## 6.2 Core Correction Stress Tensor

The core correction contribution to the total stress tensor as given in equation (6.3b) is

$$\sigma_{\alpha\beta}^{core} = -\frac{1}{2\Omega}\int_{\Omega} d^3\mathbf{r}\rho_c(\mathbf{r})(r_\beta\partial_\alpha + r_\alpha\partial_\beta)V_{eff}(\boldsymbol{r}) \tag{6.30}$$

$$= -\frac{1}{\Omega}\sum_{a\in\Omega}\int_{R_a} d^3\boldsymbol{r}_a\rho_c^a(\mathbf{r}_a)\frac{1}{2}(\mathbf{r}_{a\alpha}\partial_\beta + \mathbf{r}_{a\beta}\partial_\alpha)V_{eff}^a(\mathbf{r}_a), \tag{6.31}$$

where $\rho_c^a(\mathbf{r}_a)$ represents the core charge density, and it is confined, in principle, to the interior of the atomic spheres. $V_{eff}^a(\mathbf{r}_a)$ is the effective or total potential in the system, $\int_{R_a}$ denotes the integration domain inside an atomic sphere region, and the summation index $a$ runs over all the equivalent and non-equivalent atoms in the unit cell.

When the unit cell is deformed, the core states change in two different ways: First, the core states will move along with the nuclei to a position in the strained unit cell. Second, the total potential in the unit cell will be changed, and core states will interact with that modified potential. Equation (6.30) suggests that the core correction is coming from this second change. The following lines illustrate the necessary steps to simplify equation (6.31).

Inside an atomic sphere, the potential is expanded in terms of spherical harmonics. For the sake of brevity, in the following lines we will be using $V_{eff}^a(\mathbf{r}_a) = V(\mathbf{r})$

$$V(\mathbf{r}) = \sum_{l,m} V_{l,m}(\mathbf{r})Y_{l,m}(\hat{\boldsymbol{r}}) \tag{6.32}$$

The partial derivative of the length of a radial vector along the Cartesian direction $\alpha$ is

$$\frac{\partial r}{\partial r_\alpha} = \partial_\alpha r = \partial_\alpha\Big[\sum_\alpha \mathbf{r}_\alpha^2\Big]^{\frac{1}{2}} = \frac{\mathbf{r}_\alpha}{\sqrt{\sum_\alpha \mathbf{r}_\alpha^2}} = \hat{\boldsymbol{r}}_\alpha \tag{6.33}$$

Also,

$$\partial_\alpha = \frac{\partial}{\partial r_\alpha} = \frac{\partial}{\partial r}\frac{\partial r}{\partial r_\alpha} = \hat{\boldsymbol{r}}_\alpha\frac{\partial}{\partial r} \tag{6.34}$$

$$\begin{aligned}
\partial_\alpha V(\mathbf{r}) &= \sum_{l,m}\Big(Y_{l,m}(\hat{\boldsymbol{r}})\partial_\alpha V_{l,m}(\mathbf{r}) + V_{l,m}(\mathbf{r})\partial_\alpha Y_{l,m}(\hat{\boldsymbol{r}})\Big) \\
&= \sum_{l,m}\Big(Y_{l,m}(\hat{\boldsymbol{r}})\hat{\boldsymbol{r}}_\alpha V'_{l,m}(\mathbf{r}) + \frac{V_{l,m}(\mathbf{r})}{r}r\partial_\alpha Y_{l,m}(\hat{\boldsymbol{r}})\Big) \\
&\overset{(A.8)}{=} \sum_{l,m}\Big(Y_{l,m}(\hat{\boldsymbol{r}})\hat{\boldsymbol{r}}_\alpha V'_{l,m}(\mathbf{r}) + \frac{V_{l,m}(\mathbf{r})}{r}\sum_{s=\pm1}\sum_{t=-1}^{1} c_\alpha^{st}(l,m)Y_{l+s,m+t}(\hat{\boldsymbol{r}})\Big)
\end{aligned} \tag{6.35}$$

The prime in $V'_{l,m}(\mathbf{r})$ denotes the radial derivative, the summation over $s$ takes +1 and -1 only, and $t$ runs from -1 to +1. In the above equation, the loop over $l$ and $s$ has

to be such that $l+s$ is always positive. The expressions of $c_\alpha^{st}(l,m)$ are provided in section A.2. The angular derivative of the spherical harmonics produces a change of angular quantum number ($l$) of the spherical harmonics to its nearest value only by $\pm 1$. The implication of this result is that a `s`-like shape of the effective potential can only change to a `p`-like shape but not directly to `d`-like shape. However, a `p`-like shape can transform to `s`-like shape or `d`-like shape according to $s=-1$ or $s=+1$, respectively.

Also,

$$\partial_\alpha V(\mathbf{r}) = \sum_{l,m}\Big(V'_{l,m}(\mathbf{r})\sum_{t=-1}^{1} c_{\alpha t}Y_{1t}(\hat{\boldsymbol{r}})Y_{l,m}(\hat{\boldsymbol{r}}) + \frac{V_{l,m}(\mathbf{r})}{r}\sum_{s=\pm1}\sum_{t=-1}^{1} c_\alpha^{st}(l,m)Y_{l+s,m+t}(\hat{\boldsymbol{r}})\Big) \tag{6.36}$$

We expand the radial vector components in terms of spherical harmonics:

$$r_\beta = \hat{\boldsymbol{r}}_\beta r \overset{(A.1)}{=} r\sum_{t'=-1}^{1} c_{\beta t'}Y_{1t'}(\hat{\boldsymbol{r}}) \tag{6.37}$$

Multiplying equation (6.36) by (6.37):

$$\begin{aligned} r_\beta\partial_\alpha V(\mathbf{r}) = \sum_{l,m}\Big(&rV'_{l,m}(\mathbf{r})\sum_{t,t'=-1}^{1} c_{\alpha t}c_{\beta t'}Y_{1t'}(\hat{\boldsymbol{r}})Y_{1t}(\hat{\boldsymbol{r}})Y_{l,m}(\hat{\boldsymbol{r}}) \\ &+V_{l,m}(\mathbf{r})\sum_{s=\pm1}\sum_{t,,t'=-1}^{1} c_\alpha^{st}(l,m)c_{\beta t'}Y_{1t'}(\hat{\boldsymbol{r}})Y_{l+s,m+t}(\hat{\boldsymbol{r}})\Big) \end{aligned} \tag{6.38}$$

The product of two spherical harmonics can be replaced by a Gaunt number according to equation (A.4).

$$\begin{aligned} r_\beta\partial_\alpha V(\mathbf{r}) = \sum_{l,m}\Big(&rV'_{l,m}(\mathbf{r})\sum_{t,t'=-1}^{1} c_{\alpha t}c_{\beta t'}\sum_{s=0}^{2}\sum_{\nu=-s}^{s} G_{s,1,1}^{\nu,t,t'}Y_{s\nu}(\hat{\boldsymbol{r}})Y_{l,m}(\hat{\boldsymbol{r}}) \\ &+V_{l,m}(\mathbf{r})\sum_{s=\pm1}\sum_{t,,t'=-1}^{1} c_\alpha^{st}(l,m)c_{\beta t'}Y_{1t'}(\hat{\boldsymbol{r}})Y_{l+s,m+t}(\hat{\boldsymbol{r}})\Big) \end{aligned} \tag{6.39}$$

Interchanging $\alpha$ and $\beta$:

$$\begin{aligned} r_\alpha\partial_\beta V(\mathbf{r}) = \sum_{l,m}\Big(&rV'_{l,m}(\mathbf{r})\sum_{t,t'=-1}^{1} c_{\alpha t}c_{\beta t'}\sum_{s=0}^{2}\sum_{\nu=-s}^{s} G_{s,1,1}^{\nu,t,t'}Y_{s\nu}(\hat{\boldsymbol{r}})Y_{l,m}(\hat{\boldsymbol{r}}) \\ &+V_{l,m}(\mathbf{r})\sum_{s=\pm1}\sum_{t,,t'=-1}^{1} c_\beta^{st}(l,m)c_{\alpha t'}Y_{1t'}(\hat{\boldsymbol{r}})Y_{l+s,m+t}(\hat{\boldsymbol{r}})\Big) \end{aligned} \tag{6.40}$$

Adding the expressions (6.39) and (6.40):

$$\begin{aligned} \frac{1}{2}(r_\beta\partial_\alpha + r_\alpha\partial_\beta)V(\mathbf{r}) = \sum_{l,m}\sum_{t,t'=-1}^{1}\Big(&rV'_{l,m}(\mathbf{r})c_{\alpha t}c_{\beta t'}\sum_{s=0}^{2}\sum_{\nu=-s}^{s} G_{s,1,1}^{\nu,t,t'}Y_{s\nu}(\hat{\boldsymbol{r}})Y_{l,m}(\hat{\boldsymbol{r}}) \\ &+V_{l,m}(\mathbf{r})\sum_{s=\pm1}\frac{c_\beta^{st}(l,m)c_{\alpha t'}+c_\alpha^{st}(l,m)c_{\beta t'}}{2}Y_{1t'}(\hat{\boldsymbol{r}})Y_{l+s,m+t}(\hat{\boldsymbol{r}})\Big) \end{aligned} \tag{6.41}$$

The total charge density is a real quantity:

$$\rho(\mathbf{r}) = \sum_{l',m'} \rho_{l',m'}(r) Y_{l',m'}(\hat{\boldsymbol{r}}) = \sum_{l',m'} \rho^*_{l',m'}(r) Y^*_{l',m'}(\hat{\boldsymbol{r}}) \tag{6.42}$$

Substituting equation (6.41) in (6.31):

$$\begin{aligned}\Omega\sigma^C_{\alpha\beta} = \sum_{l,m}\sum_{l',m'}\sum_{t,t'=-1}^{1}\Big(& I_1 c_{\alpha t} c_{\beta t'} \sum_{s=0}^{2}\sum_{\nu=-s}^{s} G^{\nu,t,t'}_{s,1,1} G^{m',m,\nu}_{l',l,s} \\ & + I_2 \sum_{s=\pm 1} \frac{c^{st}_{\beta}(l,m) c_{\alpha t'} + c^{st}_{\alpha}(l,m) c_{\beta t'}}{2} G^{m',t',m+t}_{l',1,l+s}\Big),\end{aligned} \tag{6.43}$$

where $I_1$ and $I_2$ are the abbreviation of the following integrals:

$$I_1 = -\int_0^{R_a} r_a^3 dr_a \rho^*_{l',m'}(r_a) \frac{dV_{l,m}(r_a)}{dr_a} \tag{6.44}$$

$$I_2 = -\int_0^{R_a} r_a^2 dr_a \rho^*_{l',m'}(r_a) V_{l,m}(r_a) \tag{6.45}$$

In the APW based methods, the core density is assumed to be spherically symmetric and confined within a spherical region. It is also assumed that its spherical nature remains intact even for the strained system, which means that $l'$ and $m'$ of the charge density in equation (6.43) are zero . The underlying assumption is that when a system is deformed, the core states simply move to a new position along with the nucleus, and the stress contribution comes through the change in the shape of the potential. Core states are lying so deep in energy and are so localized that their spherical nature persists even after the system is deformed. On the other hand, the total potential is spreading over the entire crystal, and thus the indexes $l, m$ of potential can have both spherical and non-spherical indexes. However, due to the product of two Gaunt numbers $G^{\nu,t,t'}_{s,1,1} G^{m',m,\nu}_{l',l,s}$, $l$ and $m$ can have only very few non-spherical components. This concept is similar to the core correction for the force calculation. In the calculation of forces, densities are assumed to be spherical too, but the potential they interact with has both spherical ($l = 0$) and non-spherical components ($l = 1$), see equation (A4) in Ref.[31].

The product of two Gaunt numbers with $l', m' = 0$ is:

$$\begin{aligned} G^{\nu,t,t'}_{s,1,1} G^{m',m,\nu}_{l',l,s} &= G^{\nu,t,t'}_{s,1,1} G^{0,m,\nu}_{0,l,s} \\ &= G^{\nu,t,t'}_{s,1,1} \int_S dS\ Y^*_{00}(\hat{\boldsymbol{r}}) Y_{lm}(\hat{\boldsymbol{r}}) Y_{s\nu}(\hat{\boldsymbol{r}}) \\ &= G^{\nu,t,t'}_{s,1,1} \frac{(-1)^m}{\sqrt{4\pi}} \delta_{l,s} \delta_{-m,\nu} \\ &= \frac{(-1)^m}{\sqrt{4\pi}} G^{-m,t,t'}_{l,1,1} \end{aligned} \tag{6.46}$$

$$
\begin{aligned}
G^{m',t',m+t}_{l',1,l+s} &= G^{0,t',m+t}_{0,1,l+s} \\
&= \frac{(-1)^{t'}}{\sqrt{4\pi}}\delta_{1,l+s}\delta_{-t',m+t} \qquad (6.47)
\end{aligned}
$$

The final expression of core-correction stress is obtained by substituting equations (6.46) and (6.47) in (6.43).

$$
\begin{aligned}
\Omega\sigma^{C}_{\alpha\beta} = \sum_{l,m}\sum_{t,,t'=-1}^{1}\Bigg( & I_1 c_{\alpha t}c_{\beta t'}\frac{(-1)^m}{4\pi}G^{-m,t,t'}_{l,1,1} + \\
& I_2\sum_{s=\pm1}\frac{c^{st}_{\beta}(l,m)c_{\alpha t'} + c^{st}_{\alpha}(l,m)c_{\beta t'}}{2}\frac{(-1)^{t'}}{4\pi}\delta_{1,l+s}\delta_{-t',m+t}\Bigg) \qquad (6.48)
\end{aligned}
$$

with integrals,

$$
\begin{aligned}
I_1 &= -\int_0^{R_a} r_a^3 dr_a\sqrt{4\pi}\rho^*_{00}(r_a)\frac{dV_{lm}(r_a)}{dr_a} \qquad (6.49)\\
I_2 &= -\int_0^{R_a} r_a^2 dr_a\sqrt{4\pi}\rho^*_{00}(r_a)V_{lm}(r_a) \qquad (6.50)
\end{aligned}
$$

Equation (6.48) shows that the stress components ($\alpha$, $\beta$) enter in the equation via $c_{\alpha t}$, $c_{\beta t'}$, $c^{st}_{\alpha}(l,m)$, and $c^{st}_{\beta}(l,m)$ and these coefficients result from a change in potential (radial derivative of $V_{lm}(\boldsymbol{r})$) and spherical harmonics (angular derivative of spherical harmonics $Y_{lm}(\hat{\boldsymbol{r}})$).

For a Gaunt number $G^{-m,t,t'}_{l,1,1}$, the indices $[l,1,1]$ are required to satisfy the triangle rule and their sum needs to be even [46]. These conditions restrict $l$ to be 0 and 2, $l$=0 is the primary component and $l$=2 acts as an extra correction term, which does not always exist. In a cubic structure, $l$=2 never appears because of symmetry (for example, with site symmetry $m3m$, $l$ of the charge density can be 0,4,6), a $l$=2 term appears only in the lower symmetric crystal structures (for example, a hexagonal system). As can be seen above, we assumed that the core density is always spherical, and $l = 2$ appears due to the non-spherical nature introduced in the total potential when the system is deformed. This concept is similar to the core correction of the force calculation. In the force calculation, atoms are displaced, and in the core correction, $l$=1 appears in the potential. In the stress calculation, the system is deformed and $l$=2 appears in the potential as a core correction.

Equation (6.31) is similar to corresponding expression in Refs.[12, 19]. Equation (21) in Thonhauser *et al.* has a different sign than in our expression. On the other hand, we do not see such a term in Ref.[17]. In section 4.1 in Ref. [12], the authors make an argument that "the core correction vanishes for pure pressure", but from our calculation we could not validate such a rationale. The core correction given in Thonhauser et. al. is: