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First principles study of optical properties of molybdenum disulfide: From bulk to monolayer

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ABSTRACT

In this paper, we theoretically study the optical properties of both bulk and monolayer MoS_2 using first-principles calculations. The optical characters such as: dielectric function, optical reflectivity, and electron energy-loss spectrum of MoS_2 are observed in the energy region from 0 to 15 eV. At equilibrium state the dielectric constant in the parallel $E_{\|x}$ and perpendicular $E_{\|z}$ directions are of 15.01 and 8.92 for bulk while they are 4.95 and 2.92 for monolayer MoS_2, respectively. In the case of bulk MoS_2, the obtained computational results for both real and imaginary parts of the dielectric constant are in good agreement with the previous experimental data. In the energy range from 0 to 6 eV, the dielectric functions have highly anisotropic, whereas they become isotropic when the energy is larger than 7 eV. For the adsorption spectra and optical reflectivity, both the collective plasmon resonance and $(\pi + \sigma)$ electron plasmon peaks are observed, in which the transition in $E_{\|x}$ direction is accordant with the experiment data more than the transition in $E_{\|z}$ direction is. The refractive index, extinction index, and electron energy-loss spectrum are also investigated. The observed prominent peak at 23.1 eV in the energy-loss spectra is in good agreement with experiment value. Our results may provide a useful potential application for the MoS_2 structures in electronic and optoelectronic devices.

1. Introduction

Graphene [1], a two-dimensional (2D) materials in the single atomic layer, has attracted great interest for applications in nanoelectronic technology due to their unique transport properties [2–6]. However, the clean graphene does not have a band gap in its electronic structure, which is deemed as a considerable drawback for many applications, in optics and transistor technology. This limitation of graphene leads researchers to investigate alternate materials that are similar to graphene and distinct in their electronic properties. In recent year, transition metal dichalcogenides (TMDs) have have become of great

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interest due to their novel mechanical, transport, and optical properties [7–14]. Among them, molybdenum disulfide (MoS_2) is currently one of most interesting materials for applications in nano-electronic and optoelectronic devices due to its unique electronic, mechanical, transport, and optical properties [15–20].

The MoS_2 bulk is a semiconductor with an indirect electronic band gap of the 1.24 eV opening between the highest energy state of the valence bands located at the Γ point and the lowest energy state of the conduction bands located between the Γ and *K* points. Whereas, the MoS_2 monolayer is the semiconductor with a direct band gap of the 1.80 eV [7] opening between the highest/lowest energy state of the valence/conduction bands located at the *K* point. Moreover, MoS_2 monolayer has been successfully synthesized by various experimental techniques, such as chemical vapor deposition [21], micromechanical cleavage [22], or liquid exfoliation [23]. The indirect–direct band gap transition makes MoS_2 nanomaterial being a promising potential material for application in optoelectronics [24]. Recently, the structure of both bulk and monolayer MoS_2 has been studied by density functional theory (DFT) [25]. Effect of uniaxial strain and external electric field on electronic properties of both bulk and monolayer MoS_2 has also been considered by different methods [16,26–29]. Besides, optical properties of MoS_2 have attracted many scientists [30–33]. Using DFT calculations, they have shown that the blue-shift phenomenon was observed in O–doped MoS_2 systems [11]. The static dielectric constant of the monolayer MoS_2 with neutral S and Mo vacancies is respectively 1.50 and 2.45, and the S vacancy does not effect on the static dielectric constant of the monolayer MoS_2 [34]. Recently, we theoretically studied the magneto-optical absorption coefficient of MoS_2 on polar substrates in the presence of an external magnetic field [35].

In the present work, we study the optical properties of the MoS_2 using DFT calculations. We calculate the optical characters of both bulk and monolayer MoS_2. Effect of direction of an external electric field on the dielectric constant and other optical characters is also considered and discussed.

2. Theoretical model and method

In this paper, DFT calculations of electronic and optical properties of bulk and monolayer MoS_2 were performed employing the APW + lo method [36]. The full potential which not depends on any predefined form, such as muffin-tin one was adopted in the present calculations. The muffin-tin (MT) sphere radii of atoms constituting the MoS_2 system were supposed to be equal to 2.27 a.u. for Mo and 1.95 a.u. for S in bulk MoS_2 and 2.44 a.u. for Mo and 2.1 a.u. for S in monolayer MoS_2.

Inside the atomic spheres for wave function expansion, the maximum value of orbital quantum number *l* is confined to $l_{max} = 10$. In the interstitial region, the wave functions were extended regarding plane waves with the cut-off value of $RK_{max} = 7$. Besides, magnitude of largest vector in Fourier expansion of the charge density was set to $G_{max} = 12$ (a.u)$^{-1}$. All these values have been chosen in a way to ensure the convergence of the results. These above-mentioned parameters are used further for the calculations of the electronic structure and optical properties of both bulk and monolayer MoS_2.

For calculations of the exchange-correlation potential, generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhof (PBE) [37,38] potential was used. Further, the tetrahedron method by Blochl et al. [39] was employed for integration through the Brillouin zone (BZ). The BZ sampling was made using 1000 *k*-points within the full zone. The iteration process was verified accounting changes in the integral charge difference $q = \int |\rho_n(r) - \rho_{n-1}(r)| dr$, where $\rho_{n-1}(r)$ and $\rho_n(r)$ are input previous iteration and output current iteration charge density, respectively, and the calculations were intercepted when reaching the value $q \leq 10^{-4}$.

3. Results and discussion

Atomic structure of MoS_2 is shown in Fig. 1. It can be seen that MoS_2 crystal has the hexagonal structure, which consists of S–Mo–S layers. In each layer, the Mo atoms are arranged in the hexagonal lattice and positioned in trigonal prismatic coordination with the two S layers. After relaxation, the lattice constants of bulk and monolayer MoS_2 are 3.176 Å and 3.180 Å, respectively. This result is in good agreement with the previous theoretical calculations [25,31] and the experimental measurements [7,40]. Moreover, our obtained Mo–S bond length in both MoS_2 bulk and monolayer is 1.41 Å, which is consistent with the experimental value [7]. In Fig. 2 we display the electronic band structures of both MoS_2 bulk and monolayer. We found that MoS_2 bulk is a semiconductor with an indirect band gap, opening between the highest occupied energy state of the valence band located at the Γ point and the lowest unoccupied energy state of the conduction band located at the *K* point. When MoS_2 bulk is transformed to a monolayer, it becomes a semiconductor with a direct band gap, opening between the highest occupied state of the valence band and the lowest unoccupied state of the conduction band located at the *K* point. Our calculated band gaps for the bulk and monolayer MoS_2 are respectively 1.23 eV and 1.70 eV which are in good agreement with the available data [7,41].

We next focus on the optical properties of MoS_2 bulk and monolayer in the energy range from 0 to 15 eV. Real and imaginary parts of dielectric function for bulk and monolayer MoS_2 are calculated by considering interband transition for both directions of electric field: (i) parallel $E_{\|x}$ and (ii) perpendicular $E_{\|z}$. The $\varepsilon_2(\omega)$ constituents are worth to be known for depiction of the linear optical susceptibility of the crystal and they are denoted as follows [42]: