Recent implementations of spectroscopy calculations in the all-electron mixed basis code, TOMBO

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In our all-electron mixed basis code, TOMBO, which is highly parallelized with MPI and openMP, we have extended the one-shot *GW* approximation for clusters to be applicable to crystals, and calculated the *GW* quasi-particle energies of TiO_2 (rutile) crystals. In contrast to the LDA result, there is a wide gap of about 4.1eV. We also performed a tentative calculation of TiO_2 with Nb impurities (Fig. 1). Although overall feature of the wide band gap structure is similar to the pure TiO_2, there appears a new dispersive band in the gap separated from the conduction band around the Γ point. This band has an extended character in the oxygen lines and occupied half by electron charge transfer from Nb. There is also a new band separated from the valence band around the B and Γ points, but this band is more localized. These are interesting feature of the defect states in the assumed geometry, but the new bands appearing in the band gap are quite sensitive to the unit cell geometry and atomic alignments, and further investigations are needed to derive any conclusive results.

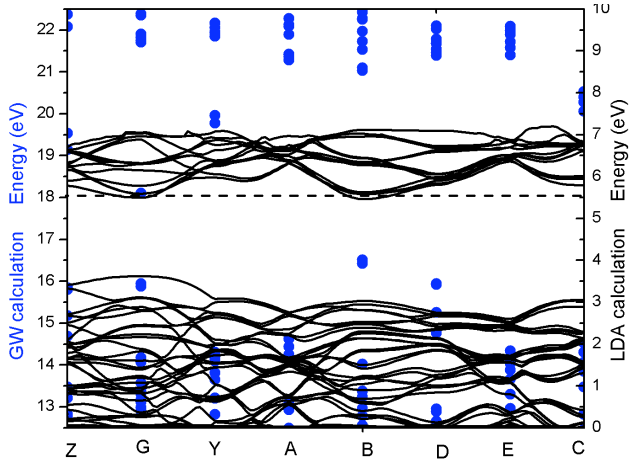

Fig. 1 Band structure of TiO_2 with Nb impurities calculated by the one-shot *GW* (dots) and LDA (curves). The dashed line is the calculated Fermi level in LDA.

We have also newly implemented the self-consistent *GWΓ* approach for clusters in the code, as well as the projection operator approach to avoid summation over empty states and plasmon pole models to avoid ω' integration and nonlocal $\boldsymbol{G}$, $\boldsymbol{G'}$ dependence of the dynamically screened Coulomb interaction $W_{\boldsymbol{GG'}}(\omega', \boldsymbol{q}=0)$. In the present calculation, the vertex Γ is consistent with Ward identity in the limit $\omega'= 0$ and $\boldsymbol{q} = 0$, and is accurate to the first order in perturabation theory for general $\omega' \neq 0$ and $\boldsymbol{q} \neq 0$. The resulting quasiparticle energies and quasiparticle wave functions are used to construct the Bethe-Salpeter equation, and from this equation, we obtained photoabsorption spectra of small sodium clusters (Fig. 2). These results are much improved compared to the results using the one-shot *GW* approximation or the self-consistent *GW* approximation without vertex correction.

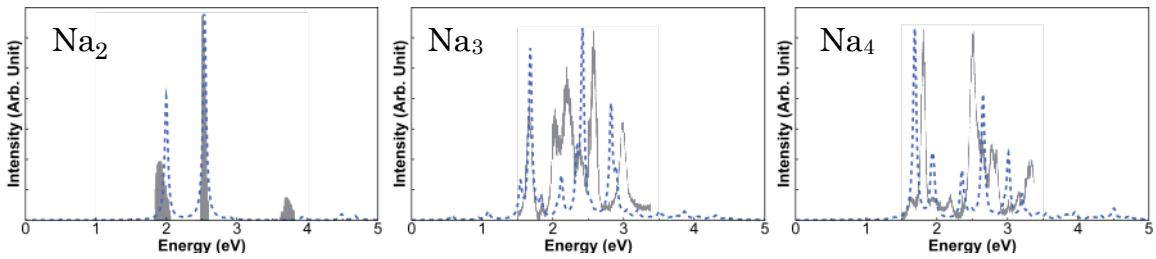

Fig. 2 Photoabsorption spectra of sodium clusters obtained by using the self-consistent *GWΓ* approach and solving the Bethe-Salpeter equation (dashed curves). The grey curves are the experimental data [1,2].

References

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[2] C. R. C. Wang et al., J. Chem. Phys. **96**, 7931 (1992).