Electronic structure and magnetic properties of $^{31}\text{P}@\text{C}_{60}$-SWCNT as peapods

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Abstract. Design of the NMR quantum computer of 1D spin chains based on $^{31}\text{P}@\text{C}_{60}$-SWCNT as peapods was studied. Electronic structure and magnetic properties of $^{31}\text{P}@\text{C}_{60}$ encapsulating fullerenes within SWCNT as peapods was investigated by quantum chemical calculation. Characterization of chemical shifts of $^{13}\text{C}$, principle $g$-tensor and $A$-tensor of hyperfine structure for phosphorus atom with electronic spin $S=3/2$ and nuclear spin $I=1/2$ were studied. The excited energy and wavelength at 1512 nm and 728 nm confirmed assignment of the first and second states as van Hove transitions. Molecular design of carbon peapods is important to control quantum spin qubits, splitting by spin-local interaction and dipole-dipole interaction based on $p$-orbital spin density distribution under hybridization of molecular orbital at excited state and grand state.

1. Introduction

Electronic structure of single-walled-carbon nanotube (SWCNT) encapsulating fullerenes have considerably been studied after the discovery of $\text{C}_{60}@\text{SWCNT}$ as peapods [1]. A scalable spin quantum computer that combines aspects of magnetic properties with the advantageous features of endohedral fullerenes within SWCNT has been proposed. Design of spin labels inside for possible molecular spintronics, which contains of 1D spin chains of magnetic endohedral fullerenes of $^{14}\text{N}@\text{C}_{60}$ and $^{31}\text{P}@\text{C}_{60}$ within SWCNT have been proposed [2]. The magnetic parameters of principle $g$-tensor, $A$-tensor for hyperfine coupling constant ($hfc$) of nitrogen, phosphorus atoms, chemical shift of $^{13}\text{C}$ in $^{14}\text{N}@\text{C}_{60}$ within SWCNT as peapods for chiral index had been investigated by ESR, ENDOR, NMR and DFT [3,4]. The magnetic endohedral fullerenes of $^{14}\text{N}@\text{C}_{60}$ and $^{31}\text{P}@\text{C}_{60}$ within SWCNT
have a high advantage of the NMR quantum computer to control spin gate with decoupling pulses in relaxation time. For instance, Morton reported the NMR quantum-computer controlled un-perturbation Rabi oscillation of spin polarization under influence of decoupling process [5, 6]. In this present work, electronic structure and magnetic properties of $^{31}$P atom encapsulating fullerenes within SWCNT as peapods was investigated by quantum chemical calculation. Characterization of chemical shifts of $^{13}$C, principle $g$-tensor and $A$-tensor for hyperfine structure of phosphorus atom with electronic spin $S=3/2$ and nuclear spin $I=1/2$ were studied. The magnetic properties were discussed on the basis of spin local interaction related on $p$-orbital spin density distribution under hybrization of molecular orbital at grand state and excite state. Especially, magnetic properties of $^{31}$P and $^{14}$N atoms encapsulating fullerenes within SWCNT as peapods based on the electronic structure at grand state and excited state was focused on controlling quantum spin qubits for NMR quantum computer.

2. Quantum chemical calculation

The molecular structures were assembled by CS ChemDraw, CS Chem3D (Cambridge Soft) and Nanotube Modeler (JCrystal Soft). Molecular orbital calculations were carried out by molecular mechanics calculations (MM2) and semi-empirical molecular orbital calculations (Hamiltonian: Parameterized Model Revision 3: PM3). In addition, the isolated molecular structures were optimized by ab-initio quantum calculation using unrestricted Hartree–Fock (UHF) and DFT using UB3LYP with hybrid function LANL2DZ and STO-3G*, 3-31G* and 6-31G* as basis set because of computational limitations (Gaussian 03 Inc.). HOMO, LUMO, LUMO+1 and the HOMO-LUMO band gap ($E_g$) were calculated. Phosphorus atomic charges of $^{31}$P@C$_{60}$ within SWCNT were estimated by Mulliken population analysis. Continuously, chemical shift ($\delta$) of $^{13}$C, principle $g$-tensor ($g_{xx}$, $g_{yy}$, $g_{zz}$) and $A$-tensor ($A_{xx}$, $A_{yy}$, $A_{zz}$) in hyperfine coupling constant ($hfc$) of nitrogen atom were calculated by DFT using NMR / GIAO with hybrid function UB3LYP and 3-31G* as basis set. Excited energy and wavelength were calculated by TD-DFT.

3. Results and Discussion

Electronic structure of molecular orbital at HOMO an LUMO and energy levels of $^{31}$P@C$_{60}$-SWCNT (9, 9) and $^{14}$N@C$_{60}$-SWCNT (9, 9) was investigated by DFT with hybrid function UB3LYP using STO-3G* as basis set. Figure 1 shows electron structure and energy levels of $^{31}$P@C$_{60}$-SWCNT (9, 9). Electron spin density distribution of $p$-orbital in phosphorus atom was localized at HOMO. The electron spin density distribution at LUMO was delocalized on surface of carbon tube. As listed in Table 1, energy levels at HOMO and LUMO and energy gap of $^{31}$P@C$_{60}$-SWCNT were -1.58 eV, -1.09 eV and 0.49 eV, which narrowed as compared with the levels of $^{14}$N@C$_{60}$-SWCNT and $^{31}$P@C$_{60}$ and $^{14}$N@C$_{60}$. Mulliken atomic charge for phosphorus atom in $^{31}$P@C$_{60}$-SWCNT was estimated to be $-1.9 \times 10^{-2}$ e, which indicated negative charge transfer from C$_{60}$ to phosphorus atom. In reference case,
the Mulliken atomic charge for the phosphorus atom in $^{31}$P@C$_{60}$ was $5.7 \times 10^2$ e, which suggested charge transfer from phosphorus to C$_{60}$. Gross orbital populations of $3s$ orbital and $3p$ orbital in the phosphorus atom inside C$_{60}$ within SWCNT were 2.03, 1.03, 1.03 and 1.03, respectively. These results indicate localization of spin orbital distribution at $3s$ orbital and principle $3p$ orbital: $p_{xx}$, $p_{yy}$, $p_{zz}$ in the phosphorus atom inside C$_{60}$ within SWCNT. In contrast case using $^{14}$N@C$_{60}$-SWCNT, gross orbital populations of $2s$ orbital and $2p$ orbital in nitrogen atom inside C$_{60}$ within SWCNT were 0.94, 0.64, 0.64 and 0.64, respectively. There was considerable delocalization of $2s$ orbital and $2p$ orbital in nitrogen atom. As reference cases using $^{31}$P@C$_{60}$ and $^{14}$N@C$_{60}$, the gross orbital populations of nitrogen and phosphorus atom inside C$_{60}$ suggested delocalization of $s$ orbital and $p$ orbital. Comparison between $^{31}$P@C$_{60}$-SWCNT and $^{31}$P@C$_{60}$ supports the assertion that spin distribution at $3p$ orbital on phosphorus atom is well screened within the C$_{60}$ cage around SWCNT. On the basis of comparison between $^{31}$P@C$_{60}$-SWCNT and $^{31}$P@C$_{60}$, coverage of SWCNT with $^{31}$P@C$_{60}$ on the electronic structure was influenced by $\pi$ orbital interaction of carbon cage between C$_{60}$ and SWCNT with hybrization of $p$-orbital spin density distribution in $^{31}$P atom covered with C$_{60}$ and SWCNT. As reported in Ref. 4, we will expect considerable influence on geometrical structure of $^{31}$P@C$_{60}$ within SWCNT varied with chirality and diameter on the electronic structure.

Table 2 lists EPR parameters of principal $g$-tensor, $A$-tensor in hyperfine coupling constant ($hfc$) for carbon peapods, calculated by DFT/UB3LYP/STO-3G*. The magnetic parameters of principal $g$-tensor ($g_{xx}$, $g_{yy}$, $g_{zz}$), $A$-tensor ($A_{xx}$, $A_{yy}$, $A_{zz}$) of $hfc$ for $^{31}$P@C$_{60}$-SWCNT (9, 9) were estimated to be 1.96509, 1.99151, 2.00298, 5.7, 5.5 and 3.5, respectively. The calculated results would be mainly attributed to hyperfine coupling interaction based on isotropic and anisotropic spin density distribution.
Table 1. Electronic structure of carbon peapods, fullerenes, and SWCNT, as calculated by DFT using UB3LYP/ STO-3G* as basis function.

| Molecule          | HOMO/LUMO (eV) | $E_g$ (eV) | Mulliken atomic charge / e | Gross orbital populations |
|-------------------|---------------|-----------|---------------------------|---------------------------|
| $^{31}$P@C$_{60}$-SWCNT | -1.58/-1.09   | 0.49      | -1.9 $\times 10^{-2}$    | $N$: 2$s^2$, 2$p^3$, $P$: 3$s^2$, 3$p^3$ |
| $^{14}$N@C$_{60}$-SWCNT | -4.05/-2.89   | 1.16      | $3.8 \times 10^{-5}$     | 0.94, 0.64, 0.64, 0.64    |
| $^{31}$P@C$_{60}$      | -6.41/-3.68   | 2.73      | $5.7 \times 10^{-2}$     | 1.49, 0.70, 0.70, 0.70    |
| $^{14}$N@C$_{60}$      | -6.60/-3.57   | 3.03      | $-4.5 \times 10^{-3}$    | 0.93, 0.64, 0.64, 0.64    |
| SWCNT (9, 9)            | -4.08/-2.84   | 1.24      | -                        | -                         |

The hyperfine coupling interaction was the sum of isotropic ($A_{iso}$) and anisotropic interaction ($A_{aniso}$). The isotropic interaction of $A_{iso}$ corresponded to Fermi contact interaction based on s spin localization on the phosphorus atom covered with the C$_{60}$ cage within SWCNT. The anisotropic hyperfine interaction of $A_{aniso}$ in $hfc$ for $^{31}$P@C$_{60}$-SWCNT was approximately 10 times as large as those of $^{14}$N@C$_{60}$-SWCNT. This result was strongly related to magnetic interaction between the electron and nuclear spin on the nucleus under a control of angle-dependence on p-orbital spin density distribution.

Nuclear quadrupole interaction is based on multiplication of nuclear quadrupole moment $Q$ and the electric field gradient ($EFG$) tensor generated by charge distribution around nucleus. There was a slight different value of $Q$ for $^{31}$P@C$_{60}$-SWCNT and $^{14}$N@C$_{60}$-SWCNT as listed in Table 2. The chemical shift of $^{14}$N@C$_{60}$-SWCNT compared with $^{31}$P@C$_{60}$-SWCNT will be shifted by nuclear quadrupole interaction between $Q$ and $EFG$ tensor, as shown in Fig. 2.

Table 2. EPR parameters of principal g-tensor and A-tensor in hfc (DFT/UB3LYP/STO-3G*).

| $^{31}$P@C$_{60}$-SWCNT (9, 9) | $^{14}$N@C$_{60}$-SWCNT (9, 9) |
|----------------------------------|---------------------------------|
| $A_{iso}/G$ | $A_{aniso}/G$ | $Q/DA$ | $A_{iso}/G$ | $A_{aniso}/G$ | $Q/DA$* |
| 5.7        | -9.13          | -0.050  | -759        | 6.0           | 10.43   | -0.002 | -813 |
| 5.5        | -0.034         | -759    | 2.00098     | 6.0           | 0.000   | -819  |
| 3.5        | 0.084          | -729    | 2.00093     | 3.8           | 0.002   | -771  |

* $Q/DA$: Quadrupole moment / Debye-Ang.

Magnetic mechanism will be discussed on the basis of the quantum calculation. Especially, geometrical effect of magnetic fullerenes within SWCNT varied with chirality and diameter on chemical shift of $^{13}$C, principal g-tensor, A-tensor for hfc of central atom and excited state transition will be considered. The magnetic properties would be originated in the spin-local interaction and dipole-dipole interaction based on p-orbital spin density distribution of central atom covered with C$_{60}$ and inner surface on SWCNT varied with chirality and diameter. Spin Hamiltonian is formulated with different terms as noted by Eq. (1). These terms represent the following interaction: electron and
nuclear Zeeman interaction, hyperfine structure of the spin-nuclear interaction, the fine structure of the spin-spin interaction and the nuclear quadrupole interaction. The magnetic parameters of principle \textit{g}-tensor and \textit{A}-tensor for \textit{hfc} are based on electron spin density distribution and dipole-dipole interaction. Magnetic parameter of \textit{g}-tensor is sum of isotropic and anisotropic parts as noted by Eq. (2)-(3). Anisotropic \textit{g}-tensor is related with extent of spin-local interaction under hybrization of molecular orbital at grand state and excited states. The \textit{A}-tensor of \textit{hfc} is sum of isotropic and anisotropic terms as noted by Eq. (4)-(5). The isotropic \textit{A}-tensor \((A_{iso})\) as Fermi contact interaction is in proportion as the \textit{s} spin density distribution. The anisotropic \textit{A}-tensor \((A_{aniso})\) as dipole-dipole interaction is under a control of angle dependence on \textit{p}-orbital electron spin distribution.

The chemical shifts of \textit{\textsuperscript{13}C} with multicity for \textit{31P@C\textsubscript{60}}-SWCNT and \textit{\textsuperscript{14}N@C\textsubscript{60}}-SWCNT had been quantitatively analyzed by \textit{ab-nitio} DFT calculation. Figure 2 show the chemical shift of \textit{\textsuperscript{13}C} with multicity for \textit{31P@C\textsubscript{60}}-SWCT and \textit{\textsuperscript{14}N@C\textsubscript{60}}-SWCNT. The chemical shift of \textit{\textsuperscript{13}C} for \textit{31P@C\textsubscript{60}}-SWCNT was shifted with multicity and multi-splitted in the range of 80-100 ppm. The chemical shifts of \textit{\textsuperscript{13}C} were confirmed as part of SWCNT and \textit{C\textsubscript{60}} at 80 ppm and 100 ppm. In contrast, the chemical shift of \textit{\textsuperscript{13}C} for \textit{\textsuperscript{14}N@C\textsubscript{60}}-SWCNT was shifted with multicity and multi-splitted in a wide spin-spin coupling as part of SWCNT and \textit{C\textsubscript{60}} at 110 ppm and 130 ppm. The chemical shifts for both cases using carbon peapods mainly had influence on the paramagnetic effect under the spin-dipole interaction.
In general case, the chemical shift of $^{13}$C with multicity for $^{31}$P@C$_{60}$-SWCNT and $^{14}$N@C$_{60}$-SWCNT can be explained by Karplus-Pople equation [7] as noted by Eq. (7). The chemical shift mainly consists with diamagnetism and paramagnetic parts in first and other terms as noted by Eq. (7). The chemical shift strongly range for $p$-orbital nuclei dominated by paramagnetic parts. The paramagnetic term has an influence on spin-local interaction under hybrization of molecular orbital at excited state and grand state. The spin-local interaction is based on the $p$-orbital spin density distribution. The chemical shift of $^{13}$C with multicity will be influenced by hybrization of molecular orbital at energy levels between excited state and grand state in second term as noted by Eq. (7).

$$\sigma = \frac{e^2}{3mc^2} \left( \sum_k \frac{1}{r_k^3} \right) \left\langle 0 \left| \sum_k \frac{L_k}{r_k^3} \right| n \right\rangle$$

$$- \frac{2}{3} \left( \frac{eh}{2mc} \right)^2 \sum_n \frac{1}{E_n - E_0} \left\{ \left\langle 0 \left| \sum_k L_k \right| n \right\rangle \left\langle n \left| \sum_k \frac{L_k}{r_k^3} \right| 0 \right\rangle + \left\langle 0 \left| \sum_k \frac{L_k}{r_k^3} \right| n \right\rangle \left\langle n \left| \sum_k L_k \right| 0 \right\rangle \right\}$$

(7)

Table 3 list excited energy level and optical wavelength of $^{31}$P@C$_{60}$-SWCNT and $^{14}$N@C$_{60}$-SWCNT, calculated by TD-DFT. The excited energy for $^{31}$P@C$_{60}$-SWCNT was in the range of 0.8199 eV-1.7042 eV, which converted to the wavelength in the range of 1512-728 nm. There were multi-state energy levels from HOMO to LUMO, LUMO+1 and band gaps, which would be assigned as first and second state as Van Hove transition at 0.8199 eV (1512 nm) and 1.6920 eV (733 nm). Similarly, the excited energy with wavelength for $^{14}$N@C$_{60}$-SWCNT confirmed assignment of the first and second state as van Hove transition on Raman spectroscopy with density of state using tight binding model as Van Hove transition at 0.728 eV (1703 nm) and 1.169 eV (1061 nm) as listed in Table 3. The
calculated results made agreement with experimental results using UV-vis-NIR spectroscopy [8]. Consequently, the magnetic properties were summarized with spin local interaction, dipole-dipole interaction, nuclear quadropole interaction and hybrization of molecular orbital at excited state and grand state. The spin density distribution and the hybrization of molecular orbital at excited state are important to control the spin gate for NMR quantum computer. Molecular design of $^{14}\text{N}@C_{60}$-SWCNT rather than $^{31}\text{P}@C_{60}$-SWCNT as the NMR quantum computer is advantage to quantum-calculate at multiple-state.

### Table 3. Excited energy levels and wavelength of $^{31}\text{P}@C_{60}$-SWCNT (9, 9) and $^{14}\text{N}@C_{60}$-SWCNT (9, 9), calculated by TD-DFT.

|          | $^{31}\text{P}@C_{60}$-SWCNT (9, 9) | $^{14}\text{N}@C_{60}$-SWCNT (9, 9) |
|----------|-------------------------------------|-------------------------------------|
| Energy   | Wavelength                         | Oscillator Strength                | Energy   | Wavelength | Oscillator |
| (eV)     | (nm)                               |                                     | (eV)     | (nm)       | Strength   |
| 1.7042   | 728                                 | 0.0006                              |          |            |            |
| 1.6920   | 733                                 | 0.0012                              |          |            |            |
| 1.5606   | 794                                 | 0.0007                              | 1.169    | 1061       | 0.0007     |
| 0.8949   | 1386                                | 0.0002                              |          |            |            |
| 0.8679   | 1429                                | 0.0002                              |          |            |            |
| 0.8199   | 1512                                | 0.0002                              | 0.728    | 1703       | 0.0001     |

### 4. Conclusion
Design of the NMR quantum computer of 1D spin chains based on $^{31}\text{P}@C_{60}$-SWCNT as peapods was studied. Comparison between $^{31}\text{P}@C_{60}$ and $^{14}\text{N}@C_{60}$ within SWCNT as peapods on electronic structure and magnetic properties was investigated. Electronic structure and magnetic properties of $^{31}\text{P}@C_{60}$ encapsulating fullerenes within SWCNT as peapods was investigated by quantum chemical calculation. Characterization of chemical shifts of $^{13}\text{C}$, principle g-tensor and A-tensor of hfc in phosphorus atom with electronic spin $S=3/2$ coupled with nuclear spin $I=1/2$ were employed. The magnetic properties were originated in spin-local interaction, dipole-dipole interaction based on $p$-orbital spin density distribution, nuclear quadropole interaction and hybridization of molecular orbital at excited state and grand state. The calculated chemical shifts were mainly dominated by paramagnetic term with spin local interaction and hybrization of molecular orbital at excited and grand state. The excited energy levels and wavelength confirmed assignment of the first and second van Hove transition, which made agreement with the experimental results of UV-vis-NIR, Raman using tight binding model. Molecular design of $^{14}\text{N}@C_{60}$-SWCNT rather than $^{31}\text{P}@C_{60}$-SWCNT as the NMR quantum computer is advantage to quantum-calculate with controlling quantum spin-qubits at multiple state.
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