1. The transformation matrix and Mathematica code for the Euler transformations

Code for Euler transformation

```
(************
  ϕ==> Rotate
  θ==> Tilt
  ψ==>Twist
  ************)

(*Transformation Matrix
*) ℝ = ( Cos[ψ] Cos[ϕ] - Cos[θ] Sin[ϕ] Sin[ψ]    -Sin[ψ] Cos[ϕ] - Cos[θ] Sin[ϕ] Cos[ψ]    Sin[θ] Sin[ϕ]
         Cos[ψ] Sin[ϕ] + Cos[θ] Cos[ϕ] Sin[ψ]    -Sin[ψ] Sin[ϕ] + Cos[θ] Cos[ϕ] Cos[ψ]    -Sin[θ] Cos[ϕ]
         Sin[θ] Sin[ψ]                            Sin[θ] Cos[ψ]                            Cos[θ]        );

(*Variables for matrix calculations*)
x = a = 1;
y = b = 2;
z = c = 3;

(*List of hyperpolarizability*)
β[l_, m_, n_] := {{{β[aaa], β[aab], β[aac]}, {β[aba], β[abb], β[abc]}, {β[aca], β[acb], β[acc]}},
    {{β[baa], β[bab], β[bac]}, {β[bba], β[bbb], β[bbc]}, {β[bca], β[bcb], β[bcc]}},
    {{β[caa], β[cab], β[cac]}, {β[cba], β[cbb], β[cbc]}, {β[cca], β[ccb], β[ccc]}}}[[l, m, n]];

(*χ[i,j,k] returns trasnformation of surface coordinated susceptibility to be expressed as a linear combination of the
 molecular coordinated hyperpolarizability *)
χ[i_, j_, k_] := ∑_{l=a}^{c} ∑_{m=a}^{c} ∑_{n=a}^{c} ℝ[[i, l]] ℝ[[j, m]] ℝ[[k, n]] β[l, m, n]
```

Example

```
χ[x, x, x]
(Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^3 β[aaa] + (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^2 β[aab] +
 Sin[θ] Sin[ϕ] (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^2 β[aac] + (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^2 β[aba] +
 (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ])^2 (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[abb] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[abc] +
 Sin[θ] Sin[ϕ] (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^2 β[aca] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[acb] +
 Sin[θ]^2 Sin[ϕ]^2 (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[acc] + (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^2 β[baa] +
 (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ])^2 (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[bab] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[bac] +
 (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ])^2 (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[bba] +
 (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ])^3 β[bbb] + Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ])^2 β[bbc] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[bca] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ])^2 β[bcb] +
 Sin[θ]^2 Sin[ϕ]^2 (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) β[bcc] + Sin[θ] Sin[ϕ] (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^2 β[caa] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[cab] +
 Sin[θ]^2 Sin[ϕ]^2 (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[cac] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[cba] +
 Sin[θ] Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ])^2 β[cbb] + Sin[θ]^2 Sin[ϕ]^2 (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) β[cbc] +
 Sin[θ]^2 Sin[ϕ]^2 (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β[cca] + Sin[θ]^2 Sin[ϕ]^2 (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) β[ccb] + Sin[θ]^3 Sin[ϕ]^3 β[ccc]
```

2. The complete list of non-zero hyperpolarizability

In second-order hyperpolarizability, β_{lmn}, the first two index, l ,and, m , are related to Raman transition dipole and they are interchangeable. The last index, n , is related to IR transition dipole. SFG transition dipoles are active only when the Raman and IR transition dipole are both active. Thus, orthogonal elements of the Raman and IR transition dipole results inactive SFG transition dipole. The orthogonality can be easily conformed using character table.

2.1. For C_{3v} symmetry molecules

(*From C3V Character Table*)

"$\beta_{a,a,a}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{a,a,c}$==A_1 ⊗ A_1==A_1, Symmetric"
"$\beta_{a,b,b}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{a,c,a}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{b,a,b}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{b,b,a}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{b,b,c}$==A_1 ⊗ A_1==A_1, Symmetric"
"$\beta_{b,c,b}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{c,a,a}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{c,b,b}$==E ⊗ E==A_1, Asymmetric"
"$\beta_{c,c,c}$==A_1 ⊗ A_1==A_1, Symmetric"

(*Non-zero Microscopic Hyperpolarizability*)

"Symmetric"
$\beta_{b,b,c} = \beta_{a,a,c}$
$\beta_{c,c,c}$
"Asymmetric"
$\beta_{b,c,b} = \beta_{a,c,a}$
$\beta_{c,b,b} = \beta_{c,a,a}$
$\beta_{b,b,a} = \beta_{a,b,b} = \beta_{b,a,b} = -\beta_{a,a,a}$

(*Zero Microscopic Hyperpolarizability*)

$\beta_{a,a,b} = \beta_{a,b,a} = \beta_{a,b,c} = \beta_{a,c,b} = \beta_{a,c,c} = 0$

$\beta_{b,a,a} = \beta_{b,a,c} = \beta_{b,b,b} = \beta_{b,c,a} = \beta_{b,c,c} = 0$

$\beta_{c,a,b} = \beta_{c,a,c} = \beta_{c,b,a} = \beta_{c,b,c} = \beta_{c,c,a} = \beta_{c,c,b} = 0$

2.2. For C_{2v} symmetry molecules

(*From C2V Character Table*)

"$\beta_{a,a,c}$==$A_1 \otimes A_1$==A_1, Symmetric"

"$\beta_{a,c,a}$==$B_1 \otimes B_1$==A_1, Asymmetric"

"$\beta_{b,b,c}$==$A_1 \otimes A_1$==A_1, Symmetric"

"$\beta_{b,c,b}$==$B_2 \otimes B_2$==A_1, Asymmetric"

"$\beta_{c,a,a}$==$B_1 \otimes B_1$==A_1, Asymmetric"

"$\beta_{c,b,b}$==$B_2 \otimes B_2$==A_1, Asymmetric"

"$\beta_{c,c,c}$==$A_1 \otimes A_1$==A_1, Symmetric"

(*Non-zero Microscopic Hyperpolarizability*)

"Symmetric"

$\beta_{a,a,c}$

$\beta_{b,b,c}$

$\beta_{c,c,c}$

"Asymmetric, B_1"

$\beta_{c,a,a} = \beta_{a,c,a}$

"Asymmetric, B_2"

$\beta_{c,b,b} = \beta_{b,c,b}$

(*Zero Microscopic Hyperpolarizability*)

$\beta_{a,a,a} = \beta_{a,a,b} = \beta_{a,b,a} = \beta_{a,b,b} = \beta_{a,b,c} = \beta_{a,c,b} = \beta_{a,c,c} = 0$

$\beta_{b,a,a} = \beta_{b,a,b} = \beta_{b,a,c} = \beta_{b,b,a} = \beta_{b,b,b} = \beta_{b,c,a} = \beta_{b,c,c} = 0$

$\beta_{c,a,b} = \beta_{c,a,c} = \beta_{c,b,a} = \beta_{c,b,c} = \beta_{c,c,a} = \beta_{c,c,b} = 0$

2.3. For $C_{\infty v}$ symmetry molecules

It is to be noted that $C_{\infty v}$ symmetry molecules such as –OH only have symmetric stretching vibration.

```
(*From C∞V Character Table*)
```

"$\beta_{a,a,c}$==$A_1 \otimes A_1$==A_1, Symmetric"
"$\beta_{b,b,c}$==$A_1 \otimes A_1$==A_1, Symmetric"
"$\beta_{c,c,c}$==$A_1 \otimes A_1$==A_1, Symmetric"

```
(*Non-zero Microscopic Hyperpolarizability*)
```

"Symmetric"

$\beta_{b,b,c} = \beta_{a,a,c}$

$\beta_{c,c,c}$

```
(*Zero Microscopic Hyperpolarizability*)
```

$\beta_{a,a,a} = \beta_{a,a,b} = \beta_{a,b,a} = \beta_{a,b,b} = \beta_{a,b,c} = \beta_{a,c,a} = \beta_{a,c,b} = \beta_{a,c,c} = 0$

$\beta_{b,a,a} = \beta_{b,a,b} = \beta_{b,a,c} = \beta_{b,b,a} = \beta_{b,b,b} = \beta_{b,c,a} = \beta_{b,c,b} = \beta_{b,c,c} = 0$

$\beta_{c,a,a} = \beta_{c,a,b} = \beta_{c,a,c} = \beta_{c,b,a} = \beta_{c,b,b} = \beta_{c,b,c} = \beta_{c,c,a} = \beta_{c,c,b} = 0$

3. The second-order susceptibility expressed as a linear combination of hyperpolarizability

First, the complete list of Euler transformations is produced. The 27 tensor elements of the susceptibility in surface coordinates are expressed as a linear combination of the molecular hyperpolarizability tensor elements in molecular coordinates. Then the four independent non-zero polarization combinations, ssp, sps, pss, and ppp are only considered (i.e. $\chi_{yyz}, \chi_{yzy}, \chi_{zyy}, \chi_{xxz}, \chi_{xzx}, \chi_{zxx}, and\ \chi_{zzz}$). The symmetric and anti-symmetric non-zero tensor elements of hyperpolarizability for each C_{3v}, C_{2v}, and $C_{\infty v}$ symmetry molecules on the isotropic interface are listed in Section 2. To simplify the procedure the hyperpolarization ratio, $R = \beta_{aac}/\beta_{ccc}$, is introduced, which can be deduced from Raman depolarization ratio. For visualize the susceptibility changes as a function of orientation angles, arbitrary values of the hyperpolarizability tensor elements, β_{lmn}, and number of vibrational modes, N_s, are used.

3.1. The susceptibility of ssp-polarization combination, $\chi_{ssp} = \chi_{yyz}$

3.1.1. C_{3v} symmetry molecules

3.1.1.a. Symmetric stretching vibration

"SSP Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{y,y,z} = \mathrm{Expand}\Big[\mathrm{Cos}[\theta]\,(\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi] + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi] - \mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{c,c,c}\Big]$$

$$= \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$= \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]^2\,\left(\mathrm{Cos}[\psi]^2 + \mathrm{Sin}[\psi]^2\right)\beta_{a,a,c} + \mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\,\left(\mathrm{Cos}[\psi]^2 + \mathrm{Sin}[\psi]^2\right)\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$= \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$= \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\left(1 - \mathrm{Cos}[\theta]^2\right)\beta_{c,c,c}$$

$$= \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\beta_{c,c,c} - \mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\,\beta_{c,c,c}$$

$$= \left(\mathrm{Cos}[\phi]^2\,\beta_{c,c,c} + \mathrm{Sin}[\phi]^2\,\beta_{a,a,c}\right)\mathrm{Cos}[\theta] - (\beta_{c,c,c} - \beta_{a,a,c})\,\mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2$$

$$= \beta_{c,c,c}\left(\left(\mathrm{Cos}[\phi]^2 + \mathrm{Sin}[\phi]^2\,\frac{\beta_{a,a,c}}{\beta_{c,c,c}}\right)\mathrm{Cos}[\theta] - \left(1 - \frac{\beta_{a,a,c}}{\beta_{c,c,c}}\right)\mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\phi]^2\right)$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{y,y,z} = \beta_{c,c,c}\,\mathrm{Cos}[\phi]^2\left(\left(1 + \left(\frac{\mathrm{Sin}[\phi]}{\mathrm{Cos}[\phi]}\right)^2 R\right)\mathrm{Cos}[\theta] - (1 - R)\,\mathrm{Cos}[\theta]^3\right)$$

"Average Over Orientation (ϕ)"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\beta_{c,c,c}\,\text{Cos}[\phi]^2\left(\left(1+\left(\frac{\text{Sin}[\phi]}{\text{Cos}[\phi]}\right)^2 R\right)\text{Cos}[\theta]-(1-R)\,\text{Cos}[\theta]^3\right)\right)d\phi\right)$$

$$=\frac{1}{2}\text{Cos}[\theta]\left(1+R+(-1+R)\,\text{Cos}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{Y,Y,Z}=\frac{1}{2}N_s\,\beta_{c,c,c}\left((1+R)\,\text{Cos}[\theta]-(1-R)\,\text{Cos}[\theta]^3\right)}$$

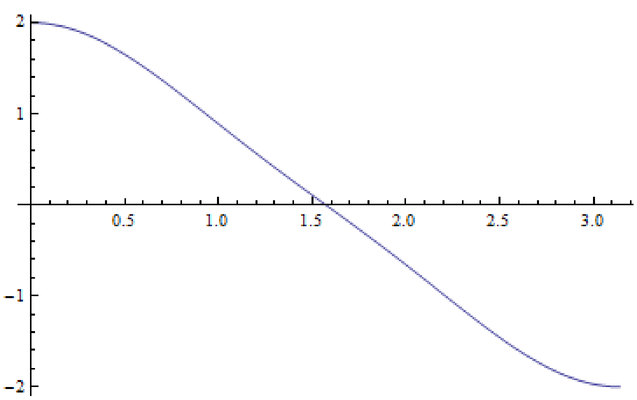
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 2$

$$\text{Plot}\left[\frac{1}{2}N_s\,\beta_{c,c,c}\left((1+R)\,\text{Cos}[\theta]-(1-R)\,\text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$$



3.1.1.b. Anti-symmetric stretching vibration

"SSP Anti-symmetric Stretching-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

$$\chi^{(2)\,as}_{y,y,z} = \mathrm{Expand}\Big[\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,(\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]+\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{a,a,a} - 2\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]\,(\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]+\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{a,a,a} - \mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{a,a,a} - \mathrm{Cos}[\phi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]\,(\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]+\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{a,c,a} - \mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{a,c,a} - \mathrm{Cos}[\phi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]\,(\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]+\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{c,a,a} - \mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{c,a,a}\Big]$$

$$= -2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]^3\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\beta_{a,a,a} - 3\,\mathrm{Cos}[\theta]^2\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,\beta_{a,a,a} + 3\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]\,\beta_{a,a,a} + 6\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,a} + \mathrm{Cos}[\theta]^2\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a} - \mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{a,c,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{c,a,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{c,a,a}$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\,\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\big(-2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]^3\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\beta_{a,a,a} - 3\,\mathrm{Cos}[\theta]^2\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,\beta_{a,a,a} + 3\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]\,\beta_{a,a,a} + 6\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,a} + \mathrm{Cos}[\theta]^2\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a} - \mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{a,c,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{c,a,a} - \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{c,a,a}\big)\,d\phi\,d\psi\right)$$

$$= -\frac{1}{2}\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,N_s\,(\beta_{a,c,a}+\beta_{c,a,a})$$

$$= -\frac{1}{2}\,\mathrm{Cos}[\theta]\,\left(1-\mathrm{Cos}[\theta]^2\right)\,N_s\,(\beta_{a,c,a}+\beta_{c,a,a})$$

$$= -\frac{1}{2}\,\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\,N_s\,(\beta_{a,c,a}+\beta_{c,a,a})$$

"Isotropic Interface--> $\beta_{c,a,a}=\beta_{a,c,a}$"

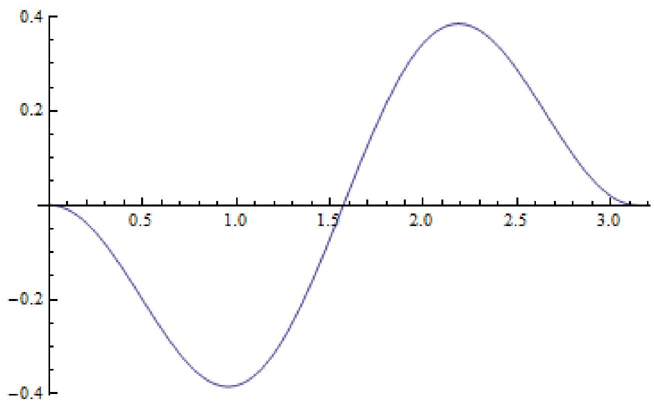
$$\boxed{\chi^{(2)\,as}_{y,y,z} = -N_s\,\beta_{a,c,a}\,\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

Plot$[-N_s\,\beta_{a,c,a}\,(\text{Cos}[\theta] - \text{Cos}[\theta]^3),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}]$



3.1.2. C_{2v} symmetry molecules

3.1.2.a. Symmetric stretching vibration

"SSP Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{b,b,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{y,y,z} = \text{Expand}\Big[\cos[\theta]\,(\cos[\psi]\sin[\phi] + \cos[\theta]\cos[\phi]\sin[\psi])^2\,\beta_{a,a,c} + \cos[\theta]\,(\cos[\theta]\cos[\phi]\cos[\psi] - \sin[\phi]\sin[\psi])^2\,\beta_{b,b,c} + \cos[\theta]\cos[\phi]^2\sin[\theta]^2\,\beta_{c,c,c}\Big]$$

$$= \cos[\theta]\cos[\psi]^2\sin[\phi]^2\,\beta_{a,a,c} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{a,a,c} + \cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\,\beta_{a,a,c} + \cos[\theta]^3\cos[\phi]^2\cos[\psi]^2\,\beta_{b,b,c} - 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{b,b,c} + \cos[\theta]\sin[\phi]^2\sin[\psi]^2\,\beta_{b,b,c} + \cos[\theta]\cos[\phi]^2\sin[\theta]^2\,\beta_{c,c,c}$$

$$= \cos[\theta]\cos[\psi]^2\sin[\phi]^2\,\beta_{a,a,c} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{a,a,c} + \cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\,\beta_{a,a,c} + \cos[\theta]^3\cos[\phi]^2\cos[\psi]^2\,\beta_{b,b,c} - 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{b,b,c} + \cos[\theta]\sin[\phi]^2\sin[\psi]^2\,\beta_{b,b,c} + \cos[\theta]\cos[\phi]^2\,\beta_{c,c,c} - \cos[\theta]^3\cos[\phi]^2\,\beta_{c,c,c}$$

$$= \left(\sin[\phi]^2\cos[\psi]^2\,\beta_{a,a,c} + \sin[\phi]^2\sin[\psi]^2\,\beta_{b,b,c} + \cos[\phi]^2\,\beta_{c,c,c}\right)\cos[\theta] + 2\,(\beta_{a,a,c} - \beta_{b,b,c})\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi] + \left(\cos[\phi]^2\sin[\psi]^2\,\beta_{a,a,c} + \cos[\phi]^2\cos[\psi]^2\,\beta_{b,b,c} - \cos[\phi]^2\,\beta_{c,c,c}\right)\cos[\theta]^3$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\,\mathrm{Cos}[\theta]\left(\int_0^{2\pi}\left(\left(\mathrm{Sin}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{a,a,c}+\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{b,b,c}+\mathrm{Cos}[\phi]^2\,\beta_{c,c,c}\right)\right)d\phi\right)+$$
$$\frac{N_s}{2\pi}\,2\,\mathrm{Cos}[\theta]^2\left(\int_0^{2\pi}\left(\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\left(\beta_{a,a,c}-\beta_{b,b,c}\right)\right)d\phi\right)+$$
$$\frac{N_s}{2\pi}\,\mathrm{Cos}[\theta]^3\left(\int_0^{2\pi}\left(\left(\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\mathrm{Cos}[\phi]^2\,\beta_{c,c,c}\right)\right)d\phi\right)$$

$$=\frac{1}{2}\,\mathrm{Cos}[\theta]^3\,N_s\,\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)+\frac{1}{2}\,\mathrm{Cos}[\theta]\,N_s\,\left(\mathrm{Cos}[\psi]^2\,\beta_{a,a,c}+\mathrm{Sin}[\psi]^2\,\beta_{b,b,c}+\beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{Y,Y,Z}=\frac{1}{2}\,N_s\,\left(\mathrm{Cos}[\psi]^2\,\beta_{a,a,c}+\mathrm{Sin}[\psi]^2\,\beta_{b,b,c}+\beta_{c,c,c}\right)\mathrm{Cos}[\theta]+\frac{1}{2}\,N_s\,\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)\mathrm{Cos}[\theta]^3}$$

"Plot"

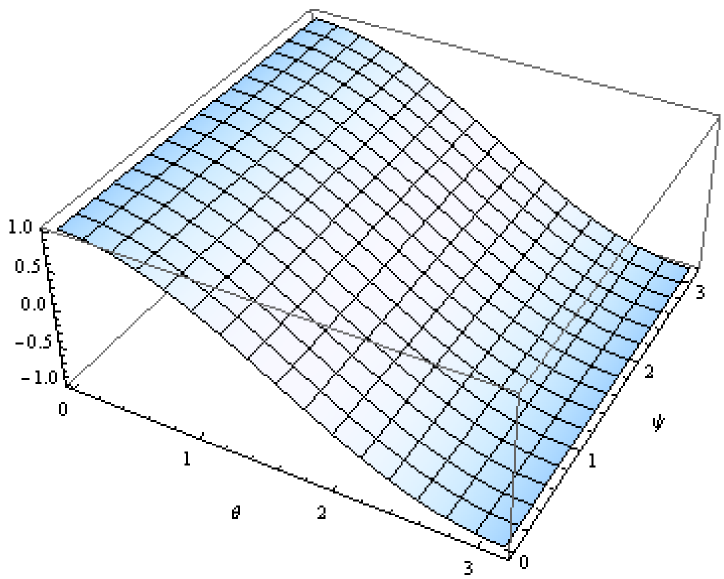
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 1$

$\beta_{c,c,c} = 1$

```
Plot3D[1/2 N_s (Cos[ψ]^2 β_{a,a,c} + Sin[ψ]^2 β_{b,b,c} + β_{c,c,c}) Cos[θ] +
  1/2 N_s (Sin[ψ]^2 β_{a,a,c} + Cos[ψ]^2 β_{b,b,c} - β_{c,c,c}) Cos[θ]^3,
  {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
  AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)-Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2}\,N_s\left(\text{Cos}[\psi]^2\,\beta_{a,a,c}+\text{Sin}[\psi]^2\,\beta_{b,b,c}+\beta_{c,c,c}\right)\text{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2}\,N_s\left(\text{Sin}[\psi]^2\,\beta_{a,a,c}+\text{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)\text{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{4}\,\text{Cos}[\theta]^3\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})+\frac{1}{4}\,\text{Cos}[\theta]\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}+2\,\beta_{c,c,c})$$

$$\boxed{\chi^{(2)\,ss}_{Y,Y,z}=\frac{1}{4}\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}+2\,\beta_{c,c,c})\,\text{Cos}[\theta]+\frac{1}{4}\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})\,\text{Cos}[\theta]^3}$$

```
"Plot"
```

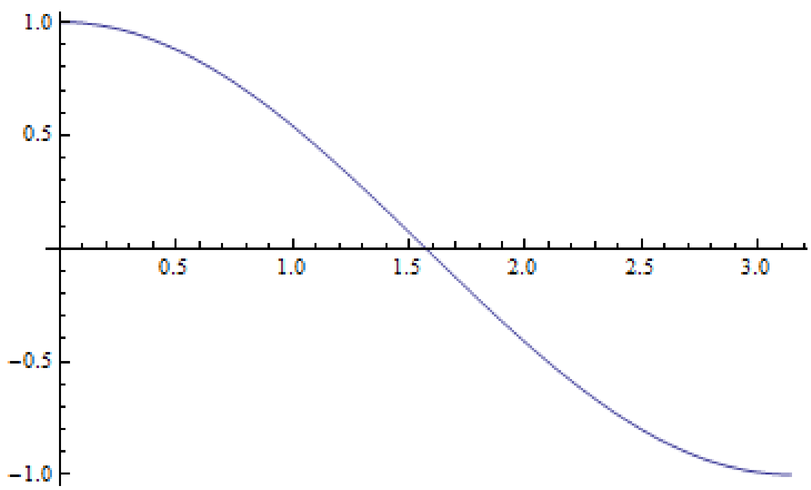
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 1$

$\beta_{c,c,c} = 1$

$$\text{Plot}\left[\frac{1}{4} N_s\,(\beta_{a,a,c} + \beta_{b,b,c} + 2\,\beta_{c,c,c})\,\text{Cos}[\theta] + \frac{1}{4} N_s\,(\beta_{a,a,c} + \beta_{b,b,c} - 2\,\beta_{c,c,c})\,\text{Cos}[\theta]^3,\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$$



3.1.2.b. Anti- symmetric stretching vibration

"SSP, B_1 Anti-symmetric Stretching-->$\beta_{a,c,a}$"

$$\chi^{(2)\,as,B_1}_{Y,Y,z} = \text{Expand}\left[-2\,\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi]+\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,c,a}\right]$$

$$= -2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} - 2\,\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

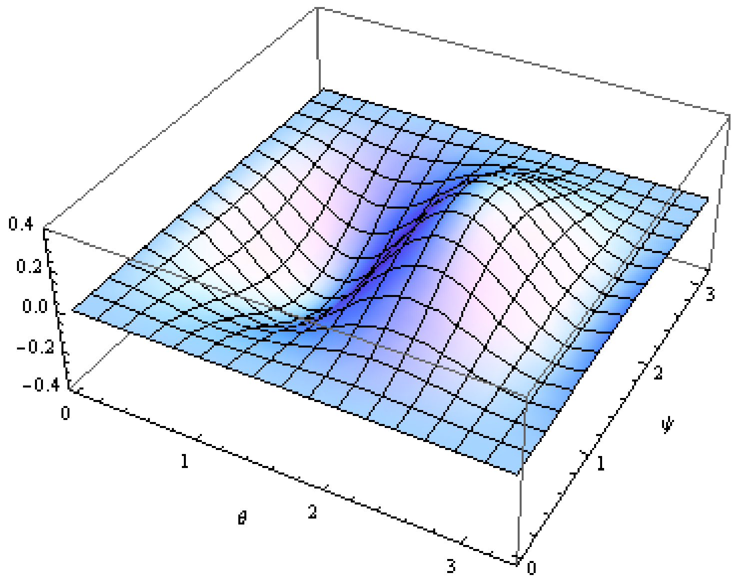
$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(-2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} - 2\,\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}\right)d\phi\right)$$

$$= -\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,N_s\,\beta_{a,c,a}$$

$$\boxed{\chi^{(2)\,as,B_1}_{Y,Y,z} = -N_s\,\beta_{a,c,a}\,\text{Sin}[\psi]^2\,\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

```
Nₛ = 1
β_{a,c,a} = 1
Plot3D[-Nₛ β_{a,c,a} Sin[ψ]^2 (Cos[θ] - Cos[θ]^3),
 {θ, 0 Degree, 190 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)-Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$= -\frac{1}{2}N_s\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\beta_{a,c,a}$$

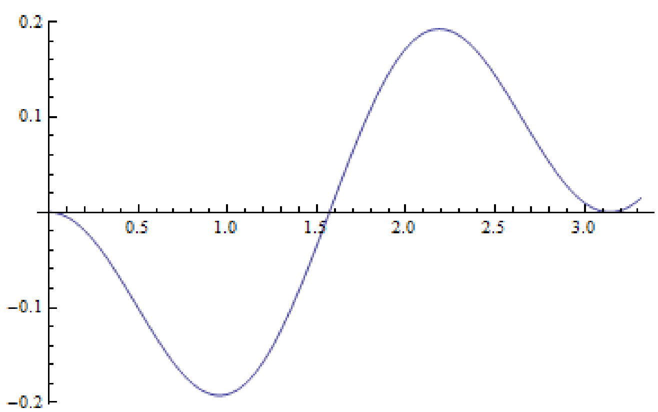
$$\boxed{\chi^{(2)\,as,B_1}_{Y,Y,Z} = -\frac{1}{2}N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

Plot$\left[-\frac{1}{2}N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 190\,\mathrm{Degree}\}\right]$



"SSP, B_2 Anti-symmetric Stretching-->$\beta_{b,c,b}$"

$\chi^{(2)\,as,B_2}_{Y,Y,z}$ =

Expand[$-2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2$
$(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi] - \mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{b,c,b}$]

$$= -2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{b,c,b} + 2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{b,c,b}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(-2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{b,c,b} + 2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{b,c,b}\right)d\phi\right)$$

$$= -\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,N_s\,\beta_{b,c,b}$$

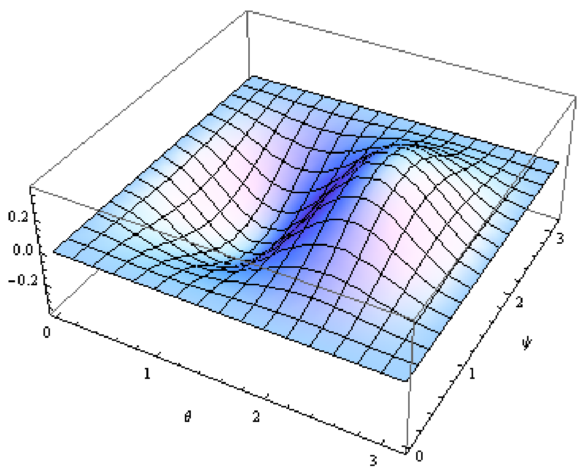
$$\boxed{\chi^{(2)\,as,B_2}_{Y,Y,z} = -N_s\,\beta_{b,c,b}\,\mathrm{Sin}[\psi]^2\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

Plot3D[$-N_s\,\beta_{b,c,b}\,\mathrm{Sin}[\psi]^2\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)$,
{θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
AxesLabel → {θ, ψ}]



"Average Over Orientation (ϕ,ψ)-Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-N_s\,\beta_{b,c,b}\,\text{Sin}[\psi]^2\,\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$=-\frac{1}{2}N_s\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\beta_{b,c,b}$$

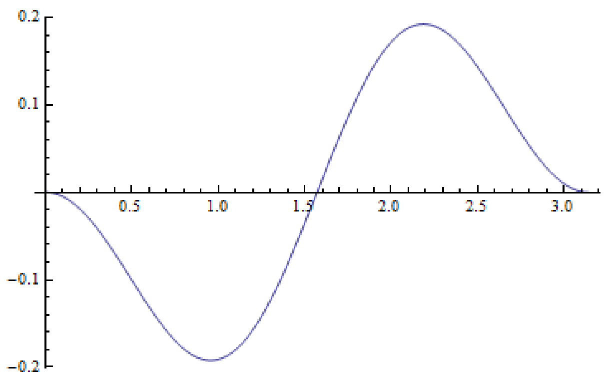
$$\boxed{\chi^{(2)\,as,B_2}_{Y,Y,z}=-\frac{1}{2}N_s\,\beta_{b,c,b}\,\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

$$\text{Plot}\left[-\frac{1}{2}N_s\,\beta_{b,c,b}\,\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$$



3.1.3. $C_{\infty v}$ symmetry molecules

3.1.3.a. Symmetric stretching vibration

"SSP Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{Y,Y,Z} =$$

$$\text{Expand}\left[\text{Cos}[\theta]\ (\text{Cos}[\psi]\ \text{Sin}[\phi] + \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ (\text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi] - \text{Sin}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]^2\ \beta_{c,c,c}\right]$$

$$= \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \text{Cos}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]^2\ \beta_{c,c,c}$$

$$= \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \left(\text{Cos}[\psi]^2 + \text{Sin}[\psi]^2\right)\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \left(\text{Cos}[\psi]^2 + \text{Sin}[\psi]^2\right)\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]^2\ \beta_{c,c,c}$$

$$= \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]^2\ \beta_{c,c,c}$$

$$= \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \left(1 - \text{Cos}[\theta]^2\right)\ \beta_{c,c,c}$$

$$= \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \beta_{c,c,c} - \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \beta_{c,c,c}$$

$$= \left(\text{Cos}[\phi]^2\ \beta_{c,c,c} + \text{Sin}[\phi]^2\ \beta_{a,a,c}\right)\ \text{Cos}[\theta] - (\beta_{c,c,c} - \beta_{a,a,c})\ \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2$$

$$= \beta_{c,c,c}\ \left(\left(\text{Cos}[\phi]^2 + \text{Sin}[\phi]^2\ \frac{\beta_{a,a,c}}{\beta_{c,c,c}}\right)\ \text{Cos}[\theta] - \left(1 - \frac{\beta_{a,a,c}}{\beta_{c,c,c}}\right)\ \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\right)$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{Y,Y,Z} = \beta_{c,c,c}\ \text{Cos}[\phi]^2\ \left(\left(1 + \left(\frac{\text{Sin}[\phi]}{\text{Cos}[\phi]}\right)^2 R\right)\ \text{Cos}[\theta] - (1 - R)\ \text{Cos}[\theta]^3\right)$$

"Average Over Orientation (ϕ)"

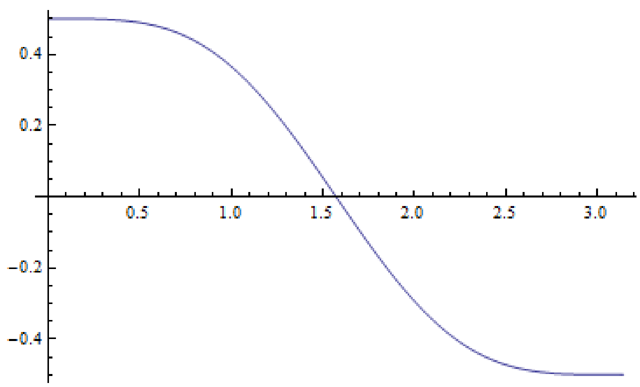
$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\beta_{c,c,c}\,\mathrm{Cos}[\phi]^2\left(\left(1+\left(\frac{\mathrm{Sin}[\phi]}{\mathrm{Cos}[\phi]}\right)^2 R\right)\mathrm{Cos}[\theta]-(1-R)\,\mathrm{Cos}[\theta]^3\right)\right)d\phi\right)$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\left(1+R+(-1+R)\,\mathrm{Cos}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{Y,Y,z}=\frac{1}{2}N_s\,\beta_{c,c,c}\left((1+R)\,\mathrm{Cos}[\theta]-(1-R)\,\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

```
Ns = 1
βc,c,c = 1
R = 0.5
Plot[1/2 Ns βc,c,c ((1 + R) Cos[θ] - (1 - R) Cos[θ]^3),
 {θ, 0 Degree, 180 Degree}]
```



3.2. The effective susceptibility of sps-polarization combination, $\chi_{sps} = \chi_{yzy}$

3.2.1. C_{3v} symmetry molecules

3.2.1.a. Symmetric stretching vibration

"SPS Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{y,z,y} = \text{Expand}\big[-\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi] + \text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,(\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}\big]$$

$$= -\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{y,z,y} = \beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)\right)d\phi\,d\psi\right)$$

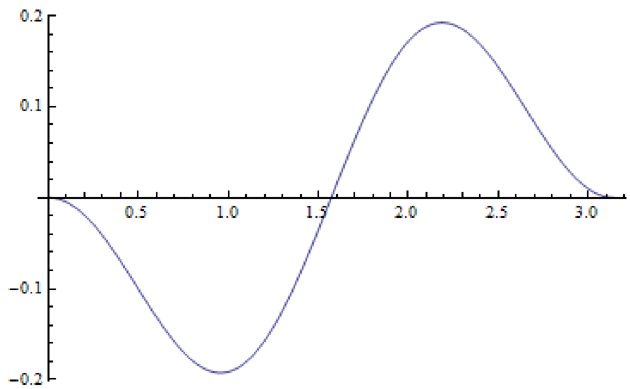
$$= -\frac{1}{2}\,(-1 + R)\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{y,z,y} = \frac{1}{2}\,N_s\,\beta_{c,c,c}\,(1 - R)\,\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

"Plot"

```
N_s = 1
β_{c,c,c} = 1
R = 2
```

$$\text{Plot}\left[\frac{1}{2} N_s\, \beta_{c,c,c}\, (1 - R)\, \left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$$



3.2.1.b. Anti- symmetric stretching vibration

"SPS Anti-symmetric Stretching-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

$$\chi^{(2)\,as}_{y,z,y} =$$

$$\text{Expand}\big[\text{Sin}[\theta]\ \text{Sin}[\psi]\ (\text{Cos}[\psi]\ \text{Sin}[\phi] + \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,a,a} - 2\ \text{Cos}[\psi]\ \text{Sin}[\theta]\ (\text{Cos}[\psi]\ \text{Sin}[\phi] + \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Sin}[\psi])\ (\text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi] - \text{Sin}[\phi]\ \text{Sin}[\psi])\ \beta_{a,a,a} - \text{Sin}[\theta]\ \text{Sin}[\psi]\ (\text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi] - \text{Sin}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,a,a} + \text{Cos}[\theta]\ (\text{Cos}[\psi]\ \text{Sin}[\phi] + \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,c,a} + \text{Cos}[\theta]\ (\text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi] - \text{Sin}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,c,a} - \text{Cos}[\phi]\ \text{Sin}[\theta]^2\ \text{Sin}[\psi]\ (\text{Cos}[\psi]\ \text{Sin}[\phi] + \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Sin}[\psi])\ \beta_{c,a,a} - \text{Cos}[\phi]\ \text{Cos}[\psi]\ \text{Sin}[\theta]^2\ (\text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi] - \text{Sin}[\phi]\ \text{Sin}[\psi])\ \beta_{c,a,a}\big]$$

$$= -2\ \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi]^3\ \text{Sin}[\theta]\ \text{Sin}[\phi]\ \beta_{a,a,a} - 3\ \text{Cos}[\theta]^2\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \text{Sin}[\theta]\ \text{Sin}[\psi]\ \beta_{a,a,a} + 3\ \text{Cos}[\psi]^2\ \text{Sin}[\theta]\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]\ \beta_{a,a,a} + 6\ \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi]\ \text{Sin}[\theta]\ \text{Sin}[\phi]\ \text{Sin}[\psi]^2\ \beta_{a,a,a} + \text{Cos}[\theta]^2\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]\ \text{Sin}[\psi]^3\ \beta_{a,a,a} - \text{Sin}[\theta]\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]^3\ \beta_{a,a,a} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \beta_{a,c,a} + \text{Cos}[\theta]\ \text{Cos}[\psi]^2\ \text{Sin}[\phi]^2\ \beta_{a,c,a} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,c,a} + \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,c,a} - \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \text{Sin}[\theta]^2\ \beta_{c,a,a} - \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]^2\ \text{Sin}[\psi]^2\ \beta_{c,a,a}$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\big(-2\ \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi]^3\ \text{Sin}[\theta]\ \text{Sin}[\phi]\ \beta_{a,a,a} - 3\ \text{Cos}[\theta]^2\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \text{Sin}[\theta]\ \text{Sin}[\psi]\ \beta_{a,a,a} + 3\ \text{Cos}[\psi]^2\ \text{Sin}[\theta]\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]\ \beta_{a,a,a} + 6\ \text{Cos}[\theta]\ \text{Cos}[\phi]\ \text{Cos}[\psi]\ \text{Sin}[\theta]\ \text{Sin}[\phi]\ \text{Sin}[\psi]^2\ \beta_{a,a,a} + \text{Cos}[\theta]^2\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]\ \text{Sin}[\psi]^3\ \beta_{a,a,a} - \text{Sin}[\theta]\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]^3\ \beta_{a,a,a} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \beta_{a,c,a} + \text{Cos}[\theta]\ \text{Cos}[\psi]^2\ \text{Sin}[\phi]^2\ \beta_{a,c,a} + \text{Cos}[\theta]^3\ \text{Cos}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,c,a} + \text{Cos}[\theta]\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,c,a} - \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \text{Sin}[\theta]^2\ \beta_{c,a,a} - \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Sin}[\theta]^2\ \text{Sin}[\psi]^2\ \beta_{c,a,a}\big)\, d\phi\, d\psi\right)$$

$$= \frac{1}{4}\ \text{Cos}[\theta]\ N_s\ \big((3 + \text{Cos}[2\theta])\ \beta_{a,c,a} - 2\ \text{Sin}[\theta]^2\ \beta_{c,a,a}\big)$$

"Isotropic Interface--> $\beta_{c,a,a}=\beta_{a,c,a}$"

$\beta_{c,a,a} = \beta_{a,c,a}$

$\text{Simplify}\left[\frac{1}{4}\,\text{Cos}[\theta]\,N_s\,\left((3+\text{Cos}[2\,\theta])\,\beta_{a,c,a} - 2\,\text{Sin}[\theta]^2\,\beta_{c,a,a}\right)\right]$

$= \text{Cos}[\theta]^3\,N_s\,\beta_{a,c,a}$

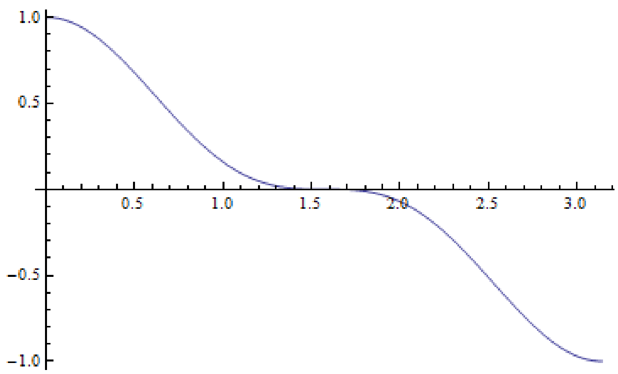
$\boxed{\chi^{(2)\,as}_{y,z,y} = N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$\text{Plot}\left[N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3,\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$



3.2.2. C_{2v} symmetry molecules

3.2.2.a. Symmetric stretching vibration

"SPS Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{b,b,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{Y,Z,Y} = \text{Expand}\Big[-\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi] + \text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,(\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}\Big]$$

$$= -\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{b,b,c} + \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$= -\text{Cos}[\phi]\,\text{Cos}[\psi]\,(1-\text{Cos}[\theta]^2)\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,(1-\text{Cos}[\theta]^2)\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,(1-\text{Cos}[\theta]^2)\,\beta_{b,b,c} + \text{Cos}[\phi]\,\text{Cos}[\psi]\,(1-\text{Cos}[\theta]^2)\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,(1-\text{Cos}[\theta]^2)\,\beta_{c,c,c}$$

$$= -\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} + \text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]^3\,\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{b,b,c} + \text{Cos}[\theta]^3\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{b,b,c} + \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} - \text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\beta_{c,c,c} - \text{Cos}[\theta]^3\,\text{Cos}[\phi]^2\,\beta_{c,c,c}$$

$$= -\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\beta_{a,a,c} - \beta_{b,b,c}) - \text{Cos}[\theta]\,(\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{b,b,c} - \text{Cos}[\phi]^2\,\beta_{c,c,c}) + \text{Cos}[\theta]^2\,(\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c}) + \text{Cos}[\theta]^3\,(\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{b,b,c} - \text{Cos}[\phi]^2\,\beta_{c,c,c})$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}(-\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,(\beta_{a,a,c}-\beta_{b,b,c}))\,d\phi\right)-$$
$$\frac{N_s}{2\pi}\mathrm{Cos}[\theta]\left(\int_0^{2\pi}\left(\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\mathrm{Cos}[\phi]^2\,\beta_{c,c,c}\right)d\phi\right)+$$
$$\frac{N_s}{2\pi}\mathrm{Cos}[\theta]^2\left(\int_0^{2\pi}(\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{a,a,c}-\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{b,b,c})\,d\phi\right)+$$
$$\frac{N_s}{2\pi}\mathrm{Cos}[\theta]^3\left(\int_0^{2\pi}\left(\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\mathrm{Cos}[\phi]^2\,\beta_{c,c,c}\right)d\phi\right)$$

$$=-\frac{1}{2}\mathrm{Cos}[\theta]\,N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)+\frac{1}{2}\mathrm{Cos}[\theta]^3\,N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{y,z,y}=-\frac{1}{2}N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

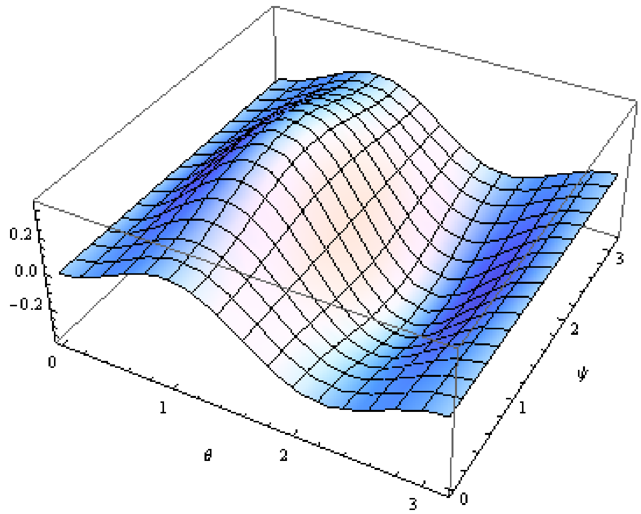
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 2$

$\beta_{c,c,c} = 3$

$$\text{Plot3D}\left[-\frac{1}{2}\ N_s\ \left(\text{Sin}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\psi]^2\ \beta_{b,b,c} - \beta_{c,c,c}\right)\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\},\ \{\psi,\ 0\,\text{Degree},\ 180\,\text{Degree}\},\ \text{AxesLabel} \to \{\theta,\ \psi\}\right]$$



"Average Over Orientation (ϕ,ψ)-Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2}N_s\left(\mathrm{Sin}[\psi]^2\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\beta_{b,b,c}-\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$=-\frac{1}{4}\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2 N_s^2\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})$$

$$\boxed{\chi^{(2)\,ss}_{y,z,y}=-\frac{1}{4}N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

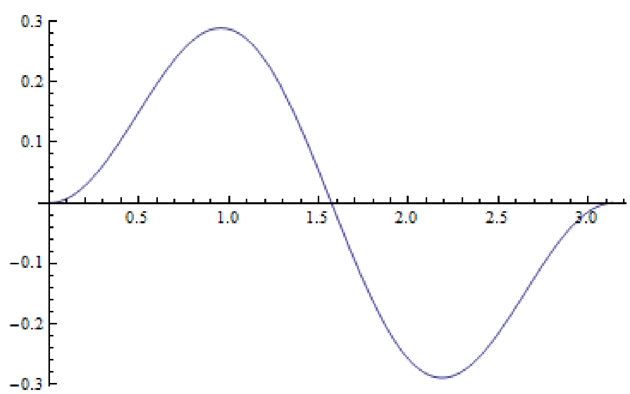
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 2$

$\beta_{c,c,c} = 3$

$$\mathrm{Plot}\left[-\frac{1}{4}N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



3.2.2.b. Anti- symmetric stretching vibration

"SPS, B_1 Anti-symmetric Stretching-->$\beta_{a,c,a}$"

$$\chi^{(2)\,as,B_1}_{Y,Z,Y} =$$

$$\text{Expand}\big[-\cos[\phi]\sin[\theta]^2\sin[\psi]\,(\cos[\psi]\sin[\phi]+\cos[\theta]\cos[\phi]\sin[\psi])\,\beta_{a,c,a} + \cos[\theta]\,(\cos[\psi]\sin[\phi]+\cos[\theta]\cos[\phi]\sin[\psi])^2\,\beta_{a,c,a}\big]$$

$$= \cos[\theta]\cos[\psi]^2\sin[\phi]^2\beta_{a,c,a} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} - \cos[\phi]\cos[\psi]\sin[\theta]^2\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a} - \cos[\theta]\cos[\phi]^2\sin[\theta]^2\sin[\psi]^2\beta_{a,c,a}$$

$$= \cos[\theta]\cos[\psi]^2\sin[\phi]^2\beta_{a,c,a} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} - \cos[\phi]\cos[\psi]\left(1-\cos[\theta]^2\right)\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a} - \cos[\theta]\cos[\phi]^2\left(1-\cos[\theta]^2\right)\sin[\psi]^2\beta_{a,c,a}$$

$$= \cos[\theta]\cos[\psi]^2\sin[\phi]^2\beta_{a,c,a} - \cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + 3\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} - \cos[\theta]\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a} + 2\cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a}$$

$$= -\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]\left(\cos[\psi]^2\sin[\phi]^2 - \sin[\psi]^2\cos[\phi]^2\right)\beta_{a,c,a} + 3\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + 2\cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a}$$

$$= -\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]\left(\cos[\psi]^2\left(1-\cos[\phi]^2\right) - \left(1-\cos[\psi]^2\right)\cos[\phi]^2\right)\beta_{a,c,a} + 3\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + 2\cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a}$$

$$= -\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]\left(\cos[\psi]^2 - \cos[\psi]^2\cos[\phi]^2 - \cos[\phi]^2 + \cos[\psi]^2\cos[\phi]^2\right)\beta_{a,c,a} + 3\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + 2\cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a}$$

$$= -\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]\left(\cos[\psi]^2 - \cos[\phi]^2\right)\beta_{a,c,a} + 3\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + 2\cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\beta_{a,c,a}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}(-\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{a,c,a})\,d\phi\right)+$$
$$\frac{N_s}{2\pi}\mathrm{Cos}[\theta]\left(\int_0^{2\pi}\left(\left(\mathrm{Cos}[\psi]^2-\mathrm{Cos}[\phi]^2\right)\beta_{a,c,a}\right)d\phi\right)+$$
$$\frac{N_s}{2\pi}\mathrm{Cos}[\theta]^2\left(\int_0^{2\pi}(\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{a,c,a})\,d\phi\right)+$$
$$\frac{N_s}{2\pi}2\,\mathrm{Cos}[\theta]^3\left(\int_0^{2\pi}\left(\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}\right)d\phi\right)$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\,\mathrm{Cos}[2\psi]\,N_s\,\beta_{a,c,a}+\mathrm{Cos}[\theta]^3\,\mathrm{Sin}[\psi]^2\,N_s\,\beta_{a,c,a}$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)N_s\,\beta_{a,c,a}+\mathrm{Cos}[\theta]^3\,\mathrm{Sin}[\psi]^2\,N_s\,\beta_{a,c,a}$$

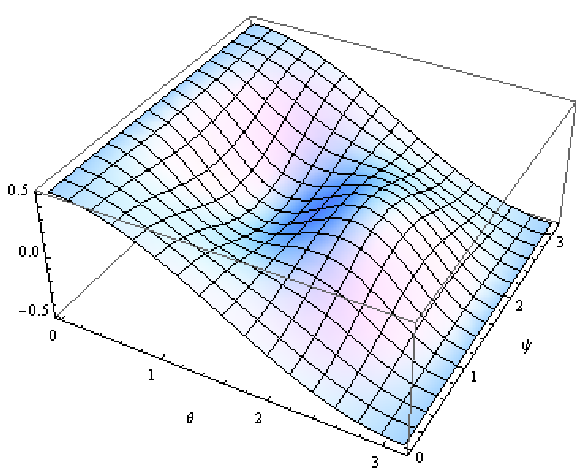
$$\boxed{\chi_{Y,z,Y}^{(2)\,as,B_1}=\frac{1}{2}N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$$\mathrm{Plot3D}\left[\frac{1}{2}N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\,\mathrm{Cos}[\theta]^3,\right.$$
$$\{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\},\ \{\psi,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\},$$
$$\left.\mathrm{AxesLabel}\rightarrow\{\theta,\ \psi\}\right]$$



"Average Over Orientation (ϕ,ψ)-Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2}N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\,\mathrm{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]^3\,N_s\,\beta_{a,c,a}$$

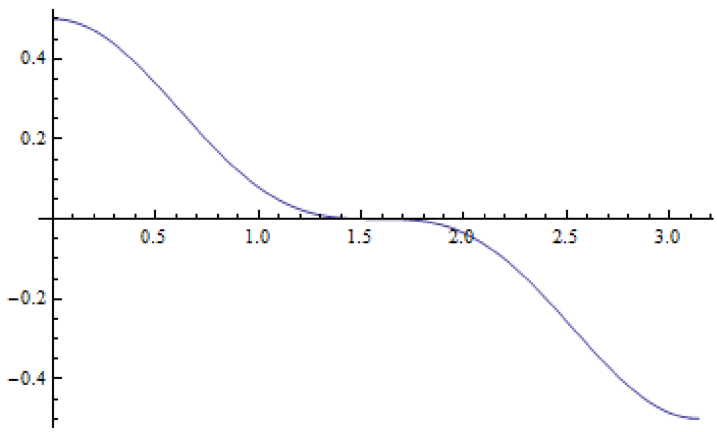
$$\boxed{\chi^{(2)\,as,B_1}_{Y,z,Y}=\frac{1}{2}N_s\,\beta_{a,c,a}\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$$\mathrm{Plot}\left[\frac{1}{2}N_s\,\beta_{a,c,a}\,\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



"SPS, B_2 Anti-symmetric Stretching-->$\beta_{b,c,b}$"

$$\chi^{(2)\,as,B_2}_{Y,z,Y} =$$
$$-\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{b,c,b}+\mathrm{Cos}[\theta]\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{b,c,b}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

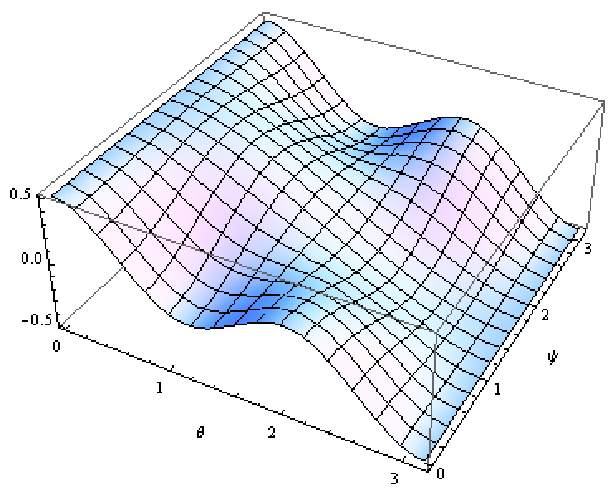
$$\boxed{\chi^{(2)\,as,B_2}_{Y,z,Y} = -\frac{1}{2}N_s\,\beta_{b,c,b}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

$$\mathrm{Plot3D}\left[-\frac{1}{2}N_s\,\beta_{b,c,b}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\},\ \{\psi,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\},\ \mathrm{AxesLabel}\to\{\theta,\ \psi\}\right]$$



"Average Over Orientation (ϕ,ψ)-Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2}N_s\,\beta_{b,c,b}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]^3\,N_s\,\beta_{b,c,b}$$

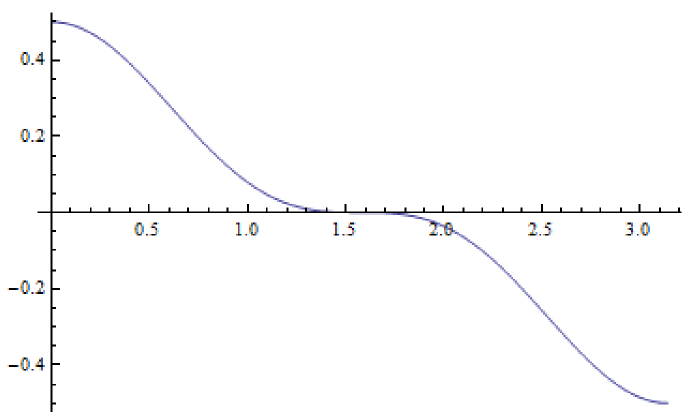
$$\boxed{\chi^{(2)\,as,B_2}_{Y,z,Y}=\frac{1}{2}N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

Plot$\left[\frac{1}{2}N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$



3.2.3. $C_{\infty v}$ symmetry molecules

3.2.3.a. Symmetric stretching vibration

"SPS Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{Y,Z,Y} =$$
$$\text{Expand}[-\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi]+\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,(\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi]-\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}]$$

$$= -\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{Y,Z,Y} = \beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)\right)d\phi\,d\psi\right)$$

$$= -\frac{1}{2}(-1+R)\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{Y,Z,Y} = \frac{1}{2}N_s\,\beta_{c,c,c}\,(1-R)\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

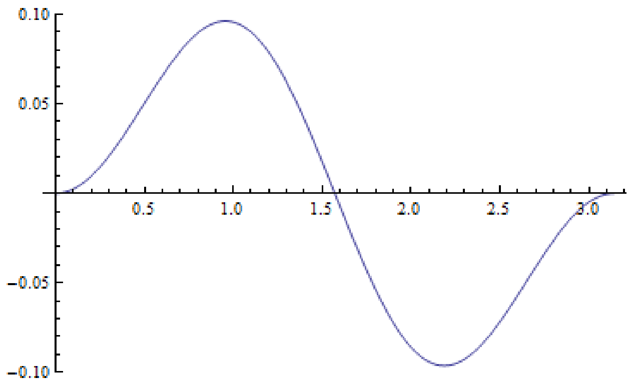
$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 0.5$

```
Plot[1/2 Ns β_{c,c,c} (1 - R) (Cos[θ] - Cos[θ]^3), {θ, 0 Degree, 180 Degree}]
```

$$\text{Plot}\left[\frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R)\, \left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$$



3.3. The effective susceptibility of pss-polarization combination, $\chi_{pss} = \chi_{zyy}$

3.3.1. C_{3v} symmetry molecules

3.3.1.a. Symmetric stretching vibration

"PSS Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{z,Y,Y} = \text{Expand}\big[-\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi] + \text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,(\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}\big]$$

$$= -\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{z,Y,Y} = \beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)\right)d\phi\,d\psi\right)$$

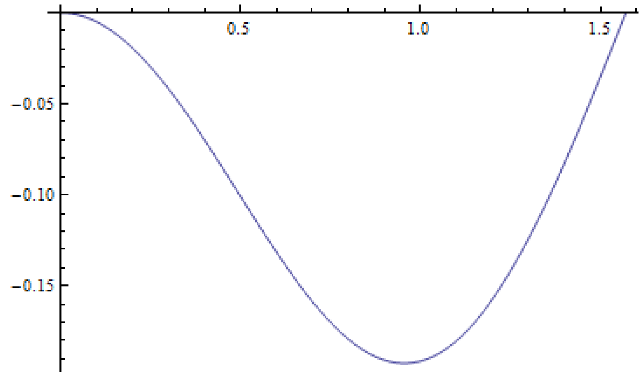
$$= -\frac{1}{2}\,(-1 + R)\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{z,Y,Y} = \frac{1}{2}\,N_s\,\beta_{c,c,c}\,(1 - R)\,\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

"Plot"

```
N_s = 1
β_{c,c,c} = 1
R = 2
```

$$\text{Plot}\left[\frac{1}{2} N_s \beta_{c,c,c} (1 - R) \left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right), \{\theta, 0\,\text{Degree}, 90\,\text{Degree}\}\right]$$



3.3.1.b. Anti- symmetric stretching vibration

"SPS Anti-symmetric Stretching-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

$$
\begin{aligned}
\chi^{(2)\,as}_{z,y,y} = \ & \text{Expand}\big[\sin[\theta]\sin[\psi]\,(\cos[\psi]\sin[\phi]+\cos[\theta]\cos[\phi]\sin[\psi])^2\,\beta_{a,a,a} - \\
& 2\cos[\psi]\sin[\theta]\,(\cos[\psi]\sin[\phi]+\cos[\theta]\cos[\phi]\sin[\psi]) \\
& (\cos[\theta]\cos[\phi]\cos[\psi]-\sin[\phi]\sin[\psi])\,\beta_{a,a,a} - \\
& \sin[\theta]\sin[\psi]\,(\cos[\theta]\cos[\phi]\cos[\psi]-\sin[\phi]\sin[\psi])^2\,\beta_{a,a,a} - \\
& \cos[\phi]\sin[\theta]^2\sin[\psi]\,(\cos[\psi]\sin[\phi]+\cos[\theta]\cos[\phi]\sin[\psi])\,\beta_{a,c,a} - \\
& \cos[\phi]\cos[\psi]\sin[\theta]^2\,(\cos[\theta]\cos[\phi]\cos[\psi]-\sin[\phi]\sin[\psi])\,\beta_{a,c,a} + \\
& \cos[\theta]\,(\cos[\psi]\sin[\phi]+\cos[\theta]\cos[\phi]\sin[\psi])^2\,\beta_{c,a,a} + \\
& \cos[\theta]\,(\cos[\theta]\cos[\phi]\cos[\psi]-\sin[\phi]\sin[\psi])^2\,\beta_{c,a,a}\big]
\end{aligned}
$$

$$
\begin{aligned}
= \ & -2\cos[\theta]\cos[\phi]\cos[\psi]^3\sin[\theta]\sin[\phi]\,\beta_{a,a,a} - \\
& 3\cos[\theta]^2\cos[\phi]^2\cos[\psi]^2\sin[\theta]\sin[\psi]\,\beta_{a,a,a} + \\
& 3\cos[\psi]^2\sin[\theta]\sin[\phi]^2\sin[\psi]\,\beta_{a,a,a} + \\
& 6\cos[\theta]\cos[\phi]\cos[\psi]\sin[\theta]\sin[\phi]\sin[\psi]^2\,\beta_{a,a,a} + \\
& \cos[\theta]^2\cos[\phi]^2\sin[\theta]\sin[\psi]^3\,\beta_{a,a,a} - \sin[\theta]\sin[\phi]^2\sin[\psi]^3\,\beta_{a,a,a} - \\
& \cos[\theta]\cos[\phi]^2\cos[\psi]^2\sin[\theta]^2\,\beta_{a,c,a} - \\
& \cos[\theta]\cos[\phi]^2\sin[\theta]^2\sin[\psi]^2\,\beta_{a,c,a} + \cos[\theta]^3\cos[\phi]^2\cos[\psi]^2\,\beta_{c,a,a} + \\
& \cos[\theta]\cos[\psi]^2\sin[\phi]^2\,\beta_{c,a,a} + \cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\,\beta_{c,a,a} + \\
& \cos[\theta]\sin[\phi]^2\sin[\psi]^2\,\beta_{c,a,a}
\end{aligned}
$$

"Average Over Orientation (ϕ,ψ)"

$$
\begin{aligned}
\frac{N_s}{(2\pi)^2}\Bigg(\int_0^{2\pi}\!\!\int_0^{2\pi} \big(& -2\cos[\theta]\cos[\phi]\cos[\psi]^3\sin[\theta]\sin[\phi]\,\beta_{a,a,a} - \\
& 3\cos[\theta]^2\cos[\phi]^2\cos[\psi]^2\sin[\theta]\sin[\psi]\,\beta_{a,a,a} + \\
& 3\cos[\psi]^2\sin[\theta]\sin[\phi]^2\sin[\psi]\,\beta_{a,a,a} + \\
& 6\cos[\theta]\cos[\phi]\cos[\psi]\sin[\theta]\sin[\phi]\sin[\psi]^2\,\beta_{a,a,a} + \\
& \cos[\theta]^2\cos[\phi]^2\sin[\theta]\sin[\psi]^3\,\beta_{a,a,a} - \\
& \sin[\theta]\sin[\phi]^2\sin[\psi]^3\,\beta_{a,a,a} - \\
& \cos[\theta]\cos[\phi]^2\cos[\psi]^2\sin[\theta]^2\,\beta_{a,c,a} - \\
& \cos[\theta]\cos[\phi]^2\sin[\theta]^2\sin[\psi]^2\,\beta_{a,c,a} + \\
& \cos[\theta]^3\cos[\phi]^2\cos[\psi]^2\,\beta_{c,a,a} + \cos[\theta]\cos[\psi]^2\sin[\phi]^2\,\beta_{c,a,a} + \\
& \cos[\theta]^3\cos[\phi]^2\sin[\psi]^2\,\beta_{c,a,a} + \cos[\theta]\sin[\phi]^2\sin[\psi]^2\,\beta_{c,a,a}\big) \\
& d\phi\, d\psi\Bigg)
\end{aligned}
$$

$$
= \frac{1}{4}\cos[\theta]\,N_s\,\big(-2\sin[\theta]^2\,\beta_{a,c,a} + (3+\cos[2\theta])\,\beta_{c,a,a}\big)
$$

"Isotropic Interface--> $\beta_{c,a,a}=\beta_{a,c,a}$"

$\beta_{c,a,a} = \beta_{a,c,a}$

Simplify$\left[\frac{1}{4} \mathrm{Cos}[\theta]\, N_s \left(-2\,\mathrm{Sin}[\theta]^2 \beta_{a,c,a} + (3 + \mathrm{Cos}[2\,\theta])\, \beta_{c,a,a}\right)\right]$

$= \mathrm{Cos}[\theta]^3\, N_s\, \beta_{a,c,a}$

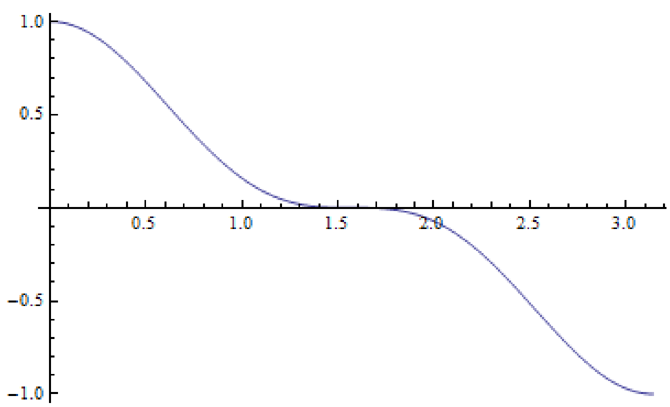
$\boxed{\chi^{(2)\,as}_{z,y,y} = N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3}$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

Plot$[N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}]$



3.3.2. C_{2v} symmetry molecules

3.3.2.a. Symmetric stretching vibration

"SSP Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{b,b,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{z,y,y} = \text{Expand}\Big[-\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi] + \text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,(\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}\Big]$$

$$= -\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{b,b,c} + \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\Big(-\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{b,b,c} + \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}\Big)\,d\phi\right)$$

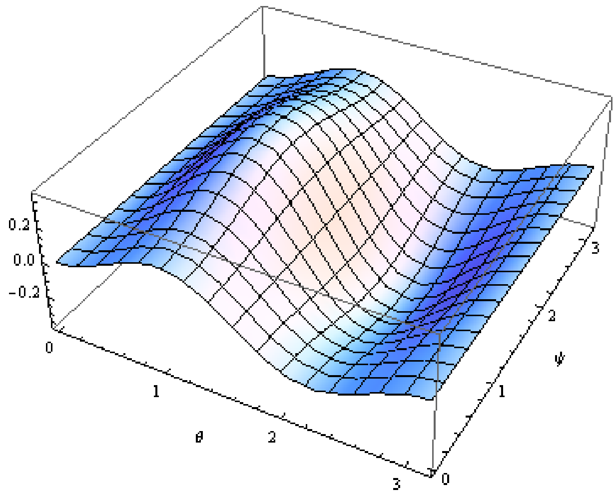
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\left(-\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\psi]^2\,\beta_{b,b,c} + \beta_{c,c,c}\right)$$

$$= \frac{1}{2}\,\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)\,N_s\,\left(-\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\psi]^2\,\beta_{b,b,c} + \beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{z,y,y} = -\frac{1}{2}\,N_s\,\left(\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\psi]^2\,\beta_{b,b,c} - \beta_{c,c,c}\right)\,\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

```
"Plot"

Ns = 1
βa,a,c = 1
βb,b,c = 2
βc,c,c = 3
Plot3D[-1/2 Ns (Sin[ψ]^2 βa,a,c + Cos[ψ]^2 βb,b,c - βc,c,c) (Cos[θ] - Cos[θ]^3),
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ) - Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2}\,N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$= -\frac{1}{4}\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})$$

$$\boxed{\chi^{(2)\,ss}_{z,y,y} = -\frac{1}{4}\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

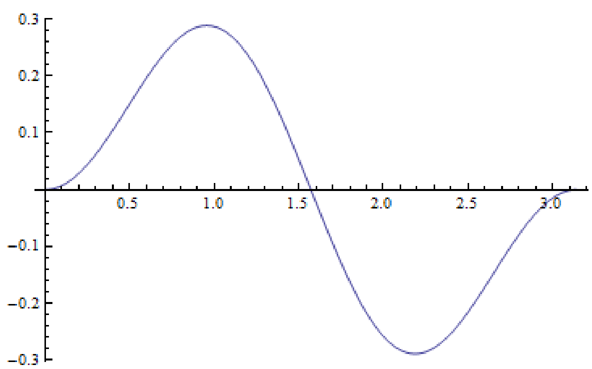
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 2$

$\beta_{c,c,c} = 3$

$$\mathrm{Plot}\left[-\frac{1}{4}\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



3.3.2.b. Anti- symmetric stretching vibration

"PSS, B_1 Anti-symmetric Stretching-->$\beta_{a,c,a}$"

$$\chi^{(2)\,as,B_1}_{z,y,y} = $$

$$\text{Expand}\left[-\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi] + \text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,c,a} + \text{Cos}[\theta]\,(\text{Cos}[\psi]\,\text{Sin}[\phi] + \text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])^2\,\beta_{a,c,a}\right]$$

$$= \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\phi]^2\,\beta_{a,c,a} + 2\,\text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} + \text{Cos}[\theta]^3\,\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\phi]^2\,\beta_{a,c,a} + 2\,\text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} + \text{Cos}[\theta]^3\,\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}\right)d\phi\right)$$

$$= \frac{1}{2}\,\text{Cos}[\theta]\,\left(\text{Cos}[\psi]^2 + \text{Cos}[2\,\theta]\,\text{Sin}[\psi]^2\right)\,N_s\,\beta_{a,c,a}$$

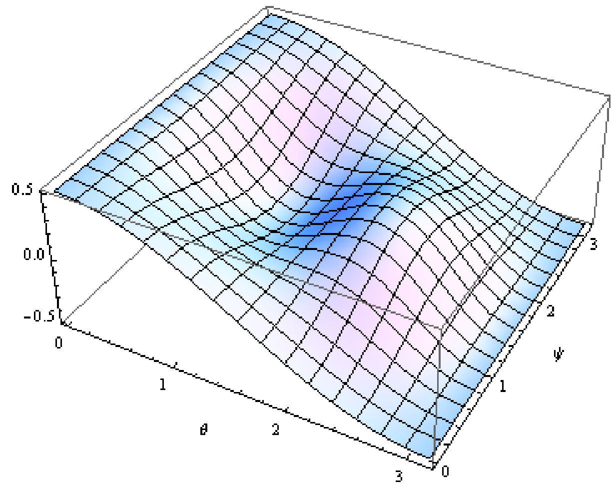
$$= \frac{1}{2}\,\left(\text{Cos}[\theta]\,\text{Cos}[\psi]^2 + \text{Cos}[\theta]^3\,\text{Sin}[\psi]^2 - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\right)\,N_s\,\beta_{a,c,a}$$

$$= \frac{1}{2}\,\left(\text{Cos}[\theta]\,\left(\text{Cos}[\psi]^2 - \text{Sin}[\psi]^2\right) + 2\,\text{Cos}[\theta]^3\,\text{Sin}[\psi]^2\right)\,N_s\,\beta_{a,c,a}$$

$$\boxed{\chi^{(2)\,as,B_1}_{z,y,y} = \frac{1}{2}\,N_s\,\beta_{a,c,a}\,\left(\text{Cos}[\psi]^2 - \text{Sin}[\psi]^2\right)\,\text{Cos}[\theta] + N_s\,\beta_{a,c,a}\,\text{Sin}[\psi]^2\,\text{Cos}[\theta]^3}$$

"Plot"

```
N_s = 1
β_{a,c,a} = 1
Plot3D[1/2 N_s β_{a,c,a} (Cos[ψ]^2 - Sin[ψ]^2) Cos[θ] + N_s β_{a,c,a} Sin[ψ]^2 Cos[θ]^3,
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2} N_s\, \beta_{a,c,a}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\, \beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\,\mathrm{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2} N_s\,\mathrm{Cos}[\theta]^3\,\beta_{a,c,a}$$

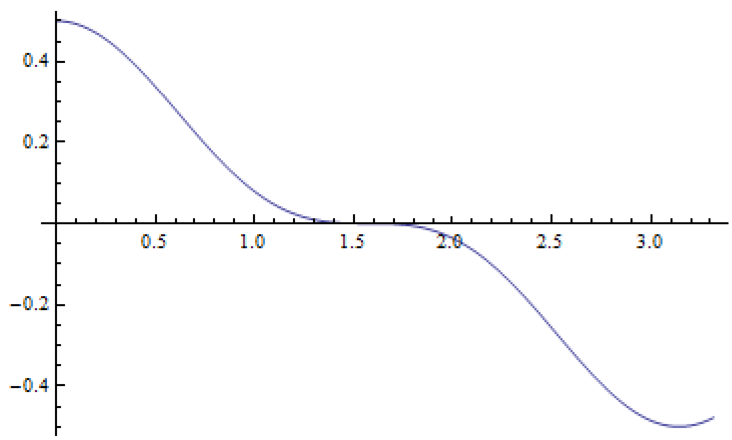
$$\boxed{\chi^{(2)\,as,B_1}_{z,y,y}=\frac{1}{2} N_s\,\beta_{a,c,a}\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$\mathrm{Plot}\left[\frac{1}{2} N_s\, \beta_{a,c,a}\,\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 190\,\mathrm{Degree}\}\right]$



"SSP, B_2 Anti-symmetric Stretching-->$\beta_{b,c,b}$"

$$\chi^{(2)\,as,B_2}_{Y,Y,z} =$$
$$-\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{b,c,b}+\mathrm{Cos}[\theta]\,(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{b,c,b}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

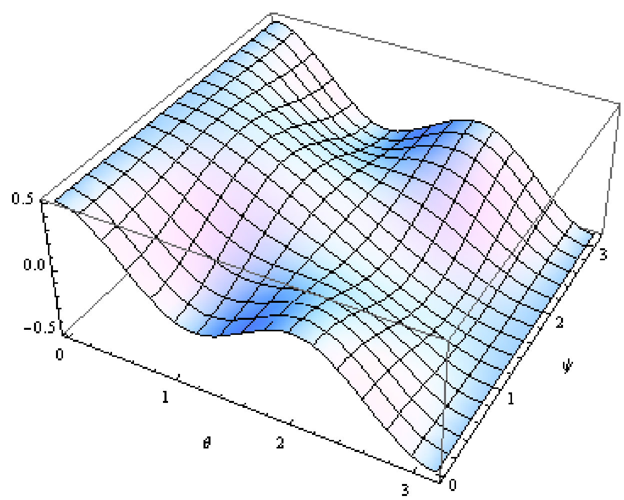
$$\boxed{\chi^{(2)\,as,B_2}_{z,Y,Y} = -\frac{1}{2}\,N_s\,\beta_{b,c,b}\,\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

$$\mathrm{Plot3D}\Big[-\frac{1}{2}\,N_s\,\beta_{b,c,b}\,\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\},\ \{\psi,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\},\ \mathrm{AxesLabel}\to\{\theta,\ \psi\}\Big]$$



"Average Over Orientation (ϕ,ψ) - Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2}N_s\,\beta_{b,c,b}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2}N_s\,\mathrm{Cos}[\theta]^3\,\beta_{b,c,b}$$

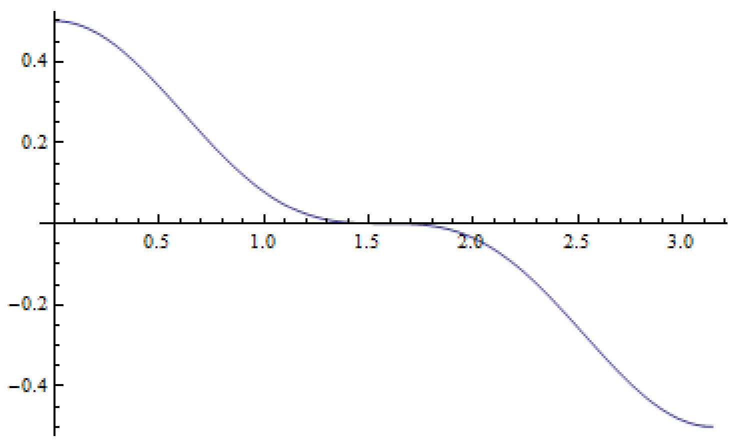
$$\boxed{\chi^{(2)\,as,B_2}_{z,y,y}=\frac{1}{2}N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

$\mathrm{Plot}\left[\frac{1}{2}N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$



3.3.3. C$_{\infty v}$ symmetry molecules

3.3.3.a. Symmetric stretching vibration

"PSS Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{z,y,y} =$$

$$\text{Expand}\big[-\text{Cos}[\phi]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]\,(\text{Cos}[\psi]\,\text{Sin}[\phi] + \text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,(\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}\big]$$

$$= -\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{z,y,y} = \beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)\right)d\phi\,d\psi\right)$$

$$= -\frac{1}{2}(-1 + R)\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{z,y,y} = \frac{1}{2}N_s\,\beta_{c,c,c}\,(1 - R)\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

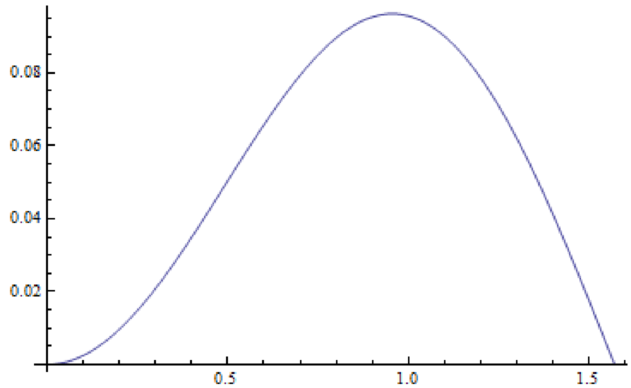
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 0.5$

$\text{Plot}\left[\frac{1}{2} N_s \beta_{c,c,c} (1 - R) \left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right), \{\theta, 0\,\text{Degree}, 90\,\text{Degree}\}\right]$



3.4. The effective susceptibility of ppp-polarization combination, χ_{ppp}

3.4.1. C_{3v} symmetry molecules

3.4.1.a. Symmetric stretching vibration

"PPP,xxz Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{x,x,z} =$$

$$\text{Expand}\big[+\text{Cos}[\theta]\ (-\text{Cos}[\theta]\ \text{Cos}[\psi]\ \text{Sin}[\phi] - \text{Cos}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ (\text{Cos}[\phi]\ \text{Cos}[\psi] - \text{Cos}[\theta]\ \text{Sin}[\phi]\ \text{Sin}[\psi])^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Sin}[\theta]^2\ \text{Sin}[\phi]^2\ \beta_{c,c,c}\big]$$

$$= \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Cos}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Sin}[\phi]^2\ \text{Cos}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Sin}[\phi]^2\ \text{Sin}[\psi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Sin}[\theta]^2\ \text{Sin}[\phi]^2\ \beta_{c,c,c}$$

$$= \text{Cos}[\theta]\ \text{Cos}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]^3\ \text{Sin}[\phi]^2\ \beta_{a,a,c} + \text{Cos}[\theta]\ \text{Sin}[\theta]^2\ \text{Sin}[\phi]^2\ \beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{x,x,z} =$$

$$\beta_{c,c,c}\ \left(\text{Cos}[\theta]\ \text{Cos}[\phi]^2\ R + \text{Cos}[\theta]^3\ \text{Sin}[\phi]^2\ R + \text{Cos}[\theta]\ \text{Sin}[\theta]^2\ \text{Sin}[\phi]^2\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2 R+\mathrm{Cos}[\theta]^3\,\mathrm{Sin}[\phi]^2 R+\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\right)\right)d\phi\, d\psi\right)$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\left(R+R\,\mathrm{Cos}[\theta]^2+\mathrm{Sin}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\left(R+R\,\mathrm{Cos}[\theta]^2+1-\mathrm{Cos}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

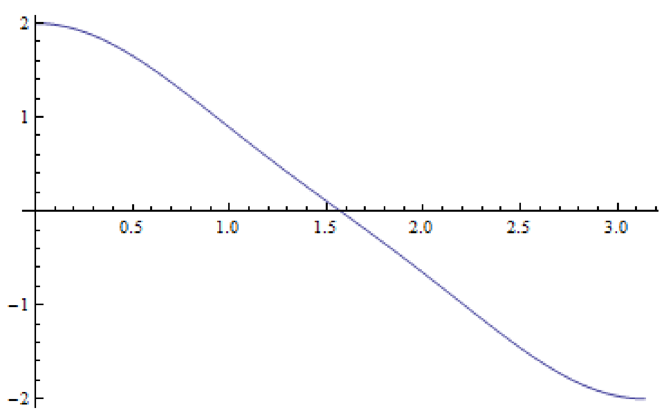
$$=\frac{1}{2}\mathrm{Cos}[\theta]\left((1+R)-(1-R)\,\mathrm{Cos}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{z,z,z}=\frac{1}{2}N_s\,\beta_{c,c,c}\left((1+R)\,\mathrm{Cos}[\theta]-(1-R)\,\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$
$\beta_{c,c,c} = 1$
$R = 2$

$$\mathrm{Plot}\left[\frac{1}{2}N_s\,\beta_{c,c,c}\left((1+R)\,\mathrm{Cos}[\theta]-(1-R)\,\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



"PPP,xzx Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{x,z,x} = \text{Expand}\Big[\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi] - \text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}\Big]$$

$$= -\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{x,z,x} = \beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,R - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,R-\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,R+\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\right)\right)d\phi\,d\psi\right)$$

$$=-\frac{1}{2}(-1+R)\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{x,z,x}=\frac{1}{2}N_s\,\beta_{c,c,c}\,(1-R)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

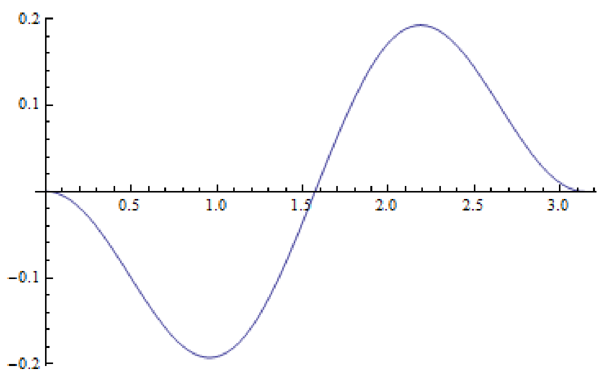
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 2$

$$\mathrm{Plot}\left[\frac{1}{2}N_s\,\beta_{c,c,c}\,(1-R)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



"PPP,zxx Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$\chi^{(2)\,ss}_{z,x,x}$ =
 Expand[
  Cos[ψ] Sin[θ]^2 Sin[ϕ] (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) $\beta_{a,a,c}$ +
   Sin[θ]^2 Sin[ϕ] Sin[ψ] (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) $\beta_{a,a,c}$ +
   Cos[θ] Sin[θ]^2 Sin[ϕ]^2 $\beta_{c,c,c}$]

= -Cos[θ] Cos[ψ]^2 Sin[θ]^2 Sin[ϕ]^2 $\beta_{a,a,c}$ -
  Cos[θ] Sin[θ]^2 Sin[ϕ]^2 Sin[ψ]^2 $\beta_{a,a,c}$ + Cos[θ] Sin[θ]^2 Sin[ϕ]^2 $\beta_{c,c,c}$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$\chi^{(2)\,ss}_{z,x,x}$ =
 $\beta_{c,c,c}$
  (-Cos[θ] Cos[ψ]^2 Sin[θ]^2 Sin[ϕ]^2 R -
    Cos[θ] Sin[θ]^2 Sin[ϕ]^2 Sin[ψ]^2 R + Cos[θ] Sin[θ]^2 Sin[ϕ]^2)

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,R-\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,R+\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\right)\right)d\phi\,d\psi\right)$$

$$=-\frac{1}{2}\,(-1+R)\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{z,x,x}=\frac{1}{2}\,N_s\,\beta_{c,c,c}\,(1-R)\,\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

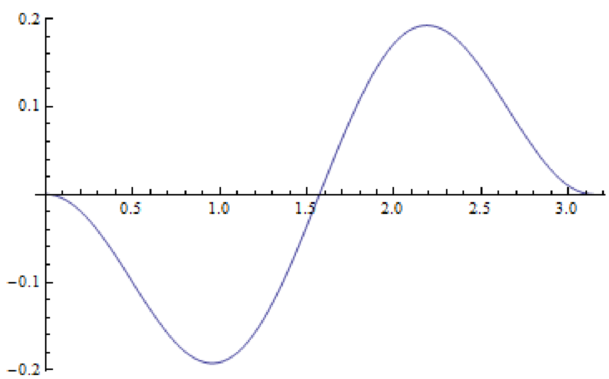
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 2$

$$\mathrm{Plot}\left[\frac{1}{2}\,N_s\,\beta_{c,c,c}\,(1-R)\,\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



"PPP,zzz Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{z,z,z} = \text{Expand}\left[\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]^3\,\beta_{c,c,c}\right]$$

$$= \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]^3\,\beta_{c,c,c}$$

$$= \text{Cos}[\theta]\,\text{Sin}[\theta]^2\left(\text{Cos}[\psi]^2 + \text{Sin}[\psi]^2\right)\beta_{a,a,c} + \text{Cos}[\theta]^3\,\beta_{c,c,c}$$

$$= \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\beta_{a,a,c} + \text{Cos}[\theta]^3\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{z,z,z} = \beta_{c,c,c}\left(\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,R + \text{Cos}[\theta]^3\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,R + \text{Cos}[\theta]^3\right)\right)d\phi\,d\psi\right)$$

$$= \left(\text{Cos}[\theta]^3 + R\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$= \left(\text{Cos}[\theta]^3 + R\,\text{Cos}[\theta] - R\,\text{Cos}[\theta]^3\right)N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{z,z,z} = N_s\,\beta_{c,c,c}\left(R\,\text{Cos}[\theta] + (1-R)\,\text{Cos}[\theta]^3\right)}$$

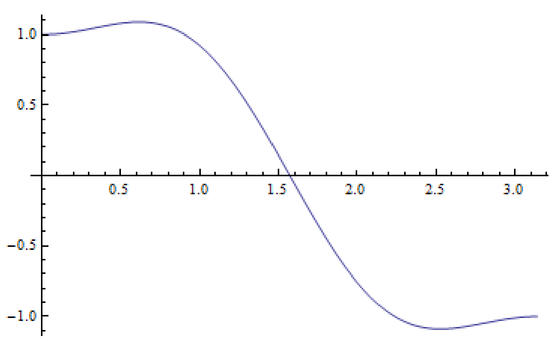
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 2$

Plot[$N_s\,\beta_{c,c,c}\left(R\,\text{Cos}[\theta] + (1-R)\,\text{Cos}[\theta]^3\right)$, {$\theta$, 0 Degree, 180 Degree}]



3.4.1.b. Anti- symmetric stretching vibration

"PPP,xxz Anti-symmetric Stretching-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

$$\chi^{(2)\,as}_{x,x,z} =$$

$$\text{Expand}\Big[-\text{Sin}[\theta]\,\text{Sin}[\psi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi]-\text{Cos}[\phi]\,\text{Sin}[\psi])^2\,\beta_{a,a,a}-2\,\text{Cos}[\psi]\,\text{Sin}[\theta]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi]-\text{Cos}[\phi]\,\text{Sin}[\psi])\,(\text{Cos}[\phi]\,\text{Cos}[\psi]-\text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,a}+\text{Sin}[\theta]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi]-\text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])^2\,\beta_{a,a,a}+\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi]-\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,c,a}+\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi]-\text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,c,a}+\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi]-\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{c,a,a}+\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi]-\text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{c,a,a}\Big]$$

$$= 2\,\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi]^3\,\text{Sin}[\theta]\,\text{Sin}[\phi]\,\beta_{a,a,a}+3\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]\,\text{Sin}[\psi]\,\beta_{a,a,a}-3\,\text{Cos}[\theta]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]\,\beta_{a,a,a}-6\,\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi]^2\,\beta_{a,a,a}-\text{Cos}[\phi]^2\,\text{Sin}[\theta]\,\text{Sin}[\psi]^3\,\beta_{a,a,a}+\text{Cos}[\theta]^2\,\text{Sin}[\theta]\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^3\,\beta_{a,a,a}-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{a,c,a}-\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,a,a}-\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{c,a,a}$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\big(2\,\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi]^3\,\text{Sin}[\theta]\,\text{Sin}[\phi]\,\beta_{a,a,a}+3\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]\,\text{Sin}[\psi]\,\beta_{a,a,a}-3\,\text{Cos}[\theta]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]\,\beta_{a,a,a}-6\,\text{Cos}[\theta]\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi]^2\,\beta_{a,a,a}-\text{Cos}[\phi]^2\,\text{Sin}[\theta]\,\text{Sin}[\psi]^3\,\beta_{a,a,a}+\text{Cos}[\theta]^2\,\text{Sin}[\theta]\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^3\,\beta_{a,a,a}-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{a,c,a}-\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,a,a}-\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{c,a,a}\big)\,d\phi\,d\psi\right)$$

$$= -\frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,(\beta_{a,c,a}+\beta_{c,a,a})$$

"Isotropic Interface--> $\beta_{c,a,a}=\beta_{a,c,a}$"

$\beta_{c,a,a} = \beta_{a,c,a}$

$$\text{Simplify}\left[-\frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,(\beta_{a,c,a}+\beta_{c,a,a})\right]$$

$$= -\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{a,c,a}$$

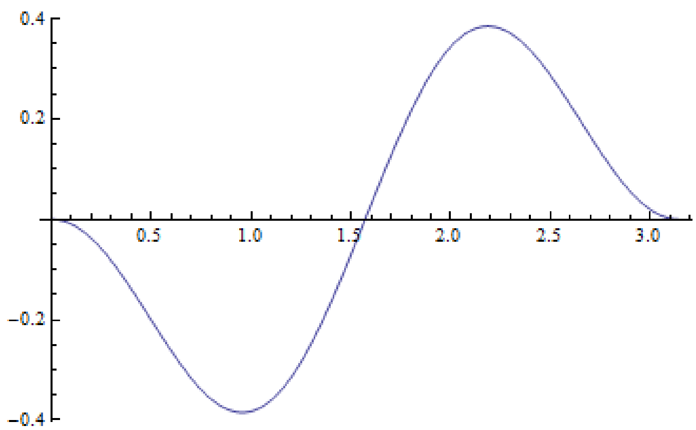
$$\boxed{\chi^{(2)\,as}_{x,x,z} = -N_s\,\beta_{a,c,a}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$$\text{Plot}\left[-N_s\,\beta_{a,c,a}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$$



"PPP,xzx Anti-symmetric Stretching-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

$$
\begin{aligned}
\chi^{(2)\,as}_{x,z,x} = {} & \mathrm{Expand}\Big[-\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]-\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])^2 \\
& \quad \beta_{a,a,a}-2\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]\,(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]-\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi]) \\
& \quad (\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{a,a,a}+ \\
& \quad \mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,(\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{a,a,a}+ \\
& \quad \mathrm{Cos}[\theta]\,(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]-\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{a,c,a}+ \\
& \quad \mathrm{Cos}[\theta]\,(\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])^2\,\beta_{a,c,a}+ \\
& \quad \mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]-\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi]) \\
& \quad \beta_{c,a,a}+\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi] \\
& \quad (\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{c,a,a}\Big]
\end{aligned}
$$

$$
\begin{aligned}
= {} & 2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]^3\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\beta_{a,a,a}+ \\
& 3\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,\beta_{a,a,a}- \\
& 3\,\mathrm{Cos}[\theta]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]\,\beta_{a,a,a}- \\
& 6\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,a}- \\
& \mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a}+\mathrm{Cos}[\theta]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a}+ \\
& \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{a,c,a}+\mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\phi]^2\,\beta_{a,c,a}+ \\
& \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}+\mathrm{Cos}[\theta]^3\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}- \\
& \mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\beta_{c,a,a}- \\
& \mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{c,a,a}
\end{aligned}
$$

"Average Over Orientation (ϕ,ψ)"

$$
\begin{aligned}
& \frac{N_s}{(2\pi)^2} \\
& \Big(\int_0^{2\pi}\int_0^{2\pi}\big(2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]^3\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\beta_{a,a,a}+ \\
& \qquad 3\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]\,\beta_{a,a,a}- \\
& \qquad 3\,\mathrm{Cos}[\theta]^2\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]\,\beta_{a,a,a}- \\
& \qquad 6\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,a}- \\
& \qquad \mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a}+ \\
& \qquad \mathrm{Cos}[\theta]^2\,\mathrm{Sin}[\theta]\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^3\,\beta_{a,a,a}+ \\
& \qquad \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{a,c,a}+\mathrm{Cos}[\theta]^3\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\phi]^2\,\beta_{a,c,a}+ \\
& \qquad \mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}+\mathrm{Cos}[\theta]^3\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}- \\
& \qquad \mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\beta_{c,a,a}- \\
& \qquad \mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{c,a,a}\big)\,d\phi\,d\psi\Big)
\end{aligned}
$$

$$
= \frac{1}{4}\,\mathrm{Cos}[\theta]\,N_s\,\big((3+\mathrm{Cos}[2\,\theta])\,\beta_{a,c,a}-2\,\mathrm{Sin}[\theta]^2\,\beta_{c,a,a}\big)
$$

"Isotropic Interface--> $\beta_{c,a,a}$=$\beta_{a,c,a}$"

$\beta_{c,a,a} = \beta_{a,c,a}$

Simplify$\left[\frac{1}{4}\, \mathrm{Cos}[\theta]\, N_s \left((3 + \mathrm{Cos}[2\,\theta])\, \beta_{a,c,a} - 2\, \mathrm{Sin}[\theta]^2\, \beta_{c,a,a}\right)\right]$

$= \mathrm{Cos}[\theta]^3\, N_s\, \beta_{a,c,a}$

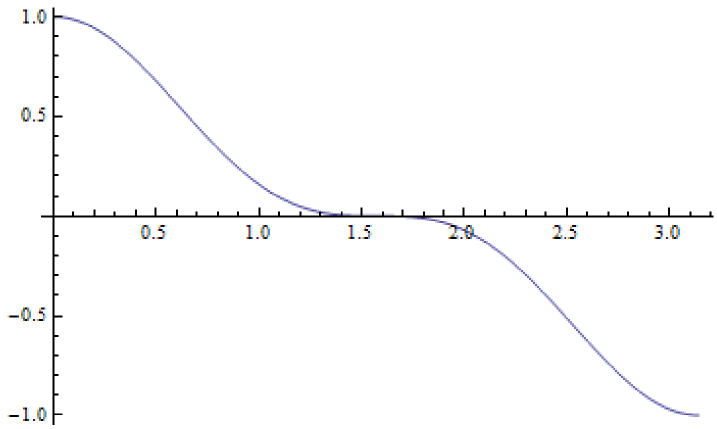
$\boxed{\chi^{(2)\,as}_{x,z,x} = N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3}$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

Plot$\left[N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3, \{\theta, 0\,\mathrm{Degree}, 180\,\mathrm{Degree}\}\right]$



"PPP,zxx Anti-symmetric Stretching-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

$$
\begin{aligned}
\chi^{(2)\,as}_{z,x,x} = \mathrm{Expand}\Big[& -\sin[\theta]\sin[\psi]\,(-\cos[\theta]\cos[\psi]\sin[\phi]-\cos[\phi]\sin[\psi])^2\,\beta_{a,a,a} - 2\cos[\psi]\sin[\theta]\,(-\cos[\theta]\cos[\psi]\sin[\phi]-\cos[\phi]\sin[\psi]) \\
& (\cos[\phi]\cos[\psi]-\cos[\theta]\sin[\phi]\sin[\psi])\,\beta_{a,a,a} + \\
& \sin[\theta]\sin[\psi]\,(\cos[\phi]\cos[\psi]-\cos[\theta]\sin[\phi]\sin[\psi])^2\,\beta_{a,a,a} + \\
& \cos[\psi]\sin[\theta]^2\sin[\phi]\,(-\cos[\theta]\cos[\psi]\sin[\phi]-\cos[\phi]\sin[\psi])\,\beta_{a,c,a} + \sin[\theta]^2\sin[\phi]\sin[\psi] \\
& (\cos[\phi]\cos[\psi]-\cos[\theta]\sin[\phi]\sin[\psi])\,\beta_{a,c,a} + \\
& \cos[\theta]\,(-\cos[\theta]\cos[\psi]\sin[\phi]-\cos[\phi]\sin[\psi])^2\,\beta_{c,a,a} + \\
& \cos[\theta]\,(\cos[\phi]\cos[\psi]-\cos[\theta]\sin[\phi]\sin[\psi])^2\,\beta_{c,a,a}\Big]
\end{aligned}
$$

$$
\begin{aligned}
= & \; 2\cos[\theta]\cos[\phi]\cos[\psi]^3\sin[\theta]\sin[\phi]\,\beta_{a,a,a} + \\
& 3\cos[\phi]^2\cos[\psi]^2\sin[\theta]\sin[\psi]\,\beta_{a,a,a} - \\
& 3\cos[\theta]^2\cos[\psi]^2\sin[\theta]\sin[\phi]^2\sin[\psi]\,\beta_{a,a,a} - \\
& 6\cos[\theta]\cos[\phi]\cos[\psi]\sin[\theta]\sin[\phi]\sin[\psi]^2\,\beta_{a,a,a} - \\
& \cos[\phi]^2\sin[\theta]\sin[\psi]^3\,\beta_{a,a,a} + \cos[\theta]^2\sin[\theta]\sin[\phi]^2\sin[\psi]^3\,\beta_{a,a,a} - \\
& \cos[\theta]\cos[\psi]^2\sin[\theta]^2\sin[\phi]^2\,\beta_{a,c,a} - \\
& \cos[\theta]\sin[\theta]^2\sin[\phi]^2\sin[\psi]^2\,\beta_{a,c,a} + \cos[\theta]\cos[\phi]^2\cos[\psi]^2\,\beta_{c,a,a} + \\
& \cos[\theta]^3\cos[\psi]^2\sin[\phi]^2\,\beta_{c,a,a} + \cos[\theta]\cos[\phi]^2\sin[\psi]^2\,\beta_{c,a,a} + \\
& \cos[\theta]^3\sin[\phi]^2\sin[\psi]^2\,\beta_{c,a,a}
\end{aligned}
$$

"Average Over Orientation (ϕ,ψ)"

$$
\begin{aligned}
\frac{N_s}{(2\pi)^2}\Bigg(\int_0^{2\pi}\!\!\int_0^{2\pi} \Big(& 2\cos[\theta]\cos[\phi]\cos[\psi]^3\sin[\theta]\sin[\phi]\,\beta_{a,a,a} + \\
& 3\cos[\phi]^2\cos[\psi]^2\sin[\theta]\sin[\psi]\,\beta_{a,a,a} - \\
& 3\cos[\theta]^2\cos[\psi]^2\sin[\theta]\sin[\phi]^2\sin[\psi]\,\beta_{a,a,a} - \\
& 6\cos[\theta]\cos[\phi]\cos[\psi]\sin[\theta]\sin[\phi]\sin[\psi]^2\,\beta_{a,a,a} - \\
& \cos[\phi]^2\sin[\theta]\sin[\psi]^3\,\beta_{a,a,a} + \\
& \cos[\theta]^2\sin[\theta]\sin[\phi]^2\sin[\psi]^3\,\beta_{a,a,a} - \\
& \cos[\theta]\cos[\psi]^2\sin[\theta]^2\sin[\phi]^2\,\beta_{a,c,a} - \\
& \cos[\theta]\sin[\theta]^2\sin[\phi]^2\sin[\psi]^2\,\beta_{a,c,a} + \\
& \cos[\theta]\cos[\phi]^2\cos[\psi]^2\,\beta_{c,a,a} + \cos[\theta]^3\cos[\psi]^2\sin[\phi]^2\,\beta_{c,a,a} + \\
& \cos[\theta]\cos[\phi]^2\sin[\psi]^2\,\beta_{c,a,a} + \cos[\theta]^3\sin[\phi]^2\sin[\psi]^2\,\beta_{c,a,a}\Big) \\
& d\phi\, d\psi\Bigg)
\end{aligned}
$$

$$
= \frac{1}{4}\cos[\theta]\,N_s\left(-2\sin[\theta]^2\,\beta_{a,c,a} + (3+\cos[2\theta])\,\beta_{c,a,a}\right)
$$

"Isotropic Interface--> $\beta_{c,a,a}=\beta_{a,c,a}$"

$\beta_{c,a,a} = \beta_{a,c,a}$

$\text{Simplify}\left[\frac{1}{4}\,\text{Cos}[\theta]\,N_s\left(-2\,\text{Sin}[\theta]^2\,\beta_{a,c,a} + (3 + \text{Cos}[2\,\theta])\,\beta_{c,a,a}\right)\right]$

$= \text{Cos}[\theta]^3\,N_s\,\beta_{a,c,a}$

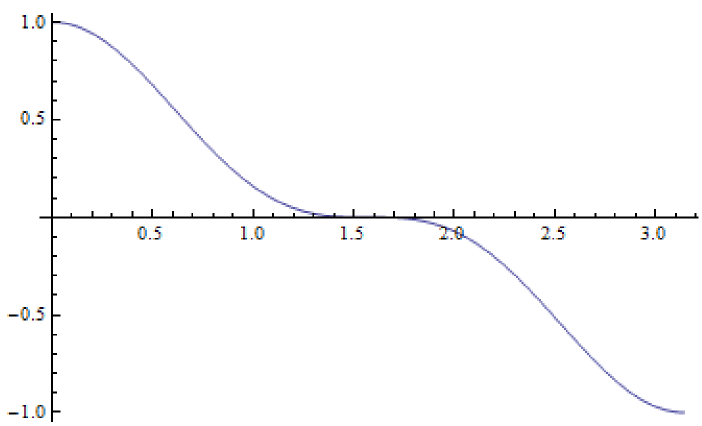
$\boxed{\chi^{(2)\,as}_{z,x,x} = N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$\text{Plot}\left[N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3,\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$



"PPP,zzz Anti-symmetric Stretching-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

$$\chi^{(2)\,as}_{z,z,z} =$$

$$\text{Expand}\left[-3\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^3\,\text{Sin}[\psi]\,\beta_{a,a,a} + \text{Sin}[\theta]^3\,\text{Sin}[\psi]^3\,\beta_{a,a,a} + \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,c,a} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a} + \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{c,a,a} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{c,a,a}\right]$$

$$= -3\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^3\,\text{Sin}[\psi]\,\beta_{a,a,a} + \text{Sin}[\theta]^3\,\text{Sin}[\psi]^3\,\beta_{a,a,a} + \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,c,a} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a} + \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{c,a,a} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{c,a,a}$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(-3\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^3\,\text{Sin}[\psi]\,\beta_{a,a,a} + \text{Sin}[\theta]^3\,\text{Sin}[\psi]^3\,\beta_{a,a,a} + \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{a,c,a} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a} + \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{c,a,a} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,\beta_{c,a,a}\right) d\phi\, d\psi\right)$$

$$= \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,(\beta_{a,c,a} + \beta_{c,a,a})$$

$$= \left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)\,N_s\,(\beta_{a,c,a} + \beta_{c,a,a})$$

"Isotropic Interface--> $\beta_{c,a,a}=\beta_{a,c,a}$"

$\beta_{c,a,a} = \beta_{a,c,a}$

Simplify[(Cos[θ] - Cos[θ]^3) N_s (β_{a,c,a} + β_{c,a,a})]

$= 2\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right) N_s\, \beta_{a,c,a}$

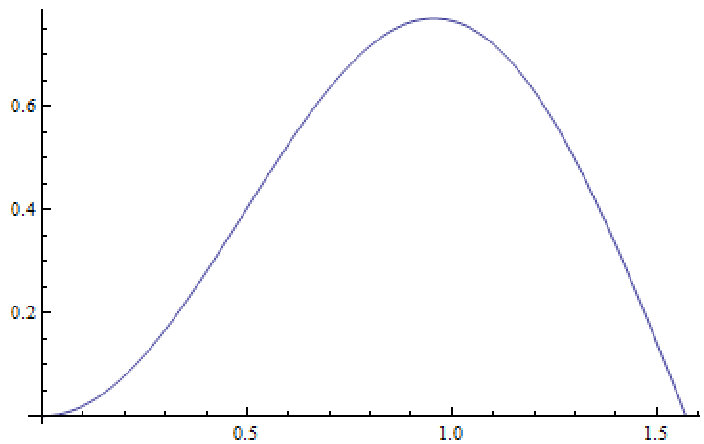
$$\boxed{\chi^{(2)\,as}_{z,z,z} = 2\, N_s\, \beta_{a,c,a} \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

Plot[2 N_s β_{a,c,a} (Cos[θ] - Cos[θ]^3), {θ, 0 Degree, 90 Degree}]



3.4.2. C_{2v} symmetry molecules

3.4.2.a. Symmetric stretching vibration

"PPP,xxz Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{b,b,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{x,x,z} = \text{Expand}\big[\cos[\theta]\,(\cos[\phi]\cos[\psi] - \cos[\theta]\sin[\phi]\sin[\psi])^2\,\beta_{a,a,c} + \cos[\theta]\,(-\cos[\theta]\cos[\psi]\sin[\phi] - \cos[\phi]\sin[\psi])^2\,\beta_{b,b,c} + \cos[\theta]\sin[\theta]^2\sin[\phi]^2\,\beta_{c,c,c}\big]$$

$$= \cos[\theta]\cos[\phi]^2\cos[\psi]^2\,\beta_{a,a,c} - 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{a,a,c} + \cos[\theta]^3\sin[\phi]^2\sin[\psi]^2\,\beta_{a,a,c} + \cos[\theta]^3\cos[\psi]^2\sin[\phi]^2\,\beta_{b,b,c} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{b,b,c} + \cos[\theta]\cos[\phi]^2\sin[\psi]^2\,\beta_{b,b,c} + \cos[\theta]\sin[\theta]^2\sin[\phi]^2\,\beta_{c,c,c}$$

$$= \cos[\theta]\cos[\phi]^2\cos[\psi]^2\,\beta_{a,a,c} - 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{a,a,c} + \cos[\theta]^3\sin[\phi]^2\sin[\psi]^2\,\beta_{a,a,c} + \cos[\theta]^3\cos[\psi]^2\sin[\phi]^2\,\beta_{b,b,c} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,\beta_{b,b,c} + \cos[\theta]\cos[\phi]^2\sin[\psi]^2\,\beta_{b,b,c} + \cos[\theta]\sin[\phi]^2\,\beta_{c,c,c} - \cos[\theta]^3\sin[\phi]^2\,\beta_{c,c,c}$$

$$= \cos[\theta]\,\left(\cos[\phi]^2\cos[\psi]^2\,\beta_{a,a,c} + \cos[\phi]^2\sin[\psi]^2\,\beta_{b,b,c} + \sin[\phi]^2\,\beta_{c,c,c}\right) - 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\,(\beta_{a,a,c} - \beta_{b,b,c}) + \cos[\theta]^3\left(\sin[\phi]^2\sin[\psi]^2\,\beta_{a,a,c} + \cos[\psi]^2\sin[\phi]^2\,\beta_{b,b,c} - \sin[\phi]^2\,\beta_{c,c,c}\right)$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\operatorname{Cos}[\theta]\left(\int_0^{2\pi}\left(\operatorname{Cos}[\phi]^2\operatorname{Cos}[\psi]^2\beta_{a,a,c}+\operatorname{Cos}[\phi]^2\operatorname{Sin}[\psi]^2\beta_{b,b,c}+\operatorname{Sin}[\phi]^2\beta_{c,c,c}\right)d\phi\right)-$$
$$\frac{N_s}{2\pi}2\operatorname{Cos}[\theta]^2\left(\int_0^{2\pi}(\operatorname{Cos}[\phi]\operatorname{Cos}[\psi]\operatorname{Sin}[\phi]\operatorname{Sin}[\psi](\beta_{a,a,c}-\beta_{b,b,c}))\,d\phi\right)+$$
$$\frac{N_s}{2\pi}\operatorname{Cos}[\theta]^3\left(\int_0^{2\pi}\left(\operatorname{Sin}[\phi]^2\operatorname{Sin}[\psi]^2\beta_{a,a,c}+\operatorname{Cos}[\psi]^2\operatorname{Sin}[\phi]^2\beta_{b,b,c}-\operatorname{Sin}[\phi]^2\beta_{c,c,c}\right)d\phi\right)$$

$$=\frac{1}{2}\operatorname{Cos}[\theta]^3 N_s\left(\operatorname{Sin}[\psi]^2\beta_{a,a,c}+\operatorname{Cos}[\psi]^2\beta_{b,b,c}-\beta_{c,c,c}\right)+\frac{1}{2}\operatorname{Cos}[\theta]N_s\left(\operatorname{Cos}[\psi]^2\beta_{a,a,c}+\operatorname{Sin}[\psi]^2\beta_{b,b,c}+\beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{z,z,z}=\frac{1}{2}N_s\left(\operatorname{Cos}[\psi]^2\beta_{a,a,c}+\operatorname{Sin}[\psi]^2\beta_{b,b,c}+\beta_{c,c,c}\right)\operatorname{Cos}[\theta]+\frac{1}{2}N_s\left(\operatorname{Sin}[\psi]^2\beta_{a,a,c}+\operatorname{Cos}[\psi]^2\beta_{b,b,c}-\beta_{c,c,c}\right)\operatorname{Cos}[\theta]^3}$$

"Plot"

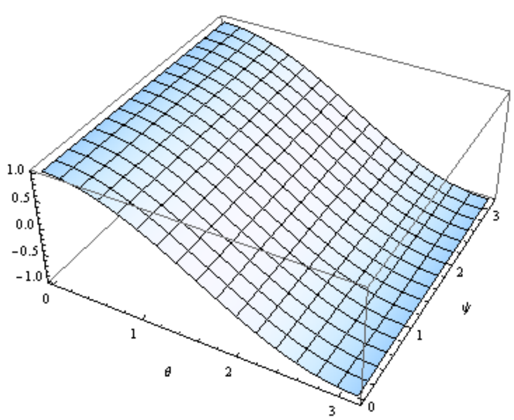
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 1$

$\beta_{c,c,c} = 1$

$$\text{Plot3D}\left[\frac{1}{2}N_s\left(\operatorname{Cos}[\psi]^2\beta_{a,a,c}+\operatorname{Sin}[\psi]^2\beta_{b,b,c}+\beta_{c,c,c}\right)\operatorname{Cos}[\theta]+\frac{1}{2}N_s\left(\operatorname{Sin}[\psi]^2\beta_{a,a,c}+\operatorname{Cos}[\psi]^2\beta_{b,b,c}-\beta_{c,c,c}\right)\operatorname{Cos}[\theta]^3,\ \{\theta, 0\,\text{Degree}, 180\,\text{Degree}\},\ \{\psi, 0\,\text{Degree}, 180\,\text{Degree}\},\ \text{AxesLabel}\to\{\theta,\psi\}\right]$$



"Average Over Orientation (ϕ,ψ) - Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2}N_s\left(\mathrm{Cos}[\psi]^2\beta_{a,a,c}+\mathrm{Sin}[\psi]^2\beta_{b,b,c}+\beta_{c,c,c}\right)\mathrm{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2}N_s\left(\mathrm{Sin}[\psi]^2\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\beta_{b,b,c}-\beta_{c,c,c}\right)\mathrm{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{4}\mathrm{Cos}[\theta]^3 N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)+\frac{1}{4}\mathrm{Cos}[\theta]N_s\left(\beta_{a,a,c}+\beta_{b,b,c}+2\beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{z,z,z}=\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}+2\beta_{c,c,c}\right)\mathrm{Cos}[\theta]+\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)\mathrm{Cos}[\theta]^3}$$

"Plot"

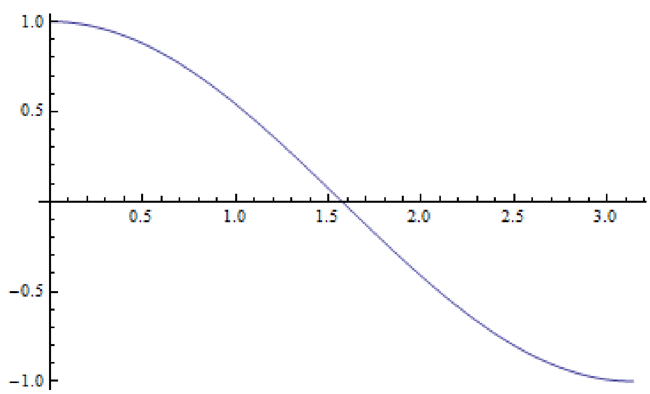
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 1$

$\beta_{c,c,c} = 1$

$$\mathrm{Plot}\left[\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}+2\beta_{c,c,c}\right)\mathrm{Cos}[\theta]+\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



"PPP,xzx Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{b,b,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{x,z,x} = \text{Expand}\big[\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi] - \text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}\big]$$

$$= \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{b,b,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\big(\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{b,b,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}\big)\,d\phi\right)$$

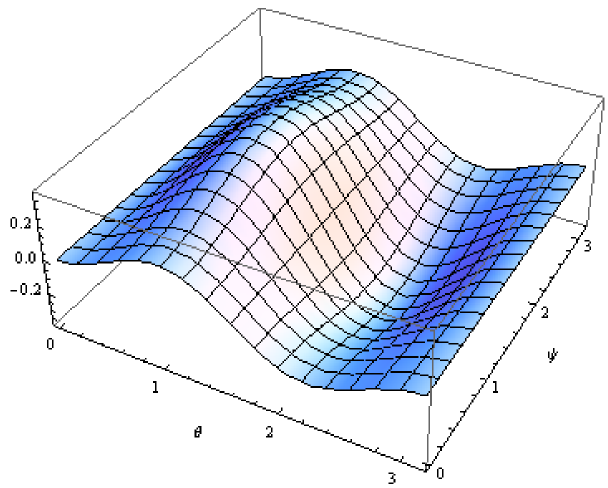
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\left(-\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\psi]^2\,\beta_{b,b,c} + \beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{x,z,x} = -\frac{1}{2}\,N_s\,\left(\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\psi]^2\,\beta_{b,b,c} - \beta_{c,c,c}\right)\,\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

"Plot"

```
Ns = 1
βa,a,c = 1
βb,b,c = 2
βc,c,c = 3
```

$$\text{Plot3D}\left[-\frac{1}{2} N_s \left(\text{Sin}[\psi]^2 \beta_{a,a,c} + \text{Cos}[\psi]^2 \beta_{b,b,c} - \beta_{c,c,c}\right) \left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right),\right.$$
$$\{\theta,\ 0\ \text{Degree},\ 180\ \text{Degree}\},\ \{\psi,\ 0\ \text{Degree},\ 180\ \text{Degree}\},$$
$$\left.\text{AxesLabel} \to \{\theta,\ \psi\}\right]$$



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2}N_s\left(\mathrm{Sin}[\psi]^2\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\beta_{b,b,c}-\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$-\frac{1}{4}\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2 N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{x,z,x}=-\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

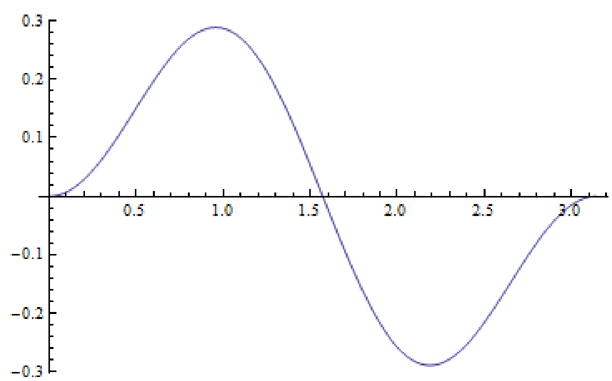
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 2$

$\beta_{c,c,c} = 3$

$$\mathrm{Plot}\left[-\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



"PPP,zxx Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{b,b,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{z,x,x} = \text{Expand}\Big[\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c} + \text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi] - \text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}\Big]$$

$$= \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{b,b,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\big(\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{b,b,c} - \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,b,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}\big)\,d\phi\right)$$

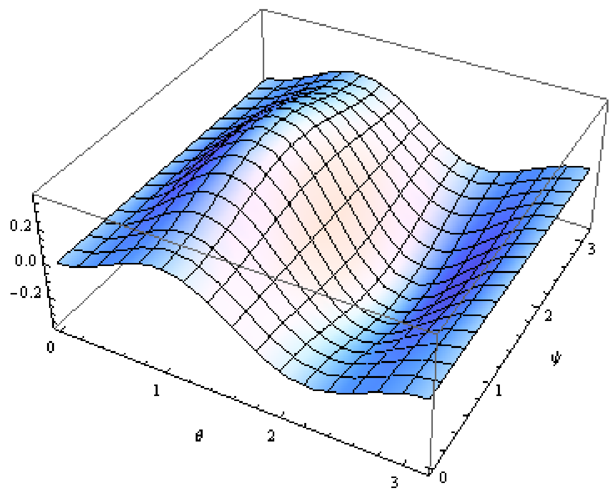
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\left(-\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\psi]^2\,\beta_{b,b,c} + \beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{z,x,x} = -\frac{1}{2}\,N_s\,\left(\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\psi]^2\,\beta_{b,b,c} - \beta_{c,c,c}\right)\,\left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

"Plot"

```
N_s = 1
β_{a,a,c} = 1
β_{b,b,c} = 2
β_{c,c,c} = 3
```

$$\text{Plot3D}\left[-\frac{1}{2}\,N_s\left(\text{Sin}[\psi]^2\,\beta_{a,a,c}+\text{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right),\right.$$
$$\{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\},\ \{\psi,\ 0\,\text{Degree},\ 180\,\text{Degree}\},$$
$$\left.\text{AxesLabel}\to\{\theta,\ \psi\}\right]$$



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2}N_s\left(\mathrm{Sin}[\psi]^2\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\beta_{b,b,c}-\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$=-\frac{1}{4}\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2 N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)$$

$$\boxed{\chi^{(2)\,ss}_{z,x,x}=-\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

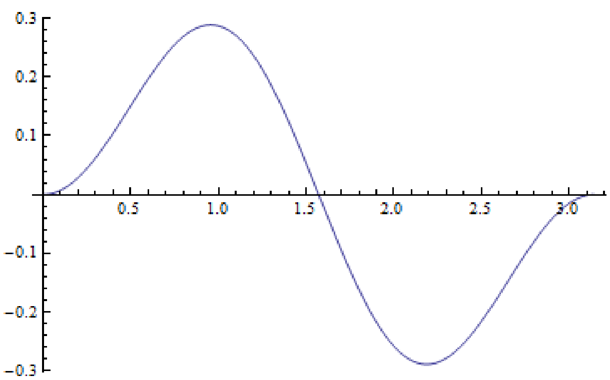
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 2$

$\beta_{c,c,c} = 3$

$$\mathrm{Plot}\left[-\frac{1}{4}N_s\left(\beta_{a,a,c}+\beta_{b,b,c}-2\beta_{c,c,c}\right)\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



"PPP,zzz Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{b,b,c}$, $\beta_{c,c,c}$"

$\chi^{(2)\,ss}_{z,z,z} =$

Expand$\left[\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{b,b,c} + \mathrm{Cos}[\theta]^3\,\beta_{c,c,c}\right]$

$= \mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{b,b,c} + \mathrm{Cos}[\theta]^3\,\beta_{c,c,c}$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{b,b,c} + \mathrm{Cos}[\theta]^3\,\beta_{c,c,c}\right) d\phi\right)$$

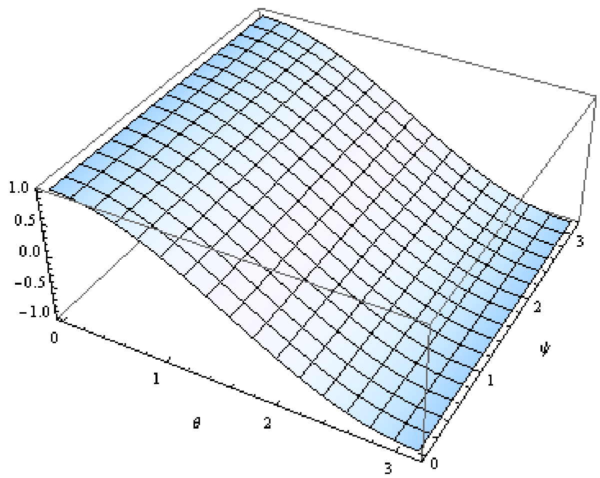
$$= N_s\left(\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{b,b,c} + \mathrm{Cos}[\theta]^3\,\beta_{c,c,c}\right)$$

$$= N_s\left(\mathrm{Cos}[\theta]\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\psi]^2\,\beta_{b,b,c}\right) - \mathrm{Cos}[\theta]^3\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\psi]^2\,\beta_{b,b,c} - \beta_{c,c,c}\right)\right)$$

$$\boxed{\chi^{(2)\,ss}_{z,z,z} = N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\psi]^2\,\beta_{b,b,c}\right)\mathrm{Cos}[\theta] - N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c} + \mathrm{Cos}[\psi]^2\,\beta_{b,b,c} - \beta_{c,c,c}\right)\mathrm{Cos}[\theta]^3}$$

"Plot"

```
Ns = 1
βa,a,c = 1
βb,b,c = 1
βc,c,c = 1
Plot3D[Ns (Sin[ψ]^2 βa,a,c + Cos[ψ]^2 βb,b,c) Cos[θ] -
  Ns (Sin[ψ]^2 βa,a,c + Cos[ψ]^2 βb,b,c - βc,c,c) Cos[θ]^3,
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}\right)\mathrm{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-N_s\left(\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\beta_{c,c,c}\right)\mathrm{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c})-\frac{1}{2}\mathrm{Cos}[\theta]^3\,N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})$$

$$\boxed{\chi^{(2)\,ss}_{z,z,z}=\frac{1}{2}N_s\,(\beta_{a,a,c}+\beta_{b,b,c})\,\mathrm{Cos}[\theta]-\frac{1}{2}N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})\,\mathrm{Cos}[\theta]^3}$$

"Plot"

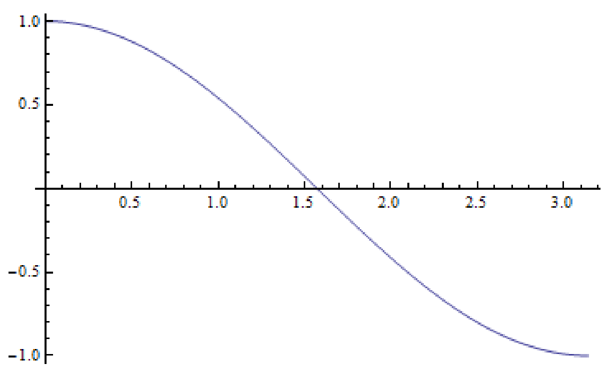
$N_s = 1$

$\beta_{a,a,c} = 1$

$\beta_{b,b,c} = 1$

$\beta_{c,c,c} = 1$

$$\mathrm{Plot}\left[\frac{1}{2}N_s\,(\beta_{a,a,c}+\beta_{b,b,c})\,\mathrm{Cos}[\theta]-\frac{1}{2}N_s\,(\beta_{a,a,c}+\beta_{b,b,c}-2\,\beta_{c,c,c})\,\mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$$



3.4.2.b. Anti- symmetric stretching vibration

"PPP,xxz, B_1 Anti-symmetric Stretching-->$\beta_{a,c,a}$"

$\chi^{(2)\,as,B_1}_{x,x,z} =$
Expand$[+2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,(\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi] - \mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{a,c,a}]$

$= 2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{a,c,a} - 2\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

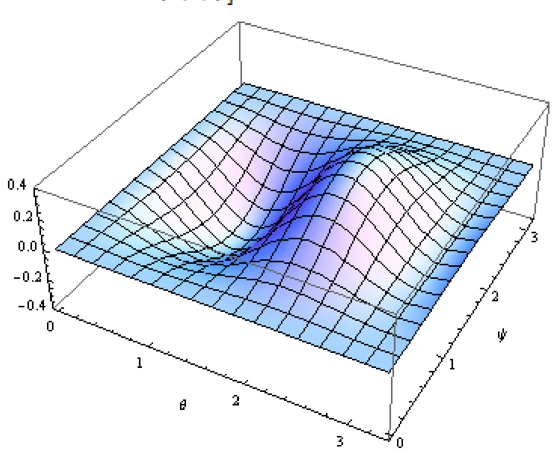
$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{a,c,a} - 2\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}\right)d\phi\right)$$

$= -\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,N_s\,\beta_{a,c,a}$

$$\boxed{\chi^{(2)\,as,B_1}_{x,x,z} = -N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\,(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3)}$$

"Plot"

$N_s = 1$
$\beta_{a,c,a} = 1$
Plot3D$[-N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\,(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3)$,
{θ, 0 Degree, 190 Degree}, {ψ, 0 Degree, 180 Degree},
AxesLabel → {θ, ψ}]



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$-\frac{1}{2}\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,N_s\,\beta_{a,c,a}$$

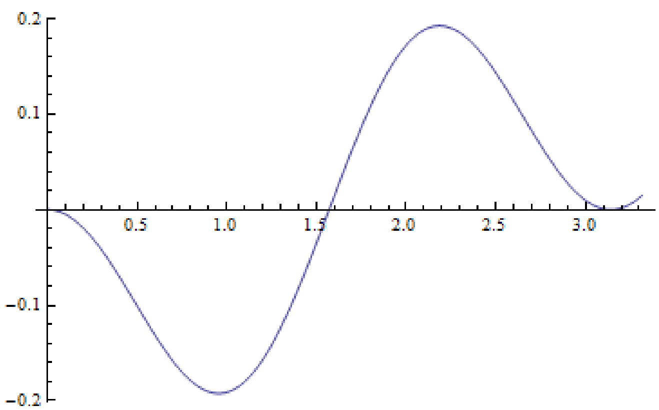
$$\boxed{\chi^{(2)\,as,B_1}_{x,x,z} = -\frac{1}{2}\,N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$$\mathrm{Plot}\left[-\frac{1}{2}\,N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 190\,\mathrm{Degree}\}\right]$$



"PPP,xxz, B_2 Anti-symmetric Stretching-->$\beta_{b,c,b}$"

$\chi^{(2)\,as,B_2}_{x,x,z}$ =

```
Expand[2 Cos[ψ] Sin[θ]^2 Sin[ϕ]
   (-Cos[θ] Cos[ψ] Sin[ϕ] - Cos[ϕ] Sin[ψ]) β_{b,c,b}]
```

$$= -2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\beta_{b,c,b} - 2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{b,c,b}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(-2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\beta_{b,c,b} - 2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{b,c,b}\right)d\phi\right)$$

$$= -\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,N_s\,\beta_{b,c,b}$$

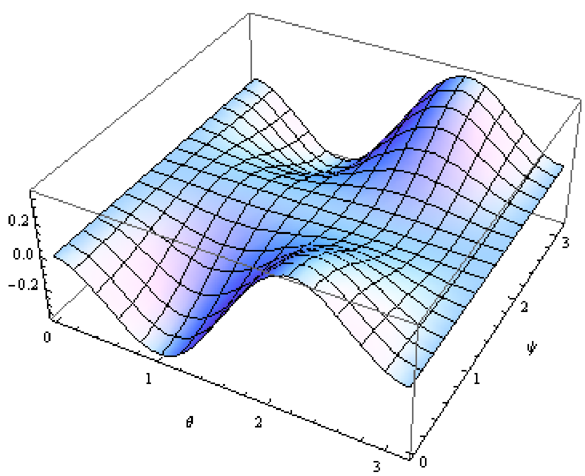
$$\boxed{\chi^{(2)\,as,B_2}_{x,x,z} = -N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)}$$

"Plot"

N_s = 1

$\beta_{b,c,b}$ = 1

```
Plot3D[-N_s β_{b,c,b} Cos[ψ]^2 (Cos[θ] - Cos[θ]^3),
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-N_s\,\beta_{b,c,b}\,\text{Cos}[\psi]^2\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)\right)d\psi\right)$$

$$= -\frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{b,c,b}$$

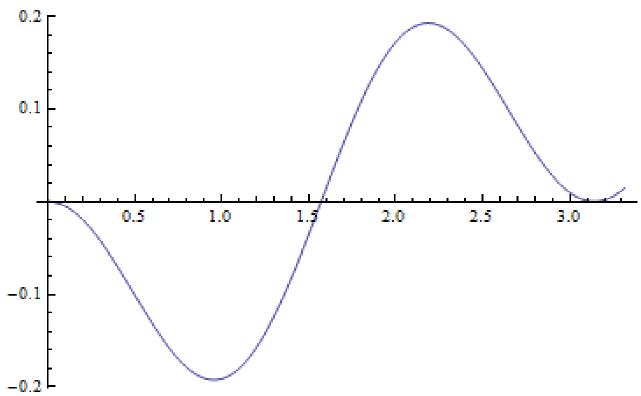
$$\boxed{\chi^{(2)\,as,B_2}_{x,x,z} = -\frac{1}{2}\,N_s\,\beta_{b,c,b}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

$$\text{Plot}\left[-\frac{1}{2}\,N_s\,\beta_{b,c,b}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 190\,\text{Degree}\}\right]$$



"PPP,xzx, B_1 Anti-symmetric Stretching-->$\beta_{a,c,a}$"

$$\chi^{(2)\,as,B_1}_{x,z,x} =$$

Expand[
Sin[θ]^2 Sin[ϕ] Sin[ψ] (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) β_{a,c,a} +
Cos[θ] (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ])^2 a, c, a]

$$= \cos[\theta]\cos[\phi]^2\cos[\psi]^2\beta_{a,c,a} - 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\phi]\cos[\psi]\sin[\theta]^2\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]^3\sin[\phi]^2\sin[\psi]^2\beta_{a,c,a} - \cos[\theta]\sin[\theta]^2\sin[\phi]^2\sin[\psi]^2\beta_{a,c,a}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\cos[\theta]\cos[\phi]^2\cos[\psi]^2\beta_{a,c,a} - 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\phi]\cos[\psi]\sin[\theta]^2\sin[\phi]\sin[\psi]\beta_{a,c,a} + \cos[\theta]^3\sin[\phi]^2\sin[\psi]^2\beta_{a,c,a} - \cos[\theta]\sin[\theta]^2\sin[\phi]^2\sin[\psi]^2\beta_{a,c,a}\right)d\phi\right)$$

$$= \frac{1}{2}\cos[\theta]\left(\cos[\psi]^2 + \cos[2\theta]\sin[\psi]^2\right)\beta_{a,c,a}$$

$$= \frac{1}{2}\left(\cos[\theta]\left(\cos[\psi]^2 - \sin[\psi]^2\right) + 2\cos[\theta]^3\sin[\psi]^2\right)N_s\,\beta_{a,c,a}$$

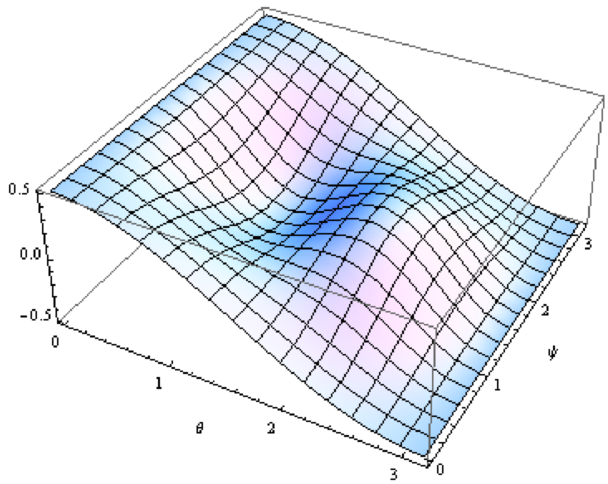
$$\boxed{\chi^{(2)\,as,B_1}_{x,z,x} = \frac{1}{2}N_s\,\beta_{a,c,a}\left(\cos[\psi]^2 - \sin[\psi]^2\right)\cos[\theta] + N_s\,\beta_{a,c,a}\sin[\psi]^2\cos[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

```
Plot3D[1/2 Ns β_{a,c,a} (Cos[ψ]^2 - Sin[ψ]^2) Cos[θ] + Ns β_{a,c,a} Sin[ψ]^2 Cos[θ]^3,
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2}N_s\,\beta_{a,c,a}\left(\text{Cos}[\psi]^2-\text{Sin}[\psi]^2\right)\text{Cos}[\theta]\right)d\psi\right)+$$
$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\,\beta_{a,c,a}\,\text{Sin}[\psi]^2\,\text{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2}\text{Cos}[\theta]^3\,N_s\,\beta_{a,c,a}$$

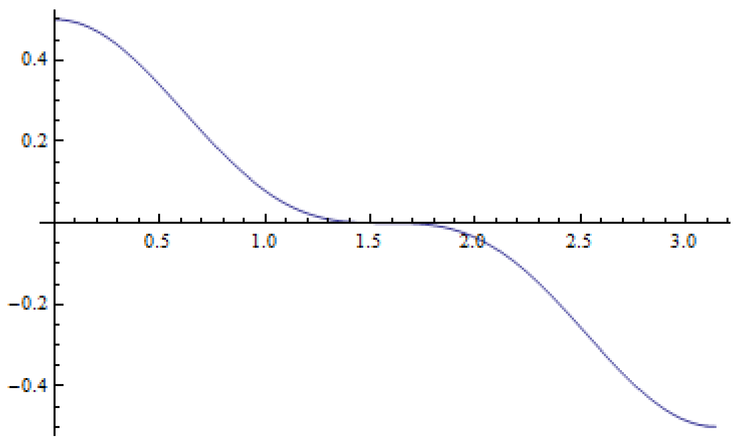
$$\boxed{\chi^{(2)\,as,B_1}_{x,z,x}=\frac{1}{2}N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$\text{Plot}\left[\frac{1}{2}N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3,\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$



"PPP,xzx, B_2 Anti-symmetric Stretching-->$\beta_{b,c,b}$"

$$\chi^{(2)\,as,B_2}_{x,z,x} = \text{Expand}\big[\cos[\psi]\sin[\theta]^2\sin[\phi]\,(-\cos[\theta]\cos[\psi]\sin[\phi]-\cos[\phi]\sin[\psi])\,\beta_{b,c,b} + \cos[\theta]\,(-\cos[\theta]\cos[\psi]\sin[\phi]-\cos[\phi]\sin[\psi])^2\,\beta_{b,c,b}\big]$$

$$= \cos[\theta]^3\cos[\psi]^2\sin[\phi]^2\beta_{b,c,b} - \cos[\theta]\cos[\psi]^2\sin[\theta]^2\sin[\phi]^2\beta_{b,c,b} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{b,c,b} - \cos[\phi]\cos[\psi]\sin[\theta]^2\sin[\phi]\sin[\psi]\beta_{b,c,b} + \cos[\theta]\cos[\phi]^2\sin[\psi]^2\beta_{b,c,b}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\cos[\theta]^3\cos[\psi]^2\sin[\phi]^2\beta_{b,c,b} - \cos[\theta]\cos[\psi]^2\sin[\theta]^2\sin[\phi]^2\beta_{b,c,b} + 2\cos[\theta]^2\cos[\phi]\cos[\psi]\sin[\phi]\sin[\psi]\beta_{b,c,b} - \cos[\phi]\cos[\psi]\sin[\theta]^2\sin[\phi]\sin[\psi]\beta_{b,c,b} + \cos[\theta]\cos[\phi]^2\sin[\psi]^2\beta_{b,c,b}\right)d\phi\right)$$

$$= \frac{1}{2}\cos[\theta]\left(\cos[\theta]^2 - \left(\cos[\psi]^2-\sin[\psi]^2\right)\sin[\theta]^2\right)N_s\,\beta_{b,c,b}$$

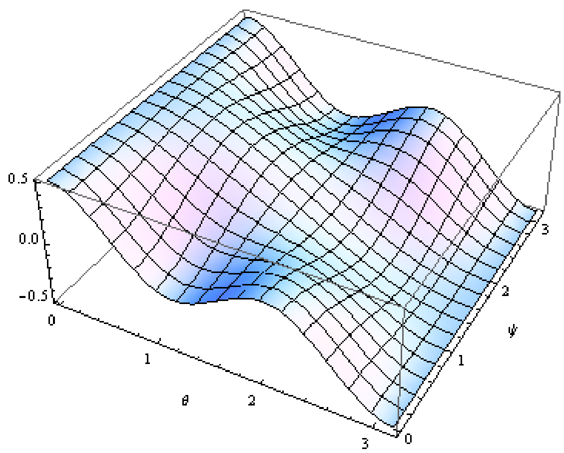
$$= \frac{1}{2}\left(\cos[\theta]^3\left(1+\cos[\psi]^2-1+\cos[\psi]^2\right) - \cos[\theta]\left(\cos[\psi]^2-\sin[\psi]^2\right)\right)N_s\,\beta_{b,c,b}$$

$$= \frac{1}{2}\left(2\cos[\psi]^2\cos[\theta]^3 - \left(\cos[\psi]^2-\sin[\psi]^2\right)\cos[\theta]\right)N_s\,\beta_{b,c,b}$$

$$\boxed{\chi^{(2)\,as,B_2}_{x,z,x} = -\frac{1}{2}N_s\,\beta_{b,c,b}\left(\cos[\psi]^2-\sin[\psi]^2\right)\cos[\theta] + N_s\,\beta_{b,c,b}\cos[\psi]^2\cos[\theta]^3}$$

```
"Plot"

Ns = 1
βb,c,b = 1
Plot3D[-1/2 Ns βb,c,b (Cos[ψ]^2 - Sin[ψ]^2) Cos[θ] +
   Ns βb,c,b Cos[ψ]^2 Cos[θ]^3, {θ, 0 Degree, 180 Degree},
  {ψ, 0 Degree, 180 Degree}, AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)-Non Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2}N_s\,\beta_{b,c,b}\left(\text{Cos}[\psi]^2-\text{Sin}[\psi]^2\right)\text{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\,\beta_{b,c,b}\,\text{Cos}[\psi]^2\,\text{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2}\text{Cos}[\theta]^3\,N_s\,\beta_{b,c,b}$$

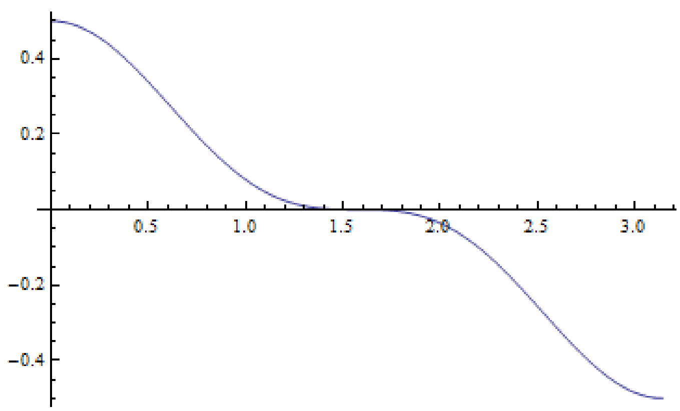
$$\boxed{\chi^{(2)\,as,B_2}_{x,z,x}=\frac{1}{2}N_s\,\beta_{b,c,b}\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

$\text{Plot}\left[\frac{1}{2}N_s\,\beta_{b,c,b}\,\text{Cos}[\theta]^3,\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$



"PPP,zxx, B_1 Anti-symmetric Stretching-->$\beta_{a,c,a}$"

$$\chi^{(2)\,as,B_1}_{z,x,x} =$$

Expand[

$$\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,c,a} + \text{Cos}[\theta]\,(\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])^2\,\beta_{a,c,a}]$$

$$= \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{a,c,a} - 2\,\text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} + \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} + \text{Cos}[\theta]^3\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{a,c,a} - 2\,\text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} + \text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,c,a} + \text{Cos}[\theta]^3\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,c,a}\right)d\phi\right)$$

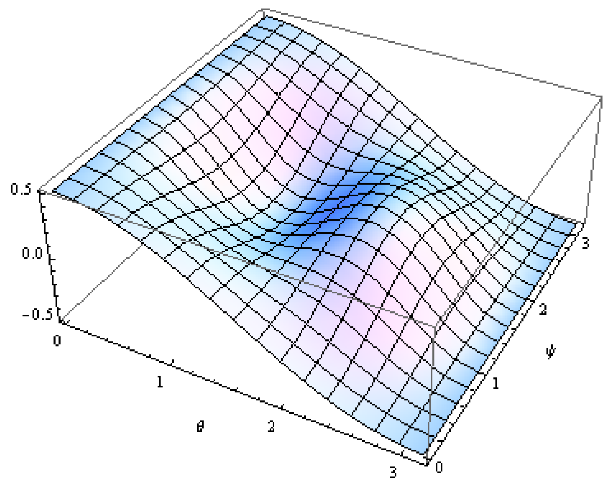
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\left(\text{Cos}[\psi]^2 + \text{Cos}[2\,\theta]\,\text{Sin}[\psi]^2\right)\,N_s\,\beta_{a,c,a}$$

$$= \frac{1}{2}\,\left(\text{Cos}[\theta]\,\left(\text{Cos}[\psi]^2 - \text{Sin}[\psi]^2\right) + 2\,\text{Cos}[\theta]^3\,\text{Sin}[\psi]^2\right)\,N_s\,\beta_{a,c,a}$$

$$\boxed{\chi^{(2)\,as,B_1}_{z,x,x} = \frac{1}{2}\,N_s\,\beta_{a,c,a}\,\left(\text{Cos}[\psi]^2 - \text{Sin}[\psi]^2\right)\,\text{Cos}[\theta] + N_s\,\beta_{a,c,a}\,\text{Sin}[\psi]^2\,\text{Cos}[\theta]^3}$$

"Plot"

```
Ns = 1
βa,c,a = 1
Plot3D[1/2 Ns βa,c,a (Cos[ψ]^2 - Sin[ψ]^2) Cos[θ] + Ns βa,c,a Sin[ψ]^2 Cos[θ]^3,
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(\frac{1}{2}N_s\,\beta_{a,c,a}\left(\text{Cos}[\psi]^2-\text{Sin}[\psi]^2\right)\text{Cos}[\theta]\right)d\psi\right)+\frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\,\beta_{a,c,a}\,\text{Sin}[\psi]^2\,\text{Cos}[\theta]^3\right)d\psi\right)$$

$$=\frac{1}{2}\text{Cos}[\theta]^3 N_s\,\beta_{a,c,a}$$

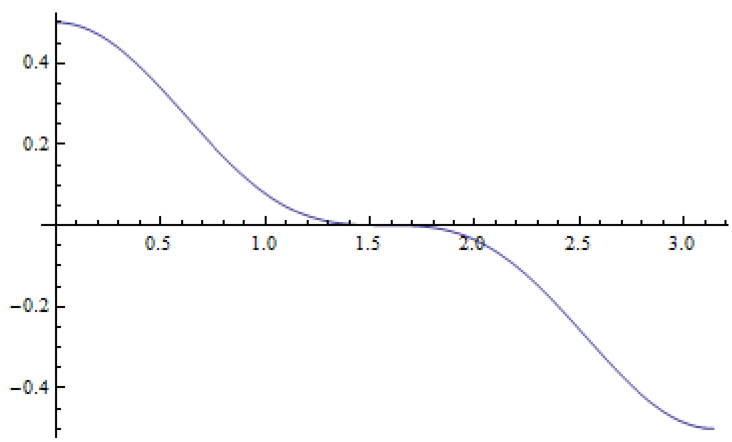
$$\boxed{\chi^{(2)\,as,B_1}_{z,x,x}=\frac{1}{2}N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

$\text{Plot}\left[\frac{1}{2}N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3,\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$



"PPP,zxx, B_2 Anti-symmetric Stretching-->$\beta_{b,c,b}$"

$$\chi^{(2)\,as,B_2}_{z,x,x} =$$

$$\text{Expand}\big[\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi]-\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{b,c,b}+\text{Cos}[\theta]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi]-\text{Cos}[\phi]\,\text{Sin}[\psi])^2\,\beta_{b,c,b}\big]$$

$$= \text{Cos}[\theta]^3\,\text{Cos}[\psi]^2\,\text{Sin}[\phi]^2\,\beta_{b,c,b}-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{b,c,b}+2\,\text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,c,b}-\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,c,b}+\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{b,c,b}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\big(\text{Cos}[\theta]^3\,\text{Cos}[\psi]^2\,\text{Sin}[\phi]^2\,\beta_{b,c,b}-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{b,c,b}+2\,\text{Cos}[\theta]^2\,\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,c,b}-\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{b,c,b}+\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{b,c,b}\big)\,d\phi\right)$$

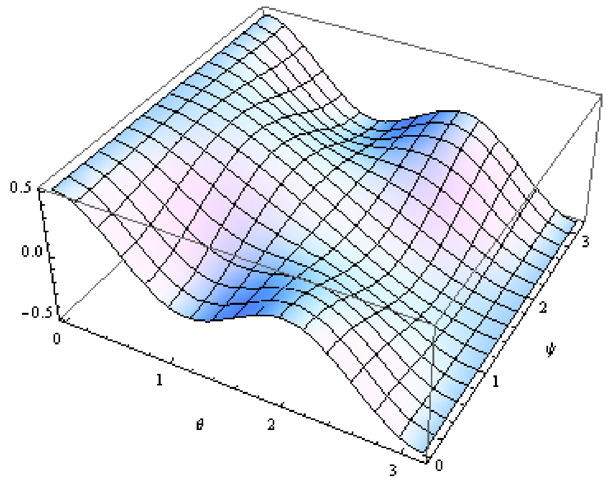
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\left(\text{Cos}[\theta]^2-\text{Cos}[2\,\psi]\,\text{Sin}[\theta]^2\right)\,N_s\,\beta_{b,c,b}$$

$$= \frac{1}{2}\,\left(2\,\text{Cos}[\psi]^2\,\text{Cos}[\theta]^3-\left(\text{Cos}[\psi]^2-\text{Sin}[\psi]^2\right)\,\text{Cos}[\theta]\right)\,N_s\,\beta_{b,c,b}$$

$$\boxed{\chi^{(2)\,as,B_2}_{z,x,x} = -\frac{1}{2}\,N_s\,\beta_{b,c,b}\,\left(\text{Cos}[\psi]^2-\text{Sin}[\psi]^2\right)\,\text{Cos}[\theta]+N_s\,\beta_{b,c,b}\,\text{Cos}[\psi]^2\,\text{Cos}[\theta]^3}$$

"Plot"

```
Ns = 1
βb,c,b = 1
Plot3D[-1/2 Ns βb,c,b (Cos[ψ]^2 - Sin[ψ]^2) Cos[θ] +
  Ns βb,c,b Cos[ψ]^2 Cos[θ]^3, {θ, 0 Degree, 180 Degree},
 {ψ, 0 Degree, 180 Degree}, AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\int_0^{2\pi}\left(-\frac{1}{2} N_s\, \beta_{b,c,b} \left(\mathrm{Cos}[\psi]^2 - \mathrm{Sin}[\psi]^2\right) \mathrm{Cos}[\theta]\right) d\psi\right) + \frac{1}{2\pi}\left(\int_0^{2\pi}\left(N_s\, \beta_{b,c,b}\, \mathrm{Cos}[\psi]^2\, \mathrm{Cos}[\theta]^3\right) d\psi\right)$$

$$\frac{1}{2}\, \mathrm{Cos}[\theta]^3\, N_s\, \beta_{b,c,b}$$

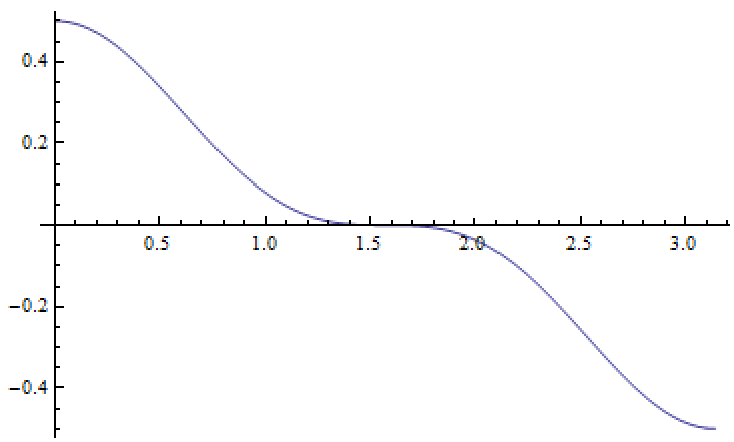
$$\boxed{\chi^{(2)\,as,B_2}_{z,x,x} = \frac{1}{2}\, N_s\, \beta_{b,c,b}\, \mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

$$\mathrm{Plot}\left[\frac{1}{2}\, N_s\, \beta_{b,c,b}\, \mathrm{Cos}[\theta]^3,\ \{\theta,\ 0\ \mathrm{Degree},\ 180\ \mathrm{Degree}\}\right]$$



"PPP,zzz, B_1 Anti-symmetric Stretching-->$\beta_{a,c,a}$"

$$\chi^{(2)\,as,B_1}_{z,z,z} = 2\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(2\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}\right)d\phi\right)$$

$$= 2\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\psi]^2\,N_s\,\beta_{a,c,a}$$

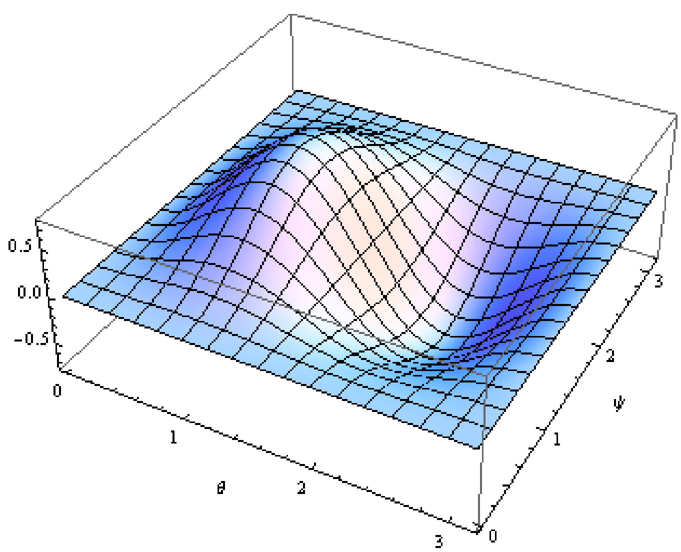
$$\boxed{\chi^{(2)\,as,B_1}_{z,z,z} = 2\,N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{a,c,a} = 1$

```
Plot3D[2 Ns βa,c,a Sin[ψ]^2 (Cos[θ] - Cos[θ]^3),
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

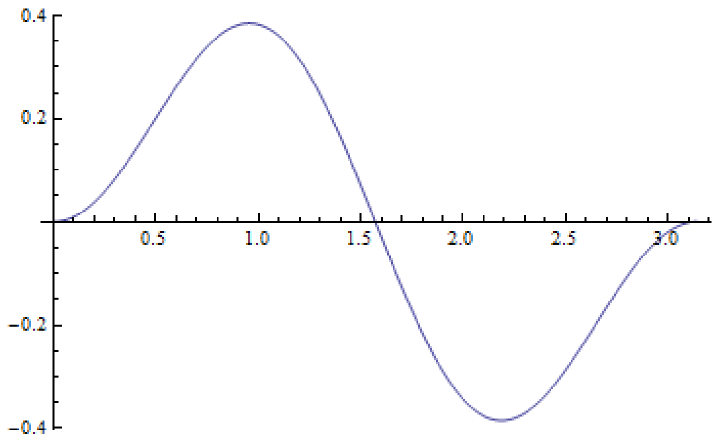
$$\frac{1}{2\pi}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)\left(\int_0^{2\pi}\left(2\,N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\right)d\psi\right)$$

$$=\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)N_s\,\beta_{a,c,a}$$

$$\boxed{\chi^{(2)\,as,B_1}_{z,z,z}=N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

```
Ns = 1
βa,c,a = 1
Plot[Ns βa,c,a (Cos[θ] - Cos[θ]^3), {θ, 0 Degree, 180 Degree}]
```



"PPP,zzz, B_2 Anti-symmetric Stretching-->$\beta_{b,c,b}$"

$$\chi^{(2)\,as,B_2}_{z,z,z} = 2\,\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{b,c,b}$$

"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(2\,\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\beta_{b,c,b}\right)d\phi\right)$$

$$= 2\,\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,N_s\,\beta_{b,c,b}$$

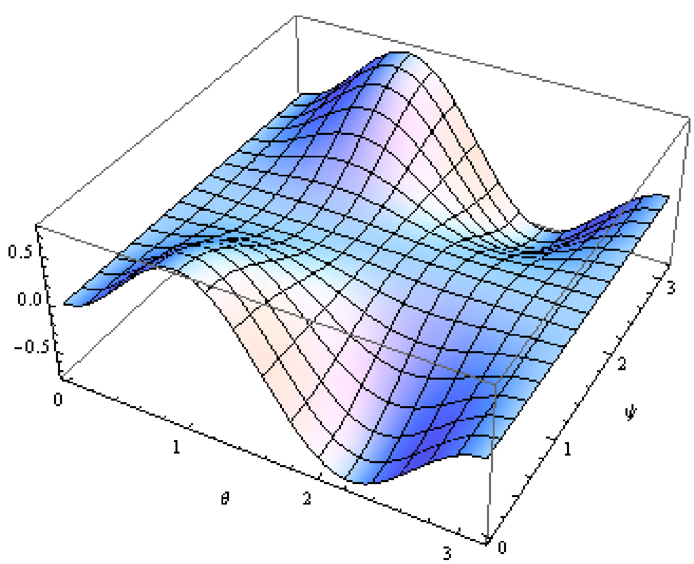
$$\boxed{\chi^{(2)\,as,B_2}_{z,z,z} = 2\,N_s\,\beta_{b,c,b}\,\text{Cos}[\psi]^2\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

```
Plot3D[2 Ns βb,c,b Cos[ψ]^2 (Cos[θ] - Cos[θ]^3),
 {θ, 0 Degree, 180 Degree}, {ψ, 0 Degree, 180 Degree},
 AxesLabel → {θ, ψ}]
```



"Average Over Orientation (ϕ,ψ)- Free Rotation of C2V Group"

$$\frac{1}{2\pi}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)\left(\int_0^{2\pi}\left(2\,N_s\,\beta_{b,c,b}\,\text{Cos}[\psi]^2\right)d\psi\right)$$

$$=\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)N_s\,\beta_{b,c,b}$$

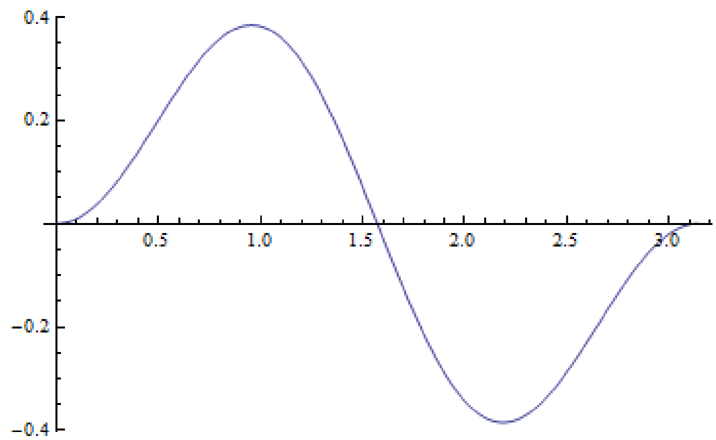
$$\boxed{\chi^{(2)\,as,B_2}_{z,z,z}=N_s\,\beta_{b,c,b}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

$\beta_{b,c,b} = 1$

Plot$\left[N_s\,\beta_{b,c,b}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right),\{\theta,0\,\text{Degree},180\,\text{Degree}\}\right]$



3.4.3. $C_{\infty v}$ symmetry molecules

3.4.3.a. Symmetric stretching vibration

"PPP,xxz Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{x,x,z} =$$
$$\text{Expand}\left[\text{Cos}[\theta]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi] - \text{Cos}[\phi]\,\text{Sin}[\psi])^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,(\text{Cos}[\phi]\,\text{Cos}[\psi] - \text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}\right]$$

$$= \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]^3\,\text{Sin}[\phi]^2\,\text{Cos}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]^3\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}$$

$$= \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]^3\,\text{Sin}[\phi]^2\,\beta_{a,a,c} + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{x,x,z} =$$
$$\beta_{c,c,c}\left(\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,R + \text{Cos}[\theta]^3\,\text{Sin}[\phi]^2\,R + \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\right)$$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(\mathrm{Cos}[\theta]\,\mathrm{Cos}[\phi]^2\,R+\mathrm{Cos}[\theta]^3\,\mathrm{Sin}[\phi]^2\,R+\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\right)\right)d\phi\, d\psi\right)$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\left(R+R\,\mathrm{Cos}[\theta]^2+\mathrm{Sin}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\left(R+R\,\mathrm{Cos}[\theta]^2+1-\mathrm{Cos}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$=\frac{1}{2}\mathrm{Cos}[\theta]\left((1+R)-(1-R)\,\mathrm{Cos}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{x,x,z}=\frac{1}{2}N_s\,\beta_{c,c,c}\left((1+R)\,\mathrm{Cos}[\theta]-(1-R)\,\mathrm{Cos}[\theta]^3\right)}$$

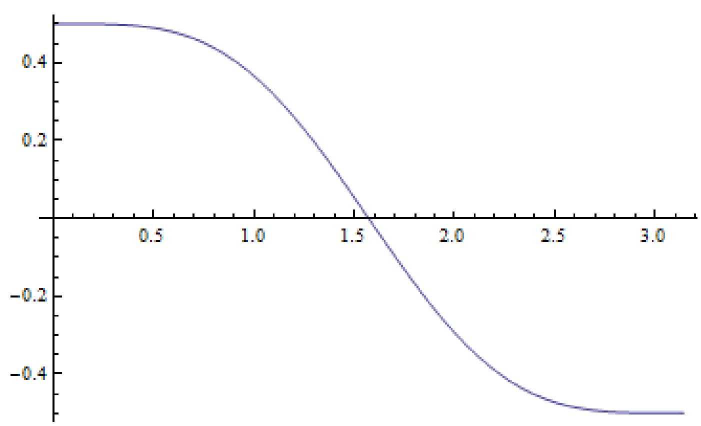
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 0.5$

$\mathrm{Plot}\left[\frac{1}{2}N_s\,\beta_{c,c,c}\left((1+R)\,\mathrm{Cos}[\theta]-(1-R)\,\mathrm{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\mathrm{Degree},\ 180\,\mathrm{Degree}\}\right]$



"PPP,xzx Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$\chi^{(2)\,ss}_{x,z,x}$ =

Expand[

$\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]-\mathrm{Cos}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{a,a,c}+$
$\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,(\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]-\mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi])\,\beta_{a,a,c}+$
$\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\beta_{c,c,c}$]

$= -\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\beta_{a,a,c}-$
$\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\beta_{c,c,c}$

$$\boxed{R=\frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$\chi^{(2)\,ss}_{x,z,x}$ =

$\beta_{c,c,c}$
$\big(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,R-$
$\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,R+\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\big)$

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,R-\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,R+\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\right)\right)d\phi\,d\psi\right)$$

$$=-\frac{1}{2}(-1+R)\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{x,x,x}=\frac{1}{2}N_s\,\beta_{c,c,c}\,(1-R)\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

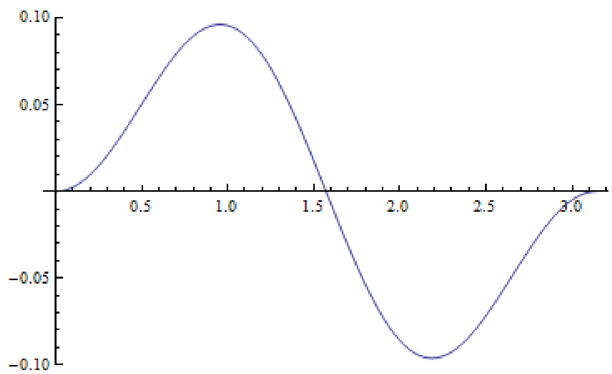
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 0.5$

$$\text{Plot}\left[\frac{1}{2}N_s\,\beta_{c,c,c}\,(1-R)\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$$



"PPP,zxx Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$$\chi^{(2)\,ss}_{z,x,x} =$$

$$\text{Expand}\left[\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,(-\text{Cos}[\theta]\,\text{Cos}[\psi]\,\text{Sin}[\phi]-\text{Cos}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c}+\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,(\text{Cos}[\phi]\,\text{Cos}[\psi]-\text{Cos}[\theta]\,\text{Sin}[\phi]\,\text{Sin}[\psi])\,\beta_{a,a,c}+\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}\right]$$

$$= -\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{a,a,c}-\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c}+\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{c,c,c}$$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$$\chi^{(2)\,ss}_{z,x,x} = \beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,R-\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,R+\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\right)$$

"Average Over Orientation (ϕ, ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,R - \mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,R + \mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\right)\right) d\phi\, d\psi\right)$$

$$= -\frac{1}{2}(-1+R)\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{z,x,x} = \frac{1}{2} N_s\,\beta_{c,c,c}\,(1-R)\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)}$$

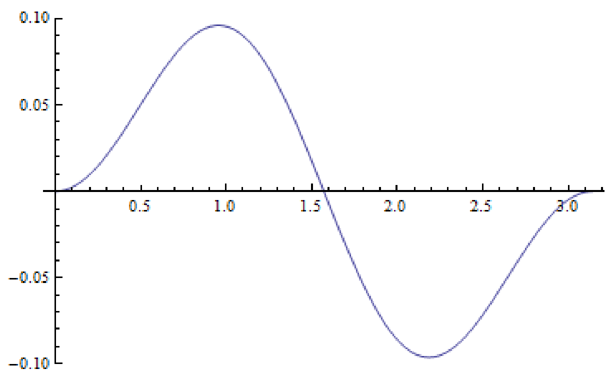
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 0.5$

$\mathrm{Plot}\left[\frac{1}{2} N_s\,\beta_{c,c,c}\,(1-R)\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right), \{\theta, 0\,\mathrm{Degree}, 180\,\mathrm{Degree}\}\right]$



"PPP,zzz Symmetric Stretching-->$\beta_{a,a,c}$, $\beta_{c,c,c}$"

$\chi^{(2)\,ss}_{z,z,z}$ =

Expand[Cos[θ] Cos[ψ]^2 Sin[θ]^2 $\beta_{a,a,c}$ + Cos[θ] Sin[θ]^2 Sin[ψ]^2 $\beta_{a,a,c}$ +
Cos[θ]^3 $\beta_{c,c,c}$]

= Cos[θ] Cos[ψ]^2 Sin[θ]^2 $\beta_{a,a,c}$ + Cos[θ] Sin[θ]^2 Sin[ψ]^2 $\beta_{a,a,c}$ +
Cos[θ]^3 $\beta_{c,c,c}$

= Cos[θ] Sin[θ]^2 (Cos[ψ]^2 + Sin[ψ]^2) $\beta_{a,a,c}$ + Cos[θ]^3 $\beta_{c,c,c}$

= Cos[θ] Sin[θ]^2 $\beta_{a,a,c}$ + Cos[θ]^3 $\beta_{c,c,c}$

$$\boxed{R = \frac{\beta_{a,a,c}}{\beta_{c,c,c}}}$$

$\chi^{(2)\,ss}_{z,z,z}$ = $\beta_{c,c,c}$ (Cos[θ] Sin[θ]^2 R + Cos[θ]^3)

"Average Over Orientation (ϕ,ψ)"

$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(\text{Cos}[\theta]\ \text{Sin}[\theta]^2\,R+\text{Cos}[\theta]^3\right)\right)d\phi\, d\psi\right)$$

$$=\left(\text{Cos}[\theta]^3+R\,\text{Cos}[\theta]\ \text{Sin}[\theta]^2\right)N_s\,\beta_{c,c,c}$$

$$=\left(\text{Cos}[\theta]^3+R\,\text{Cos}[\theta]\ -R\,\text{Cos}[\theta]^3\right)N_s\,\beta_{c,c,c}$$

$$\boxed{\chi^{(2)\,ss}_{z,z,z}=N_s\,\beta_{c,c,c}\left(R\,\text{Cos}[\theta]+(1-R)\ \text{Cos}[\theta]^3\right)}$$

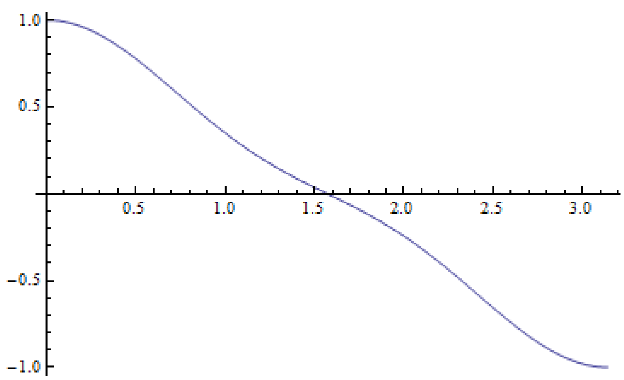
"Plot"

$N_s = 1$

$\beta_{c,c,c} = 1$

$R = 0.5$

Plot$\left[N_s\,\beta_{c,c,c}\left(R\,\text{Cos}[\theta]+(1-R)\ \text{Cos}[\theta]^3\right),\ \{\theta,\ 0\,\text{Degree},\ 180\,\text{Degree}\}\right]$



Appendix B

B.1. Mathematica codes for generating the orientation curve with Gaussian convolution

Fresnel Factors For Local Electric Field

```
(*Clear all values*)
ClearAll["`*"]
Needs["PlotLegends`"];

(*Change rad to degree
*)
β_sfg = B_sfg °;
β_vis = B_vis °;
β_ir = B_ir °;
γ_sfg = Γ_sfg °;
γ_vis = Γ_vis °;
γ_ir = Γ_ir °;

(*Refractive Index
*)
n_1,sfg = n_1,vis = n_1,ir = 1;
n_2,sfg = 0.18435 + ⅈ 5.2517;
n_2,vis = 0.28519 + ⅈ 7.3536;
n_2,ir = 2.05014 + ⅈ 21.326;
n_m,sfg = n_m,vis = n_m,ir = 1.2;

(*Other values
*)
R = 3.4;
β_a,c,a = 3.4;
β_a,a,c = β_b,b,c = β_c,c,c = 1;
N_s = 1;

(*Wavenumber
*)
ω_vis = 9400;
ω_ir = 2900;
ω_sfg = ω_vis + ω_ir;

(*Angles
*)
B_vis = 60;
B_ir = 70;
B_sfg = ArcSin[(ω_vis Sin[β_vis] + ω_ir Sin[β_ir]) / ω_sfg] / °;

(*Snell's Law
*)
γ_sfg = ArcSin[(Sin[β_sfg] n_1,sfg) / n_2,sfg];
γ_vis = ArcSin[(Sin[β_vis] n_1,vis) / n_2,vis];
γ_ir = ArcSin[(Sin[β_ir] n_1,ir) / n_2,ir];

(*Fresnel Factors
*)
L_xx,sfg = (n_1,sfg 2 Cos[γ_sfg]) / (n_1,sfg Cos[γ_sfg] + n_2,sfg Cos[β_sfg]) Cos[β_sfg];
L_xx,vis = (n_1,vis 2 Cos[γ_vis]) / (n_1,vis Cos[γ_vis] + n_2,vis Cos[β_vis]) Cos[β_vis];
L_xx,ir = (n_1,ir 2 Cos[γ_ir]) / (n_1,ir Cos[γ_ir] + n_2,ir Cos[β_ir]) Cos[β_ir];

L_yy,sfg = (n_1,sfg 2 Cos[β_sfg]) / (n_1,sfg Cos[β_sfg] + n_2,sfg Cos[γ_sfg]);
L_yy,vis = (n_1,vis 2 Cos[β_vis]) / (n_1,vis Cos[β_vis] + n_2,vis Cos[γ_vis]);
L_yy,ir = (n_1,ir 2 Cos[β_ir]) / (n_1,ir Cos[β_ir] + n_2,ir Cos[γ_ir]);

L_zz,sfg = (n_2,sfg 2 Cos[β_sfg]) / (n_1,sfg Cos[γ_sfg] + n_2,sfg Cos[β_sfg]) (n_1,sfg / n_m,sfg)^2 Sin[β_sfg];
L_zz,vis = (n_2,vis 2 Cos[β_vis]) / (n_1,vis Cos[γ_vis] + n_2,vis Cos[β_vis]) (n_1,vis / n_m,vis)^2 Sin[β_vis];
L_zz,ir = (n_2,ir 2 Cos[β_ir]) / (n_1,ir Cos[γ_ir] + n_2,ir Cos[β_ir]) (n_1,ir / n_m,ir)^2 Sin[β_ir];
```

Effective Susceptibilities

C3V

(*Susceptibilities of C3V Molecule Symmetric Stretching
*)

$$\mathrm{C3VssSSP} = L_{yy,sfg}\, L_{yy,vis}\, L_{zz,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c} \left((1+R)\, \mathrm{Cos}[\theta] - (1-R)\, \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C3VssSPS} = L_{yy,sfg}\, L_{zz,vis}\, L_{yy,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C3VssPSS} = L_{zz,sfg}\, L_{yy,vis}\, L_{yy,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C3VssPPP} = -L_{xx,sfg}\, L_{xx,vis}\, L_{zz,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c} \left((1+R)\, \mathrm{Cos}[\theta] - (1-R)\, \mathrm{Cos}[\theta]^3\right) - L_{xx,sfg}\, L_{zz,vis}\, L_{xx,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right) + L_{zz,sfg}\, L_{xx,vis}\, L_{xx,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right) + L_{zz,sfg}\, L_{zz,vis}\, L_{zz,ir}\, N_s\, \beta_{c,c,c} \left(R\, \mathrm{Cos}[\theta] + (1-R)\, \mathrm{Cos}[\theta]^3\right);$$

(*Susceptibilities of C3V Molecule Antisymmetric Stretching
*)

$$\mathrm{C3VasSSP} = -L_{yy,sfg}\, L_{yy,vis}\, L_{zz,ir}\, N_s\, \beta_{a,c,a} \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C3VasSPS} = L_{yy,sfg}\, L_{zz,vis}\, L_{yy,ir}\, N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3$$

$$\mathrm{C3VasPSS} = L_{zz,sfg}\, L_{yy,vis}\, L_{yy,ir}\, N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3$$

$$\mathrm{C3VasPPP} = L_{xx,sfg}\, L_{xx,vis}\, L_{zz,ir}\, N_s\, \beta_{a,c,a} \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right) - L_{xx,sfg}\, L_{zz,vis}\, L_{xx,ir}\, N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3 + L_{zz,sfg}\, L_{xx,vis}\, L_{xx,ir}\, N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3 + L_{zz,sfg}\, L_{zz,vis}\, L_{zz,ir}\, 2 N_s\, \beta_{a,c,a} \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$(-0.0190977 - 0.0103648\, i)\, \mathrm{Cos}[\theta]^3$$

$$(-0.0134276 - 0.00922796\, i)\, \mathrm{Cos}[\theta]^3$$

C2V

(*Susceptibilities of C2V Molecule Symmetric Stretching
*)

$$\mathrm{C2VssSSP} = L_{yy,sfg}\, L_{yy,vis}\, L_{zz,ir} \left(\frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} + 2\, \beta_{c,c,c})\, \mathrm{Cos}[\theta] + \frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} - 2\, \beta_{c,c,c})\, \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C2VssSPS} = -L_{yy,sfg}\, L_{zz,vis}\, L_{yy,ir}\, \frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} - 2\, \beta_{c,c,c}) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C2VssPSS} = -L_{zz,sfg}\, L_{yy,vis}\, L_{yy,ir}\, \frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} - 2\, \beta_{c,c,c}) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C2VssPPP} = -L_{xx,sfg}\, L_{xx,vis}\, L_{zz,ir} \left(\frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} + 2\, \beta_{c,c,c})\, \mathrm{Cos}[\theta] + \frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} - 2\, \beta_{c,c,c})\, \mathrm{Cos}[\theta]^3\right) - L_{xx,sfg}\, L_{zz,vis}\, L_{xx,ir} \left(-\frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} - 2\, \beta_{c,c,c}) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)\right) + L_{zz,sfg}\, L_{xx,vis}\, L_{xx,ir} \left(-\frac{1}{4} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} - 2\, \beta_{c,c,c}) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)\right) + L_{zz,sfg}\, L_{zz,vis}\, L_{zz,ir} \left(\frac{1}{2} N_s\, (\beta_{a,a,c} + \beta_{b,b,c})\, \mathrm{Cos}[\theta] - \frac{1}{2} N_s\, (\beta_{a,a,c} + \beta_{b,b,c} - 2\, \beta_{c,c,c})\, \mathrm{Cos}[\theta]^3\right);$$

(*Susceptibilities of C2V Molecule Antisymmetric Stretching
*)

$$\mathrm{C2VasSSP} = L_{yy,sfg}\, L_{yy,vis}\, L_{zz,ir} \left(-\frac{1}{2} N_s\, \beta_{a,c,a} \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)\right);$$

$$\mathrm{C2VasSPS} = -L_{yy,sfg}\, L_{zz,vis}\, L_{yy,ir}\, \frac{1}{2} N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3;$$

$$\mathrm{C2VasPSS} = -L_{zz,sfg}\, L_{yy,vis}\, L_{yy,ir}\, \frac{1}{2} N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3;$$

$$\mathrm{C2VasPPP} = -L_{xx,sfg}\, L_{xx,vis}\, L_{zz,ir} \left(-\frac{1}{2} N_s\, \beta_{a,c,a} \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)\right) - L_{xx,sfg}\, L_{zz,vis}\, L_{xx,ir} \left(\frac{1}{2} N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3\right) + L_{zz,sfg}\, L_{xx,vis}\, L_{xx,ir} \left(\frac{1}{2} N_s\, \beta_{a,c,a}\, \mathrm{Cos}[\theta]^3\right) + L_{zz,sfg}\, L_{zz,vis}\, L_{zz,ir}\, N_s\, \beta_{a,c,a} \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

C∞V

(*Susceptibilities of C∞V Molecule Symmetric Stretching
*)

$$\mathrm{C\infty VssSSP} = L_{yy,sfg}\, L_{yy,vis}\, L_{zz,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c} \left((1+R)\, \mathrm{Cos}[\theta] - (1-R)\, \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C\infty VssSPS} = L_{yy,sfg}\, L_{zz,vis}\, L_{yy,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C\infty VssPSS} = L_{zz,sfg}\, L_{yy,vis}\, L_{yy,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

$$\mathrm{C\infty VssPPP} = -L_{xx,sfg}\, L_{xx,vis}\, L_{zz,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c} \left((1+R)\, \mathrm{Cos}[\theta] - (1-R)\, \mathrm{Cos}[\theta]^3\right) - L_{xx,sfg}\, L_{zz,vis}\, L_{xx,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right) + L_{zz,sfg}\, L_{xx,vis}\, L_{xx,ir}\, \frac{1}{2} N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right) + L_{zz,sfg}\, L_{zz,vis}\, L_{zz,ir}\, N_s\, \beta_{c,c,c} \left(R\, \mathrm{Cos}[\theta] + (1-R)\, \mathrm{Cos}[\theta]^3\right);$$