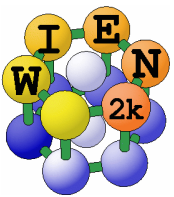
The stress tensor in the APW based methods and its implementation in the WIEN2k code.



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Outline

- Stress tensor and its importance
- Theoretical explanation
- Results
- Discussion and Outlook

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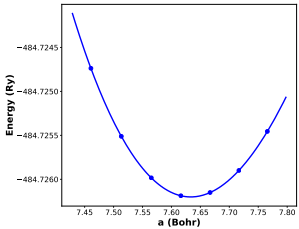
Why is stress ($\sigma_{\alpha\beta}$) so important for solid state DFT?

- Stress tensor: derivative of E with respect to strain

$$\Omega\sigma_{\alpha\beta} \equiv \frac{\partial E}{\partial \epsilon_{\alpha\beta}}\bigg|_{\epsilon=0} \qquad \alpha, \beta = 1, 2, 3$$

Structure optimization:

- **cubic** solid $\Rightarrow$ only Ω-dependence $\Rightarrow$ easy.

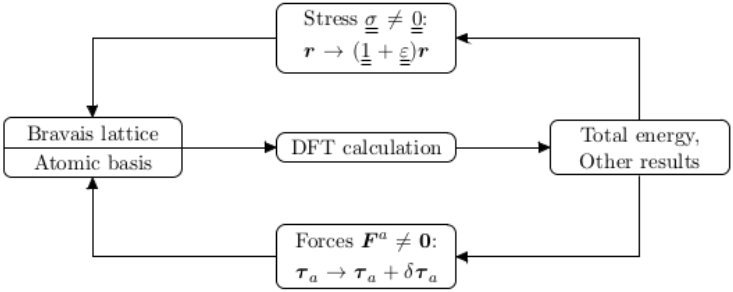


* perform DFT calculations for a number of volumes V_i

* fit resulting energies $E_i(\Omega_i)$ *to EOS*$(Murnaghan, Birch-Murnaghan, Vinet, \dots)$

- **tetragonal** solid $\Rightarrow$ expensive but still feasible.
  1. for each volume Ω_i: perform a series of DFT calculations to determine the c_i/a_i for which E_i is minimal
  2. fit resulting E_i and Ω_i to EOS
  3. perform final volume optimization for resulting volume $\Omega(P)$ at prescribed pressure P.
- symmetry **lower than tetragonal, hexagonal or rhombohedral**: possible variations in all six independent components of $\epsilon_{\alpha\beta}$ must be considered $\Rightarrow$ extremely tedious, computationally expensive or even impossible.

Determining the equilibrium state from DFT



- Solid need to relax not only forces ($F^a = -\frac{dE}{dR_a}$) but also determine equilibrium **lattice vectors** at a prescribed external stress $\sigma_{\alpha\beta}$.
- We are looking for the specific unit cell dimensions for which

$$\Omega\sigma_{\alpha\beta} \equiv \frac{\partial E}{\partial \epsilon_{\alpha\beta}}\Big|_{\epsilon=0} \qquad \alpha, \beta = 1, 2, 3$$

In most practical cases stress will be hydrostatic, so we search for a unit cell geometry for which

$$-3\Omega P\delta_{\alpha\beta} \equiv \frac{\partial E}{\partial \epsilon_{\alpha\beta}}\Big|_{\epsilon=0}$$

Review of previous attempts

- **For plane wave based methods stress tensor implementation is already available**(O. H. Nielsen & R.M. Martin Phys. Rev. Lett. **50** (1983) 697)

many attempts on the full-potential linearized augmented plane-wave (LAPW)

- **Thonhauser, Singh & Draxl** [1]
  - \+ only LDA for simple cubic systems
  - \- missing GGA, APW+lo, and semi core local orbitals.
- **Nagasako & Oguchi** [2]
  - \+ LDA and GGA
  - \- no LOs, no follow-up papers
  - \- applies to Solar-William LAPW only and can not be applied to the standard LAPW.
- **Klüppelberg & Blügel** [3]
  - \+ extensive analytical calculations are presented
  - \- calculation has a huge error and the source is untraceable
  - \- only LDA, no LOs, GGA, APW+lo

1 Solid state comm. **124**, 275 (2002)

2 J. Phys. Soc. Jpn. **80**, 024701 (2011)

3 diploma thesis, Jülich (2012)

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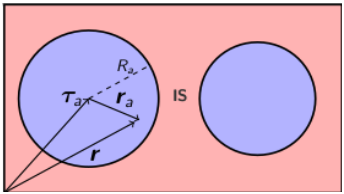
Basis function in the APW based methods

- Unit cell is divided into the atomic spheres and the interstitial region.



- Basis functions in the augmented plane wave (APW) method [Slater 1937].

$$\phi^{APW}_{\boldsymbol{kK}}(\boldsymbol{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot\boldsymbol{r}} & \boldsymbol{r} \in IS \\ \sum_{lm} a^{a\boldsymbol{kK}}_{lm} u^a_l(r,E) Y_{lm}(\hat{\boldsymbol{r}}) & \boldsymbol{r} \in R_a \end{cases}$$

- $u^a_l(r,E)$ is the numerical solution of the radial Schrödinger equation with the spherically symmetric potential (V_{00}) at the eigenenergy E
- This leads to a non-linear eigenvalue problem and a computationally very expensive process.
- Energy dependency of $u^a_l(r,E)$ needs to be linearized

Basis function: LAPW and APW+lo

- Linearization inside the atomic sphere is introduced by choosing a linear combination of $u_l^a(r, E_l^a)$ at a fixed energy E_l^a and it's energy derivative $\dot{u}_l^a(r, E_l^a)$ in linearized augmented plane wave (LAPW)[Anderson 1975].

$$\phi_{\mathbf{kK}}^{LAPW}(\boldsymbol{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot\boldsymbol{r}} & \boldsymbol{r} \in IS \\ \sum_{lm} \left[a_{lm}^{a\mathbf{kK}} u_l^a(r, E_l^a) + b_{lm}^{a\mathbf{kK}} \dot{u}_l^a(r, E_l^a) \right] Y_{lm}(\hat{\boldsymbol{r}}) & \boldsymbol{r} \in R_a \end{cases}$$

- $a_{lm}^{a\mathbf{kK}}$ and $b_{lm}^{a\mathbf{kK}}$ ensure the continuity of the value and slope of the basis functions.
- Another linearization scheme: the APW plus local orbital (APW+lo) method [E. Sjöstedt *et. al* 2000], where an APW basis is defined at a fixed energy E_l^a and the energy dependency is linearized by a set of local orbitals (lo).

$$\phi_{lo}^a(\boldsymbol{r}) = \begin{cases} 0 & \boldsymbol{r} \in IS \\ \left[a_{l,lo}^a u_{l,lo}^a(r, E_l^a) + b_{l,lo}^a \dot{u}_{l,lo}^a(r, E_l^a) \right] Y_L(\hat{\boldsymbol{r}}), & \boldsymbol{r} \in R_a \end{cases}$$

- Additional basis, the so-called LOs, only to chemically important l are added to describe the semi core states ($E_{l,LO}^a$) [Singh 1991].

Total energy in Kohn-Sham DFT

- One-electron Kohn-Sham equation is solved with $V_{\text{eff}}(\boldsymbol{r}) = \mathrm{V_C}(\boldsymbol{r}) + \mu_{\text{xc}}(\boldsymbol{r})$

$$[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r})]\psi_{v\boldsymbol{k}}(\boldsymbol{r}) = \epsilon_{v\boldsymbol{k}}\psi_{v\boldsymbol{k}}(\boldsymbol{r})$$

- For a given the charge density $\rho(\boldsymbol{r})$, the total energy per unit cell volume is

$$\begin{aligned} E &= E_{\text{kin}} + E_{\text{es}} + E_{\text{xc}} \\ &= \sum_{v\mathbf{k}} n_{v\mathbf{k}}\epsilon_{v\mathbf{k}} - \int_\Omega d^3r\ \rho(\boldsymbol{r})V_{\mathit{eff}}(\boldsymbol{r}) + \frac{1}{2}\int_\Omega d^3r\ \rho(\boldsymbol{r})V_C(\boldsymbol{r}) - \frac{1}{2}\sum_{a\in\Omega} Z_a V_M^a(\tau_a) \\ &\quad + \int_\Omega d^3r\rho(\boldsymbol{r})\epsilon_{\text{xc}}(\boldsymbol{r}) \end{aligned}$$

  * $\mu_{\text{xc}}(\boldsymbol{r}) \overset{\text{LDA}}{=} \frac{d}{d\rho}[\rho\epsilon_{\text{xc}}(\boldsymbol{r})]$ and for GGA, $\epsilon_{\text{xc}}(\boldsymbol{r}) \equiv \epsilon_{\text{xc}}(\rho, \nabla\rho)$

Effect of strain in the total energy

- A system is in an initial state with the total energy E_0 and the volume Ω_0.
- An infinitesimal amount of strain $\underline{\underline{\epsilon}}$ is applied, so that it is no longer in its initial state (E_0,Ω_0).
- Total energy of the deformed system, $E[\underline{\underline{\epsilon}}]$, is expanded around the initial state E_0 with a Taylor series expansion.

$$E[\underline{\underline{\epsilon}}] = E_0 + \Omega_0 \sum_{\alpha,\beta=1}^{3} \sigma_{\alpha\beta}\epsilon_{\alpha\beta} + \mathcal{O}(\epsilon^2)$$

- Stress tensor $\sigma_{\alpha\beta} = \frac{1}{\Omega_0} \frac{\partial E[\underline{\underline{\epsilon}}]}{\partial \epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0}$
- $E[\underline{\underline{\epsilon}}] =$
  $\sum_{v\mathbf{k}} n_{v\mathbf{k}}[\underline{\underline{\epsilon}}]\epsilon_{v\mathbf{k}}[\underline{\underline{\epsilon}}] - \int_{\Omega[\underline{\underline{\epsilon}}]} d^3r_\epsilon\ \rho[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}])V_{\mathit{eff}}[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}]) + \frac{1}{2}\int_{\Omega[\underline{\underline{\epsilon}}]} d^3r_\epsilon\ \rho[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}])V_C[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}]) -$
  $\frac{1}{2}\sum_{a\in\Omega} Z_a V_M^a[\underline{\underline{\epsilon}}](\tau_a[\underline{\underline{\epsilon}}]) + \int_{\Omega[\underline{\underline{\epsilon}}]} d^3r_\epsilon \rho[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}])\epsilon_{xc}[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}])$

Frequently used mathematical relationship

- Strain derivative of vectors and volume
  - A vector $\boldsymbol{r}$ changes as $\boldsymbol{r} \rightarrow \boldsymbol{r}[\underline{\underline{\epsilon}}] = (\underline{\underline{1}} \pm \underline{\underline{\epsilon}})\boldsymbol{r}$; + or - is for the direct or the reciprocal lattice and the unit cell volume changes as $\Omega \rightarrow \Omega[\underline{\underline{\epsilon}}] = \det(\underline{\underline{1}} + \underline{\underline{\epsilon}})\Omega$.

$$\left.\frac{d\boldsymbol{r}[\underline{\underline{\epsilon}}]}{d\epsilon_{\alpha\beta}}\right|_{\underline{\underline{\epsilon}}=0} = \pm\frac{r}{2}(\widehat{\boldsymbol{r}}_\alpha\widehat{\boldsymbol{e}}_\beta + \widehat{\boldsymbol{r}}_\beta\widehat{\boldsymbol{e}}_\alpha) = \pm r\widehat{\boldsymbol{r}}_\alpha\widehat{\boldsymbol{r}}_\beta$$

$$\left.\frac{d\Omega[\underline{\underline{\epsilon}}]}{d\epsilon_{\alpha\beta}}\right|_{\underline{\underline{\epsilon}}=0} = \delta_{\alpha\beta}\Omega$$

  - The unit vector component $\widehat{\boldsymbol{r}}_\alpha$ along Cartesian direction α can be expanded as $\widehat{\boldsymbol{r}}_\alpha = \sum_{t=-1}^{1} c_{\alpha t} Y_{1t}(\hat{\boldsymbol{r}})$.
  - The product of two spherical harmonics is expanded into Gaunt numbers times another spherical harmonics i.e.

$$Y_{1t}(\hat{\boldsymbol{r}})Y_{lm}(\hat{\boldsymbol{r}}) = \sum_{s,\nu} G^{\nu,t,m}_{s,1,l} Y_{s,\nu}(\hat{\boldsymbol{r}})$$

- The gradient component of the spherical harmonics, $\partial_\alpha Y_{lm}(\hat{\boldsymbol{r}})$, in the atomic spheres is computed as

$$\partial_\alpha Y_{lm}(\hat{\boldsymbol{r}}) = \frac{1}{r}\sum_{s=\pm1}\sum_{t=-1}^{1} c^{st}_\alpha(l,m) Y_{l+s,m+t}(\hat{\boldsymbol{r}})$$

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Strain variation of the total integration

- Strain derivative of integrals over the unit cell volume
  1. A generic integral over the unit cell $\int_\Omega d^3\boldsymbol{r} F(\boldsymbol{r})$ of an arbitrary function $F(\boldsymbol{r})$, which in practice is the charge density times potential or some other real quantity. In stress calculation

$$\frac{d}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} \int_{\Omega[\underline{\underline{\epsilon}}]} d^3\boldsymbol{r}_\epsilon F[\underline{\underline{\epsilon}}](\boldsymbol{r}_\epsilon) = \frac{d}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} \det(\underline{\underline{1}}+\underline{\underline{\epsilon}}) \int_\Omega d^3\boldsymbol{r} F[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}]) = \delta_{\alpha\beta} \int_\Omega d^3\boldsymbol{r} F(\boldsymbol{r}) + \int_\Omega d^3\boldsymbol{r} \frac{dF[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}])}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0}$$

  2. $\frac{dF[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}])}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0}$ depends on $\underline{\underline{\epsilon}}$ explicitly via linear response and implicitly via its smeared argument $\boldsymbol{r}[\underline{\underline{\epsilon}}]$,

$$\frac{dF[\underline{\underline{\epsilon}}](\boldsymbol{r}[\underline{\underline{\epsilon}}])}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} = \frac{dF[\underline{\underline{\epsilon}}](\boldsymbol{r})}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} + \frac{d\boldsymbol{r}[\underline{\underline{\epsilon}}]}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} \cdot \nabla F(\boldsymbol{r})$$

  3. With these relationship, the strain variation of an integral over the unit cell volume becomes

$$\frac{d}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} \int_{\Omega[\underline{\underline{\epsilon}}]} d^3\boldsymbol{r}_\epsilon F[\underline{\underline{\epsilon}}](\boldsymbol{r}_\epsilon) = \delta_{\alpha\beta} \int_\Omega d^3\boldsymbol{r} F(\boldsymbol{r}) + \int_\Omega d^3\boldsymbol{r} \frac{dF[\underline{\underline{\epsilon}}](\boldsymbol{r})}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} + \frac{1}{2}\int_\Omega d^3\boldsymbol{r}(r_\beta \partial_\alpha + r_\alpha \partial_\beta) F(\boldsymbol{r})$$

Total stress tensor in the APW based methods

$$\begin{aligned}\sigma_{\alpha\beta} &= \frac{1}{\Omega}\frac{dE[\underline{\underline{\epsilon}}]}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} \\ &= \sigma^{val,kin}_{\alpha\beta} + \delta_{APW}\sigma^{APW}_{\alpha\beta} + \sigma^{val,corr}_{\alpha\beta} + \sigma^{core,corr}_{\alpha\beta} + \sigma^{es}_{\alpha\beta} + \sigma^{xc}_{\alpha\beta}\end{aligned}$$

- $\sigma^{val,kin}_{\alpha\beta} = \frac{1}{2}\sum_{\upsilon\mathbf{k}} n_{\upsilon\mathbf{k}} \int_\Omega d^3\mathbf{r}\psi^*_{\upsilon\mathbf{k}}(\mathbf{r})\left(\partial_\alpha\partial_\beta + \partial_\beta\partial_\alpha\right)\psi_{\upsilon\mathbf{k}}(\mathbf{r})$
- $\sigma^{APW}_{\alpha\beta} = \frac{1}{\Omega}\oint dS \frac{d}{d\epsilon_{\alpha\beta}}\left(\psi^{*\,a}_{\upsilon\mathbf{k}}[\underline{\underline{\epsilon}}]\frac{\partial\psi^a_{\upsilon\mathbf{k}}[\underline{\underline{\epsilon}}]}{\partial r_a} - \psi^{*\,IS}_{\upsilon\mathbf{k}}[\underline{\underline{\epsilon}}]\frac{\partial\psi^{IS}_{\upsilon\mathbf{k}}[\underline{\underline{\epsilon}}]}{\partial r_a}\right)$
- $\sigma^{val,corr}_{\alpha\beta} = \frac{2}{\Omega}\sum_{\nu\mathbf{k}} n_{\nu\mathbf{k}}\Re\left\langle \frac{d\psi_{\nu\mathbf{k}}[\underline{\underline{\epsilon}}](\mathbf{r}[\underline{\underline{\epsilon}}])}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} \Big| \widehat{H}_{eff}(\mathbf{r}) - \epsilon_{\nu\mathbf{k}}\,|\psi_{\nu\mathbf{k}}(\mathbf{r})\right\rangle$
- $\sigma^{core,corr}_{\alpha\beta} = -\frac{1}{2\Omega}\sum_{a\in\Omega}\int_{R_a} d^3r_a\rho^a_c(\mathbf{r}_a)\left(\mathbf{r}_{a\alpha}\partial_\beta + \mathbf{r}_{a\beta}\partial_\alpha\right)V^a_{eff}(\mathbf{r}_a)$
- $\sigma^{es}_{\alpha\beta} = -\frac{\delta_{\alpha\beta}}{\Omega}\int_\Omega d^3\mathbf{r}\rho(\mathbf{r})V_C(\mathbf{r}) + \frac{1}{2\Omega}\frac{d}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0}\int_{\Omega[\underline{\underline{\epsilon}}]} d^3\mathbf{r}_\epsilon\rho((\underline{\underline{1}}-\underline{\underline{\epsilon}})\mathbf{r}_\epsilon)V_C[\underline{\underline{\epsilon}}](\mathbf{r}_\epsilon) - \frac{1}{2\Omega}\sum_{a\in\Omega}Z_a\frac{d}{d\epsilon_{\alpha\beta}}\Big|_{\underline{\underline{\epsilon}}=0} V^a_M[\underline{\underline{\epsilon}}](\tau_a[\underline{\underline{\epsilon}}])$
- $\sigma^{xc}_{\alpha\beta} = \frac{\delta_{\alpha\beta}}{\Omega}\int_\Omega d^3\mathbf{r}\rho(\mathbf{r})\Big(\epsilon_{\rm xc}(\rho(\mathbf{r})) - \mu_{\rm xc}(\rho(\mathbf{r}))\Big) - \frac{2\delta_{GGA}}{\Omega}\int_\Omega d^3\mathbf{r}\rho(\mathbf{r})\partial_\alpha\rho(\mathbf{r})\partial_\beta\rho(\mathbf{r})\frac{\partial\epsilon_{\rm xc}}{\partial\sigma}$

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Results

- The results of the stress tensor are compared with the least square fit of total energy vs volume using the Birch-Murnaghan (BM) equation of state.

$$E_{BM}(\Omega) = E_0 + \frac{9\Omega_0 B_0}{16}\left(\left[\left(\frac{\Omega}{\Omega_0}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{\Omega}{\Omega_0}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{\Omega}{\Omega_0}\right)^{\frac{2}{3}}\right]\right)$$

- With $E_{BM}(\Omega)$ we define the numerical pressure $P^{(E)}$

$$P^{(E)}(\Omega) \quad = \quad -\frac{\partial E_{BM}(\Omega)}{\partial \Omega}$$

- $P^{(E)}(\Omega)$ is compared to one third of the negative trace of the full stress tensor $P^{(\sigma)}(\Omega)$

$$P^{(\sigma)}(\Omega) = -\frac{1}{3}\sum_{\alpha}\sigma_{\alpha\alpha} = -\frac{1}{3}\Big(\sigma_{11} + \sigma_{22} + \sigma_{33}\Big).$$

- The difference $P^{(E)}(\Omega)$ - $P^{(\sigma)}(\Omega)$ gives the accuracy of our stress tensor formalism.

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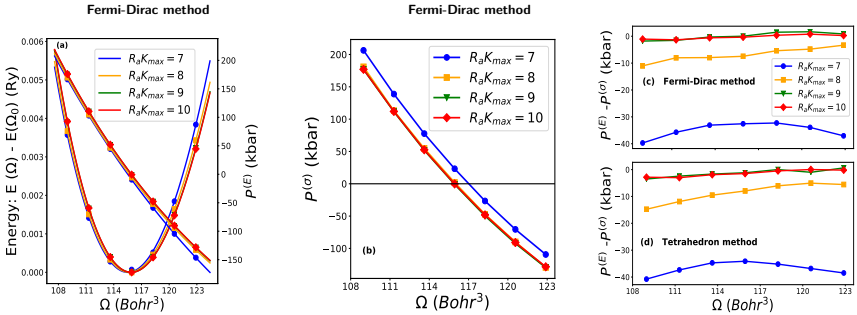
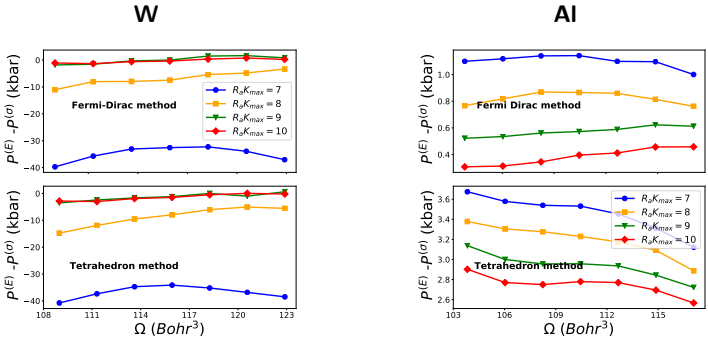
Convergence of the trace of $\sigma_{\alpha\beta}$ with R_aK_{max} for W

- (**a**) Energy-Volume curve as well as $P^{(E)}$, (**b**) $P^{(\sigma)}$ and (**c**) and (**d**) are $P^{(E)}$-$P^{(\sigma)}$



- $P^{(E)} - P^{(\sigma)}$ exhibits the same behavior in the tetrahedron method (**d**) as in the FD method (**c**).

Stress tensor with the FD and tetrahedron method.

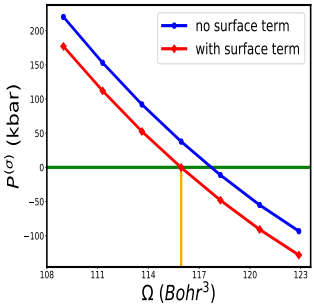


- Left panel: for W, $P^{(E)}$ - $P^{(\sigma)}$ for the FD and tetrahedron method is in the same order. With $R_aK_{max} = 10$, $a_0 = 6.143$ (σ, FD), 6.143 (E, FD), 6.145 (σ, Tetra) and 6.144 (E, Tetra).
- Right panel: for Al, $P^{(E)}$ - $P^{(\sigma)}$ is larger in the tetrahedron method than in the FD method. With $R_aK_{max} = 10$, $a_0 = 7.633$ (σ, FD), 7.634 (E, FD), 7.626 (σ, Tetra) and 7.635 (E, Tetra).

Importance of the surface term in APW+lo

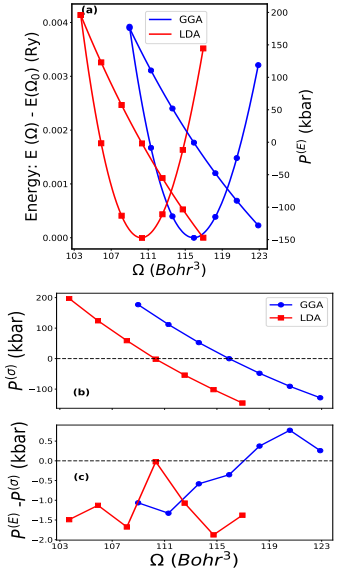
In the APW+lo method

- Basis functions are continuous but not the slope.
  - * This gives an additional surface term in the kinetic energy when calculating the total energy. $\mathcal{S} = \oint dS \left(\psi^{*\,a}_{\upsilon \boldsymbol{k}} \frac{\partial \psi^{a}_{\upsilon \boldsymbol{k}}}{\partial r_a} - \psi^{*\,IS}_{\upsilon \boldsymbol{k}} \frac{\partial \psi^{IS}_{\upsilon \boldsymbol{k}}}{\partial r_a} \right)$
  - * In stress calculation, $\mathcal{S}$ is defined in the deformed system and differentiated with respect to strain. $\sigma^{APW}_{\alpha\beta} = \frac{1}{\Omega} \oint dS \frac{d}{d\epsilon_{\alpha\beta}} \left(\psi^{*\,a}_{\upsilon \boldsymbol{k}}[\underline{\underline{\epsilon}}] \frac{\partial \psi^{a}_{\upsilon \boldsymbol{k}}[\underline{\underline{\epsilon}}]}{\partial r_a} - \psi^{*\,IS}_{\upsilon \boldsymbol{k}}[\underline{\underline{\epsilon}}] \frac{\partial \psi^{IS}_{\upsilon \boldsymbol{k}}[\underline{\underline{\epsilon}}]}{\partial r_a} \right)$



- σ^{APW}_{11} for APW+lo $\sim$ -38 kbar and for LAPW = 0 kbar. $a_0^{(E)} = 6.143$ Bohr, $a_0^{(\sigma)} = 6.143$ Bohr (red curve) and 6.174 Bohr (blue curve)

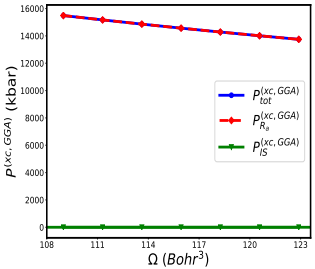
Comparison between LDA and GGA for W



- Difference between $P^{(E)}$ and $P^{(\sigma)}$ is just 1-2 kbar.
- $P^{(E)}$ - $P^{(\sigma)}$ is smaller for GGA than LDA.
- $a_0^{(\sigma)} = a_0^{(E)}$ for LDA and GGA up to three decimal place.

The additional GGA contribution is

$$\sigma_{\alpha\beta}^{xc,GGA} = -\frac{2\delta_{GGA}}{\Omega}\int_{\Omega} d^3 r\,\rho(\mathbf{r})\partial_\alpha\rho(\mathbf{r})\partial_\beta\rho(\mathbf{r})\frac{\partial\epsilon_{XC}}{\partial\sigma}$$

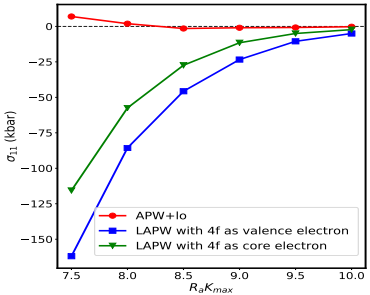


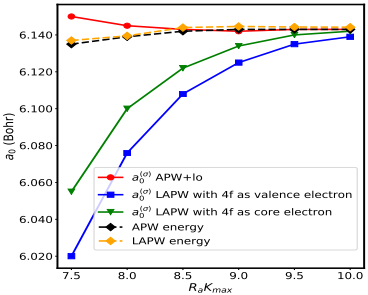
- $P_{tot}^{(xc,GGA)}$ is negative trace of $\sigma_{\alpha\beta}^{xc,GGA}$.
- $P_{tot}^{(xc,GGA)} = P_{R_a}^{(xc,GGA)} + P_{IS}^{(xc,GGA)}$
- R_a and IS denote the atomic sphere and the interstitial region.
- $P_{R_a}^{(xc,GGA)}$ is the major constituent and $P_{IS}^{(xc,GGA)}$ is within the error limit of the calculation.

J. Phys. Soc. Jap. **82**, 044701 (2013).

Comparison of convergences in APW+lo and LAPW

- Convergence of σ_{11} (left panel) and the lattice parameter (right panel) with basis set size (R_aK_{max}) for W.





- With APW+lo $R_aK_{max} = 8$ already gives an acceptable result, but for LAPW $R_aK_{max} = 10$ or more is required.
- Both the stress tensor and the lattice parameter in the APW+lo method converge much faster than two different LAPW cases.

Individual contributions of the stress tensor

- Stress tensor

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{val,kin} + \delta_{APW}\sigma_{\alpha\beta}^{APW} + \sigma_{\alpha\beta}^{val,corr} + \sigma_{\alpha\beta}^{core,corr} + \sigma_{\alpha\beta}^{es} + \sigma_{\alpha\beta}^{xc}$$

- σ_{11} component of various stress tensor contributions at $\Omega = 115.94$ $Bohr^3$.

stress	APW+lo (kbar)	LAPW (kbar)
$\sigma_{11}^{val,kin}$	1102905.56	1102971.88
σ_{11}^{APW}	-37.96	0.00
$\sigma_{11}^{val,corr}$	45.09	20.50
$\sigma_{11}^{core,corr}$	24760504.93	24760437.09
σ_{11}^{es}	-25607153.70	-25607170.14
$\sigma_{11}^{xc,LDA}$	-241699.29	-241699.56
$\sigma_{11}^{GGA,corr}$	-14564.88	-14564.78
total	-0.25	-5.01

- Conversion from the *energy per unit volume* to *kbar* for the given volume Ω is achieved by $1\frac{Ry}{Bohr^3} = 147105.16$ kbar.

Importance of non-spherical potential in core correction

- Core correction stress tensor

$$\sigma_{\alpha\beta}^{core,corr} = -\frac{1}{\Omega}\sum_{a\in\Omega}\int_{R_a} d^3 r_a \rho_c^a(\mathbf{r}_a)\frac{1}{2}(\mathbf{r}_{a\alpha}\partial_\beta + \mathbf{r}_{a\beta}\partial_\alpha)V_{eff}^a(\mathbf{r}_a) \quad (1)$$

- $V_{eff}^a \equiv V_{tot}^c = V_{00}^c + V_{2m}^c$
- V_{2m}^c is missing in Thonhauser *et al.* (2002)
- Effects due to the non-spherical component (l=2) in the potential exist only in non-cubic crystal structure.
- For the stress tensor, its importance is confirmed with results for anatase TiO_2 in body center tetragonal structure.

	a_0 (Bohr)	c_0 (Bohr)
energy	7.181	18.309
stress with V_{tot}^c	7.181	18.307
stress with V_{00}^c	7.163	18.404

- The symmetry between the equivalent atoms has been addressed correctly and the code works also for a non-symmorphic space group.

Accuracy of individual components of the stress tensor

- Cubic silicon in the diamond structure at the equilibrium volume (pressure = 0 and a_0 = 10.209 Bohr).
- Lattice parameters a_0 and $b_0 = a_0 = 10.209$ Bohr are fixed but only c_0 lattice parameter varies such that c = $c_0(1+\epsilon_{33})$.
- Using a family of tetragonal deformations without volume conserving, the stress component $\sigma_{33}^{(E)}$ is calculated using $\sigma_{33}^{(E)} = \frac{1}{\Omega_0}\frac{\partial E(\epsilon_{33})}{\partial \epsilon_{33}}$ with $\epsilon_{33} = \frac{c}{c_0}$ - 1 and compared with $\sigma_{33}^{(\sigma)}$

ϵ_{33}	$\sigma_{33}^{(E)}$	$\sigma_{33}^{(\sigma)}$
-0.020	33.12	34.28
-0.013	21.95	22.63
-0.007	10.90	11.17
0.000	0.00	0.00
0.007	-10.74	-10.99
0.013	-21.29	-21.70
0.020	-31.65	-32.16

Discussion and Outlook

- Stress tensor formalism for LAPW, APW+lo, LDA and GGA has been derived and implemented in the WIEN2k code.
- Stress tensor is accurate enough to be used for structure optimization.
- A bit larger basis set for stress calculations is needed than for total energy calculations.
- With APW+lo compared to LAPW, the stress tensor converges faster and requires a smaller value of $R_a K_{max}$.
- For metallic systems, calculations using the FD method converge faster
- Formalism and the implementation needs to be extended to the scalar relativistic kinetic energy and spin-orbit coupling.
- An automatic optimization of the lattice parameter using the stress tensor can be implemented in a similar way as the automatic optimization with force (L. D. Marks J. Chem. Theory Comput. (2021)).

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Thank you

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Non linear eigenvalue problem in the APW method

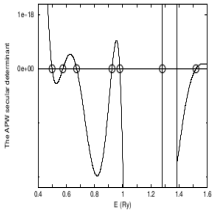

Figure 2.3: The APW determinant $\det\ \bar{T}(E) + V(E) - E\mathcal{O}(E)$, must be evaluated for a number of energies E, in order to find the solutions to the secular equation in Eqn. (2.14). The circles indicate the eigenenergies of the valence electrons in niobium, at $\mathbf{k} = \frac{2\pi}{a}(0.5, 0.25, 0.33)$, for $a = 6.236$ a.u.

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Why the Fermi-Dirac smearing method is better for calculating stresses

- For a system with partial occupation, the total energy discussed above is no longer variational. In such a case, the total energy must be replaced by a more general expression as given in Eq. (2). This argument is based on the force calculation and we assume that the same argument is valid for the stress tensor calculation.

$$F = E - \sum_{vk} n_{vk} \sigma S \tag{2}$$

- The derivative of the occupation number with respect to strain will be canceled with a similar expression from the entropy-like term (second term in Eq. (2)).

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Linearization in the LAPW method

- Energy dependent radial function $u_l(r, E)$ of APW is expanded in LAPW.

$$\begin{aligned} u_l(r, E) &= u_l(r, E_l^a + (E - E_l^a)) \\ &= u_l(r, E_l^a) + (E - E_l^a)\dot{u}_l(r, E_l^a) + \mathcal{O}((E - E_l^a)^2) \end{aligned}$$

- All higher order terms are neglected by assuming that the difference $E - E_l^a$ is very small.
- Linearization scheme of LAPW is able to solve the non-linear eigenvalue problem of APW but optimal shape of the basis function inside the atomic spheres is sacrificed.

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Total wave function and charge density

- The linear combination of the basis functions $\phi_{\mathbf{k}\mathbf{K}}(\boldsymbol{r})$ are used to define the total wave function $\psi_{v\boldsymbol{k}}(\boldsymbol{r})$ for the band v and given $\boldsymbol{k}$ vector

$$\psi_{v\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{K}} c_{v\boldsymbol{k}\boldsymbol{K}} \phi^{(L)APW}_{\boldsymbol{k}\boldsymbol{K}}(\boldsymbol{r}) + \sum_{lo} c_{v\boldsymbol{k},lo} \phi^{a}_{lo}(\boldsymbol{r}) + \sum_{LO} c_{v\boldsymbol{k},LO} \phi^{a}_{LO}(\boldsymbol{r})$$

- $c_{v\boldsymbol{k}\boldsymbol{K}}$ are expansion coefficients and $\boldsymbol{K}$ is the reciprocal lattice vector such that $|\boldsymbol{K}| \leq K_{\max}$.
- $\psi_{v\boldsymbol{k}}(\boldsymbol{r})$ are used to define the charge density as

$$\rho(\boldsymbol{r}) = \sum_{v\boldsymbol{k}} n_{v\boldsymbol{k}} \psi^{*}_{v\boldsymbol{k}}(\boldsymbol{r}) \psi_{v\boldsymbol{k}}(\boldsymbol{r})$$

- After simplification, $\rho(\boldsymbol{r})$ in the APW based methods can be expressed as follow

$$\rho(\boldsymbol{r}) = \begin{cases} \sum_{\boldsymbol{G}}^{G_{\max}} \rho(\boldsymbol{G}) e^{i\boldsymbol{G}.\boldsymbol{r}} & \boldsymbol{r} \in IR \\ \sum_{\mathrm{LM}} \rho_{\mathrm{LM}}(r) Y_{\mathrm{LM}}(\hat{\boldsymbol{r}}_a) & \boldsymbol{r} \in R_a, \end{cases}$$

- $G_{\max}$ must be at least $2K_{\max}$. The total potential $V(\boldsymbol{r})$ is expanded similar to $\rho(\boldsymbol{r})$.