brillouin zone was 41. The geometry optimization was performed until the force on each atom is less than 0.01 eV/Å.

We have considered three different structures of BN porous sheets. Similar to the porous C sheet, the porous BN sheet can be considered as the BN sheet with periodical BN hexagonal vacancies [25]. In the unit cell of the porous BN sheet, two BN hexagons are joined together via a B-N bond, or a B-B bond or a N-N bond. We have named BN porous sheets with homoelemental B-N bond (Fig. 1a), B-B bond (Fig. 1b) and N-N bond (Fig. 1c) as hBN, hB and hN, respectively. A supercell of 3×3 (Fig. 1) was used to study adsorption of nicotine molecule on these sheets. This was chosen to keep the separate distance (15 Å) between nicotine molecules large enough to eliminate their interaction in neighboring supercells. A vacuum layer 20 Å was set in the vertical direction to avoid interaction between the layer and its images.

3. RESULTS AND DISCUSSIONS

The bond lengths of the optimized structures (Fig. 1) are listed in Table 1. In hBN structure, there are two B-N bonds: The B-N bonds as a part of the rings are labeled by (*r*) and B-N bonds linking different rings are labeled by (*l*) in Table 1. The bond lengths are in good agreement with previous theoretical and experimental estimates [21-23, 25].

Table 1
Optimized bond lengths (Å).

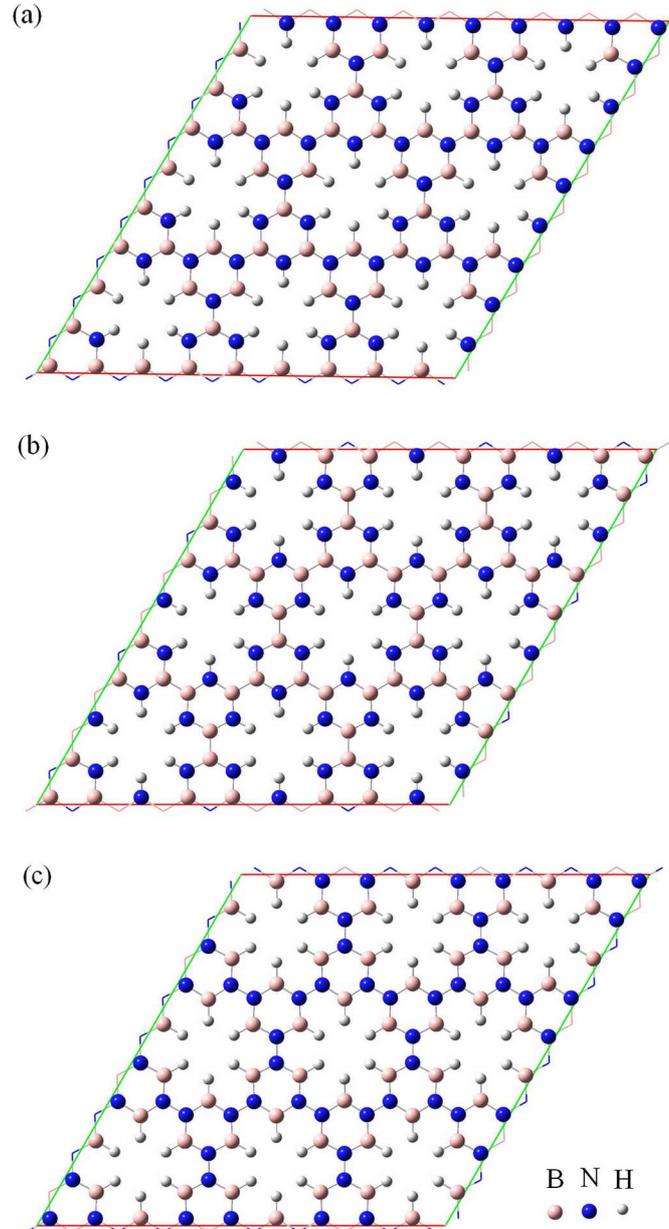|	hBN	hB	hN
B-N	1.43 (*r*), 1.45 (*l*)	1.04	1.44
B-B	-	1.52	-
N-N	-	-	1.44
B-H	1.23	-	1.18
N-H	1.05	1.05	-

Fig. 1 - Atomic structures of (a) hBN, (b) hB and (c) hN.

The stability of each structure was investigated by calculation of the cohesive energy (E_{coh}). This quantity is defined as

$$E_{coh} = \frac{\sum_x n_x E_x - E_T}{\sum_x n_x} \qquad (1)$$

where, E_T represents total energy of the BN system, n_x and E_x stands for the number and energy of an isolated atom of type x (x = B, N and H), respectively. Here, a larger cohesive energy indicates a more stable structure. The cohesive

energy of BN porous sheets is given in Table 2. The results are in good agreement with previous reports [22, 25, 29]. The cohesive energies indicate that these structures are stable in thermodynamics and they may be synthesized in ambient temperature. Here, hBN structure is more stable than hB and hN structures.

Table 2
Cohesive energy (E_{coh}), adsorption distance (d), adsorption energy (E_{ads}), energy band gap (E_g), and charge transfer, q.

	hBN	hB	hN
E_{coh} (eV/atom)	5.3	5.0	4.8
d (Å)	3.2	3.1	3.1
E_{ads} (eV)	1.1	1.2	1.2
E_g (eV)	4.1	3.1	3.0
q (e)	0.23	0.22	0.25

To define the electronic properties of BN porous sheets, the electronic band structures and density of states (DOS) of hBN, hB and hN structures were calculated. As shown in Fig. 2, these BN porous structures are insulator with large energy band gap of 4.1, 3.1 and 3.0 eV. According to the previous studies, the band gaps of hBN, hB and hN were reported 4.4, 3.4 and 3.9 eV, respectively [22, 25, 29]. The large band gaps of these BN structures are attributed to the strong ionicity of B-N bonds [25]. Our results indicate that the homoelemental bond has a considerable effect on the energy band gap. Wang and Ding [30] indicated that homoelemental bond can reduce the band gap distinctly because of the contribution of p_z orbital of N-N pair to valence bond maximum and the contribution of π orbital of B-B bond to conduction band minimum. The partial density of states (pDOS) of BN porous structures are also presented in Fig. 2. Here, the top conduction bands come mainly from the N atoms, while the bottom conduction bands are mainly from the B atoms. To evaluate stability of adsorbed molecule on BN porous sheet, adsorption energy (E_{ads}) is calculated as

$$E_{ads} = E_{nicotine+sheet} - E_{sheet} - E_{nicotine} \qquad (2)$$

where $E_{nicotine+sheet}$ is the total energy of BN porous sheet with adsorbed molecule, E_{sheet} is the total energy of BN sheet and $E_{nicotine}$ is the total energy of an isolated nicotine molecule. The negative values of the adsorption energy reveal that the adsorption is exothermic. A more negative value of adsorption energy indicates a stronger interaction between molecule and sheet. To determine the most stable adsorption configurations, we have considered nicotine molecule parallel and perpendicular to the sheets at different adsorption sites on the sheets. The adsorption energy of each configuration was calculated and compared. The results indicate nicotine molecule prefer to place parallel on the BN porous sheets. As an example, the most stable adsorption configuration of nicotine adsorbed on hBN sheet is shown in Fig. 3. To determine the optimal distance between nicotine molecule and BN porous sheet, adsorption energy as a function of adsorption distance was calculated. The optimal adsorption distance and adsorption energy of the most stable structure are listed in Table 2. The large adsorption distance and small adsorption energy indicate physisorption of nicotine molecule on BN porous sheets. All the atomic structures were fully relaxed. It was found that nicotine physisorption induces no significant change in the atomic structures of BN sheets.
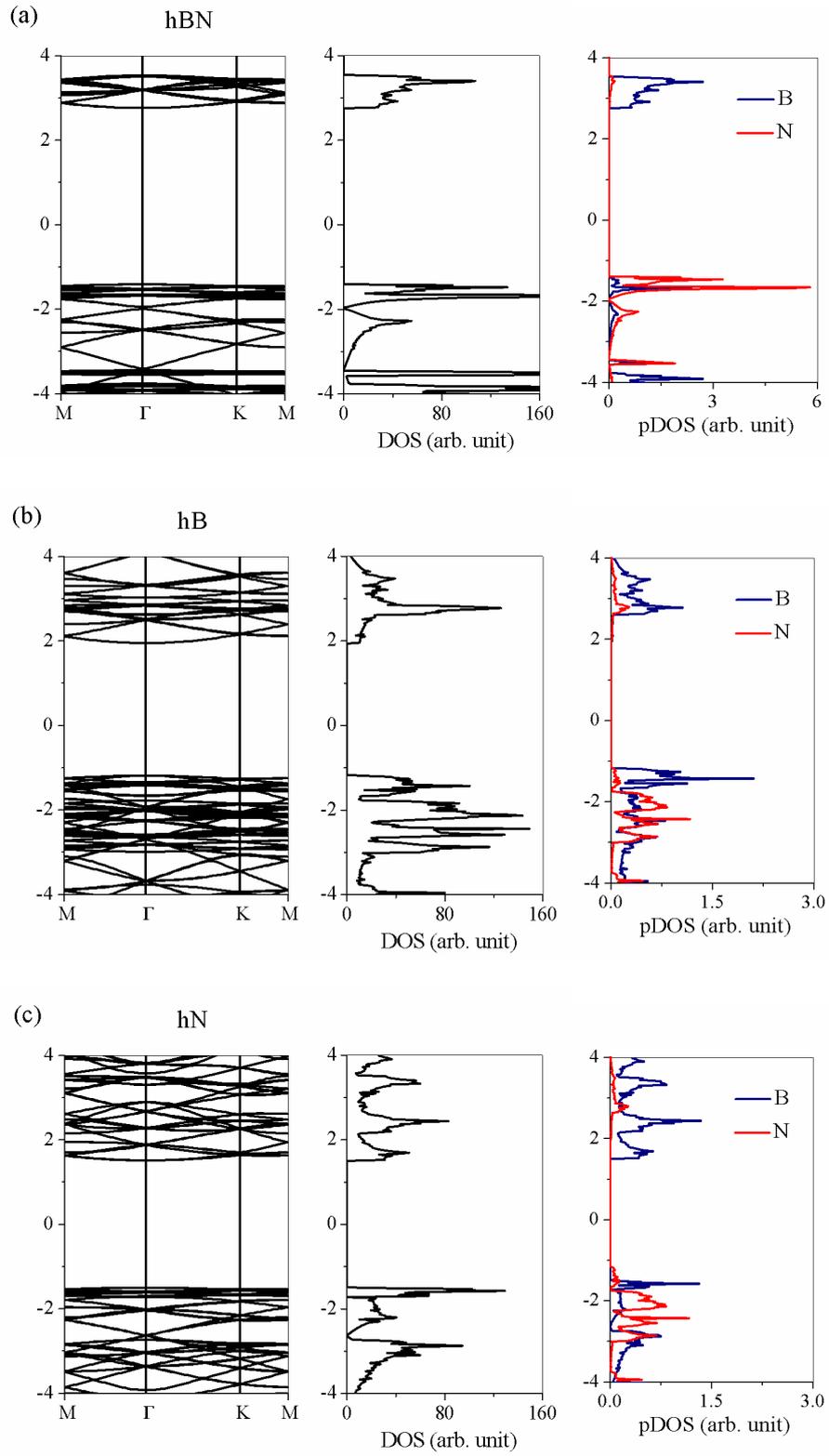
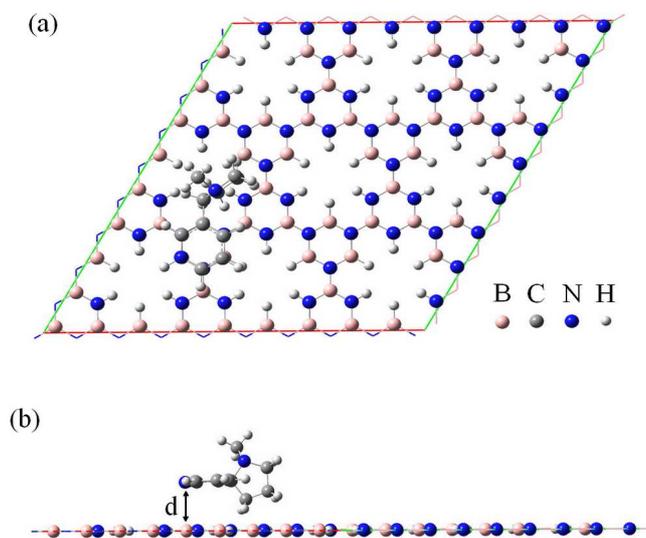Fig. 2 - Electronic band structures, DOS and pDOS of (a) hBN, (b) hB and (c) hN.

Fig. 3 - (a) Top and (b) side view of the most stable adsorption configuration of nicotine adsorbed on hBN sheet.

To clarify the effect of nicotine adsorption on the electronic properties of BN porous sheets, the electronic band structures and DOS of hBN, hB and hN structures in the presence of nicotine molecule are shown in Fig. 4. Here, adsorption of nicotine molecule leads to appearance of occupied states and sharp DOS peaks below the Fermi level (The Fermi level is at 0 eV). In the presence of nicotine molecule, hBN, hB and hN sheets become n-type semiconductors with energy band gap of 1.6, 1.0, and 1.1 eV, respectively. The Mulliken population analysis clarify that electrons are transferred from nicotine molecule to BN sheets. It means concentration of electrons and consequently electrical conductivity of BN porous sheets is increased by nicotine adsorption. The amount of charge transfer between adsorbed molecule and sheets is presented in Table 2. The charge transfer from molecule to BN porous sheets also reveals the n-type semiconducting properties of these sheets in the presence of nicotine molecule.

4. CONCLUSIONS

The effect of nicotine adsorption on the electronic properties of BN porous sheets was investigated. Three different structures of BN porous sheets were considered: hBN, hB and hN. The cohesive energy, adsorption energy, charge transfer, electronic band structures and DOS were calculated. It was found that these BN porous sheets were stable. The nicotine molecule was physisorbed on BN porous sheets. The charge was transferred from nicotine molecule to BN porous sheets. These BN porous sheets with insulating properties become n-type semiconductors with adsorption of a donor molecule such as nicotine molecule. The results indicate the electronic properties of BN porous sheets were sensitive to the presence of nicotine molecule. These results may provide new ideas to develop sensors based on BN nanomaterials for nicotine detection.
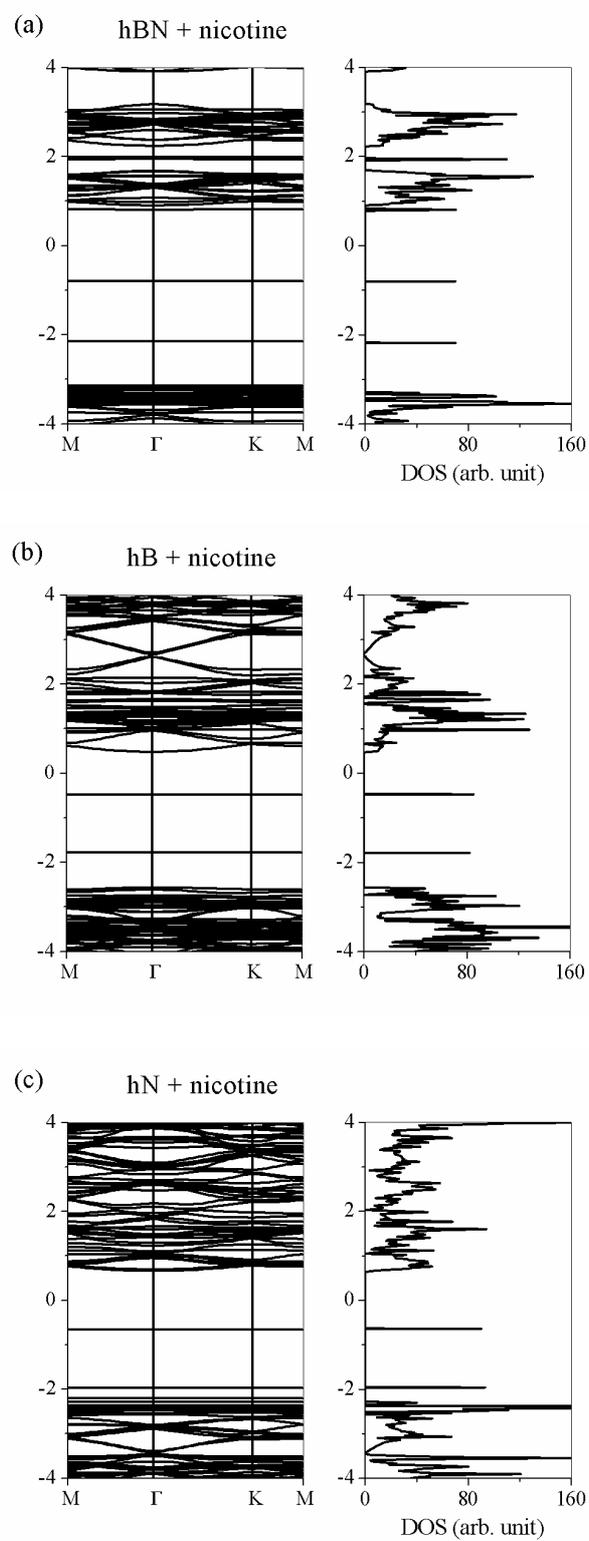
Fig. 4 - Electronic band structures and DOS of (a) hBN, (b) hB and (c) hN in the presence of nicotine.

5. ACKNOWLEDGEMENT

REFERENCES

1. J. Rusted, L. Graupner, N. O'Connell, C. Nicholls, Psychopharmacology **115**, 547 (1994).
2. Y. Xu, J.H. Zhu, L.L. Ma, J.A. An, Y.L. Wei, X.Y. Shang, Microporous and Mesoporous Mater. **60**, 125 (2003).
3. M. N. Howe, I. Price, Int. Psychogeriatr. **13**, 465 (2001).
4. V.E. Moran, Frontiers in Pharmacology **3**, 173 (2013).
5. http://www.livestrong.com/article/91383-caffeine-nicotine/
6. J. Zhao, A. Buldum, J. Han, J.P. Lu, Nanotechnology **13**, 195 (2002).
7. M. Chi, Y.P. Zhao, Comput. Mater. Sci. **56**, 79 (2012).
8. M. Chi, Y.P. Zhao, Comput. Mater. Sci. **46**, 1085 (2009).
9. R. Majidi, Mol. Phys. **111**, 89 (2012).
10. O. Leenaerts, B. Partoens, F.M. Peeters, Phys. Rev. B **77**, 125416 (2008).
11. R. Majidi, A.R. Karami, Physica E **54**, 177 (2013).
12. R. Majidi, A. R. Karami, Indian J. Phys. **88**, 483 (2014).
13. R. Majidi, A.R. Karami, Physica E **59**, 169 (2014).
14. A.R. Karami, R. Majidi, Chem. Lett. **44**, 1071 (2015).
15. A. R. Karami, R. Majidi, Rom. Journ. Phys. **60**, 1474 (2015).
16. E.C. Girao, S.B. Fagan, I. Zanella, A.G.S. Filho, J. Hazard. Mater. **184**, 78 (2010).
17. H.J. Lee, G. Kim, Y.K. Kwon, Chem. Phys. Lett. **580**, 57 (2013).
18. M. Baei, P. Torabi, H. Mohammadian, S. Hashemian, Full. Nanotube Carb. Nanostruct. **23**, 874 (2015).
19. Z.G. Chen, L.S. Zhang, Y.W. Tang, Z. J. Lia, Apl. Surf. Sci. **252**, 2933 (2006).
20. E. C. Girao, S.B. Fagan, I. Zanellab, A. G. Souza Filho, J. Hazard. Mater. **184**, 678 (2010).
21. R. Majidi, A.R. Karami, (submited).
22. J-R. Feng, G-C. Wang, Compt. Mat. Sci. **11**, 366 (2010).
23. E. Perim, R. Paupitz, P.A.S. Autreto, D.S. Galvao, J. Phys. Chem. C **118**, 23670 (2014).
24. P. Kuhn, A. Forget, D. Su, A. Thomas, M. Antoniette, J. Am. Chem. Soc. **130**, 13333 (2008).
25. Y. Ding, Y. Wang, S. Shi, W. Tang, J. Phys. Chem. C **115**, 5334 (2011).
26. R. Majidi, Cand. J. Phys. Doi: 10.1139/cjp-2015-0445.
27. T. Ozaki, H. Kino, J. Yu, M.J. Han, N. Kobayashi, M. Ohfuti, F. Ishii, et al. User's manual of OpenMX version 3.7. <http://www.openmx-square.org>.
28. J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. **77**, 3865 (1996).
29. G. Brunetto, P.A.S. Autreto, L.D. Machado, B.I. Santos, R.P.B. dos Santos, D.S. Galvao, J. Phys. Chem. C **116**, 12810 (2012).
30. Y.L. Wangm Y. Ding, Ann. Phys. **526**, 415 (2014).