PRECISE AND EFFICIENT HYBRIDS IN ALL-ELECTRON LINEARIZED AUGMENTED PLANE WAVES

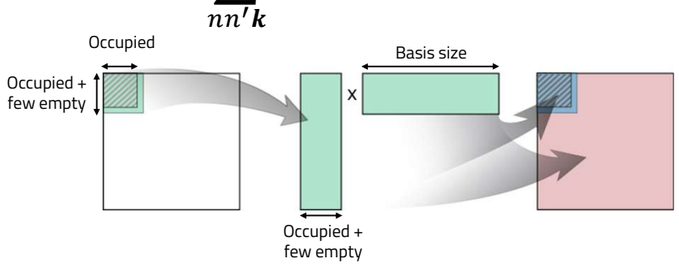
UNIVERSITY OF LATVIA

Andris Gulans, Jānis Užulis and Kristiāns Kacars

Challenges

All-electron LAPW is the reference method for electronic-structure calculations in solids. Hybrid functionals still present a few difficulties to LAPW. We make a bet on the low-rank approximation employing adaptively compressed exchange (ACE) and fully restore the control over precision.

$$\hat{V}_x^{ACE} = \sum_{nn'\mathbf{k}}^{n_{occ}} \hat{V}_x^{HF}|\psi_{n\mathbf{k}}\rangle\langle\psi_{n\mathbf{k}}|\hat{V}_x^{HF}|\psi_{n'\mathbf{k}}\rangle^{-1}\langle\psi_{n'\mathbf{k}}|\hat{V}_x^{HF} = -\sum_{\alpha}|\xi_\alpha\rangle\langle\xi_\alpha|$$



We address the following challenges:

- ~~dependence on empty bands~~ – actually not a problem specifically in ACE,
- performance (quartic scaling),
- screened (range-separated) exchange that required an implementation,
- the radial basis and core orbitals are generated with a local functional.

Reference: D. Zavickis, K. Kacars, J. Cimurs, A. Gulans, Phys. Rev. B 106, 165101 (2022)

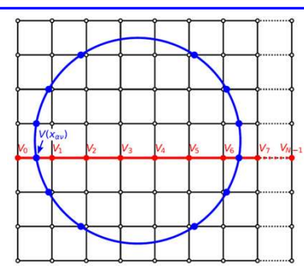
Complexity

The overall complexity of computing $\hat{V}_x^{ACE}$ is $O(N_{at}^4)$ with $O(N_{occ}^2)$ Poisson solves costing $O(N_{at}N_{\boldsymbol{G}}) \sim O(N_{at}^2)$ FLOPs each. The quadratic cost of the Poisson solve is due to the pseudocharge method needed for the density and potential representation employed in LAPW. We reduce the cost of each individual solve.

Exact calculation in G-space

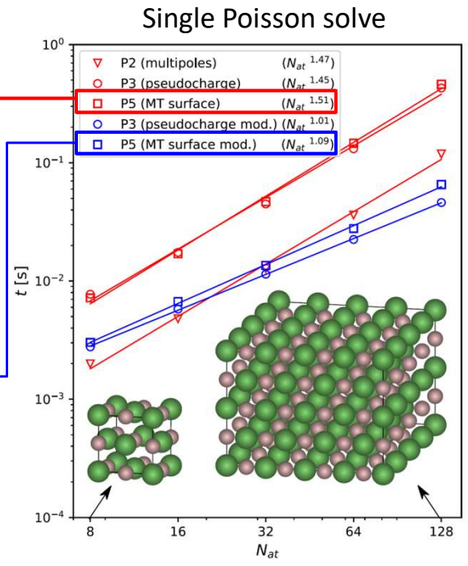
$$V_{\alpha;\ell m}^{\text{surf}} = 4\pi i^\ell \sum_{\mathbf{G}} j_\ell(GR_\alpha)V^{\text{I}}(\mathbf{G})e^{i\mathbf{G}\mathbf{R}_\alpha}Y_{\ell m}^*(\hat{G})$$

1D Fourier interpolation



Least-squares fit $V(\hat{r}_{\alpha v}) = \sum_{\ell m} V_{\alpha;\ell m}^{\text{surf}} Y_{\ell m}(\hat{r}_{\alpha v})$

Single Poisson solve



Reference: J. Užulis, A. Sorokin, A. Gulans, npj computational materials (accepted but not online yet) https://doi.org/10.1038/s41524-025-01733-z

Range separation

We implement screened functionals in two ways:

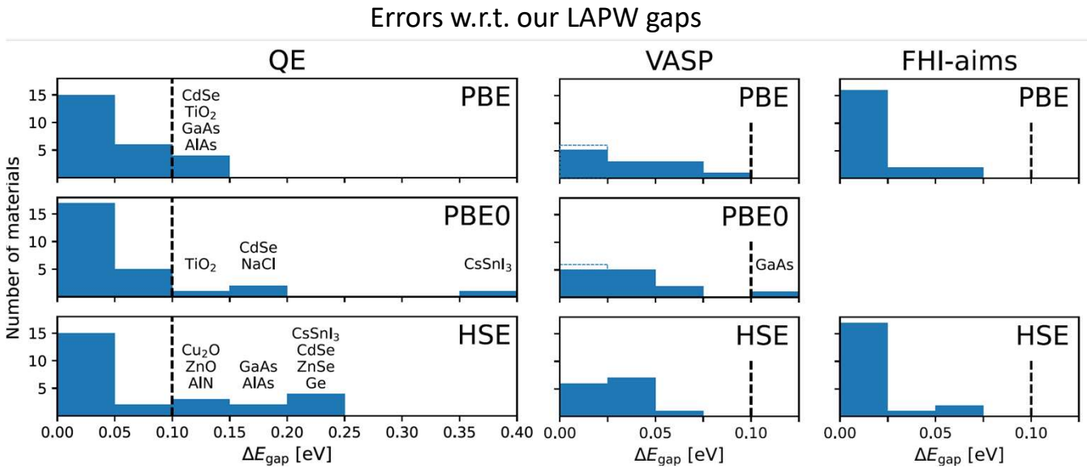
- $\text{erfc}(\mu r)/r \approx \frac{\sum_n A_n e^{\alpha_n r}}{r}$ with complex fitted parameters A_n and α_n. This way, the problem reduces to solving the screened Poisson equation several times and can be addressed using the pseudocharge method.
- $\text{erfc}(\mu r)/r = 1/r - \text{erf}(\mu r)/r$. The first term is usual Coulomb kernel, whereas the second one decays rapidly in the reciprocal space.

Both methods yield nearly identical results. In production, we use the first method for computing the core-valence contribution and the second one for the valence-valence part.

We use the implementation for calculating band gaps of 26 materials and comparing with literature:

- J. Yang, S. Falletta, A. Pasquarello, npj Comput. Mater. 9, 108 (2023) – Quantum Espresso + ONCVPSP,
- M. A. L. Marques et al. Phys. Rev. B 83, 035119 (2011) – VASP,
- W.P. Huhn, V. Blum, Phys. Rev. Mater. 1, 033803 (2017) – FHI-AIMS all-electron.

Errors w.r.t. our LAPW gaps



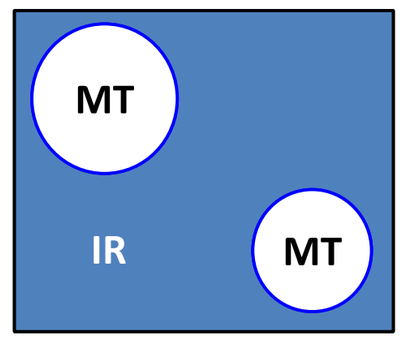
Reference: J. Užulis, A. Sorokin, A. Gulans, npj computational materials (accepted but not online yet) https://doi.org/10.1038/s41524-025-01733-z

Optimal basis and proper core

LAPW+lo basis:

$$\phi_{\boldsymbol{G}+\boldsymbol{k}}^{\text{LAPW}}(\boldsymbol{r}) = \begin{cases} \sum_{\xi lm} A_{\xi lm}^{\boldsymbol{G}+\boldsymbol{k}} u_{\xi l}(r)Y_{lm}(\hat{\boldsymbol{r}}) & \boldsymbol{r} \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\boldsymbol{G}+\boldsymbol{k})\boldsymbol{r}} & \boldsymbol{r} \in \text{IR} \end{cases},$$

$$\phi_\nu^{\text{LO}}(\boldsymbol{r}) = \begin{cases} \sum_{\xi lm} a_{\xi lm}^\nu u_{\xi l}(r)Y_{lm}(\hat{\boldsymbol{r}}) & \text{if } \boldsymbol{r} \in \text{MT} \\ 0 & \text{if } \boldsymbol{r} \in \text{IR} \end{cases}.$$



The functions $u_{\xi l}(r)$ come from the radial Schrödinger equation with the trial (self-consistent) Kohn-Sham potential. The standard approach is to use $v_{\text{PBE}}(r)$. Instead, we propose to generate $u_{\xi l}(r)$ with $\hat{v} = v_{\text{loc}}(r) + \hat{v}_{\text{nl}}^{\text{x}}$.

Example: the HF molecule in a Hartree-Fock calculation.

Method	Total energy [Ha]	Heat of formation [kcal/mol]
Reference	-100.0708025	-73.587
$u_{\xi l}^{HF}(r)$, high cut	-100.0708*11*	-73.587
$u_{\xi l}^{HF}(r)$, med. cut	-100.0702*452*	-73.590
$u_{\xi l}^{PBE}(r)$, med. cut	-100.0692*182*	-73.586

S. Lehtola, Fully numerical Hartree-Fock and density functional calculations. II. Diatomic molecules.

Example: CdSe band gap from PBE0 calculation (4×4×4 k-points and large atomic spheres).

$u_{\xi l}^{?}(r)$	Core	Gap [eV]
PBE0	PBE0+ZORA	2.2084
PBE	PBE0+ZORA	2.2048
PBE	PBE+ZORA	2.2058
PBE	PBE+Dirac	2.2058
PBE+HELOs	PBE+Dirac	2.2085

The standard approach in those benchmarks works well enough.

But can you rely on it blindly?

References: J. Užulis, A. Gulans, J. Phys. Commun. 6, 085002 (2022), J. Užulis, A. Gulans, work in progress

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Latvian Council of Science, Precise methods for modelling quantum materials, project No. LZP-2024/1-0202