Optical properties of CeO$_2$ using screened hybrid functional and $GW+U$ methods

Hongliang Shi,[1,2] Ping Zhang,[2,3,*] and Shu-Shen Li[1]

^{1}*State Key Laboratory for Superlattices and Microstructures,*
Institute of Semiconductors, Chinese Academy of Sciences,
P. O. Box 912, Beijing 100083, People's Republic of China
^{2}*LCP, Institute of Applied Physics and Computational Mathematics,*
P.O. Box 8009, Beijing 100088, People's Republic of China
^{3}*Center for Applied Physics and Technology, Peking University, Beijing 100871, People's Republic of China*

The optical spectra of CeO$_2$ have been systematically investigated using three first-principles computational approaches for comparison, namely, the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional, HSE+U, and $GW+U$. Our results show that by using the HSE+U method, the calculated electronic structures are in good agreement with experimental spectra and the resulting imaginary part of the optical dielectric function spectrum well reproduces the main features exhibited in experimental observations. The important adsorption spectrum and energy loss function also accord well with the experimental results.

Cerium oxides have been applied extensively because of the technologically important applications in industry originating from their unique physical properties. Taking CeO$_2$ for example, it is used in automobile exhaust catalysts due to its capacity of high oxygen storage. Another novel application of CeO$_2$ in the microelectronic and optoelectronic fields has been attracted more attention because of its high dielectric constant and good epitaxy on Si substrates resulted from the same cubic structure and small lattice mismatch [1]. Particularly, the dielectric function related optical properties of CeO$_2$ have been investigated intensively by several experimental work [2–4], and the complex $4f$ orbitals of Ce are also proved to be unoccupied locating within the band gap formed between the O $2p$ and Ce $5d$ states.

From theoretical viewpoint, accurate calculations of optical properties for $4f$ rare-earth oxide systems are hard. For example, firstly, conventional density functional theory (DFT) within standard local or semilocal functionals always underestimates the band gaps of insulators or semiconductors, consequently, the resulting optical spectra are unsatisfactory. Secondly, an accurate description of electronic structures for rare-earth oxides containing $4f$ electrons is also a great challenge to DFT due to the simultaneous itinerant and localized behaviors exhibited by the f orbitals. Many efforts have been devoted to overcoming these intractable issues.

One successful method to remedy the drawback of the standard local or semilocal functionals is the newly developed hybrid functionals [5] which introduces 25% of the nonlocal Hartree-Fock (HF) exchange into the otherwise exact semilocal exchange functional. In order to apply this method to large molecules or extended systems, an improved version of the HSE screened Coulomb hybrid functional [6] has been developed, in which the slowly decaying long-ranged (LR) part of the HF exchange term is replaced by the corresponding density functional counterpart. Taking Perdew-Burke-Ernzerhof (PBE) potentials for example, the resulting exchange is given by

$$E_{\mathrm{x}}^{\mathrm{HSE}} = \frac{1}{4}E_{\mathrm{x}}^{\mathrm{HF,SR}}(\mu) + \frac{3}{4}E_{\mathrm{x}}^{\mathrm{PBE,SR}}(\mu) + E_{\mathrm{x}}^{\mathrm{PBE,LR}}(\mu), \quad (1)$$

where $E_{\mathrm{x}}^{\mathrm{HF,SR}}$ is the short-ranged (SR) HF exchange, $E_{\mathrm{x}}^{\mathrm{PBE,SR}}$ and $E_{\mathrm{x}}^{\mathrm{PBE,LR}}$ are the SR and LR components of the PBE exchange functional, respectively.

Another successful method for determination of excited states is the GW approximation [7], which is based on the quasiparticle concept and the Green function method. In this approximation, the self-energy Σ is expanded linearly in terms of the screened interaction W, i.e., $\Sigma \approx GW$. Here, G is the single-particle Green's function and W is the screened Coulomb interaction. In order to describe the localized f orbitals more accurately, we also adopt the PBE plus a Hubbard U correction (PBE+U) method [8] as the starting point, which gives a qualitative improvement compared to PBE not only for excited states such as band gap but also for ground-state properties such as Mott insulator.

In this letter, we systematically investigate the optical spectra of CeO$_2$ using the HSE, HSE+U and $GW+U$ methods as implemented in the first-principles vienna *ab initio* simulation package (VASP) [9]. The electron and core interactions are included using the frozen-core projected augmented wave (PAW) approach [10]. The gradient corrected PBE functional [11] for the exchange correlation potential is used. The cerium $5s$, $6s$, $5p$, $5d$ and $4f$ as well as the oxygen $2s$ and $2p$ electrons are explicitly treated as valence electrons. The electron wave function is expanded in plane waves up to a cutoff energy of 500 eV. For the Brillouin zone integration, the 6 × 6 × 6 Γ-centered k-mesh is adopted and a good convergence can be obtained. In the HSE calculations, 25% HF exchange and 75 % PBE exchange are used, and the range-separation parameter is set to μ=0.3 Å^{-1}. The GW calculations are carried out using a total number of 166 bands and four iterations for accurate quasiparticle shifts. The strong on-site Coulomb repulsion among the