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Core-electron forces within the FLAPW Method

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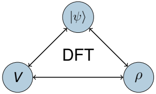
Motivation

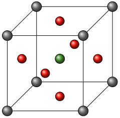
- Forces with Density Functional Theory



- All-electron full-potential LAPW method

www.flapw.de

- Accuracy sufficient for lattice relaxation



- Not so for reliable force-constant matrix

$$\begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix}$$

Goal: Increase accuracy to $\mu\text{Htr}/a_0$

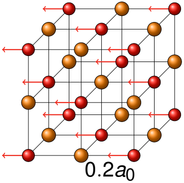
Current accuracy of forces

- Translational invariance: $\sum_\alpha \boldsymbol{F}_\alpha = \mathbf{0}$

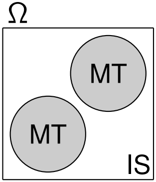
	Mg	O	total	relative
Force [mHtr/a_0]	-11.611	11.192	0.419	3.67%

- Force-constant matrix: $C^{ij}_{\alpha\beta} := \frac{\partial^2 E}{\partial \tau^i_\alpha \partial \tau^j_\beta} = -\frac{F^\alpha_i}{u^\beta_j} = -\frac{F^\beta_j}{u^\alpha_i}$
  - $\underline{\boldsymbol{C}}$ has to be symmetric by Young's theorem

$$\underline{\boldsymbol{C}}_{\text{MgO}} = \begin{pmatrix} -11.611 & 11.192 \\ 11.611 & -11.192 \end{pmatrix} \frac{\text{mHtr}}{a_0}$$



LAPW in a nutshell



- Core electrons:
  Solutions of fully relativistic Dirac-equation
- Valence electrons:
  Constructed from piece-wise basis functions

$$\phi_{\boldsymbol{K}}(\boldsymbol{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \exp(i\boldsymbol{K}\cdot\boldsymbol{r}) & \boldsymbol{r} \in \mathrm{IS} \\ \sum_L^{\ell_{\max}} \left(a_L^{\alpha\boldsymbol{K}} u_\ell^\alpha(r_\alpha) + b_L^{\alpha\boldsymbol{K}} \dot{u}_\ell^\alpha(r_\alpha)\right) Y_L(\hat{\boldsymbol{r}}_\alpha) & \boldsymbol{r} \in \mathrm{MT}_\alpha \end{cases}$$

- Local Orbitals:
  Enhance flexibility of basis inside a muffin-tin for selected ℓ

$$\phi_{\boldsymbol{K}_{lo}}^{\ell,lo}(\boldsymbol{r}_\alpha) = \sum_m \left(a_{L,lo}^{\alpha\boldsymbol{K}_{lo}} u_\ell^\alpha(r_\alpha) + b_{L,lo}^{\alpha\boldsymbol{K}_{lo}} \dot{u}_\ell^\alpha(r_\alpha) + c_{L,lo}^{\alpha\boldsymbol{K}_{lo}} \tilde{u}_{\ell,lo}(r_\alpha)\right) Y_L(\hat{\boldsymbol{r}}_\alpha)$$

Forces in FLAPW

$$\boldsymbol{F}_\alpha = -\frac{\partial}{\partial \boldsymbol{\tau}_\alpha} E$$

- Position-dependent basis set requires Pulay correction

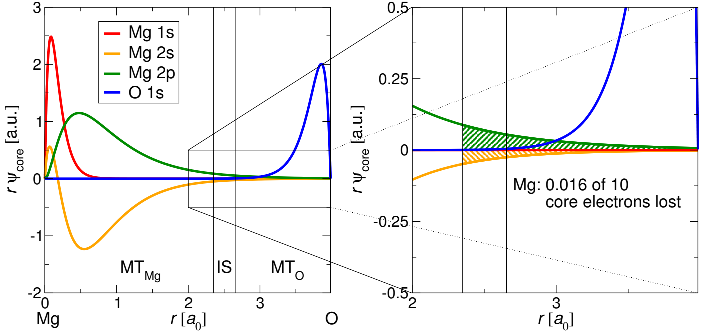
$$\begin{aligned}\boldsymbol{F}_\alpha = & -\sum_{i\boldsymbol{k}} n_{i\boldsymbol{k}} \langle \psi_{i\boldsymbol{k}} | \nabla_{\boldsymbol{\tau}_\alpha} \mathcal{H} | \psi_{i\boldsymbol{k}} \rangle \\ & - 2 \sum_{i\boldsymbol{k}} n_{i\boldsymbol{k}} \, \mathrm{Re} \, \langle \nabla_{\boldsymbol{\tau}_\alpha} \psi_{i\boldsymbol{k}} | \mathcal{H} - \epsilon_{i\boldsymbol{k}} | \psi_{i\boldsymbol{k}} \rangle \\ = & \boldsymbol{F}_\alpha^{\mathrm{HF}} + \boldsymbol{F}_{\alpha,\mathrm{core}}^{\mathrm{Pulay}} + \boldsymbol{F}_{\alpha,\mathrm{val}}^{\mathrm{Pulay}}\end{aligned}$$

- Core correction: $\boldsymbol{F}_{\alpha,\mathrm{core}}^{\mathrm{Pulay}} = -\int_{\mathrm{MT}_\alpha} d^3 \boldsymbol{r}_\alpha \rho_{\mathrm{core}}^\alpha(\boldsymbol{r}_\alpha) \nabla V_{\mathrm{eff}}^\alpha(\boldsymbol{r}_\alpha)$

(R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991))

Losing core electrons

- Core states do not necessarily vanish at MT boundary



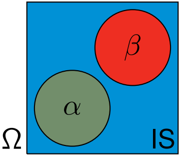
- Include complete unit cell in calculation of $\boldsymbol{F}^{\text{Pulay}}_{\alpha,\text{core}}$

Core forces over whole unit cell

$$-\int_{\Omega} d^3\boldsymbol{r}\,\rho^{\alpha}_{\text{core}}(\boldsymbol{r})\nabla V_{\text{eff}}(\boldsymbol{r}) = \underbrace{-\int_{MT_\alpha} d^3\boldsymbol{r}_\alpha\,\rho^{\alpha}_{\text{core}}(\boldsymbol{r}_\alpha)\nabla V^{\alpha}_{\text{eff}}(\boldsymbol{r}_\alpha)}_{\text{core correction in original muffin tin}}$$

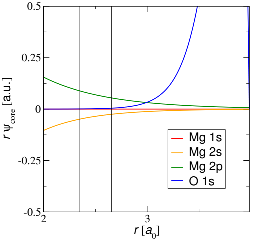
$$\underbrace{+\sum_{\beta\neq\alpha}\int_{MT_\beta} d^3\boldsymbol{r}\,\rho^{\alpha}_{\text{core}}(\boldsymbol{r}-\boldsymbol{\tau}_\alpha)\nabla V_{\text{eff}}(\boldsymbol{r})}_{\text{core correction in other muffin tins}}$$

$$\underbrace{+\int_{IS} d^3\boldsymbol{r}\,\rho^{\alpha}_{\text{core}}(\boldsymbol{r}-\boldsymbol{\tau}_\alpha)\nabla V_{\text{eff}}(\boldsymbol{r})}_{\text{core correction in interstitial}}$$

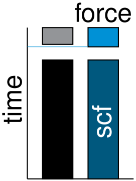


Results on MgO

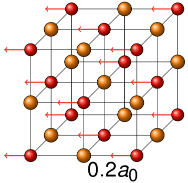
Force [mHtr/a_0]	$\text{Mg}_{2.35a_0}$	$\text{O}_{1.33a_0}$	total
no correction	-11.611	11.192	0.419
full core-correction	-11.191	11.191	0.000



$$\underline{c}^{new}_{MgO} = \begin{pmatrix} -11.191 & 11.191 \\ 11.191 & -11.191 \end{pmatrix} \frac{\text{mHtr}}{a_0}$$

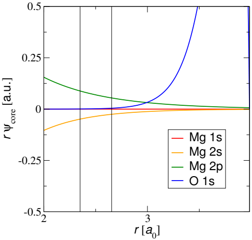


LDA	VWN
ℓ_{max}	16
k_{max}	$5.5a_0^{-1}$
a	$7.97a_0$
kpt-Grid	10x10x10

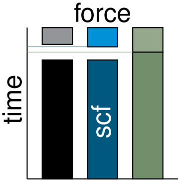


Results on MgO

Force [mHtr/a_0]	$Mg_{2.35a_0}$	$O_{1.33a_0}$	total
no correction	-11.611	11.192	0.419
full core-correction	-11.191	11.191	0.000
LOs: Mg_{2s2p}, O_{1s}	-10.808	10.807	0.001



$$\underline{C}^{new}_{MgO} = \begin{pmatrix} -11.191 & 11.191 \\ 11.191 & -11.191 \end{pmatrix} \frac{\mathrm{mHtr}}{a_0}$$



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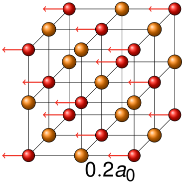
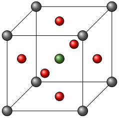


Results on $EuTiO_3$



Compare old to new force-constant matrix:

$$\underline{C}^{\text{old}}_{\text{EuTiO}_3} = \begin{pmatrix} -0.297 & 0.639 & -0.295 & -0.295 & 0.203 \\ 0.645 & -1.978 & 0.237 & 0.237 & 0.787 \\ -0.274 & 0.233 & -0.877 & -0.196 & 1.133 \\ -0.274 & 0.233 & -0.196 & -0.877 & 1.133 \\ 0.200 & 0.873 & 1.131 & 1.131 & -3.253 \end{pmatrix} \frac{\text{mHtr}}{a_0}$$

$$\underline{C}^{\text{new}}_{\text{EuTiO}_3} = \begin{pmatrix} -0.238 & 0.626 & -0.295 & -0.295 & 0.2018 \\ 0.626 & -1.591 & 0.251 & 0.251 & 0.4631 \\ -0.295 & 0.251 & -0.889 & -0.196 & 1.129 \\ -0.295 & 0.251 & -0.196 & -0.889 & 1.129 \\ 0.2014 & 0.4640 & 1.129 & 1.129 & -2.923 \end{pmatrix} \frac{\text{mHtr}}{a_0}$$

New force-constant matrix symmetric up to less than $1\mu\text{Htr}/a_0$

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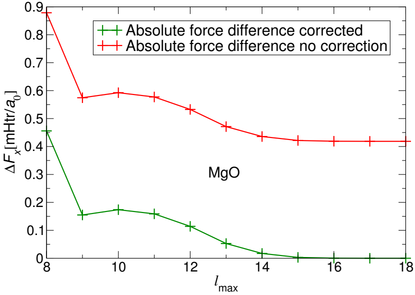
Conclusion & Outlook

- Correction only necessary in actual force step
- Drift forces vanish for high ℓ_{max}
- Calculation of highly precise force-constant matrices achieved



- To be done: Reduction of necessary ℓ_{max}-cutoff

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Appendix

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Results on NaCl and GaAs

Force [mHtr/a_0]	$\text{Na}_{2.77a_0}$	$\text{Cl}_{2.17a_0}$	total
no correction	-3.633	3.351	0.282
full core-correction	-3.351	3.351	0.000
LOs: Na_{2s2p}, Cl_{none}	-3.196	3.196	0.000
displacement along [100]: $0.27a_0$, $a = 10.69a_0$			
	$\text{Ga}_{2.21a_0}$	$\text{As}_{2.21a_0}$	total
no correction	-12.001	12.229	0.228
full core-correction	-11.982	11.982	0.000
LOs: Ga_{3s3p3d}, As_{3s3p3d}	-14.514	14.522	0.008
displacement along [100]: $0.13a_0$, $a = 10.68a_0$			
$\ell_{\max} = 16$, $8 \times 8 \times 8$ kpt-Grid, $k_{\max} = 4.2a_0^{-1}$			

Setup of $EuTiO_3$

	shared	no correction	full core-correction
Eu	$R_{MT} = 2.60a_0$	$\ell_{max} = 12$	$\ell_{max} = 16$
	local orbitals:	5p	5s5p
Ti	$R_{MT} = 2.21a_0$	$\ell_{max} = 8$	$\ell_{max} = 12$
	local orbitals:	3p	3s3p
O	$R_{MT} = 1.41a_0$	$\ell_{max} = 8$	$\ell_{max} = 12$
displacement along [100]: $0.02a_0$, $a = 7.37a_0$			
LDA VWN, $8 \times 8 \times 8$ kpt-Grid, $k_{max} = 4.0a_0^{-1}$			