# FORCES AND DFPT

## The All-Electron FLAPW Realization in FLEUR

Monday 9th September, 2019 | Picking flowers: Hands-on FLEUR | IAS 1 & PGI 1

MAX DRIVING THE EXASCALE TRANSITION

www.flapw.de fleur

cecam Centre Européen de Calcul Atomique et Moléculaire

JÜLICH Forschungszentrum

# GEOMETRY OPTIMIZATIONS

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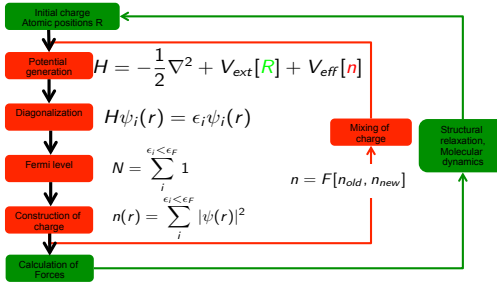


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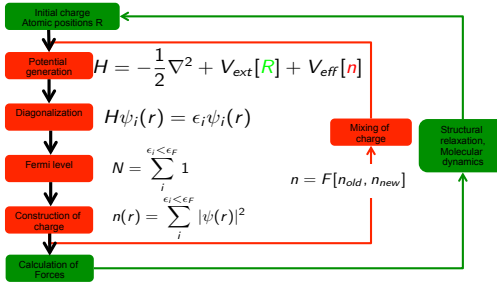


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**Note:**

- Energy landscape might contain several minima / stable geometries
- Calculation of forces combinable with optimization algorithms

# DFT FORCE CALCULATION

## Theory (Hellmann–Feynman Force)

- Force from negative gradient of Kohn–Sham total energy $\boldsymbol{F}_\alpha = -\frac{\mathrm{d}E^{\mathsf{KS}}_{\mathsf{tot}}}{\mathrm{d}\boldsymbol{\tau}_\alpha}$
- The Hellmann–Feynman (HF) contribution incorporates 2 resulting terms

$$E^{\mathsf{KS}}_{\mathsf{tot}}[\rho(\boldsymbol{r})] = \sum_n f_n \epsilon^{\mathsf{KS}}_n - \int \mathrm{d}^3 r\, \rho_0(\boldsymbol{r}) V_{\mathsf{eff}}(\boldsymbol{r}) + \frac{1}{2} \iint \mathrm{d}^3 r'\, \mathrm{d}^3 r\, \frac{\rho_0(\boldsymbol{r})\rho_0(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$
$$+ \frac{1}{2} \sum_{\alpha \neq \beta}^{N_{\mathsf{at}}} \frac{Z_\alpha Z_\beta}{|\boldsymbol{\tau}_\alpha - \boldsymbol{\tau}_\beta|} - \sum_\alpha^{N_{\mathsf{at}}} \int \mathrm{d}^3 r'\, \frac{Z_\alpha \rho_0(\boldsymbol{r}')}{|\boldsymbol{\tau}_\alpha - \boldsymbol{r}'|} + \int \mathrm{d}^3 r'\, \rho_0(\boldsymbol{r}') \epsilon_{xc}[\rho_0(\boldsymbol{r}')]$$

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- Applying Weinert method delivers HF force as implemented in FLEUR

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$$\boldsymbol{F}^{\mathsf{HF}}_{\alpha,\mathsf{Yu}} = Z_\alpha \sum_{m=-1}^{1} \frac{(-1)^m}{\sqrt{12\pi}} \underline{T}\hat{\boldsymbol{e}}_m \left( \frac{4\pi}{3} \int_0^{R_\alpha} \mathrm{d}s_\alpha\, \rho^\alpha_{1m}(s_\alpha) \left[1 - \left(\frac{s_\alpha}{R_\alpha}\right)^3\right] + \frac{V^\alpha_{\mathsf{C},1m}(R_\alpha)}{R_\alpha} \right)$$

Hellmann, Einführung in die Quantenchemie, Deuticke, 1937. | Feynman, Phys. Rev., 1939, **56**, 340-343. | Yu et al., Phys. Rev. B. 1991, **43**, 6411-6422.

# THE WEINERT METHOD

## Example: Coulomb potential

- Goal: Solve Poisson equation
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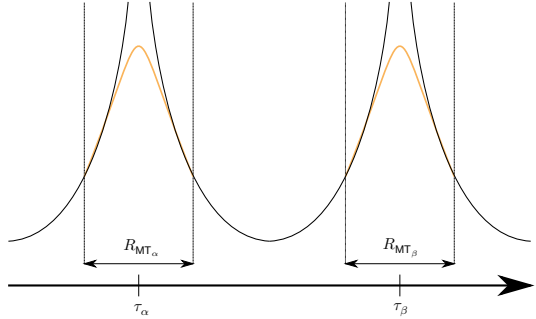
- Fourier transform appliable to smooth pseudo-charge density

$$\Rightarrow \quad V_{\text{IR, Coul}}^{\alpha}(\boldsymbol{r}) = \sum_{\boldsymbol{G}\neq\boldsymbol{0}} \frac{4\pi}{G^2} \rho_{\text{ps}}(\boldsymbol{G}) \mathrm{e}^{\mathrm{i}\boldsymbol{G}\cdot\boldsymbol{r}}$$




M. Weinert, J. Math. Phys, **22**, 2433 (1981).

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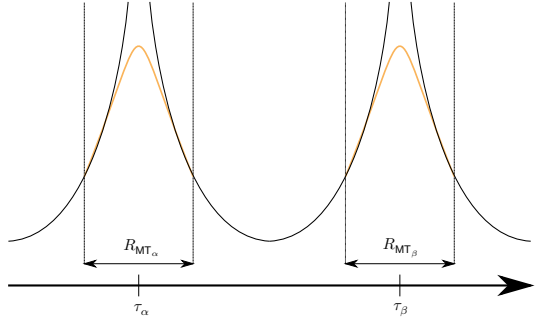


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- Muffin-tin potential from boundary-value problem

$$V_{\text{MT, Coul}}^{\alpha}(\boldsymbol{r}_\alpha + \boldsymbol{\tau}_\alpha) = \int_{\text{MT}} \mathrm{d}^3 r'_\alpha \, \rho(\boldsymbol{r}'_\alpha) G(\boldsymbol{r}_\alpha, \boldsymbol{r}'_\alpha) - \frac{1}{4\pi} \oint_{\partial\text{MT}} \mathrm{d}S V_{\text{IR, Coul}}^{\alpha}(\boldsymbol{r}'_\alpha + \boldsymbol{\tau}_\alpha) \nabla_{r'_\alpha} G(\boldsymbol{r}_\alpha, \boldsymbol{r}'_\alpha)$$

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# DFT FORCE CALCULATION

## Theory: (Pulay Force)

- FLEUR uses the LAPW basis set dependent on $\boldsymbol{r}$ (see previous talk)

$\Rightarrow$ **Gradient also acts on basis-functions!**

$$\begin{aligned} \boldsymbol{F}_\alpha^{\text{Pulay}} &= \sum_n f_n \frac{\partial \epsilon_n^{\text{KS}}}{\partial \boldsymbol{\tau}} - \int \mathrm{d}^3 r \, \rho_0(\boldsymbol{r}) \frac{\partial V_{\text{eff}}(\boldsymbol{r})}{\partial \boldsymbol{\tau}} \\ &= \sum_{n\boldsymbol{k}} f_{n\boldsymbol{k}} \left\langle \frac{\partial \Psi_{n\boldsymbol{k}}}{\partial \boldsymbol{\tau}_\alpha} \middle| \mathcal{H} - \epsilon_{n\boldsymbol{k}} \middle| \Psi_{n\boldsymbol{k}} \right\rangle + \text{c.c.} \end{aligned}$$

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**Background knowledge:**

- Pulay terms compensate Kohn–Sham solutions to be variational
- Pulay terms involve LAPW-valence state and non-LAPW core states (later)
- General (LAPW-independent) formulation up to now!

Pulay, Mol. Phys., 1969, **17**, 197-204
Yu, R., Singh, D. & Krakauer, H., Phys. Rev. B, 1991, **43**, 6411-6422

# BASIS SET CORRECTION

## Beyond plane-wave codes

- LAPW basis $\rightarrow$ Basis correction term required

$$\frac{\partial \Psi_{n\boldsymbol{k}}(\boldsymbol{r})}{\partial \boldsymbol{\tau}} = \sum_G \frac{\partial z_G(n\boldsymbol{k})}{\partial \boldsymbol{\tau}_\alpha} \phi_{\boldsymbol{kG}}(\boldsymbol{r}) + z_{\boldsymbol{G}}(n\boldsymbol{k}) \frac{\partial \phi_{\boldsymbol{kG}}(\boldsymbol{r})}{\partial \boldsymbol{\tau}} \; ; \quad \phi_{\boldsymbol{kG}}^{\mathrm{MT}(\alpha)}(\boldsymbol{r}) = \sum_{lm\lambda} a_{lm\lambda}^{\alpha \boldsymbol{kG}} u_{l\lambda}^{\alpha} \mathrm{Y}_{lm}(\hat{\boldsymbol{r}}_\alpha)$$

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- Frozen-augmentation approximation: $u^{\alpha}_{l\lambda}(\tau) \approx u^{\alpha}_{l\lambda}$

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# THE INP.XML FILE

## Relevant Extract for Relaxation Algorithm

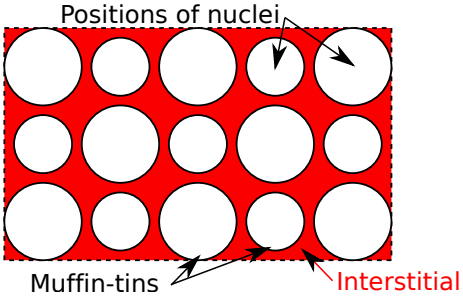
```
<calculationSetup>
   <geometryOptimization l_f="F" forcealpha="1.0" forcemix="BFGS"
      epsdisp=".00001" epsforce=".00001"/>
</calculationSetup>

<atomGroups>
   <atomGroup species="foo">
      <force calculate="T" relaxXYZ="TTT"/>
   </atomGroup>
   <!-- more atom groups here depending on geometry setup-->
</atomGroups>

<xi:include xmlns:xi="http://www.w3.org/2001/XInclude"
   href="relax.xml"> <xi:fallback/> </xi:include>
```

# SURFACE TERMS

## Compensating discontinuities

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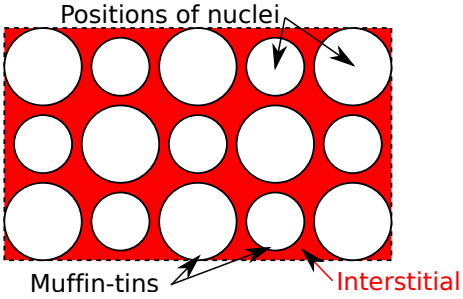


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⇒ Correction term to …

- …fix discontinuity of integration
- …correct discontinuous potential, density and xc-energy density terms

⇒ Alternative: Reduce discontinuity

D. Wortmann, DFT in practice, 45th IFF Spring School (2014).

$$\boldsymbol{F}_\alpha^{\text{surf}} = \oint_{\partial\text{MT}(\alpha)} \mathrm{d}S\, \hat{\boldsymbol{e}} \left[\boldsymbol{\rho}^{\text{MT}}\left(\epsilon_{\text{xc}}^{\text{MT}} + V_{\text{eff}}^{\text{MT}} + \mu_{\text{xc}}^{\text{MT}}\right)\right] - \left[\boldsymbol{\rho}^{\text{IR}}\left(\epsilon_{\text{xc}}^{\text{IR}} + V_{\text{eff}}^{\text{IR}} + \mu_{\text{xc}}^{\text{IR}}\right)\right]$$
$$+ \sum_{n\boldsymbol{k}} f_{n\boldsymbol{k}} \oint_{\partial\text{MT}(\alpha)} \left[\Psi_{n\boldsymbol{k}}^{\text{MT}\,*}(\mathcal{T} - \epsilon_{n\boldsymbol{k}})\Psi_{n\boldsymbol{k}}^{\text{MT}} - \Psi_{n\boldsymbol{k}}^{\text{IR}\,*}(\mathcal{T} - \epsilon_{n\boldsymbol{k}})\Psi_{n\boldsymbol{k}}^{\text{IR}}\right]$$

Klüppelberg et al., Phys. Rev. B, 2015, **91**, 035105

# DFT FORCE CALCULATION

## Pulay Core Force

$$\boldsymbol{F}_{\alpha}^{\text{Pu.,core}} = -\int_{\Omega} V_{\text{eff}}(\boldsymbol{r}) \nabla \rho_{\text{core}}^{\alpha}(\boldsymbol{r}) \, \mathrm{d}^3 r$$

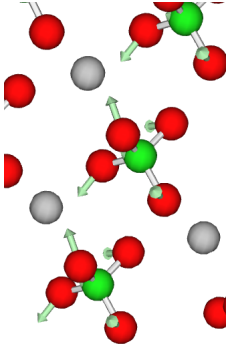
- Dependence on $\tau_\alpha$ from local coordinate frame
- In practise, core states are not perfectly confined to muffin-tins.
- Core-tail interstitial solution with help from a gaussian pseudo-density which is smoother than the original spherical core density
- Area integrated over is whole unit cell $\rightarrow$ Increase of user friendness, as result not dependent on mufin-tin radii

# DRIFT FORCE

## Violation of the acoustic sum rule

**Acoustic sum rule:** $\boldsymbol{F}_{\mathrm{D}} = \sum_{\alpha} \boldsymbol{F}_{\alpha} = \mathbf{0}$

The sum of the forces on all atoms adds up to zero.

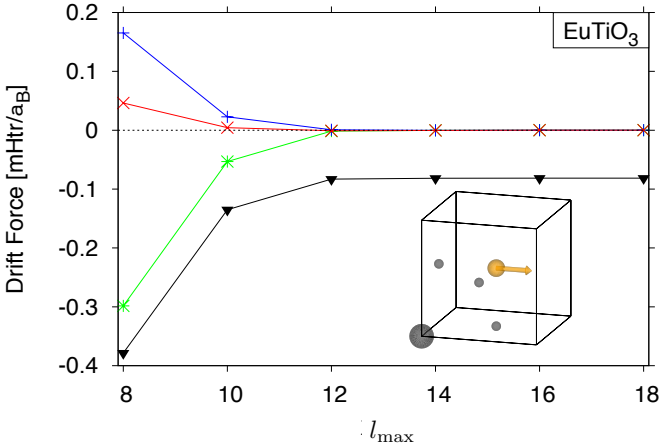


materialscloud.org

- Usually non-vanishing drift force $\boldsymbol{F}_{\mathrm{D}}$ in practise
- Contradicts Newton's 3rd law of motion!
- Sometimes out-convergable by using higher lmax-cutoff and LOs
- **Shown correction terms let the drift force vanish while using a relatively small lmax cutoff**
- Tradeoff between accuracy and performance in practise (Force calculation levels)

# FORCE CORRECTION TERMS

## Effect on Drift Force




- black: Yu et al.
- green: Core-tail correction
- blue : Surface terms (kinetic)
- red : More surface terms

D. A. Klüppelberg, Key Technologies (Schriften des Forschungszentrums Jülich), **119**, PhD Thesis (2015).

# PHONONS

## Brief Reminder

- Dynamics in solid ← Coulomb interaction between electrons and nuclei
- Decoupled dynamics ← Mass difference of electrons and nuclei (Born–Oppenheimer)

$$\mathcal{H}_{\mathsf{BO}}(\boldsymbol{\tau}) = -\frac{1}{2}\sum_i \frac{\partial^2}{\partial \boldsymbol{r}_i^2} + \frac{1}{2}\sum_{i\neq j}\frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} - \sum_{i,\kappa}\frac{Z_\kappa}{\left|\boldsymbol{r}_i - \boldsymbol{\tau}_\kappa\right|} + \frac{1}{2}\sum_{\kappa\neq\mu}\frac{Z_\kappa Z_\mu}{\left|\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_\mu\right|}$$

- Wavefunctions and energies of the nuclei by solving

$$\left(-\frac{1}{2}\sum_\kappa \frac{1}{M_\kappa}\frac{\partial^2}{\partial \boldsymbol{\tau}_\kappa^2} + E_{\mathsf{BO}}(\boldsymbol{\tau})\right)\Psi(\boldsymbol{\tau}) = E\Psi(\boldsymbol{\tau})$$

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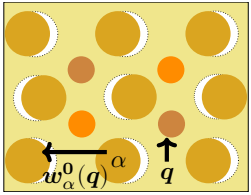
- Wavefunctions and energies of the nuclei by solving

$$\left(-\frac{1}{2}\sum_\kappa \frac{1}{M_\kappa}\frac{\partial^2}{\partial \boldsymbol{\tau}_\kappa^2} + E_{\mathrm{BO}}(\boldsymbol{\tau})\right)\Psi(\boldsymbol{\tau}) = E\Psi(\boldsymbol{\tau})$$

- Individual infinitesimal ion position shift specified by respective phonon vector

$$\boldsymbol{w}_\alpha^{\boldsymbol{R}}(\boldsymbol{q}) = \boldsymbol{Q}_\alpha(\boldsymbol{q})\mathrm{e}^{\mathrm{i}\boldsymbol{q}\boldsymbol{R}} + \boldsymbol{Q}_\alpha^*(\boldsymbol{q})\mathrm{e}^{-\mathrm{i}\boldsymbol{q}\boldsymbol{R}}$$



# FINITE DISPLACEMENT METHOD

## Phonons

- Born–Oppenheimer energy relates to total energy of ab-initio calculation
- Finite Displacement Method: Finding the Force-Constant Matrix (FCM)

$$E_{\mathrm{BO}}(\boldsymbol{u}) = E_{\mathrm{BO}}^{(0)} + \frac{1}{2} \sum_{\boldsymbol{R}\kappa\beta} \sum_{\boldsymbol{R}'\kappa'\beta'} \frac{\partial^2 E_{\mathrm{BO}}}{\partial \tau_{\boldsymbol{R}\kappa\beta}\, \partial \tau_{\boldsymbol{R}'\kappa'\beta'}}\, u_{\boldsymbol{R}\kappa\beta}\, u_{\boldsymbol{R}'\kappa'\beta'} + \ldots$$

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- Fourier transform of FCM $\rightarrow$ Dynamical Matrix (**Complete lattice dynamics!**)

$$D_{\kappa\beta,\kappa'\beta'}(\boldsymbol{q}) = \sum_{\boldsymbol{R}'} \frac{\partial^2 E_{\mathrm{BO}}}{\partial \tau_{\boldsymbol{0}\kappa\beta}\, \partial \tau_{\boldsymbol{R}'\kappa'\beta'}}\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\boldsymbol{R}'}$$

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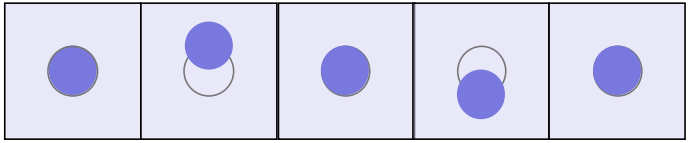
- Low Programming Effort $\Leftrightarrow$ Heavy Calculation Effort (Supercells required)
- Requires exact forces



# DENSITY FUNCTIONAL PERTURBATION THEORY (DFPT)

## Application to phonons

**Dynamical Matrix from 2nd variation of DFT total energy**

$$E^{(2)}_{\text{tot}}(\boldsymbol{q}) = \int \mathrm{d}^3 r\, \rho^{(1)}(\boldsymbol{r},\boldsymbol{q}) V^{(1)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + \int \mathrm{d}^3 r\, \rho^{(0)}(\boldsymbol{r}) V^{(2)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + E^{(2)}_{\text{ii}}(\boldsymbol{q})$$
$$= \boldsymbol{Q}^{\dagger}_{\beta}(\boldsymbol{q}) \underline{D_{\beta\alpha}}(\boldsymbol{q}) \boldsymbol{Q}_{\alpha}(\boldsymbol{q}) + \text{c.c.}$$

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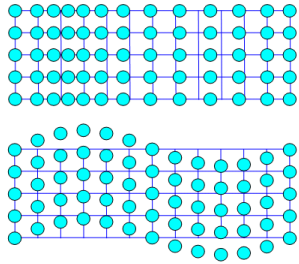
DFPT for varied quantities

- Variational ansatz $\rightarrow$ Intrinsic robustness
- Exploits lattice periodicity $\rightarrow$ One unit cell
- One unit cell $\rightarrow$ Equal complexity for any $\boldsymbol{q}$
- Only standard DFT output (wavefunctions, energies) required
- Similarities to DFT algorithm



http://www.tf.uni-kiel.de/matwis/amat/mw2_ge/index.html

S. Y. Savrasov, Phys. Rev. B **54**, 16470 (1996). | S. Baroni, Rev. Mod. Phys. **73**, 515 (2001).

# RESPONSE FUNCTIONS

## Accessable by DFPT

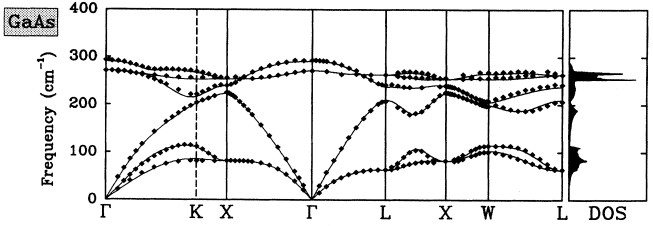
**Response functions are connected to first- or higher-order derivatives of the ground-state total energy**

# RESPONSE FUNCTIONS

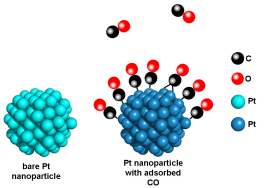
## Accessable by DFPT

**Response functions are connected to first- or higher-order derivatives of the ground-state total energy**

- Suitable perturbations for DFPT
  - Phonons
  - mechanical deformations
  - electric fields
  - magnetic fields
  - …
- DFPT gives access to
  - Dielectric / piezoelectric properties
  - Phonons / elastic properties
  - Superconductivity
  - Thermodynamic quantities
  - …




Giannozzi et al. Phys. Rev. Lett., **58**, 1861-1864, (1987)




https://www.esrf.eu/news/general-old/general-2010/platinum

# DENSITY FUNCTIONAL PERTURBATION THEORY

## General Justification

- Ground state density of effective Kohn–Sham system corresponds to ground state density of interacting system
- Valid for any external potential either unperturbed or perturbed:
  $\mathcal{H} = \mathcal{H}^{(0)} + \left(V_{\text{ext}} - V_{\text{ext}}^{(0)}\right)$
- Variations of quantities that are functionals of the density can be determined with the DFT method and the Kohn–Sham system by choosing the respective external potential

**Perturbations of real systems can be examined by applying perturbation theory to the Kohn–Sham Hamiltonian**


https://terraingallery.org

# RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

## Relevant for DFPT

- Perturbation with strenght $\lambda$ small enough so that

$$f(\lambda) = \sum_{i=0}^{\infty} \lambda^i f^{(i)}(\lambda)\,, \qquad f^{(i)}(\lambda) = \left.\frac{\mathrm{d}^i f(\lambda)}{\mathrm{d}\lambda^i}\right|_{\lambda=0}$$

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- A perturbed Hamiltonian fulfills the Schrödinger equation

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- In 1st order, the Sternheimer equation turns out

$$\left(\mathcal{H}^{(0)} - \epsilon_i^{(0)}\right)\left|\Psi_i^{(1)}\right\rangle = -\left(\mathcal{H}^{(1)} - \epsilon_i^{(1)}\right)\left|\Psi_i^{(0)}\right\rangle \Rightarrow \left|\Psi_i^{(1)}\right\rangle = \sum_{k\in\mathsf{I}^{\perp}} \left|\Psi_k^{(0)}\right\rangle \frac{\left\langle \Psi_k^{(0)} \middle| H^{(1)} \middle| \Psi_i^{(0)} \right\rangle}{\epsilon_i^{(0)} - \epsilon_k^{(0)}}$$

- Hellmann–Feynman theorem consistent with 1st order energy

$$\epsilon^{(1)} = \frac{\partial \epsilon}{\partial \lambda} = \int \mathrm{d}^3 r\, \Psi^{(0)*} \frac{\partial \mathcal{H}}{\partial \lambda} \Psi^{(0)} = \left\langle \Psi^{(0)} \middle| \frac{\partial \mathcal{H}}{\partial \lambda} \middle| \Psi^{(0)} \right\rangle = \left\langle \Psi^{(0)} \middle| \frac{\partial \mathcal{V}}{\partial \lambda} \middle| \Psi^{(0)} \right\rangle$$

# DENSITY FUNCTIONAL PERTURBATION THEORY

## Linear response and $2n+1$ theorem

- Let $V_{\text{ext}}^{\mathsf{L}}(\boldsymbol{r})$ be a general external potential with $\mathsf{L} = \{\lambda_i : i \in [1,p]\}$ minimizing

$$E_0^{\mathsf{L}} = F[\rho_0^{\mathsf{L}}] + \int \mathrm{d}^3 r \, \rho_0^{\mathsf{L}}(\boldsymbol{r}) V_{\text{ext}}^{\mathsf{L}}(\boldsymbol{r}) \, ,$$

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$$\frac{\partial^2 E_0^{\mathsf{L}}}{\partial \lambda_i \partial \lambda_j} = \int \mathrm{d}^3 r\, \rho_0^{\mathsf{L}}(\boldsymbol{r}) \frac{\partial^2 V_{\text{ext}}^{\mathsf{L}}(\boldsymbol{r})}{\partial \lambda_i \partial \lambda_j} + \int \mathrm{d}^3 r\, \frac{\partial \rho_0^{\mathsf{L}}(\boldsymbol{r})}{\partial \lambda_i} \frac{\partial V_{\text{ext}}^{\mathsf{L}}(\boldsymbol{r})}{\partial \lambda_j}$$

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**In general**: $2n+1$th deriv. of total energy $\leftrightarrow$ $n$th deriv. of electronic density

# DENSITY FUNCTIONAL PERTURBATION THEORY

## Variational character

- Sternheimer equation from minimizing $E_{\text{el}}^{(2)}$ with respect to $\Psi^{(1)}$ and given $\Psi^{(1)} \perp \Psi^{(0)}$

$$
\begin{aligned}
E_{\text{el}}^{(2)}\left[\left\{\Psi^{(0)}\right\};\,\left\{\Psi^{(1)}\right\}\right] = \sum_{i=1}^{\mathsf{c}} \Bigg( & \left\langle \Psi_i^{(0)} \middle| \left(\mathcal{T}+\mathcal{V}_{\text{ext}}\right)^{(2)} \middle| \Psi_i^{(0)} \right\rangle + \left\langle \Psi_i^{(1)} \middle| \left(\mathcal{H}-\epsilon_i\right)^{(0)} \middle| \Psi_i^{(1)} \right\rangle \\
& + \left\langle \Psi_i^{(0)} \middle| \left(\mathcal{T}+\mathcal{V}_{\text{ext}}\right)^{(1)} \middle| \Psi_i^{(1)} \right\rangle + \left\langle \Psi_i^{(1)} \middle| \left(\mathcal{T}+\mathcal{V}_{\text{ext}}\right)^{(1)} \middle| \Psi_i^{(0)} \right\rangle \Bigg) \\
& + \frac{1}{2} \int \mathrm{d}^3 r\, \mathrm{d}^3 r' \, \frac{\partial^2 E_{\text{Hxc}}\left[\rho^{(0)}\right]}{\partial\rho^{(0)}(\boldsymbol{r})\partial\rho^{(0)}(\boldsymbol{r}')} \rho^{(1)}(\boldsymbol{r})\rho^{(1)}(\boldsymbol{r}') \\
& + \int \mathrm{d}^3 r \, \frac{\mathrm{d}}{\mathrm{d}\lambda} \frac{\partial E_{\text{Hxc}}\left[\rho^{(0)}\right]}{\partial\rho^{(0)}(\boldsymbol{r}')}\bigg|_{\lambda=0} \rho^{(1)}(\boldsymbol{r}') + \frac{1}{2} \frac{\mathrm{d}^2 E_{\text{Hxc}}\left[\rho^{(0)}\right]}{\mathrm{d}\lambda^2}\bigg|_{\lambda=0}
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\end{aligned}
$$

$\Rightarrow$ 1st-order variation of the wavefunction is variational!

$\Rightarrow$ Variational solutions only on average equal to pointwise solutions of real system

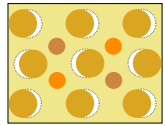
$\Rightarrow$ Small errors are damped in DFPT due to variational formulation

# ALL-ELECTRON FLAPW & DFPT

## Challenges

- Core-electron wave functions: Exact solutions of radial Schrödinger(Dirac) equation
- Full external $1$ / $r$ potential without approximations
- Valence-electron wave functions: Variational (Kohn–Sham), LAPW basis set

$$\varphi^{(0)\boldsymbol{w}}_{\boldsymbol{k},\boldsymbol{G}}(\boldsymbol{r}) = \begin{cases} \dfrac{1}{\sqrt{N\Omega}} \mathrm{e}^{\mathrm{i}(\boldsymbol{k}+\boldsymbol{G})\boldsymbol{r}}, & \boldsymbol{r} \in \mathrm{IR} \\ \dfrac{1}{\sqrt{N}} \sum\limits_{lmp} a^{\alpha \boldsymbol{R}\boldsymbol{k}\boldsymbol{G}}_{lmp\boldsymbol{w}} u^{\alpha\boldsymbol{R}}_{lp}\left(|\boldsymbol{r}-\boldsymbol{r}_{\alpha\boldsymbol{R}\boldsymbol{w}}|\right)\, \mathrm{Y}_{lm}\left(\dfrac{\boldsymbol{r}-\boldsymbol{r}_{\alpha\boldsymbol{R}\boldsymbol{w}}}{|\boldsymbol{r}-\boldsymbol{r}_{\alpha\boldsymbol{R}\boldsymbol{w}}|}\right), & \boldsymbol{r} \in \mathrm{MT}(\alpha, \boldsymbol{R}) \end{cases}$$



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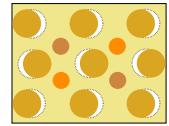

- Variation of valence-electron wavefunctions not fully covered by LAPW Hilbert space

$$\Psi^{(1)}_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{\kappa}=\pm\boldsymbol{q}} \sum_{\boldsymbol{G}} \left( z^{(1)}_{\boldsymbol{G}}(n\boldsymbol{k};\boldsymbol{\kappa},\alpha)\varphi^{(0)\boldsymbol{0}}_{\boldsymbol{k}+\boldsymbol{\kappa},\boldsymbol{G}}(\boldsymbol{r}) + z^{(0)}_{\boldsymbol{G}}(n\boldsymbol{k};\boldsymbol{\kappa})\varphi^{(1)\boldsymbol{w}}_{\boldsymbol{k}+\boldsymbol{\kappa},\boldsymbol{G}}(\boldsymbol{r}) \right), \; \varphi^{(1)}_{\boldsymbol{k}'\boldsymbol{G}}(\boldsymbol{r}) = \boldsymbol{w}^{\top}_{\alpha} \cdot [\mathrm{i}(\boldsymbol{k}'+\boldsymbol{G}) - \boldsymbol{\nabla}]\varphi^{(0)}_{\boldsymbol{k}'\boldsymbol{G}}(\boldsymbol{r}) \quad [\boldsymbol{r} \in \mathrm{MT}(\alpha, \boldsymbol{R})]$$


P. Pulay, Mol. Phys., **17**, 197 (1969).
D. A. Klüppelberg, Key Technologies (Schriften des Forschungszentrums Jülich), **119**, PhD Thesis (2015).

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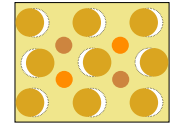

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  $\Rightarrow$ Emergence of additional terms complicating DFPT formalism
  - Pulay terms account for discrepancy between exact and variational wavefunctions
  - Surface terms correct discontinuities between interstitial and muffin-tin regions


P. Pulay, Mol. Phys., **17**, 197 (1969).
D. A. Klüppelberg, Key Technologies (Schriften des Forschungszentrums Jülich), **119**, PhD Thesis (2015).

# FIRST VARIATION OF THE DENSITY

## All-electron FLAPW & DFPT

- Let's focus on

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R. M. Sternheimer, Phys. Rev., **96**, 951 (1954).

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- Variation of the Schrödinger equation results in Sternheimer equation

$$\sum_m \left\langle \Psi^{(0)}_{\boldsymbol{k}\pm\boldsymbol{q},p} \middle| \mathcal{H}_0 - \varepsilon^{(0)}_{n,\boldsymbol{k}} \middle| \Psi^{(0)}_{\boldsymbol{k}\pm\boldsymbol{q},m} \right\rangle_V \boldsymbol{z}^{(1)}_m(n\boldsymbol{k};\alpha\pm\boldsymbol{q}) = -\sum_G \left\langle \Psi^{(0)}_{\boldsymbol{k}\pm\boldsymbol{q},p} \middle| \boldsymbol{V}^{(1)\alpha\pm}_{\text{eff}} \middle| \Psi^{(0)}_{\boldsymbol{k},n} \right\rangle_V$$
$$- \left\langle \boldsymbol{\Psi}^{(1)\alpha\mp}_{\boldsymbol{k}\pm\boldsymbol{q},p} \middle| \mathcal{H}_0 - \varepsilon^{(0)}_{n,\boldsymbol{k}} \middle| \Psi^{(0)}_{\boldsymbol{k},n} \right\rangle_V - \left\langle \Psi^{(0)}_{\boldsymbol{k}\pm\boldsymbol{q},p} \middle| \mathcal{H}_0 - \varepsilon^{(0)}_{n,\boldsymbol{k}} \middle| \boldsymbol{\Psi}^{(1)\alpha\pm}_{\boldsymbol{k},n} \right\rangle_V$$
$$- \sum_{\boldsymbol{R}} \mathrm{e}^{\pm \mathrm{i}\boldsymbol{q}\boldsymbol{R}} \oint_{\partial \mathrm{MT}(\alpha,\boldsymbol{R})} \hat{\boldsymbol{e}} \Psi^{(0)*}_{\boldsymbol{k}\pm\boldsymbol{q},p} \left[ \mathcal{H}_0 - \varepsilon^{(0)}_{n,\boldsymbol{k}} \right]_{\text{SF}} \Psi^{(0)}_{\boldsymbol{k},n}\, \mathrm{d}\boldsymbol{S} \,.$$

$\Rightarrow$ LAPW basis entails additional Pulay and surface terms

R. M. Sternheimer, Phys. Rev., **96**, 951 (1954).

# FIRST VARIATION OF THE DENSITY

## All-electron FLAPW & DFPT

- Let's focus on

$$E^{(2)}_{\text{tot}}(\boldsymbol{q}) = \int \mathrm{d}^3 r\, \rho^{(1)}(\boldsymbol{r},\boldsymbol{q}) V^{(1)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + \int \mathrm{d}^3 r\, \rho^{(0)}(\boldsymbol{r}) V^{(2)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + E^{(2)}_{\text{ii}}(\boldsymbol{q})$$

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  $\Rightarrow$ LAPW basis entails additional Pulay and surface terms

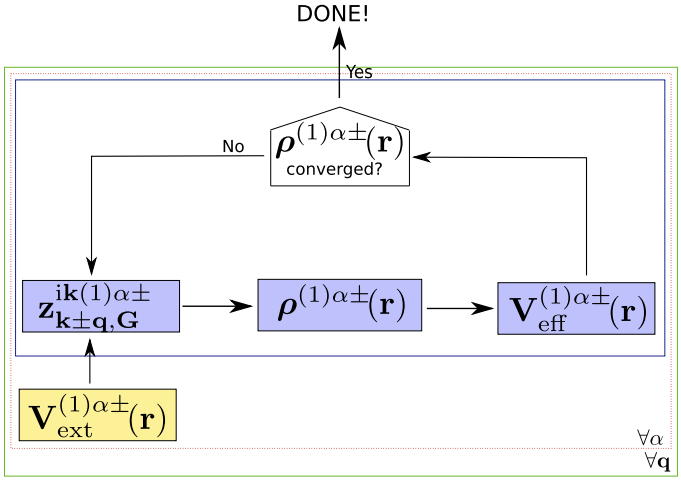
- Self-consistent solution of Sternheimer equation $\rightarrow$ 1st-order electron density

$$\rho^{(1)}(\boldsymbol{r},\boldsymbol{q}) = \sum_{\alpha n \boldsymbol{k}} 2 f^{(0)}_{n\boldsymbol{k}} \left( \Psi^{(0)}_{n\boldsymbol{k}}(\boldsymbol{r}) \right)^* \left( \boldsymbol{Q}^{\top}_{\alpha}(\boldsymbol{q}) \cdot \boldsymbol{\Psi}^{(1)\alpha}_{n\boldsymbol{k}}(\boldsymbol{r},+\boldsymbol{q}) + \boldsymbol{Q}^{\dagger}_{\alpha}(\boldsymbol{q}) \cdot \boldsymbol{\Psi}^{(1)\alpha}_{n\boldsymbol{k}}(\boldsymbol{r},-\boldsymbol{q}) \right)$$

R. M. Sternheimer, Phys. Rev., **96**, 951 (1954).

# STERNHEIMER SELF-CONSISTENCY CYCLE

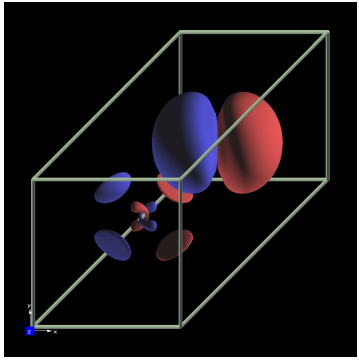
## Dynamic handling of electron screening



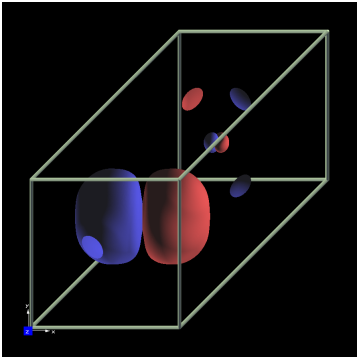
# FULL FIRST VARIATION OF THE DENSITY

## Silicon Carbide

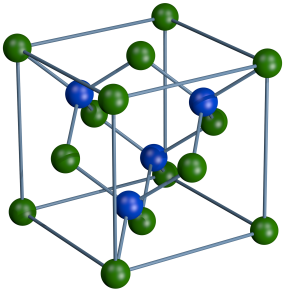
$$\rho^{(1)}(\boldsymbol{r},\boldsymbol{q}) = \sum_{\alpha n \boldsymbol{k}} 2 f^{(0)}_{n\boldsymbol{k}} \left(\Psi^{(0)}_{n\boldsymbol{k}}(\boldsymbol{r})\right)^* \left(\boldsymbol{Q}^{\top}_{\alpha}(\boldsymbol{q}) \cdot \boldsymbol{\Psi}^{(1)\alpha}_{n\boldsymbol{k}}(\boldsymbol{r},+\boldsymbol{q}) + \boldsymbol{Q}^{\dagger}_{\alpha}(\boldsymbol{q}) \cdot \boldsymbol{\Psi}^{(1)\alpha}_{n\boldsymbol{k}}(\boldsymbol{r},-\boldsymbol{q})\right)$$



Displaced atom $\alpha$: Silicon



Displaced atom $\alpha$: Carbon



https://upload.wikimedia.org/wikipedia/commons/4/45/Zincblende_structure.png, (visited 24th March 2019)

# MATRIX WEINERT METHOD

## 2nd-order external potential

- Goal: Solve Poisson equation
  $\Delta\left(\boldsymbol{\nabla}\boldsymbol{\nabla}^\top V_{\text{ext}}\right) \propto \boldsymbol{\nabla}\boldsymbol{\nabla}^\top \rho$

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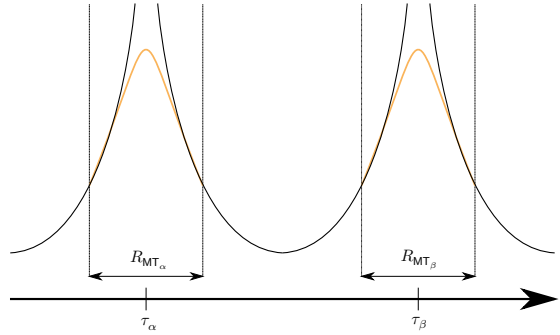
$$\underline{q_{lm}^{\alpha}} = \int_{\text{MT}_\alpha} \mathrm{d}^3 r\, \mathrm{Y}_{\mathrm{lm}}^*(\hat{\boldsymbol{r}}) \left|\boldsymbol{r}^l - \boldsymbol{\tau}_\alpha\right|^l \boldsymbol{\nabla}\boldsymbol{\nabla}^\top \rho(\boldsymbol{r})$$

$\Rightarrow$ Correct interstitial potential from pseudo-charge density

$$\underline{V_{\text{IR}}^{\alpha(2)}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}\neq\boldsymbol{0}} \frac{4\pi}{G^2} \underline{\rho_{\text{ps}}}(\boldsymbol{G}) \mathrm{e}^{\mathrm{i}\boldsymbol{G}\cdot\boldsymbol{r}}$$



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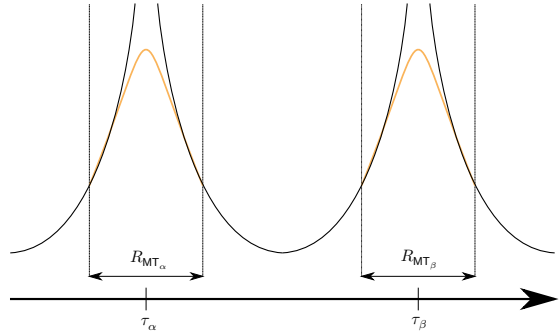


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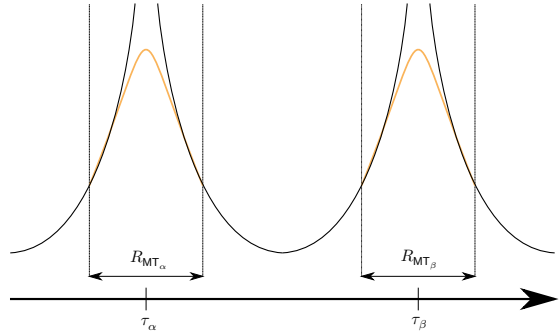


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⇒ External potential variations do not require self-consistent density variations

# SECOND-ORDER ION–ION INTERACTION

## Weinert Again

- Ion–ion interaction similar form to the electron–ion interaction

$$E^{(2)}_{\text{tot}}(\boldsymbol{q}) = \int \mathrm{d}^3 r\, \rho^{(1)}(\boldsymbol{r},\boldsymbol{q}) V^{(1)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + \int \mathrm{d}^3 r\, \rho^{(0)}(\boldsymbol{r}) V^{(2)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + E^{(2)}_{\text{ii}}(\boldsymbol{q})$$

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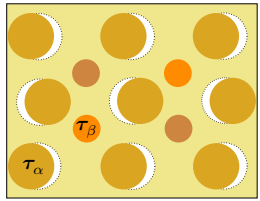

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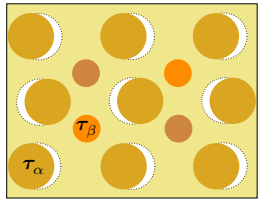


$\Rightarrow$ Suggesting, e.g., Weinert method

- Second-order ion–ion interaction can be rewritten to ($\xi(\boldsymbol{q}) = 1$ or $2$)

$$E^{(2)}_{\text{ii}}(\boldsymbol{q}) = \sum_{\alpha\beta} \xi(\boldsymbol{q}) \boldsymbol{Q}^{\dagger}_{\beta}(\boldsymbol{q}) \sum_{\substack{\boldsymbol{R}\neq\boldsymbol{0},\\ \text{if } \alpha=\beta}} \left(1 - \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}}\right) \nabla_\alpha \nabla^{\top}_{\beta} \left|\boldsymbol{\tau}_\alpha - \boldsymbol{\tau}_\beta - \boldsymbol{R}\right|^{-1} \boldsymbol{Q}_\alpha(\boldsymbol{q}) + \text{c.c.}$$

- Weinert method $\rightarrow$ interstitial and muffin-tin representation of matrix expression

D. A. Klüppelberg, Key Technologies (Schriften des Forschungszentrums Jülich), **119**, PhD Thesis (2015).

# DENSITY FUNCTIONAL PERTURBATION THEORY

## Beyond Hellmann–Feynman: Total Energy

- Calculation of Dynamical Matrix requires 2nd-order variation of total energy
- So far we discussed the basic Hellmann–Feynman contribution

$$
\begin{aligned}
E^{(2)}_{\text{tot}}(\boldsymbol{q}) &= \int \mathrm{d}^3 r\, \rho^{(1)}(\boldsymbol{r},\boldsymbol{q}) V^{(1)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + \int \mathrm{d}^3 r\, \rho^{(0)}(\boldsymbol{r}) V^{(2)}_{\text{ext}}(\boldsymbol{r},\boldsymbol{q}) + E^{(2)}_{\text{ii}}(\boldsymbol{q}) \\
&= \boldsymbol{Q}^{\dagger}_{\beta}(\boldsymbol{q}) \underline{D_{\beta\alpha}}(\boldsymbol{q}) \boldsymbol{Q}_{\alpha}(\boldsymbol{q}) + \text{c.c.}
\end{aligned}
$$

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$$= \boldsymbol{Q}^{\dagger}_{\beta}(\boldsymbol{q}) \underline{D_{\beta\alpha}}(\boldsymbol{q}) \boldsymbol{Q}_{\alpha}(\boldsymbol{q}) + \text{c.c.}$$

- LAPW basis $\rightarrow$ terms beyond basic naive contribution

$$E^{(2)}_{\text{tot}} = E^{(2)}_{\text{tot, basic}} + E^{(2)}_{\text{tot, Pulay}} + E^{(2)}_{\text{tot, surface}}$$

  - $E^{(2)}_{\text{tot, basic}}$: Naive contribution
  - $E^{(2)}_{\text{tot, Pulay}}$: Corrects deviations of the variational wave functions represented in the finite LAPW basis from the exact pointwise solutions of the Schrödinger equation
  - $E^{(2)}_{\text{tot, surface}}$: Corrects small discontinuities at the muffin-tin sphere boundary, caused by displacive perturbations

# VALENCE PULAY CONTRIBUTIONS

## Dynamical Matrix & All-Electron FLAPW

- Pulay terms also occur in second variation of total energy

$$E^{(2),\mathrm{tot}}_{\mathrm{Pulay}} = \int \mathrm{d}^3 r\, \rho^{(1)}(\boldsymbol{r}) V^{(1)}_{\mathrm{eff}}(\boldsymbol{r}) + \sum_{n\boldsymbol{k}} f^{(0)}_{n\boldsymbol{k}} \Big[ 2 \Big\langle \Psi^{(1)}_{n\boldsymbol{k}} \Big| \mathcal{H}_0 - \epsilon^{(0)}_{n\boldsymbol{k}} \Big| \Psi^{(1)}_{n\boldsymbol{k}} \Big\rangle + \Big\langle \Psi^{(0)}_{n\boldsymbol{k}} \Big| \mathcal{H}_0 - \epsilon^{(0)}_{n\boldsymbol{k}} \Big| \Psi^{(2)}_{n\boldsymbol{k}} \Big\rangle + \Big\langle \Psi^{(2)}_{n\boldsymbol{k}} \Big| \mathcal{H}_0 - \epsilon^{(0)}_{n\boldsymbol{k}} \Big| \Psi^{(0)}_{n\boldsymbol{k}} \Big\rangle \Big]$$

- Phonon with wavevector $\boldsymbol{q}$ shifts Bloch character of varied wavefunctions

$$\Psi^{(1)}_{n\boldsymbol{k}} = \sum_{\boldsymbol{\kappa}=\pm\boldsymbol{q}} \sum_{\boldsymbol{G}} \Big[ z^{(1)}_{\boldsymbol{G}}(n\boldsymbol{k};\boldsymbol{\kappa}) \phi^{(0)}_{\boldsymbol{k}+\boldsymbol{\kappa},\boldsymbol{G}} + z^{(0)}_{\boldsymbol{G}}(n\boldsymbol{k};\boldsymbol{\kappa}) \phi^{(1)}_{\boldsymbol{k}+\boldsymbol{\kappa},\boldsymbol{G}} \Big]$$

$$\Psi^{(2)}_{n\boldsymbol{k}} = \sum_{\boldsymbol{\kappa}=\boldsymbol{0},\pm 2\boldsymbol{q}} \sum_{\boldsymbol{G}} \Big[ z^{(2)}_{\boldsymbol{G}}(n\boldsymbol{k};\boldsymbol{\kappa}) \phi^{(0)}_{\boldsymbol{k}+\boldsymbol{\kappa},\boldsymbol{G}} + z^{(1)}_{\boldsymbol{G}}(n\boldsymbol{k};\boldsymbol{\kappa}) \phi^{(1)}_{\boldsymbol{k}+\boldsymbol{\kappa},\boldsymbol{G}} + z^{(0)}_{\boldsymbol{G}}(n\boldsymbol{k};\boldsymbol{\kappa}) \phi^{(2)}_{\boldsymbol{k}+\boldsymbol{\kappa},\boldsymbol{G}} \Big]$$

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# CORE PULAY AND SURFACE CONTRIBUTIONS

## Dynamical Matrix & All-Electron FLAPW

- All-Electron $\rightarrow$ core-electron terms variation

$$\sum_n \left[ 2\left\langle \Psi_n^{(1)} \middle| \mathcal{H}_0 - \epsilon_n^{(0)} \middle| \Psi_n^{(1)} \right\rangle + \left\langle \Psi_n^{(0)} \middle| \mathcal{H}_0 - \epsilon_n^{(0)} \middle| \Psi_n^{(2)} \right\rangle + \left\langle \Psi_n^{(2)} \middle| \mathcal{H}_0 - \epsilon_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle \right]$$
$$= -\boldsymbol{Q}_\alpha^\dagger \int_\Omega \mathrm{d}^3 r \, \nabla V_{\text{nsph}}^{(0)}(\boldsymbol{r}) \sum_n \nabla^\top \rho_n^{(0)}(\boldsymbol{r}) \boldsymbol{Q}_{\boldsymbol{\alpha}} + \text{c.c.}$$

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- Total energy contains discontinuities at muffin-tin surfaces
  - $\Rightarrow$ Variation generates surface terms

$$\frac{\mathrm{d}}{\mathrm{d}\boldsymbol{\tau}_\alpha} f(\boldsymbol{r}) = \left[ \sum_\beta \int_{\text{IR}(\beta)} \mathrm{d}^3 r \, \frac{\mathrm{d} f(\boldsymbol{r})}{\mathrm{d}\boldsymbol{\tau}_\alpha} + \int_{\text{MT}(\beta)} \mathrm{d}^3 r \, \frac{\mathrm{d} f(\boldsymbol{r})}{\mathrm{d}\boldsymbol{\tau}_\alpha} \right] + \oint_{\partial \text{MT}(\alpha)} \mathrm{d}S \, [f_{\text{MT}}(\boldsymbol{r}) - f_{\text{IR}}(\boldsymbol{r})] \hat{\boldsymbol{e}}_{\boldsymbol{r}}$$

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# SUMMARY

## Forces & DFPT

- Forces
  - Derivative of DFT total energy
  - FLAPW method leads to additional terms (Core, Pulay, Surface)
  - Forces for geometry optimization
  - Dynamical matrix (force-constant matrix) for phonons but inefficient
- DFPT
  - Powerful tool for ab-initio calculation of response functions
  - Dynamical matrix relates to second-order variation of total energy
  - Second-order variation of total energy contains response functions accessable by DFPT
  - FLAPW method makes DFPT more challenging

# Thank you for your attention!