Development of First-Principles GWΓ Method by Considering First-Order Three-Point Vertex Corrections

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The first-principles GW method [1], in which the three-point vertex function (Γ) is approximated as unity, is a powerful tool for simulating single-electron excitations, including band gaps in extended systems and ionization energies and electron affinities in isolated systems. However, recent systematic investigations have revealed that the standard one-shot GW (or G_0W_0) method can produce significant errors up to several electron volts in core-electron binding energies (BEs). These errors can be substantially reduced by selecting appropriate DFT functionals, such as PBEh (α = 0.45), in the one-shot approach or by incorporating (partial) self-consistency, even within the GW approximation ($\Gamma = 1$) [2,3].

To address these limitations, we developed a first-principles GWΓ method that inherently extends beyond the conventional GW by incorporating the first-order three-point vertex function ($\Gamma = 1 + iGWW$) and implemented it into our all-electron mixed basis program [4]. The Γ terms are given as

$$\begin{aligned} < n|\Sigma^{\Gamma}(E_n)|n > &= < n|\Sigma^{\Gamma-occ}(E_n)|n > + < n|\Sigma^{\Gamma-emp}(E_n)|n > \\ &= \sum_{\lambda}^{emp}\sum_{\nu}^{occ}\sum_{\mu}^{occ} \frac{v_{n,\lambda;\nu,\mu}v_{\nu,\mu;\lambda,n}}{E_n + E_\lambda - E_\nu - E_\mu - i\eta} \\ &+ \sum_{\lambda}^{occ}\sum_{\nu}^{emp}\sum_{\mu}^{emp} \frac{v_{n,\lambda;\nu,\mu}v_{\nu,\mu;\lambda,n}}{E_n + E_\lambda - E_\nu - E_\mu + i\eta} \end{aligned}$$

For simplicity, we used the bare Coulomb interaction (v) instead of the dynamically screened Coulomb interaction (W). First, we applied the GWΓ method to simulate the B1*s,* C1*s*, N1*s*, O1*s*, and F1*s* BEs for 19 small-sized molecules and compared the resulting GWΓ quasiparticle energies (with negative sign) to the available experimental BEs [5]. Second, we applied this method to simulate the first ionization energies of 96 atoms and molecules and evaluated its computational accuracy by comparing the results with experimental values. In addition, we discuss self-interaction corrections in detail in the GWΓ method [6].

References

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