



Contribution analysis of the van der Waals term on electronic structures of carbon related systems

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ABSTRACT

Contribution of the van der Waals term in the electron densities and the band structures of covalent bonding one-dimensional networks are studied. Calculations are performed with self-consistently implemented nonlocal van der Waals density functional (vdW-DF) into a first principle program. Results indicate that the contribution of the van der Waals term on band structures qualitatively depends on the bonding types, whether π orbitals are included or not in calculated systems.

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1. Introduction

Generalized gradient approximation (GGA) is an effective approximation method to evaluate the exchange–correlation energy in the density functional theory (DFT). It has been widely applied to determine the electronic states of various short-range exchange–correlation interactions. At the same time it has a serious limitation when applied to long-range (nonlocal) exchange–correlation interactions, as typified by the van der Waals (vdW) interaction. Many schemes have been developed within DFT to overcome this limitation including classical, semi-empirical and non-empirical methods [1–3]. Above all the nonlocal van der Waals density functional (vdW-DF) provided by Dion et al. [3] for non-self-consistent and Thonhauser et al. [4] following for self-consistent calculations seems one of the most valid and versatile approach. Utilities of this functional are already verified comparing with the S22 benchmark set of weakly interacting molecules and water clusters [5] in preceding calculations [6–9]. Román-Pérez et al. improved the calculating procedure using fast Fourier transforms implying further possibilities of this vdW-DF method [10]. There the nonlocal correlation term is given in terms of not only energy but also potential as non-empirical density functional formula. Thus self-consistent implementation into the Kohn–Sham equation which makes us possible to calculate various physical properties of dispersion bonded systems is also easy.

Chain molecules, like polyacetylene or polyethylene, are one of the simplest examples in which the vdW interaction plays an

important role in their physical properties. Basic properties such as lattice parameters of stacked structures of these polymers are already experimentally obtained long ago [11,12]. For the theoretical studies, Rohra et al. showed the exact-exchange approach improve the accuracy of calculating the band gap of bulk and isolated polyacetylenes than the LDA [13]. There are also many other approaches reported for accurate calculations in determining the structural optimizations and/or the electron states [14,15]. However there are no studies found analyzing how the vdW interaction contributes in determining a band structures for these systems in detail. Polyacetylenes include the π orbitals which is not included in polyethylenes. This difference is also expected to affect the contribution of the vdW interaction. In this study we analyze how the vdW interactions contribute in determining the band structures and electron densities of these typical examples of organic systems by comparing the calculation results by GGA and vdW-DF. Also comparing the difference between the results from polyacetylenes and polyethylenes, how the difference in the molecular orbital structures affect this interaction is discussed.

2. Computational method

The vdW-DF method used in this study is given by Thonhauser et al. and is able to calculate vdW potentials non-empirically [4]. The exchange–correlation potential consists from several different terms as,

$$v_{xc} = v_x^{GGA} + v_c^{LDA} + v_c^{nl} \quad (1)$$

where v_x^{GGA} is the exchange potential driven by the GGA in the Kohn–Sham equation and v_c^{LDA} is the correlation potential within the local density approximation (LDA). The last term v_c^{nl} is the

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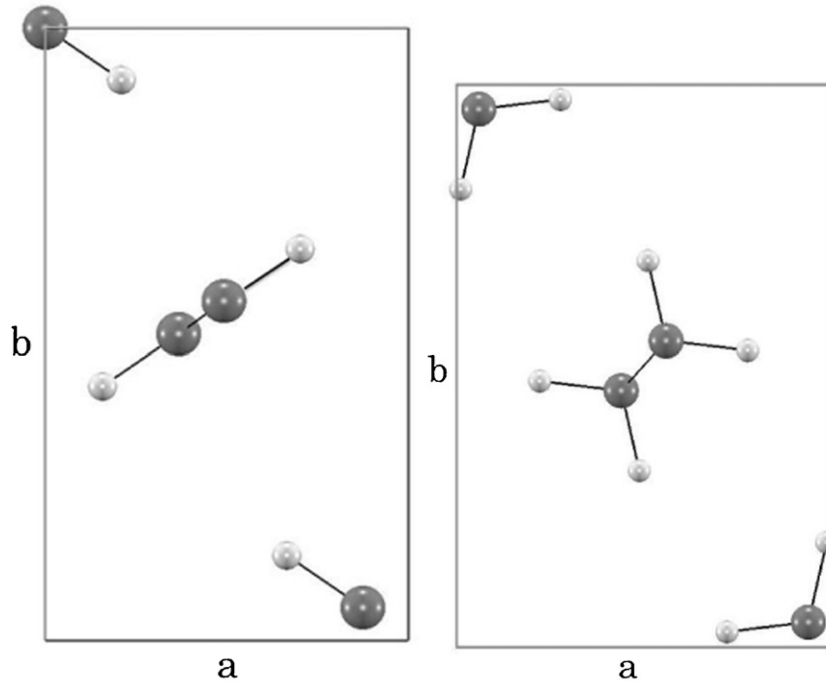


Fig. 1. Schematic projects of structure of bulk polymers. (a) Unit cell of bulk polyacetylene with $a=4.24 \text{ \AA}$ and $b=7.32 \text{ \AA}$. (b) Unit cell of bulk polyethylene with $a=4.96 \text{ \AA}$ and $b=7.42 \text{ \AA}$.

nonlocal correlation potential which is typified by the vdW term. The nonlocal correlation potential is obtained as $v_c^{nl} = \delta E_c^{nl} / \delta \rho(\mathbf{r})$ with that energy defined as

$$E_c^{nl} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') \quad (2)$$

Here $\phi(\mathbf{r}, \mathbf{r}')$ is a core function and $\rho(\mathbf{r})$ is an electron density. Since it takes time to determine $\phi(\mathbf{r}, \mathbf{r}')$ numerically, an easily determined asymptotic function

$$\phi(\mathbf{r}, \mathbf{r}') \rightarrow -\frac{12(4\pi/9)^3}{d_i^2 d_k^2 (d_i^2 + d_k^2)} = -\frac{12(4\pi/9)^3}{|\mathbf{r} - \mathbf{r}'|^6} \times \frac{1}{q_0^2(r) q_0^2(r')} (q_0^2(r) + q_0^2(r')) \quad (3)$$

is used in case $|\mathbf{r} - \mathbf{r}'|$ is large enough. Where d in this asymptotic function is a product of two functions as $d = |\mathbf{r} - \mathbf{r}'| q_0$. The former function depends only on the spatial positions \mathbf{r} and \mathbf{r}' , and the later depends directly on the electric density $\rho(\mathbf{r})$. Thus one can assume $\phi(\mathbf{r}, \mathbf{r}')$ as the function written in the second line of Eq. (3). In the right hand side of the second line in Eq. (3), the term in front of multiplication sign is an asymptotic term which does not depends on $\rho(\mathbf{r})$ while the later term depends only on $\rho(\mathbf{r})$. In periodic systems, the later term becomes a periodic term. Thus it is not necessary to calculate for the density $\rho(\mathbf{r} + \mathbf{t})$ once it has been calculated for the density $\rho(\mathbf{r})$. Here \mathbf{t} is a lattice vector. In this study we take in to account 20 unit cells for each x , y and z axis direction which is enough to regard as the calculation for infinite periodic systems. vdW-DF is self-consistently implemented into our own first principle band calculation code with ultrasoft pseudopotentials named PHASE. The plane wave basis set is truncated at 25 Ry. $1 \times 1 \times 4$ k -point and $4 \times 4 \times 4$ k -point samplings of the Brillouin zone are used for isolated and bulk systems, respectively. revpbe [16] which is more suitable than pbe [17] for dispersion bonded systems [6–8] is

used here among some other choices for the GGA exchange in Eq. (1).

3. Results and discussion

Using the self-consistently implemented vdW-DF, the electron density distributions and the band structures of isolated and bulked polymers are compared with those calculated using GGA. The atomic coordinates are taken from experimentally obtained positions [11,12] (Fig. 1). For isolated systems, unit cells are set to ensure the separation between two lateral polymers more than 8 \AA . Although in experiment, the ab plane in Fig. 1 (a) is slightly distorted for 1.5° to parallelogram from rectangle, we assumed as rectangle because of restriction in our vdW-DF program. However we consider that this factor is ignorable because the differences in electronic structures are confirmed to be limited by the GGA. The surfaces in Figs. 2–4 are the constant-height surfaces. Increases (by $0.014/\text{\AA}^3$ for Figs. 2(a), 4(a) and $0.012/\text{\AA}^3$ for Fig. 3) and decreases (by $0.014/\text{\AA}^3$ for Figs. 2(b) and 4(b)) of the electron densities in polymers when the vdW-DF is implemented are shown. In the case of the polyacetylene, since the increased area is localized around the π bonds (Fig. 2(a)) and the decreased area is localized around the σ bonds (Fig. 2(b)), the electrons tend to shift from σ orbital to π orbital by the vdW-DF implementation. This biased tendency corresponds to the shift in relative energy levels of σ and π bands. The band structure of an isolated polyacetylene is shown in Fig. 2(c). Each line is drawn with reference to the level of the lowest σ bands. There the π bands shift downward to the solid lines (vdW-DF) from the broken lines (GGA), while the σ bands shift upward slightly. Similar shifts are also seen the in bulked polyacetylenes. (Fig. 2(d)) The same band shifts seen in isolated and bulked systems indicate that the effects of self-consistently implemented vdW-DF on the electron states are limited mainly in range of a single individual molecule. The electron density shift in bulked polyacetylene is also compared with that in isolated one. As shown in Fig. 3 the same tendency is regarded, which also supports this interpretation.

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