Phase transition in one-dimensional hydrogen chain: A dependence on basis orbitals, cut off radius, and doping

T B Prayitno* and R Fahdiran

Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Jakarta, Kampus A Jl. Rawamangun Muka, Jakarta Timur 13220, Indonesia

*tteguh-budi@unj.ac.id

Abstract. We demonstrated the dependence of the phase transition in the one-dimensional hydrogen chain on the basis orbitals, the cut off radius, and the doping. For reducing the computational cost, we employed the so-called generalized Bloch theorem, where a hydrogen atom was used in the unit cell. For the non-doped case, we showed a strong dependence of the phase transition on the basis orbitals and the cut off radius, which yields either the antiferromagnetic ground state or the ferromagnetic ground state. When the doping was considered, the spiral ground state appeared between the antiferromagnetic state and the ferromagnetic state. Therefore, we showed that the doping induced the spiral ground state.

1. Introduction

The hydrogen atom, which is considered as the simplest system, has given a good description of how to obtain the energy levels in the appropriate orbitals in quantum mechanics. Indeed, this needs an available approximation to obtain the analytical solution. This result can be used then to calculate some more complex systems, i.e., the systems containing two electrons or more.

The early discussion revealed that the one-dimensional hydrogen chain, which is constructed by a set of hydrogen atoms, showed interesting phenomena. Some authors justified that this system has a metallic property by using either the perturbative approach or the density functional theory (DFT) [1-3]. This consideration suggests that the one-dimensional hydrogen chain may be used as a toy model to understand the complex systems.

In this paper, we discuss the phase transition in the one-dimensional hydrogen chain in the framework of DFT, in which the pseudo-atomic orbitals are regarded as the basis sets. To overcome the high computational cost, we utilize the generalized Bloch theorem (GBT) [4-11], with which we only use one hydrogen atom in the unit cell. We will show that the phase transition strongly depends on some parameters, such as the number of bases, the cutoff radius, and the doping.

Phase transition in materials is an important indicator to verify if the materials produce the interesting properties. In perovskite manganite, there are several ground states, such as the ferromagnetic, antiferromagnetic, canted, and spiral states, which form a phase transition when introducing the carriers [12]. Evidently, the phase transition in perovskite manganite originates the so-called giant magnetoresistance, which is very useful for the nanotechnology.

For further discussion, we briefly explain the GBT and its application to the one-dimensional hydrogen chain in Sec. 2. We provide the phase transition dependence on the number of bases, the cut
off radius, and the doping in Sec. 3. At last, we give the conclusions based on the given phase transition of the one-dimensional hydrogen chain.

### 2. Method

The self-consistent noncollinear calculation was carried out by utilizing the linear combination of pseudo-atomic orbitals (LCPAO) [13,14] and the norm-conserving pseudopotentials [15], as implemented in the OpenMX code [16]. To use the GBT, we expand the noncollinear wavefunction in terms of LCPAO as [17]

\[
\psi_{\nu\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n} \sum_{\alpha} \left[ e^{i(k-0.5\mathbf{q}) \cdot \mathbf{R}_n} \psi_{\nu\mathbf{k},\alpha}^1 \left( \begin{array}{c} 1 \\ 0 \end{array} \right) + e^{i(k+0.5\mathbf{q}) \cdot \mathbf{R}_n} \psi_{\nu\mathbf{k},\alpha}^1 \left( \begin{array}{c} 0 \\ 1 \end{array} \right) \right] \times \phi_{\nu\alpha}(\mathbf{r} - \tau_i - \mathbf{R}_n)
\]

where \( \phi_{\nu\alpha} \) is addressed to the localized orbital function. At the same time, the magnetic moment of the hydrogen atom will rotate continuously from one cell to the other cells satisfying

\[
\mathbf{M}_i = M_i \{ \cos(\mathbf{q} \cdot \mathbf{R}_i) \sin \theta_i + \sin(\mathbf{q} \cdot \mathbf{R}_i) \sin \theta_i + \cos \theta_i \}
\]

To create a phase transition, we establish the planar spiral by setting \( \theta = \pi/2 \) with the constraint method [18,19], as shown in Figure 1.

**Figure 1**. Planar spiral in the one-dimensional hydrogen chain with \( \mathbf{q} \) along the \( x \) direction. The figures of atomic structures, as well as the magnetic moments, were produced by using XCrysSDen [20,21].

Here, the spiral state lies between the ferromagnetic and antiferromagnetic states. In this case, we vary the lattice constant, the number of orbitals, and the cut off radius. Note that the cut off radius is a boundary region, in which the orbitals will overlap each other. The constrained DFT calculations were performed by using a \( 40 \times 1 \times 1 \) k-point grid, the cut off energy of 200 Ryd, and the generalized gradient approximation (GGA) for the exchange potential [22]. Note that the GGA functional is usually more accurate than the LDA functional for the magnetic system, especially when the electron density is rapidly varied.

### 3. Result and discussions

Figure 2 shows the phase transition in the one-dimensional hydrogen chain from the antiferromagnetic state to the ferromagnetic state for different orbitals when the number of orbitals increases. We deduce...
that the phase transition is not influenced by varying the cutoff radius, as shown in Figures 2(a) and 2(b). Note that the orbitals of s1 and s1p1 give one and four orbitals, respectively.

![Figure 2](image1.png)

**Figure 2.** Phase transition of the one-dimensional hydrogen chain for the lattice constant of 2.0 Å with the cutoff radius of 6.0 Bohr (a) and 7.0 Bohr (b).

The same situation appears when we vary the lattice constant and fix the cutoff radius of 6.0 Bohr, as shown in Figure 3. All the lattice constants give the antiferromagnetic ground state for the orbital of s1 while the ferromagnetic ground state is induced by the orbitals of s1p1. This means that the phase transition is robust with respect to the lattice constant.

![Figure 3](image2.png)

**Figure 3.** Phase transition of the one-dimensional hydrogen chain as varying the lattice constant for the orbitals of s1 (a) and s1p1 (b), respectively. Here, we used the cutoff radius of 6.0 Bohr.
The new ground state, i.e., the spiral ground state then appears when the doping is introduced, as shown in Figure 4. For the non-doped case, the ground state is indeed the antiferromagnetic state, while the spiral ground state does exist for 0.1 e/cell and 0.2 e/cell hole doping. One can also prove that increasing the hole doping yields the ferromagnetic state, as discussed previously in Ref. [17]. In addition, if we add the orbital of \( p \), both the antiferromagnetic state and the spiral state will be replaced by the ferromagnetic state. This is due to only an \( s \) orbital in the hydrogen atom that really exists.

![Figure 4](image)

**Figure 4.** Phase transition of the one-dimensional hydrogen chain when the doping is introduced for the lattice constant of 2 Å and the orbital of \( s1 \) with the cutoff radii of 6.0 Bohr (a) and 7.0 Bohr (b).

Here, we give some comments on the relationship between the perovskite manganite and the one-dimensional hydrogen chain for the case of the phase transition. Since at the \( e_g \) state there is only one electron possessed by the Mn site in the perovskite manganite, the phase transition in perovskite manganite can be approached by using the one-dimensional hydrogen chain model. We obtain a phase transition, as shown in Figure 4, which is a good agreement with Ref. [12].

4. Conclusion

We have investigated the phase transition of the one-dimensional hydrogen chain by varying the basis orbitals, the cut off radius, and the doping. We find three different ground states, i.e., the ferromagnetic, spiral, and antiferromagnetic states, when the treatment above is employed. We also show that the phase transition strongly depends on the number of orbitals and the doping while varying lattice constant does not create a phase transition.

Acknowledgment

The detailed computations were carried out by utilizing the high computer at the Universitas Negeri Jakarta.

References

[1] Suhai S and Ladik J 1982 Perturbation theoretical calculation of the correlation energy in an infinite metallic hydrogen chain *J. Phys. C Solid State Phys.* **15** 4327

[2] Poshusta R D and Kelin D J 1982 Novel Ab Initio Correlated Calculations for an Infinite Chain of Hydrogen Atoms *Phys. Rev. Lett.* **48** 1555

[3] Suhai S 1994 Electron correlation in extended systems: Fourth-order many-body perturbation
theory and density-functional methods applied to an infinite chain of hydrogen atoms Phys. Rev. B 50 14791
[4] Sandratskii L M 1998 Adv. Phys.
[5] Halilov S V, Eschrig H, Perlov A Y and Oppeneer P M 1998 Adiabatic spin dynamics from spin-density-functional theory: Application to Fe, Co, and Ni Phys. Rev. B 58 293
[6] Knöpfle K, Sandratskii I M and Kübler J 2000 Spin spiral ground state of γ-iron Phys. Rev. B 62 5564
[7] García-Suárez V M, Newman C M, Lambert C J, Pruneda J M and Ferrer J 2004 First principles simulations of the magnetic and structural properties of Iron Eur. Phys. J. B-Condensed Matter Complex Syst. 40 371–7
[8] Heide M, Bihlmayer G and Blügel S 2009 Describing Dzyaloshinskii–Moriya spirals from first principles Phys. B Condens. Matter 404 2678–83
[9] Jacobsson A, Sanyal B, Ležaić M and Blügel S 2013 Exchange parameters and adiabatic magnon energies from spin-spiral calculations Phys. Rev. B 88 134427
[10] Jakobsson A, Mavropoulos P, Şaşıoğlu E, Blügel S, Ležaić M, Sanyal B and Galanakis I 2015 First-principles calculations of exchange interactions, spin waves, and temperature dependence of magnetization in inverse-Heusler-based spin gapless semiconductors Phys. Rev. B 91 174439
[11] Prayitno T B and Ishii F 2019 Carrier-induced antisymmetric-symmetric tendencies of spin stiffness in zigzag graphene nanoribbons J. Phys. Condens. Matter
[12] Inoue J and Maekawa S 1995 Spiral state and giant magnetoresistance in perovskite Mn oxides Phys. Rev. Lett. 74 3407
[13] Ozaki T. 2003 Phys. Rev. B. 67 155108
[14] Ozaki T, Kino H 2004 Phys. Rev. B. 69 195113
[15] Troullier N and Martins J L 1991 Efficient pseudopotentials for plane-wave calculations Phys. Rev. B 43 1993
[16] Ozaki T, Kino H, Yu J, Han M J, Kobayashi N, Ohfuti M, Ishii F, Ohwaki T, Weng H and Terakura K 2011 User’s manual of OpenMX version 3.6 D http://www.openmx-square.orgŠ
[17] Prayitno TB, Ishii F. 2018 J. Phys. Soc. Jpn. 87: 114709
[18] Gebauer R and Baroni S 2000 Magnons in real materials from density-functional theory Phys. Rev. B 61 R6459
[19] Kurz P, Förster F, Nordström L, Bihlmayer G and Blügel S 2004 Ab initio treatment of noncollinear magnets with the full-potential linearized augmented plane wave method Phys. Rev. B 69 24415
[20] Kokalj A, Lesar A, Hodošcek M and Causa M 1999 Periodic DFT study of the Pt (111): A p (1×1) atomic oxygen interaction with the surface J. Phys. Chem. B 103 7222–32
[21] Kokalj A 2003 Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale Comput. Mater. Sci. 28 155–68
[22] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865