Modelling Exchange-Correlation Function in DFT

The success of Density Functional Theory (DFT) lays on the **functional** used to **approximate the unknown exact exchange-correlation functional** (Vxc).

$$\hat{H} = \hat{T} + \sum_{\alpha} \hat{V}_{\alpha}^{PS} + V^{H}(\vec{r}) + V^{xc}(\vec{r})$$

term unknown

Several approximations:

- **LDA** (CA/PW92) - LDA works well for systems with slowly varying electron densities like simple metals and bulk solids.

$$V_{xc}\left(\rho(\mathbf{r})\right)$$

- **GGA** (PW91/PBE /revPBE /RPBE/WC/AM05/PBEsol/BLYP) - GGA improves accuracy for molecules and materials with more complex, rapidly changing densities, such as surfaces and molecular systems.

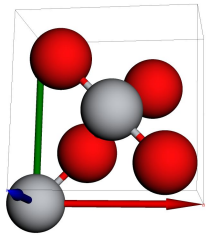
$$V_{xc}\left(\rho(\mathbf{r}),|\nabla\rho(\mathbf{r})|\right)$$

Modelling Exchange-Correlation Function in DFT

➢ **Hybrid functionals**, an advanced class of exchange-correlation functionals. They address the limitations of standard functionals (like LDA and GGA) by incorporating a portion of the exact exchange energy from Hartree-Fock theory.
This inclusion of a small amount of exact exchange significantly improves the functional performance for specific systems and properties:

- Reaction Barriers in chemical reactions
- Electron Localization, especially in systems with strong correlation
- Band Gaps in semiconductors and insulators, often correcting the underestimation by standard functionals

Key application: They are particularly important for the accurate description of **oxides and other systems with localized electrons.**



TiO_2

Hybrid Functionals in ASAP

ASAP interfaces with both SIESTA and Quantum ESPRESSO, each with its own capabilities

Quantum ESPRESSO

The code has a robust implementation of hybrid functionals

ASAP's status: Hybrid functionals are accessible through the ASAP interface.

SIESTA

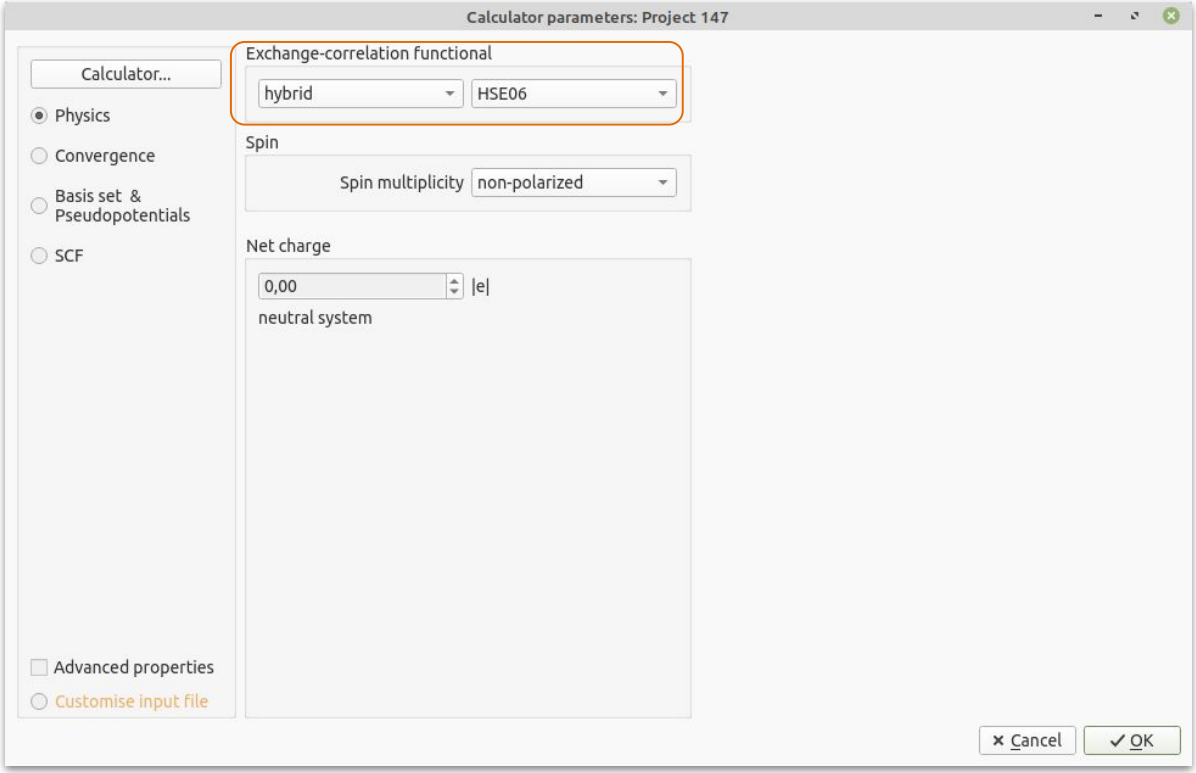
Hybrid Functionals in SIESTA are implemented in a branch that it is not yet publicly available. This is scheduled for an upcoming official release.

SIESTA offers a key advantage in terms of scalability and computational efficiency for large or complex systems.

ASAP's status: **A preview version of SIESTA with hybrid functionals is available in ASAP 2025.1** for testing and production.

Hybrid Functional in ASAP: SIESTA

Screenshot of the calculator widget for SIESTA, now with the possibility of selecting hybrid functionals.



SIESTA hybrid Functionals

The hybrid XC functionals that have been recently implemented in SIESTA are HSE06 and PBE0, two of the most widely used and successful hybrid functionals in quantum chemistry and materials science

HSE06*: Known for its good balance between accuracy and computational cost, especially for predicting band gaps.

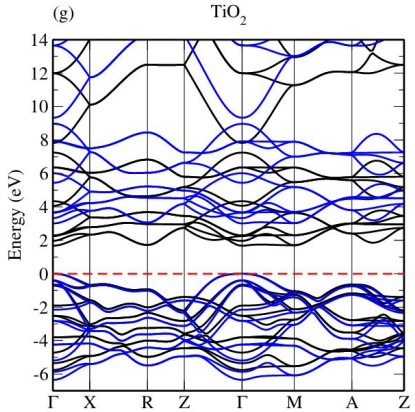
PBE0**: A global hybrid functional that provides improved accuracy for thermochemistry and molecular properties

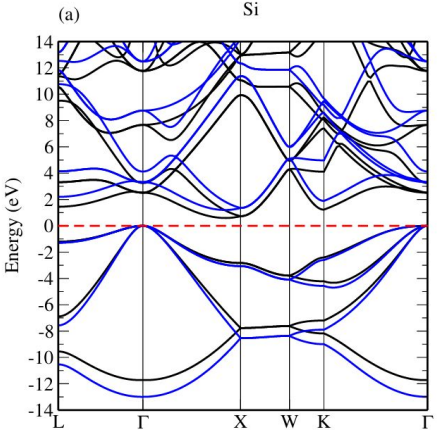
* J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118, 8207 (2003).
** C. Adamo and V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, J. Chem. Phys. 110, 6158 (1999)

SIESTA hybrid Functionals: Validation

The **hybrids functionals** implemented in SIESTA **have been thoroughly tested and benchmarked** on several systems by computing the band structure and band gap.

System	PBE	HSE06	G_0W_0	Expt.
Si	0.59	1.20	1.17 [70]	1.12 [71]
Diamond	4.20	5.31	5.95 [72]	5.47 [73]
LiF	8.96	11.23	13.6 [74]	13.04 [75]
c-BN	4.51	5.84	6.1 [76]	6.36 [77]
monolayer h-BN	4.60	5.74	7.06 [78]	5.95 [79]
TiO_2	1.67	3.01	3.14 [80]	3.03 [81]
ZnO	1.14	2.73	3.26 [80]	3.24 [82]
Black Phosphorus	0.00	0.29	0.43 [83]	0.33 [84, 85]

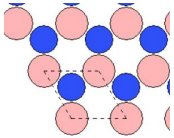


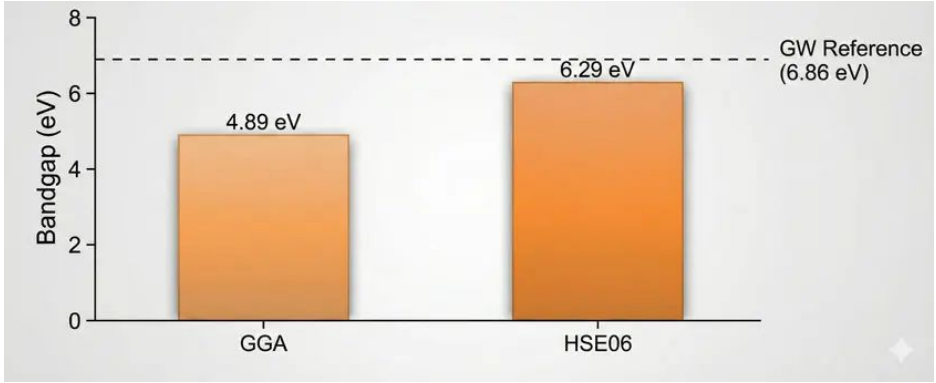


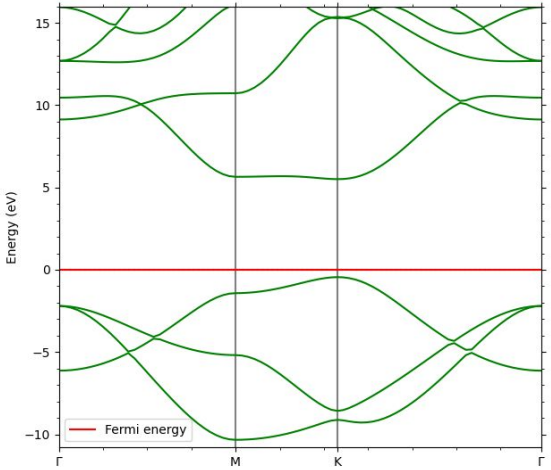
"Implementation of the hybrid exchange-correlation functionals in the siesta code"
Yann Pouillon, Javier Junquera et al.
The publication detailing this work is currently in progress, with submission expected in the coming months.

SIESTA hybrid Functionals: Validation

The HSE06 hybrid functional, implemented within ASAP/SIESTA, was successfully tested in monolayer Hexagonal Boron Nitride hBN, yielding a more accurate bandgap (6.29eV) compared to the standard GGA functional (4.89eV).







This project have been a collaboration between SIMUNE and Università degli Studi di Milano (Karina Madela, Prof. Simona Achilli, Physics Department "Aldo Pontremoli"). The "TIMES" Project received funding from the EU's Horizon Europe programme; Grant Agreement No. 101118915

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