Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The band structure and optical absorption of hematite (α-Fe_2O_3): a first-principles GW-BSE study

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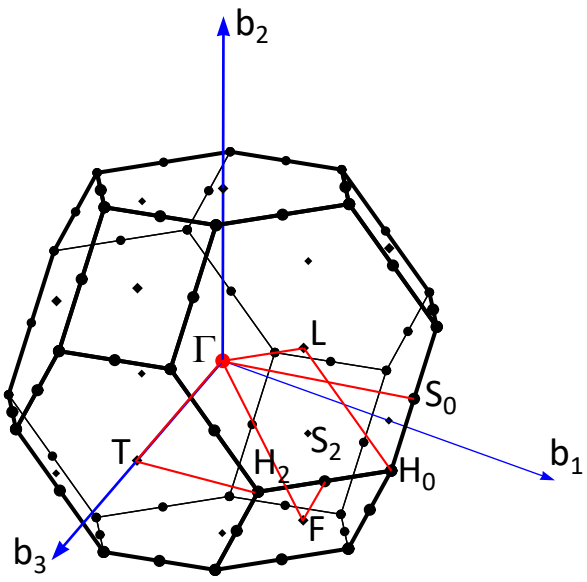

Figure S1: The Brillouin zone of the 10-atom rhombohedral unit cell of hematite and the path (red line) along which the bandstructure is computed.

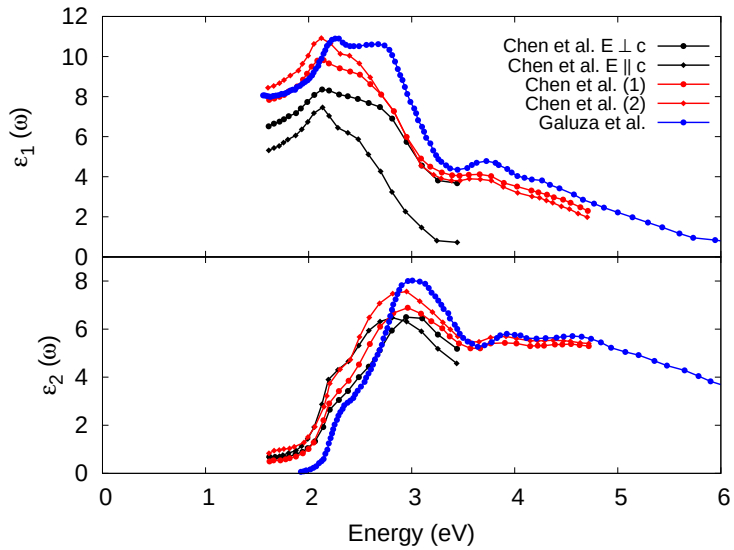

Figure S2: Experimental measurements of the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function. The data are extracted from the graphs in the works of Chen *et al.*[1] and Galuza *et al.*[2] The labels (1) and (2) refer to two different polycrystalline samples obtained through sintering at different temperatures.

Fig. S1 displays the Brillouin zone of bulk hematite and the path employed to plot the the bandstructure. In Fig. S2 we report experimental measurements of the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function obtained by Chen *et al.*[1] and Galuza *et al.*[2]

Convergence tests

Table 1: Convergence of the G_0W_0@PBE quasiparticle gap at Gamma (Gap(Γ)) as a function of the cutoff for the dielectric matrix (E^{χ}_{cut}), the number of bands considered in the sum over empty states in the calculation of the dielectric matrix (N^{χ}_{bands}) and of the self energy (N^{Σ}_{bands}).

E^{χ}_{cut}(Ry)	N^{χ}_{bands}	N^{Σ}_{bands}	Gap(Γ)
50	1994	100	2.019
50	1994	202	2.065
50	1994	300	2.063
50	1994	694	2.056
50	1994	996	2.062
50	1994	1500	2.074
50	1994	1994	2.088
50	100	1994	2.200
50	202	1994	2.170
50	300	1994	2.162
50	694	1994	2.132
50	996	1994	2.116
50	1500	1994	2.100
50	1994	1994	2.088
10	1994	1994	2.361
20	1994	1994	2.266
30	1994	1994	2.175
40	1994	1994	2.119
50	1994	1994	2.088
40	300	300	2.155

In Table 1 we show the converge tests on the quasiparticle gap obtained with the G_0W_0@PBE approach. To accelerate the convergence of the sum over empty states in the calculation of the Coulomb-hole self-energy term, we exploit the static remainder method.[3]

In Fig. S3 we show the convergence of dielectric function with k-point sampling and with the number of bands employed in the sum over empty states.

In Fig. S4 we show the convergence of the dielectric function with respect to the cutoff of the wavefunction.

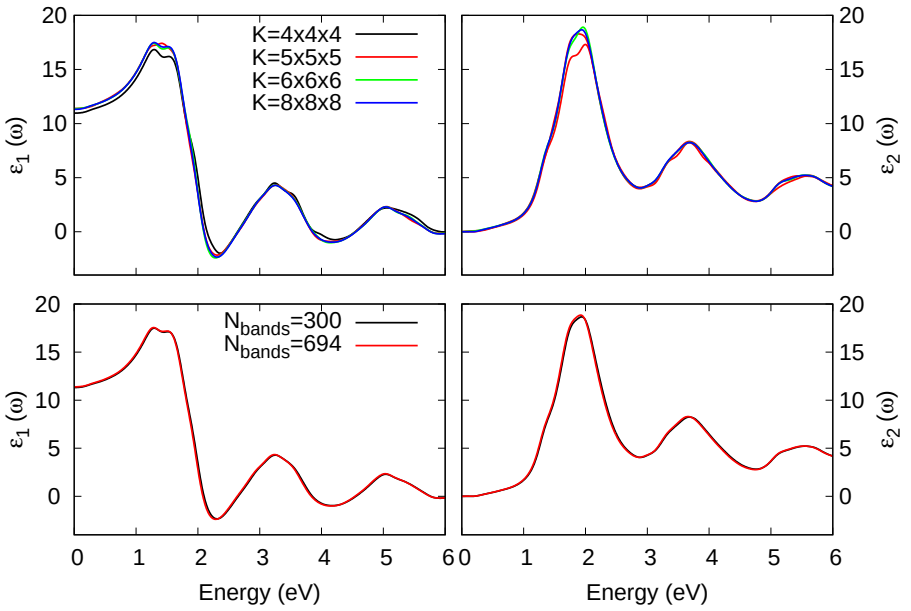

Figure S3: Convergence of the real and imaginary part of the dielectric function with k-point sampling (top panels) and number of bands (bottom panels). The SCF calculation is performed with the PBE functional. The SCF, G_0W_0 and kernel calculations are performed on a 4×4×4 grid. In the top panels, the kernel has then been interpolated on finer k-point grids where the Bethe-Salpeter equation is solved, while using N^{ϵ}_{bands}=N^{Σ}_{bands}=300. In the bottom panels the kernel is interpolated on a 8×8×8 grid while testing for convergence with respect to the number of bands.

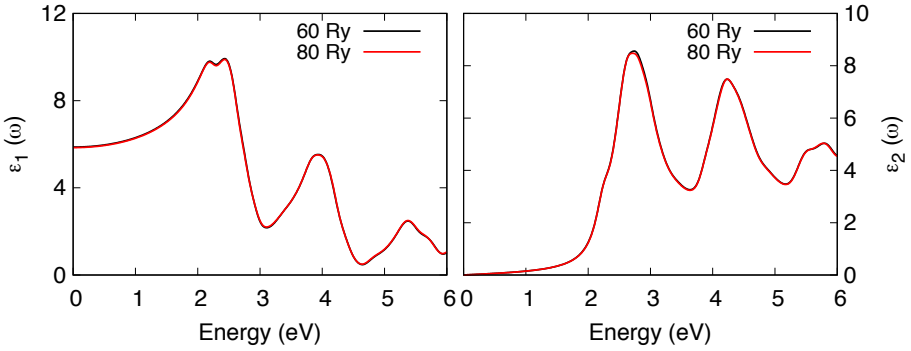

Figure S4: Convergence of the real and imaginary part of the dielectric function with the cutoff of the wavefunction. The BSE calculation has been performed starting from a PBE0(α=1/8) calculation with a 4×4×4 grid k-point grid. The kernel has then been interpolated on finer 5×5×5 k-point grid.

References

(1) Chen, C. T.; Cahan, B. D. *J. Opt. Soc. Am.* **1981**, *71*, 932–934.

(2) Galuza, A. I.; Eremenko, V. V.; Kirichenko, A. I. *Sov. Phys. Solid State* **1979**, *21*, 654.

(3) Deslippe, J.; Samsonidze, G.; Jain, M.; Cohen, M. L.; Louie, S. G. *Phys. Rev. B* **2013**, *87*, 165124.