



Recent progress in predicting structural and electronic properties of organic solids with the van der Waals density functional



Susumu Yanagisawa^{a,*}, Koji Okuma^a, Takeshi Inaoka^a, Ikutaro Hamada^b

^a Department of Physics and Earth Sciences, Faculty of Science, University of the Ryukyus, 1 Senbaru, Nishihara, Okinawa 903-0213, Japan

^b International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan

ARTICLE INFO

Article history:

Available online 17 April 2015

Keywords:

van der Waals interaction

Organic solids

First-principles method

Density functional

Cohesive property

Band structure

ABSTRACT

We review recent studies on electronic properties of the organic solids with the first-principles electronic structure methods, with the emphasis on the roles of the intermolecular van der Waals (vdW) interaction in electronic properties of the organic semiconductors. After a brief summary of the recent vdW inclusive first-principle theoretical methods, we discuss their performance in predicting cohesive properties of oligoacene crystals as examples of organic crystals. We show that a variant of the van der Waals density functional describes structure and energetics of organic crystals accurately. In addition, we review our recent study on the zinc phthalocyanine crystal and discuss the importance of the intermolecular distance and orientational angle in the band dispersion. Finally, we draw some general conclusions and the future perspectives.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Organic semiconductors, important ingredients of the organic electronics, play crucial roles in the devices such as organic light-emitting diodes (OLED), field-effect transistors (OFET), and organic photovoltaic cells (OPVC): charge carriers (electron and hole) are injected from the electrode into the organic layer, and they are transported in case of the OLED and OFET, or the holes and the electrons are separated at the donor-acceptor interface in the OPVC. Thus, it is of primary importance to elucidate the nature of the charge carriers in the bulk and at the organic–electrode and organic–organic interfaces.

The effect of configurations of the constituent molecules on the charge transport in organic semiconductors was theoretically demonstrated by Brédas et al. [1]. By quantum-chemical calculations the electronic splitting or the transfer integral was shown to depend quite sensitively on the geometrical parameters in the molecular packing: intermolecular distance, orientation angle of a molecule relative to the adjacent molecule, and the degree of translation along the long axis of a molecule [1]. The crystalline band formation in organic semiconductors from the interaction between the adjacent molecules was examined, and the effect of the intermolecular interaction on electronic and optical properties

of organic crystals under high pressure was clarified by band structure calculations [2–4].

While the roles of the configuration and conformation on the electronic structure of organic molecule dimers are pointed out based on the quantum chemical calculations, the factors governing the electronic structures of the organic solids are not yet fully understood. This is in part because the periodic density functional theory (DFT) within the (semi-)local approximation, such as the local density approximation (LDA) and generalized gradient approximation (GGA), is not able to describe the dispersion forces, which play a vital role in the cohesion of the organic crystal. Ambrosch-Draxl and co-workers have studied the electronic structures of organic crystals at ambient and high pressures by employing the experimental lattice constants, and pointed out the importance of the intermolecular distance [2,3,5]. Very recently, several methods have been proposed [6–8], which enable accurate prediction of equilibrium structures of organic crystals and their cohesive energies within the chemical accuracy, i.e. the deviation from the experimental value within 1 kcal/mol. These methods may allow one to explore the geometric and electronic structures of organic crystals without experimental inputs and to clarify the important factors determining their electronic structures.

Intrinsic electronic properties of organic semiconductors, i.e. electronic structures of the thin films and the single crystals, have been examined in recent years, thanks to the development of the precise measurement of the band dispersion with the angle-resolved photoelectron spectroscopy (ARPES). Not only the electronic properties of the constituent organic molecules, for

* Corresponding author. Tel.: +81 988958888.

E-mail addresses: shou@sci.u-ryukyu.ac.jp (S. Yanagisawa), Hamada.ikutaro@nims.go.jp (I. Hamada).

instance, the energy gap between the frontier molecular orbitals and their spatial distributions, but also their configuration or conformation in the crystals, have been highlighted. The interplay between the intermolecular configuration or orientation, which is dominated by the intermolecular van der Waals (vdW) interaction, and the electronic states determines the electronic properties of the organic semiconductors [9].

The hopping carrier transport mechanism was conventionally assumed for molecular crystals with negligibly small overlap between the neighboring molecules. On the other hand, it has been reported that some organic semiconductor single crystals and thin films have unexpectedly large bandwidth or high carrier mobility comparable to the amorphous silicon-based inorganic semiconductors. Rubrene [10,11], pentacene [12–14], picene [15], sexiphenyl [16], tetrakis(thiadiazole)porphyrine [17], and anthracene [18] were reported to have highest-occupied molecular orbital (HOMO) bandwidth larger than 100 meV. The hole mobility in some of the materials was determined to exceed 1–10 cm²/Vs [17,19–24]. The results signify the contribution of the band transport mechanism to the carrier transport in the organic crystals. To gain more insights into the electronic origins dominating the band structure and the carrier transport, theoretical studies of band structures are indispensable. First-principles electronic structure methods can reproduce the atomic-scale structures and the electronic properties therein, such as the orbital energies, the density of states, the band dispersion, and the spatial distribution of the electronic charge.

In this article, we first review the dispersion correction methods based on DFT [25–37], and the first principles van der Waals density functional (vdW-DF) [38–40]. Then, to illustrate the applicability of a vdW-inclusive DFT, we present results of the cohesive properties of series of oligoacene crystals by using the variant [8] of the vdW-DF. Finally, we draw concluding remarks with future perspective.

2. Recent developments in the first-principles theoretical methods for treating the van der Waals interaction in solids

The vdW force originates from the non-local electron correlation arising from the dynamical charge fluctuation. Such non-local and dynamical effect is inherently missing in LDA and GGA, as these approximations are local and static by construction. Thus in order to describe the non-local vdW forces, one needs to employ a method which goes beyond LDA and GGA or many body perturbation theory.

2.1. Grimme's dispersion corrected density functional theory

The lowest order of the dispersion force is $1/R^6$, where R is the distance between two fragments, and adding the pairwise $1/R^6$ term to the DFT total energy is a widely used strategy to incorporate the missing dispersion forces. The correction term is given by

$$E_{\text{vdW}} = -\frac{1}{2} \sum_{A,B} f_{\text{damp}}(R_{AB}, R_A^0, R_B^0) C_{6AB} R_{AB}^{-6}, \quad (1)$$

where R_{AB} is the distance between atoms A and B , C_{6AB} is the corresponding C_6 coefficient, R_A^0 and R_B^0 are the vdW radii, respectively. The singularity of R_{AB}^{-6} at the origin is eliminated by the short-ranged damping function $f_{\text{damp}}(R_{AB}, R_A^0, R_B^0)$, implying that at the medium and short ranges this approach works together with the exchange-correlation functionals of the DFT method. Approaches of similar type have been proposed by several authors in the last decade [25,26,41–43]. The approaches have been shown to be accurate for

a wide range of molecular systems by Grimme, which are known as the series of DFT-D [25,26]. They require C_6 coefficients of the atomic pairs and the vdW radii to be obtained by fitting to accurate theoretical data, independently of the electronic structure of the system of interest, which may limit their applicability. For the third version of DFT-D (DFT-D3), effort has been made to include system (geometry)-dependent information, along with the inclusion of the three-body term of the long-range interaction [27]. There have been a body of applications of the DFT-D methods to solids or molecules on surfaces [44–55].

For molecular applications, Sato and Nakai have proposed the local response dispersion (LRD) method [56,57] based on the local response approximation of Dobson and Dinte [58]. The method treats the distributed multipole polarizabilities of atoms in a molecule, from which the dispersion coefficients rather than the C_6 coefficients of free atoms are calculated.

2.2. Tkatchenko and Scheffler's approach to the van der Waals interaction

Tkatchenko and Scheffler (TS) proposed another approach to the vdW interaction based on the C_6 coefficients depending on the bonding environment of an atom in a molecule. The coefficients are calculated based on the accurate atomic C_6 values, which are scaled using the neutral free atom and the Hirshfeld atomic volumes based on the ground-state electron density obtained with DFT [28]. The method successfully illustrates the determination of the coefficients dependent on the bonding environment, and the subsequent interaction energies for the test data set of vdW complexes are found to be accurate. The applicability of the TS method is extended by introducing the iterative Hirshfeld scheme, where the reference atomic state is determined self-consistently [59–61]. Furthermore, TS and other authors have proposed to include long-ranged screening effects in the atomic polarizability in a self-consistent manner. As for the non-additive three-body interactions in the vdW interaction energy, the approximate model for the many-body screening effect based on the adiabatic-connection fluctuation-dissipation theorem (ACFDT) is used, and it is coupled with the existing exchange-correlation functional of DFT [29]. The proposed methodology, which the authors refer to as density-functional approximation + many-body dispersion (DFA+MBD), is found to accurately reproduce the binding energies of the benchmark systems. For cohesive properties of molecular systems, there have been successful results of those methods, reported recently [4,7,62–67].

2.3. Exchange-hole dipole moment (XDM) model

Becke and Johnson proposed the exchange-hole dipole moment (XDM) model, which describes the dispersion energy of two neutral fragments as the electronic interaction of the dipoles formed by electrons and their associated exchange holes [30–36]. The dispersion energy E_{disp} added to the DFT energy is formulated as

$$E_{\text{disp}} = -\frac{1}{2} \sum_{ij} \sum_{n=6,8,10} \frac{C_{n,ij}}{R_{\text{vdW},ij}^n + R_{ij}^n}, \quad (2)$$

implying that the atomic-pairwise terms are included from the usual R^{-6} leading term to higher-order ones. The fundamental ingredients in the equation are the interatomic coefficients $C_{n,ij}$, depending on the atomic polarizabilities and the expectation values of the atomic l -elements $\langle M_l^2 \rangle_i$, which are calculated from first-principles based on the second-order perturbation theory [35]. The spatial partitioning to define the atomic quantities is done with the Hirshfeld scheme. The vdW radii $R_{\text{vdW},ij}$ in the above E_{disp} , which control the distance at which the pairwise dispersion

Download English Version:

<https://daneshyari.com/en/article/5395608>

Download Persian Version:

<https://daneshyari.com/article/5395608>

[Daneshyari.com](https://daneshyari.com)