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Quasi-particle energies and excitonic effects in bilayer of hexagonal boron nitride

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ABSTRACT

First-principles calculations based on the density functional theory (DFT), GW and Bethe–Salpeter equations are performed on the bilayer of hexagonal boron nitride (bilayer h-BN) to investigate the electronic structure and optical properties. Due to the quantum confinement effect and the less efficient electronic screening, the value of direct (indirect) band gap increases from a value of 4.45 eV (4.37 eV) within the density functional theory to a value of 6.74 eV (6.67 eV) within the GW many-body Green's function theory. The calculated optical absorption spectra are dominated by exciton states with a binding energy about of 1.67 eV. The enhanced excitonic effects in bilayer h-BN have the potential to be used in optoelectronic and excitonic devices.

1. Introduction

The atomic structure of two-dimensional crystal membranes can modulate their electronic and optical properties, making these materials desirable for a variety of applications [1,2]. Recent developments in graphene research have stimulated intense interest in the study of other two-dimensional materials such as hexagonal boron nitride (h-BN). The structure of h-BN is analogous to graphene but their physical properties are quite different from those of their carbon counterpart. h-BN present highly appealing electronic and optical properties due to their tunable electronic energy gap, which is structurally derived from the large bandgap difference between pristine hexagonal BN, ~5 eV, and graphene, with zero-bandgap [3]. Recently, the hexagonal boron nitride layers have also been made by ultrasonication [4] and high-energy electron beam irradiation of BN particles [5]. There are few first-principles calculations about optical response properties of bilayer h-BN, though a number of relevant experiments, which use optical approaches to study bilayer h-BN [6–8], have been developed. Therefore, a first-principles calculation about the optical response properties of bilayer h-BN (Fig. 1(a) and (b)) is of great interest to the graphene community.

Electronic structure and optical response of nanostructures are two of these properties, which still require an appropriate description. Many-body interaction effects play an important role in study of electronic and optical properties in low-dimensional systems such as hexagonal BN single layer [9], BN nanotubes [10] and 2D monolayers [11,12], due to the reduced charge screening and the enhanced electron–electron correlation. Therefore, many-body interaction effects may provide useful information about the electronic structure and optical response of bilayer h-BN.

The structure of bilayer h-BN is expected to have various remarkable properties and might be a potential elementary structure for future boron nitride-based nanoelectronics. In particular, as a fundamental factor in determining the electronic and optical properties, the electronic band structure and optical absorption spectra of bilayer h-BN has been the subject of great interest. In this study, the electronic and optical properties of the hexagonal boron nitride bilayer have been calculated using the Bethe–Salpeter equation (BSE) approach. Also quasi-particle (QP) corrections within the GW approximation have been computed [13,14].

This paper is organized as follows. Section 2 introduces the theoretical method for calculating the electronic and optical properties. The results and discussion are presented in Section 3, followed by the conclusion in Section 4.

2. Theoretical method

In this study, first the ground state electronic properties of bilayer h-BN are calculated using the DFT [15,16] within the local

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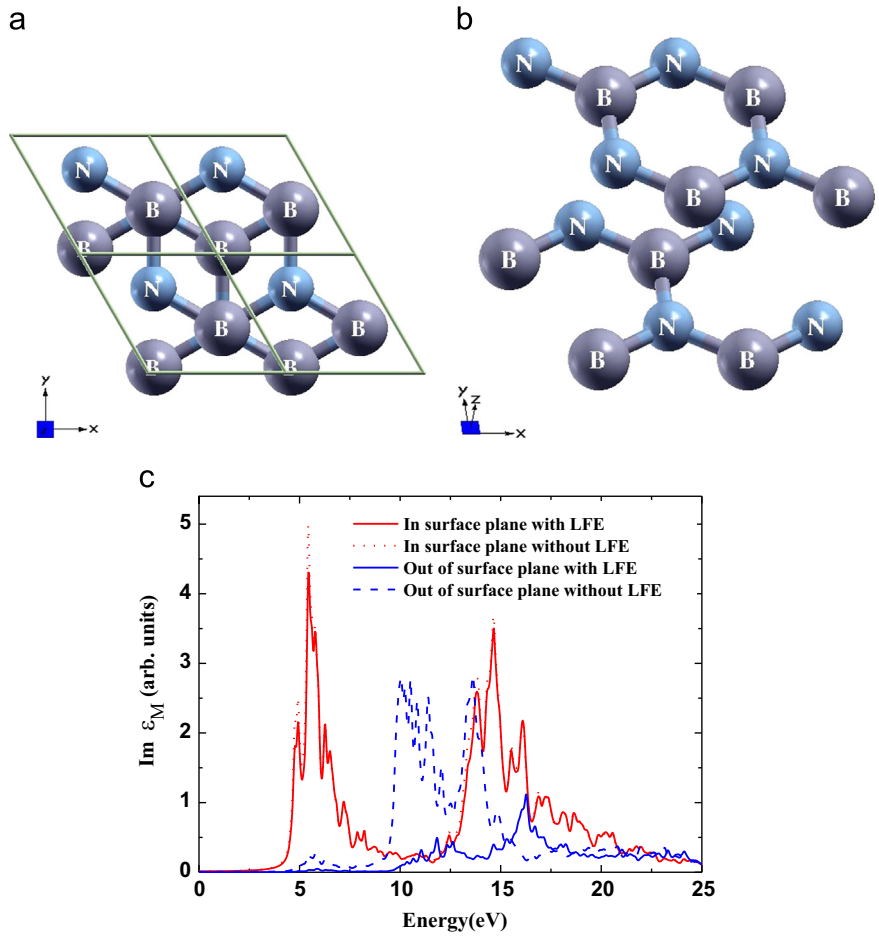

Fig. 1. (Color online) (a) Top and (b) side view of BN bilayer. Gray and blue spheres represent boron and nitride atoms. (c) Optical absorption spectra of BN bilayer calculated using the LDA–RPA level for light polarization parallel and perpendicular to the surface plane. All the spectra are computed with (solid line) and without (dash-dotted line) considering crystal local field effects (LFE).

density approximation (LDA). To do so QUANTUM-ESPRESSO computational package is used [17]. The plane-wave calculations are done with a 55 Ry energy cutoff and norm-conserving pseudopotentials. Also, to ensure convergency, the Brillouin zone integrations have been performed using a 16∗16∗1 Monkhorst–Pack [18] k-point mesh. The cell parameter and atomic positions were fully relaxed until an energy convergence of about 10^{-6} eV and a force convergence of 0.001 Ry (a.u.)$^{-1}$ were reached. A supercell with hexagonal symmetry was also used. The bond length obtained for BN is 1.43 Å, which is consistent with the experimentally-measured value (1.45 Å) [19] and the interlayer distance of bilayer h-BN is 3.31 Å. The interlayer distance calculated here is consistent with the experimentallymeasured value, i.e., ∼3.3 Å [19,20]. The distance between neighboring h-BN layers was kept at 20 Å to avoid artificial interaction.

Then, the QP energies within the GW approximation were computed using the following equation:

$$E^{QP}_{n\mathbf{k}} = \varepsilon^{KS}_{n\mathbf{k}} + Z_{n\mathbf{k}}(\varepsilon^{KS}_{n\mathbf{k}})\left\langle \psi_{n\mathbf{k}}\left|\Sigma(\varepsilon^{KS}_{n\mathbf{k}}) - V^{LDA}_{xc}\right|\psi_{n\mathbf{k}}\right\rangle,$$
$$Z_{n\mathbf{k}}(\varepsilon^{KS}_{nk}) = [1 - \partial\Sigma/\partial E|_{\varepsilon^{KS}_{n\mathbf{k}}}]^{-1}, \quad (1)$$

where $Z_{n\mathbf{k}}$ is the renormalization factor. For the exchange–correlation potential V_{xc}, the local density approximation (LDA) was utilized. Here, the self-energy Σ is calculated within the GW approximation [13,14]

$$\sum = iGW, \quad (2)$$

where G is the one-particle Green's function and W is the screened Coulomb interaction. In this study, the Plasmon-pole approximation has been used to construct the screened Coulomb interaction W. Finally, the electron–hole interaction is included by solving the Bethe–Salpeter equation [13,21]

$$(E_{c\mathbf{k}} - E_{v\mathbf{k}})A^S_{vc\mathbf{k}} + \sum_{\mathbf{k}v'c'}\left\langle vck\left|K^{eh}\right|v'c'\mathbf{k}'\right\rangle A^S_{v'c'\mathbf{k}'} = \Omega^S A^S_{vc\mathbf{k}}, \quad (3)$$

where $A^S_{vc\mathbf{k}}$ are the electron–hole amplitudes, Ω^S is the excitation energy, K^{eh} is the kernel describing the screened interaction between excited electrons and holes [13,14], $E_{c\mathbf{k}}$ and $E_{v\mathbf{k}}$ are the quasiparticle energies of the electron and hole states and ν, c, and $\mathbf{k}$ indicate the valance band, conduction band and $\mathbf{k}$ vector respectively.

The GW and Bethe–Salpeter calculations converged with respect to the number of bands, the energy cutoff and the number of k-points used to sample the first Brillouin zone. For the GW and Bethe–Salpeter calculations, we used 200 bands for the expansion of Green's function, 3000 G vectors for the exchange and 200 G for the correlation part of the self-energy. The dielectric constant was calculated in bilayer h-BN using 200 bands. 200 G vectors and 3000 G vectors were utilized for the dielectric matrix and the wave functions entering in the calculation respectively. The optical absorption spectra were calculated including 8 valence bands and 27 conduction bands, and a box-shape truncated Coulomb interaction was used to simulate the isolated bilayer h-BN in the direction perpendicular to planar surface [22]. All the GW and BSE calculations were implemented with the code YAMBO [23].