Using the density-functional toolkit (DFTK) to design black-box DFT methods

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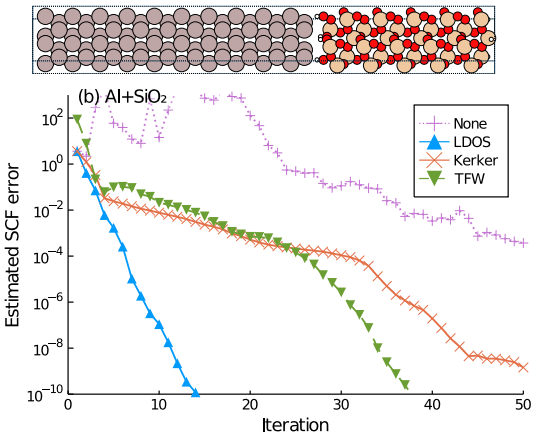
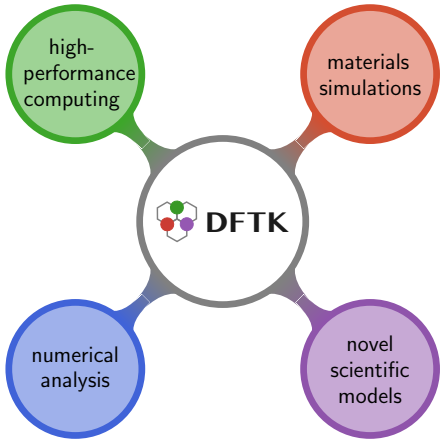
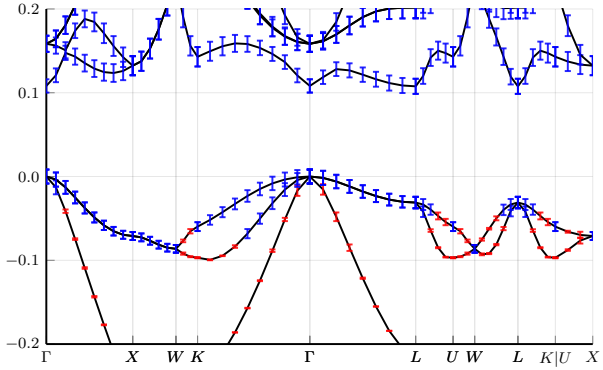






Societal challenges of 21st century

- Renewable energy
- Green chemistry and catalysts
- Drug design
- Transportation
- Data storage and communication

⇒ Need for novel materials

⇒ High-throughput computational screening

⇒ Common approach: Density-functional theory (DFT)

Typical scale

- One DFT calculation: $\mathcal{O}$(hours) to $\mathcal{O}$(days)
- E.g. Open Catalyst Project[1]
  - 1.3 million DFT calculations
  - > 250 million DFT energy evaluations
  - Workflow success rate: $\simeq 50\%$[2]

$\Rightarrow$ Need high degree of automation

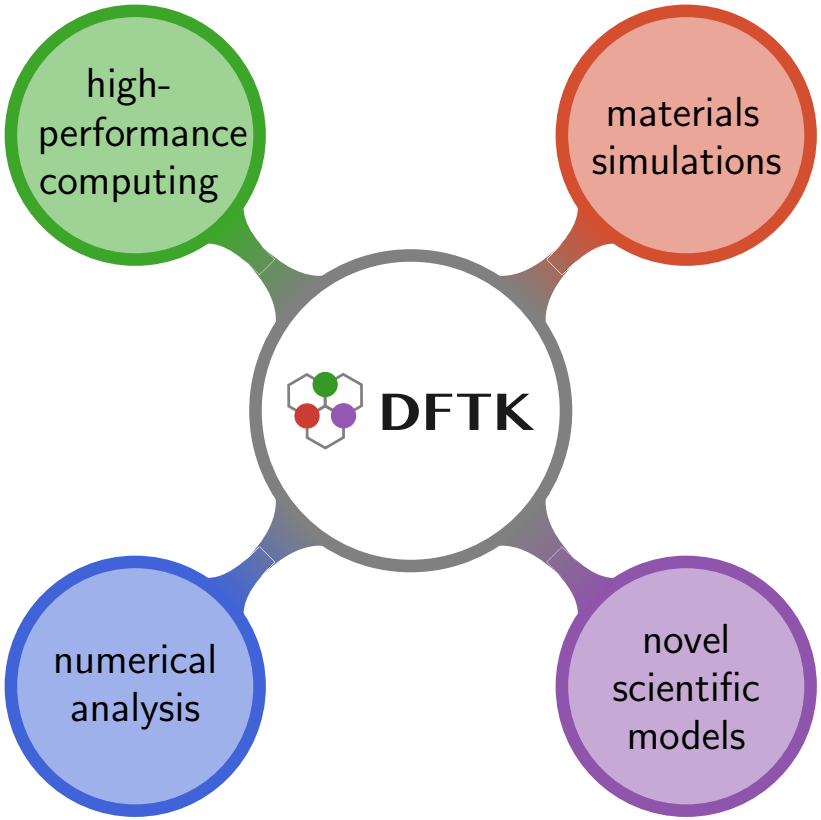
$\Rightarrow$ Reliability needs to be improved!

- Multidisciplinary research problem

[1] L. Chanussot *et. al.* The Open Catalyst 2020 (OC20) Dataset, 2020, arXiv 2010.09990.

[2] Z. Ulissi, private communication in ARPAE differentiate group seminar, Dec 2020.

Density-functional toolkit (DFTK)[1]



- `https://dftk.org`
- 2 years of development
- Pure julia code

- Supports mathematical developments *and* scale-up to regime relevant to applications
- Low entrance barrier: Only 6k lines of code!

[1] M. F. Herbst, A. Levitt and E. Cancès. JuliaCon Proc., **3**, 69 (2021).

DFTK — https://dftk.org

- Ground state (LDA, GGA) and a bit of response theory
- Compose your model (e.g. analytic potentials, . . .)
- 1D / 2D / 3D systems
- Arbitrary floating point type

- Mixed MPI-Thread-based parallelism
- > 800 electrons possible
- Integration with materials-related python modules

- Performance: Within factor 2 of established codes
- Documentation and examples: `https://docs.dftk.org`

Current research with DFTK

⇒ Vision: Improve high-throughput workflows:

- Use maths: Error analysis and automatic error balancing[1]
- Use physics: Reliable black-box SCF preconditioners[2]
- Better algorithms: Numerical analysis of SCF methods[3]

⇒ Reliable automatic selection of parameters in DFT workflows

- International and interdisciplinary user base:
  - ENPC Paris, CMU, MIT, RWTH Aachen, TUM, ...
- Involved in multidisciplinary research projects:
  - ACED-DIFFERENTIATE, EMC2 erc synergy, CESMIX

[1] M. F. Herbst, A. Levitt and E. Cancès. Faraday Discuss. **224**, 227 (2020).
[2] M. F. Herbst, A. Levitt. J. Phys. Condens. Matter **33**, 085503 (2021).
[3] E. Cancès, G. Kemlin, A. Levitt. arXiv 2004.09088 (2020).

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- Use physics: Reliable black-box SCF preconditioners[2]
- Better algorithms: Numerical analysis of SCF methods[3]
  (→ Gaspard's talk, Room A 14:20 tomorrow)

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Perspective of rigorous error analysis in DFT

- Sources of error in DFT:
  - Model error
  - Discretisation error
  - Algorithm error
  - Arithmetic error
- *A posteriori* bound on errors:
  - Total error known $\Rightarrow$ Error bars
  - Error-guided adaptive numerics $\Rightarrow$ Efficiency gain
- For DFT: Error estimation not fully developed

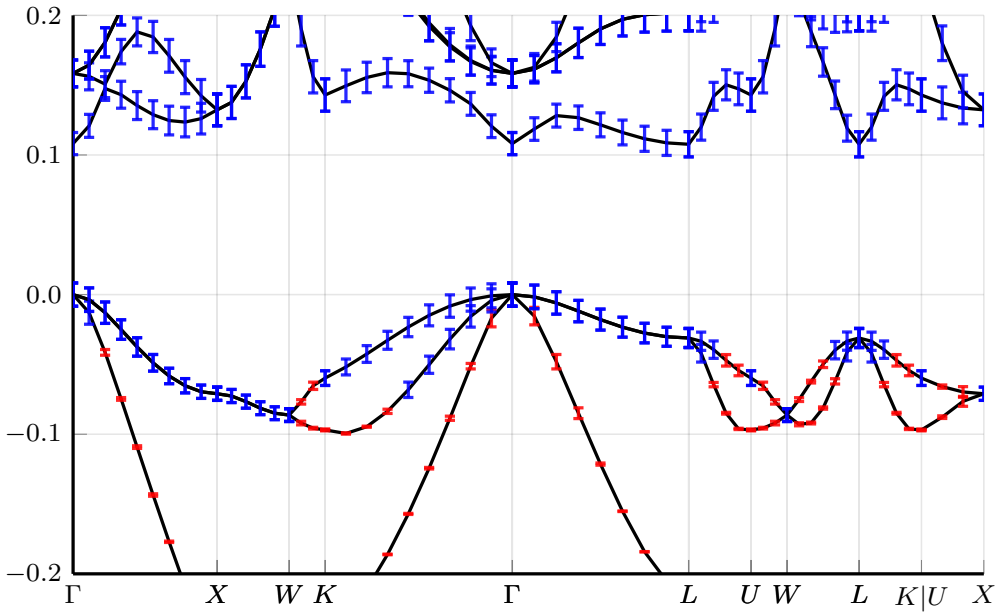
A posteriori error analysis with DFTK

- Requirements:
  - Mathematical theory can only treat reduced models
  - Step-by-step expansion (with guidance from physics)
  - Ingredients not yet clear (e.g. form of integrals for bounds)

  ⇒ Need toolbox for experimentation
  - Arithmetic error: Interval arithmetic, elevated precision
- DFTK offers:
  - Fully customisable model
  - Support for arbitrary floating-point types
  - Use julia ecosystem on DFTK datastructures:
    - Numerical quadrature, forward-mode AD, ...

    ⇒ Rapid prototyping in numerical linear algebra

A posteriori error analysis: First results with DFTK[1]



- Reduced model: Non-self-consistent Kohn-Sham
- Estimation of arithmetic error (`IntervalArithmetic.jl`)
- Used elevated floating-point type (`DoubleFloats.jl`)
- Time to submission: 10 weeks

[1] M. F. Herbst, A. Levitt and E. Cancès. Faraday Discuss. **224**, 227 (2020).

Kohn-Sham DFT

- Coupled set of non-linear elliptic partial differential equations:

$$\Big(-\frac{1}{2}\Delta + \mathcal{V}(\rho)\Big)\psi_i = \varepsilon_i \psi_i, \qquad \int \psi_i^* \psi_j = \delta_{ij}$$

$$\rho = \sum_{i=1}^{\infty} f\left(\frac{\varepsilon_i - \varepsilon_F}{T}\right) |\psi_i|^2, \quad \text{with } \varepsilon_F \text{ such that } \int \rho = N$$

- Density-dependent potential

$$\mathcal{V}(\rho) = V_{\mathsf{Nuc}} + \int (v_C \rho) + V_{\mathsf{xc}}(\rho)$$

with Coulomb kernel $v_C(\underline{\boldsymbol{r}}, \underline{\boldsymbol{r}}') = \|\underline{\boldsymbol{r}} - \underline{\boldsymbol{r}}'\|^{-1}$

- Fermi-Dirac function $f(x) = 1/(1+e^x)$
- Temperature T, electron count N
- Exchange-correlation potential V_{xc}, nuclear attraction V_{Nuc}

Self-consistent field (SCF) as a fixed-point problem

- Density-dependent potential

$$\mathcal{V}(\rho) = V_{\mathsf{Nuc}} + \int (v_C \rho) + V_{\mathsf{xc}}(\rho)$$

- Potential-to-density map F

$$F(V) = \sum_{i=1}^{\infty} f\left(\frac{\varepsilon_i - \varepsilon_F}{T}\right) |\psi_i|^2$$

with (ε_i, ψ_i) eigenpairs of $-\frac{1}{2}\Delta + V$.

$\Rightarrow$ SCF solves $\rho = F(\mathcal{V}(\rho))$

- Numerically: Damped fixed-point scheme

$$\rho_{n+1} = \rho_n + \alpha P^{-1} \left[F(\mathcal{V}(\rho_n)) - \rho_n\right]$$

with preconditioner ("mixing") P

SCF convergence (1)

$$\rho_{n+1} = \rho_n + \alpha P^{-1} \left[F(\mathcal{V}(\rho_n)) - \rho_n \right]$$

- Near a fixed-point the error goes as

$$e_{n+1} \simeq \left[1 - \alpha P^{-1} \epsilon^\dagger \right] e_n$$

  where $\epsilon^\dagger = 1 - \chi_0 (v_C + f_{\text{xc}})$ (dielectric matrix)
- χ_0: Independent-particle susceptibility (derivative of F)
- f_{xc}: XC kernel (derivative of V_{xc})

SCF convergence (2)

$$e_{n+1} \simeq \left[1 - \alpha P^{-1}\epsilon^\dagger\right] e_n, \qquad \epsilon^\dagger = 1 - \chi_0(v_C + f_{\text{xc}})$$

- Assume RPA: $\sigma(\epsilon^\dagger) > 0$ and real
- Assume $P > 0$
- λ_{min}, λ_{max}: Extremal eigenvalues of $P^{-1}\epsilon^\dagger$
- Optimal damping $\quad \alpha = \dfrac{2}{\lambda_{\text{min}} + \lambda_{\text{max}}}$
- Optimal rate $\quad R = \dfrac{\kappa - 1}{\kappa + 1}, \quad \kappa = \dfrac{\lambda_{\text{max}}}{\lambda_{\text{min}}}$

$\Rightarrow$ SCF convergence linked to dielectric properties

SCF instabilities

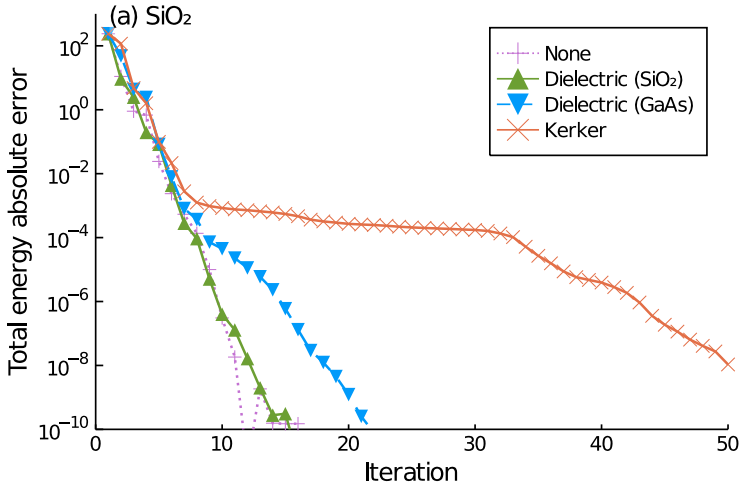
$$e_{n+1} \simeq \left[1 - \alpha P^{-1} \epsilon^\dagger\right] e_n, \qquad \epsilon^\dagger = 1 - \chi_0 (v_C + f_{\text{xc}})$$

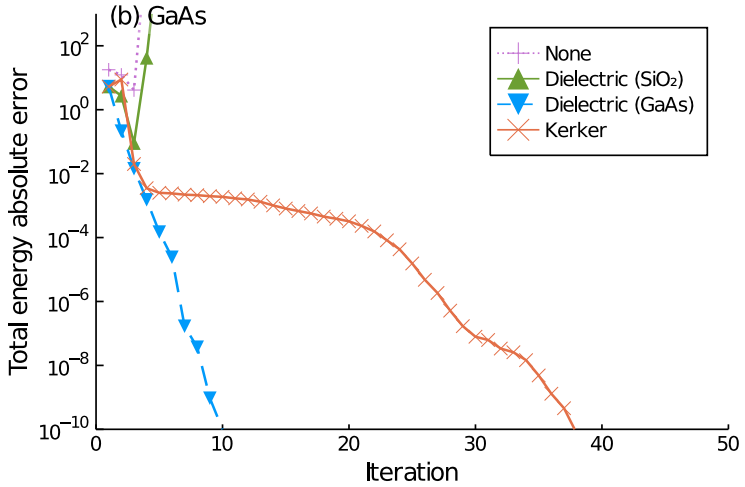
- SCF instabilities increase condition number κ:
  - $\epsilon^\dagger$ has small eigenvalues (e.g. symmetry breaking)
  - χ_0 has large eigenvalues (localised states)
  - Large charge-sloshing modes of v_C are uncompensated by χ_0 (metals)

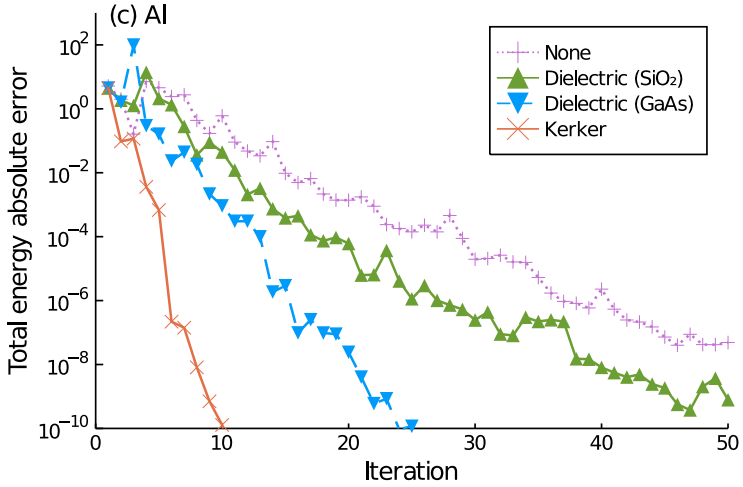
$\Rightarrow$ Need infeasibly small α or good P

- Physics where a good mixing P is known:
  - *Bulk* insulators ($P = I$)
  - *Bulk* metals (Kerker mixing)
  - *Bulk* semiconductors (e.g. Resta's dielectric model)

Convergence results for bulk materials[1]







- silica (SiO_2) insulator
- gallium arsenide (GaAs) semiconductor
- aluminium (Al) metal

[1] M. F. Herbst, A. Levitt. J. Phys. Condens. Matter **33**, 085503 (2021).

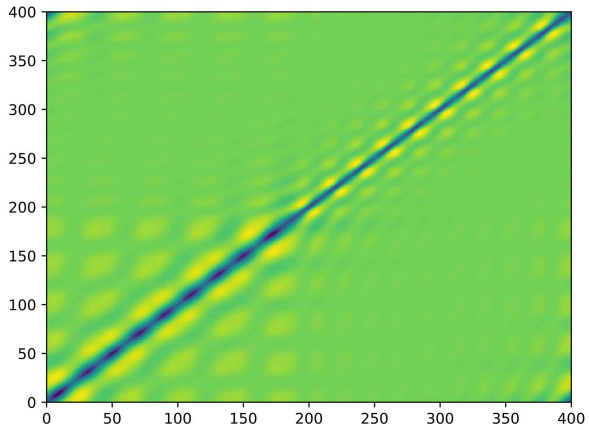
Problems with established mixing methods

- Preconditioner P manually chosen
  - Rough idea of dielectric properties needed *a priori*
- Which P for inhomogeneous materials?
  - Either bulk or non-trivial parameters
  - E.g. metal clusters, metallic surfaces, passivated surfaces
- Which P for localised states?
  - None I know of ...
  - E.g. d-metal alloys (Heuslers), surface states
- Damping α manually chosen
  - Trial and error ... (especially if P unsuitable)

Preconditioning inhomogeneous systems

$$\rho_{n+1} = \rho_n + \alpha P^{-1} \left[F(\mathcal{V}(\rho_n)) - \rho_n, \right]$$

- Bulk preconditioning models tackle directly $P^{-1} \approx \left(\varepsilon^\dagger\right)^{-1}$
- Plot of χ_0 (Chain of 10 Sodium atoms and 10 helium atoms):



$\Rightarrow$ Diagonal-dominant, try an approximation $\chi_0(\underline{\boldsymbol{r}}, \underline{\boldsymbol{r}}') \simeq \widetilde{\chi_0}(\underline{\boldsymbol{r}})$

- Apply preconditioner iteratively:

$$P^{-1}\rho_n = \left(1 - \widetilde{\chi_0} v_C\right)\right)^{-1} \rho_n$$

Local density of states (LDOS) approximation for χ_0[1]

- Main interest: Large-scale variations from ρ_n to ρ_{n+1}

$\Rightarrow$ $\underline{\boldsymbol{r}} \mapsto \chi_0(\underline{\boldsymbol{r}}, \underline{\boldsymbol{r}}')$ more localised around $\underline{\boldsymbol{r}}'$ than $V(\underline{\boldsymbol{r}}')$.

- "Row-sum mass lumping":

$$\int \chi_0(\underline{\boldsymbol{r}}, \underline{\boldsymbol{r}}') V(\underline{\boldsymbol{r}}') \, \mathrm{d}\underline{\boldsymbol{r}}' \simeq V(\underline{\boldsymbol{r}}) \int \chi_0(\underline{\boldsymbol{r}}, \underline{\boldsymbol{r}}') \, \mathrm{d}\underline{\boldsymbol{r}}'$$
$$= -V(\underline{\boldsymbol{r}}) D_{\mathsf{loc}}(\underline{\boldsymbol{r}})$$

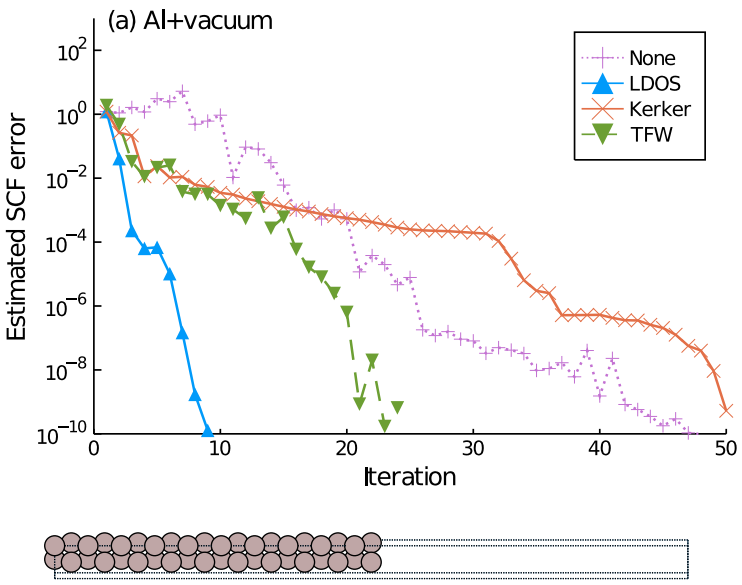
with local density of states

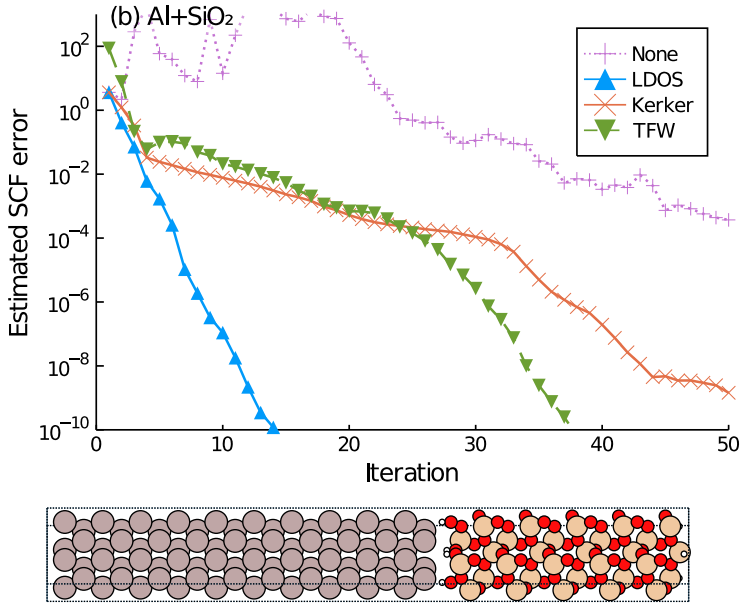
$$D_{\mathsf{loc}}(\underline{\boldsymbol{r}}) = \frac{1}{T} \sum_i f'\left(\frac{\varepsilon_i - \varepsilon_F}{T}\right) |\psi_i(\underline{\boldsymbol{r}})|^2$$

using Adler-Wiser formula.

[1] M. F. Herbst, A. Levitt. J. Phys. Condens. Matter **33**, 085503 (2021).

LDOS preconditioning (examples)





- 20 repeats of aluminium + 20 repeats vacuum / silica
- TFW: local Thomas-Fermi-von Weizsäcker mixing[1]
- LDOS automatically interpolates between Kerker mixing (in the metallic region) and no mixing (insulating region)

⇒ Parameter-free and black-box

[1] D. Raczkowski, A. Canning, L. W. Wang, Phys. Rev. B. **64**, 121101 (2001).

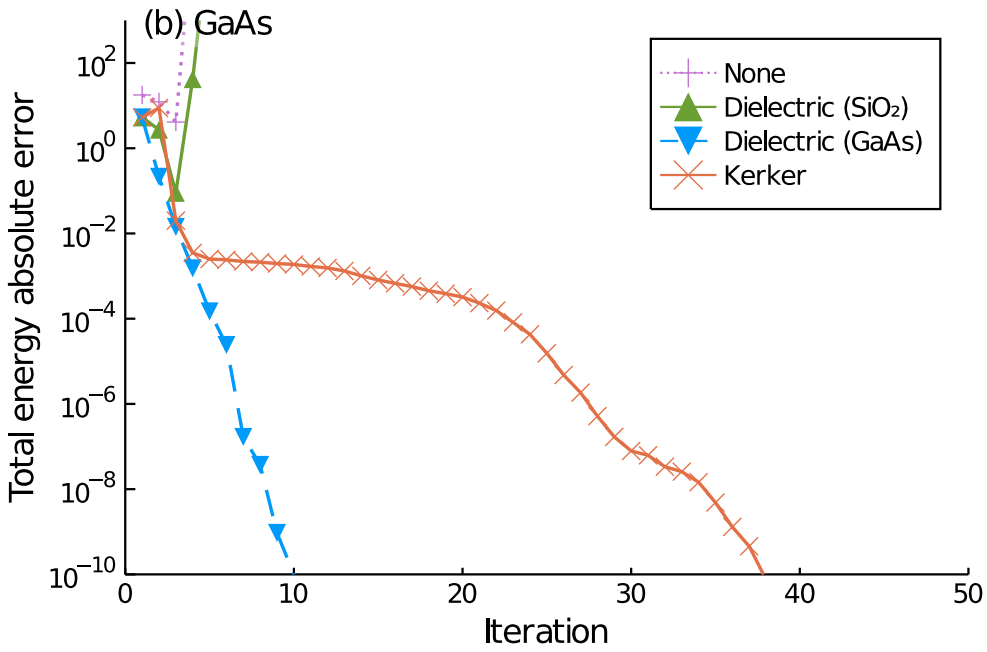
LDOS preconditioning results[1]

		None		Dielectric		Kerker		LDOS		LDOS+ Dielectric	
	$\mathcal{N}$	it	κ	it	κ	it	κ	it	κ	it	κ
SiO_2+vacuum	10	11	3.3	26	19.7	50	95.7	11	3.3	26	19.7
	20	12	3.4	30	24.4	n.c.	351.5	12	3.4	30	21.7
GaAs+vacuum	10	17	13.4	18	6.2	23	67.0	17	12.4	18	10.4
	20	20	15.5	22	12.9	n.c.	312.2	20	15.5	22	12.9
Al+vacuum	10	19	51.5	24	44.3	22	64.4	9	3.7	16	10.3
	20	47	170.8	49	168.5	n.c.	323.9	9	3.5	20	10.5
GaAs+SiO_2[a]	10	45	13.7	19	8.9	34	52.4	45	13.4	19	8.8
	20	n.c.	18.2	20	10.2	n.c.	170.1	n.c.	18.2	20	10.2
Al+SiO_2	10	43	93.1	29	33.6	30	50.9	17	6.1	20	9.2
	20	n.c.	316.6	n.c.	118.4	n.c.	159.4	14	5.4	20	10.1
Al+GaAs	10	n.c.	144.0	24	22.4	16	9.0	15	7.2	11	3.5
	20	n.c.	485.0	40	59.0	26	28.8	26	21.4	13	5.0
Al+GaAs+SiO_2	10	n.c.	149.5	34	50.4	36	62.9	26	21.5	19	9.0

- Coloured: Condition number κ less than doubled on doubling system size

[1] M. F. Herbst, A. Levitt. J. Phys. Condens. Matter **33**, 085503 (2021).

Revisiting a "simple" case



- What happens here for "None" and "Dielectric (SiO_2)"?
- GaAs strong non-linearity

⇒ Anderson acceleration (DIIS) messes up

- Can we detect this and reduce damping α to save the SCF?

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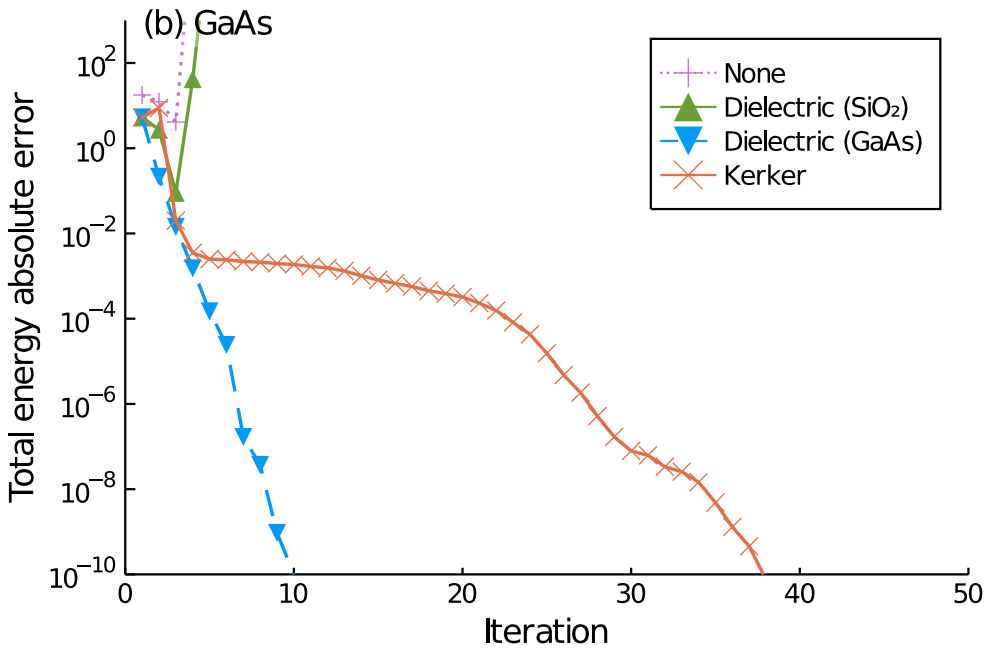

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Adaptive damping (1)

- Potential mixing:

$$V_{n+1} = V_n + \alpha\, \delta V_n$$
$$\delta V_n = P^{-1}\left[\mathcal{V}(F(V_n)) - V_n\right]$$

- Quadratic model for DFT energy:

$$E(V_n + \alpha\, \delta V_n) \simeq E(V_n) + \alpha \left\langle \nabla E_{|V=V_n} \middle| \delta V_n \right\rangle + \frac{\alpha^2}{2} \left\langle \delta V_n \middle| \nabla^2 E_{|V=V_n} \delta V_n \right\rangle$$

- Following[1]

$$\nabla E_{|V=V_n} = -\chi_0 \left(V_n^{\text{out}} - V_n\right)$$
$$\nabla^2 E_{|V=V_n} \simeq -\chi_0 \left[1 - (v_C + f_{\text{xc}})\chi_0\right]$$

[1] X. Gonze Phys. Rev. B **54**, 4383 (1996).

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[1] X. Gonze Phys. Rev. B **54**, 4383 (1996).

Adaptive damping (2)

$$V_{n+1} = V_n + \alpha\,\delta V_n, \quad \delta V_n = P^{-1}\left[V_n^{\text{out}} - V_n\right], \quad V_n^{\text{out}} = \mathcal{V}(F(V_n))$$

- Quadratic model (after some algebra):

$$E(V_n + \alpha\,\delta V_n) \simeq E(V_n) - \alpha\,\langle V_n^{\text{out}} - V_n | \delta\rho_n\rangle + \frac{\alpha^2}{2}\Big[-\langle \delta V_n | \delta\rho_n\rangle + \Big\langle \delta\rho_n \Big| \Big(v_C + f_{\text{xc}}\Big)\,\delta\rho_n\Big\rangle\Big]$$

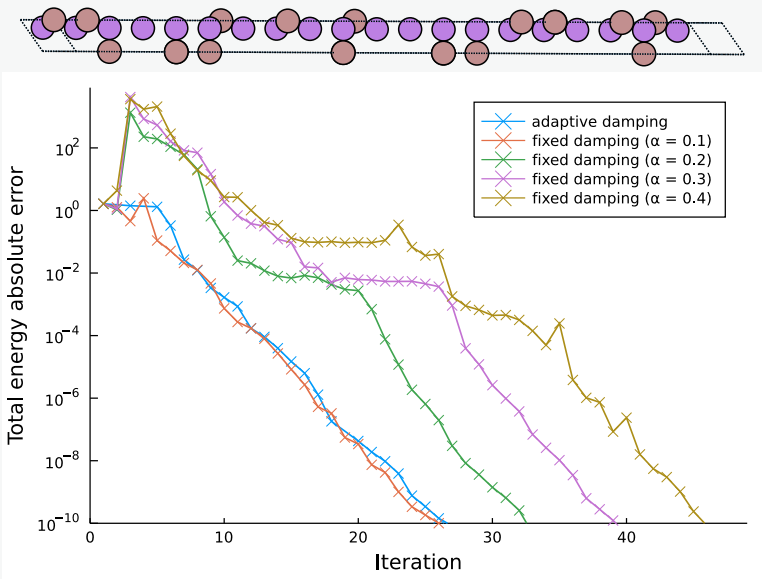
  where $\delta\rho_n = F(V_{n+1}) - F(V_n)$.

- Given V_n, V_n^{out}, V_{n+1}, $F(V_{n+1})$: Find δV_n and $\delta\rho_n$ then optimal damping α

- Sketch of adaptive damping algorithm (WIP):
  - Choose trial α
  - Accept if energy or residual decreases
  - Else: Find optimal damping, recompute V_{n+1} and $F(V_{n+1})$

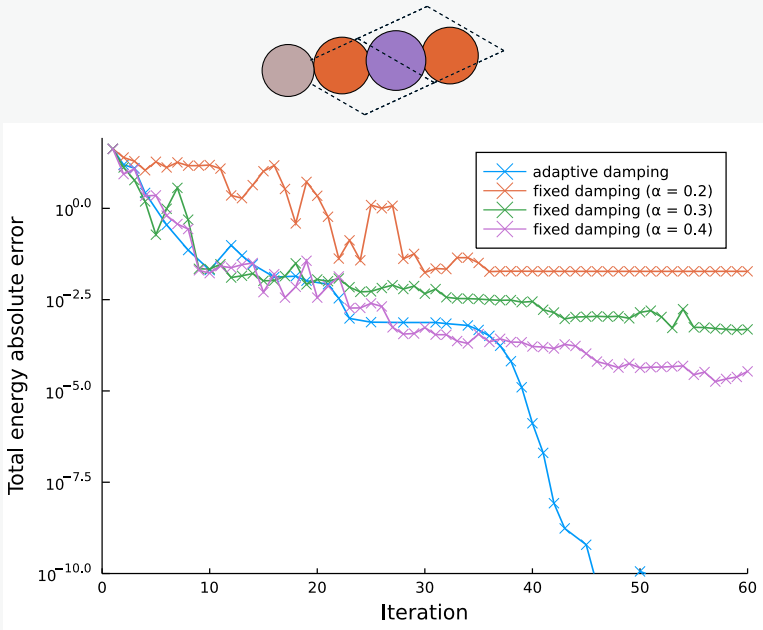
Adaptive damping (WIP examples)

GaAs (Gallium arsenide)



- Non-linear SCF behaviour in initial steps
- Anderson extrapolation fails

Fe_2MnAl Heusler alloy structure



- Localised states, spin
- No suitable preconditioner P

- Adaptive damping as safeguard
- But: Tends to be slightly more expensive for "simple" cases

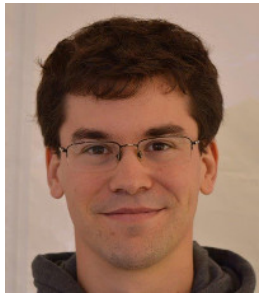
Summary

https://michael-herbst.com/slides/siamms21

- **DFTK** usage:
  - First develop LDOS scheme on test systems (1D, toy problems)
  - Tests on > 800 electrons (in the same code!)
  - Key quantities (χ_0, f_{xc}) fully accessible
  - E.g. routine computation of λ_{min} and λ_{max}
- LDOS preconditioner:
  - Parameter-free $\Rightarrow$ Highly suitable for high-throughput
  - Adaptive preconditioning for inhomogeneous systems
- Adaptive damping scheme:
  - Safe guard if preconditioner not perfect / tricky system
  - Reduction of the human factor

Acknowledgements

https://michael-herbst.com/slides/siamms21



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Questions?

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