A.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_] := Sum[R[[i, l]] R[[j, m]] R[[k, n]] β[l, m, n], {l, a, c}, {m, a, c}, {n, a, c}]
```

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]
```

A.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.

A.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*)

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

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

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

A.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*)

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

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

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

A.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*)
```

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

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

First, the complete list of Euler transformations is produced using A.1. 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 A.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.

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

A.3.1.1. C_{3v} symmetry molecules

A.3.1.1.a. Symmetric stretching vibration

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

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

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

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

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

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

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

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

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

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

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

"Average Over Orientation (ϕ)"

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

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

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

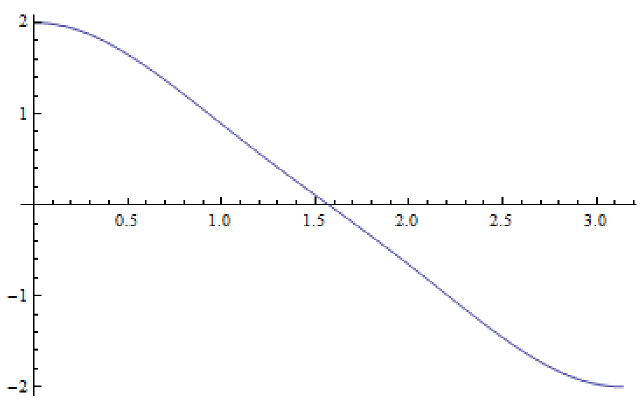
"Plot"

$N_s = 1$

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

$R = 2$

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



A.3.1.1.b. Anti-symmetric stretching vibration

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

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

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

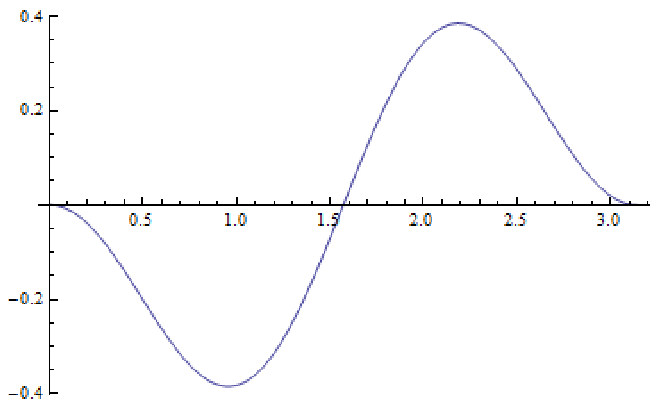
$$\boxed{\chi^{(2)\,as}_{y,y,z} = -N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

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

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



A.3.1.2. C_{2v} symmetry molecules

A.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"

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

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

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

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

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

"Plot"

```
Nₛ = 1
β_{a,a,c} = 1
β_{b,b,c} = 1
β_{c,c,c} = 1
```

$N_s = 1$

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

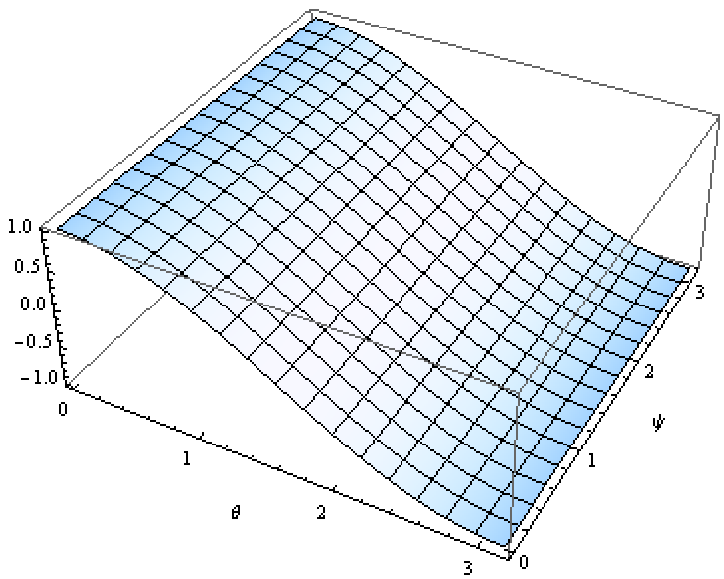
$\beta_{b,b,c} = 1$

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

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

$\{\theta,$ 0 Degree, 180 Degree$\}$, $\{\psi,$ 0 Degree, 180 Degree$\}$,

AxesLabel $\rightarrow \{\theta, \psi\}\Big]$



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

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

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

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

"Plot"

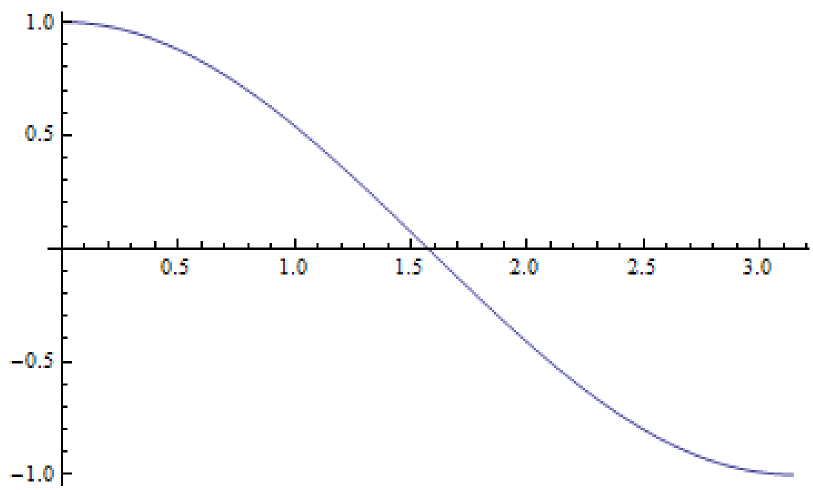
$N_s = 1$

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

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

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

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



A.3.1.2.b. Anti- symmetric stretching vibration

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

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

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

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

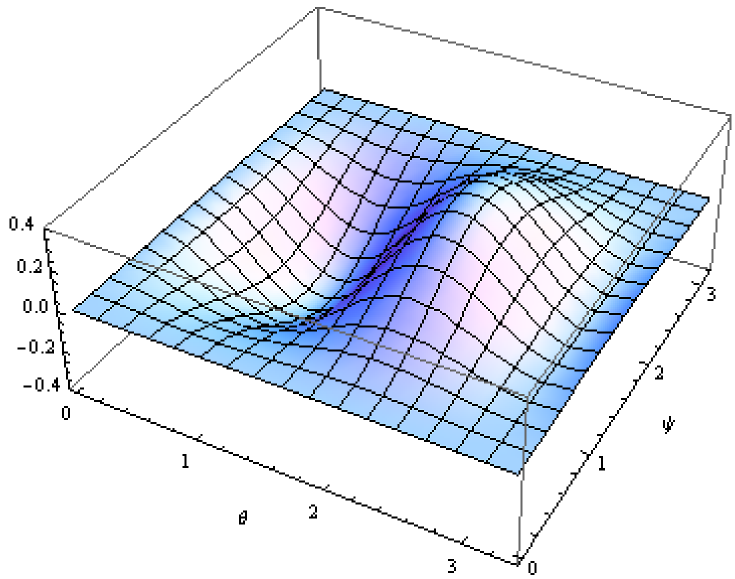
"Average Over Orientation (ϕ)-Non Free Rotation of C2V Group"

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

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

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

```
"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"

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

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

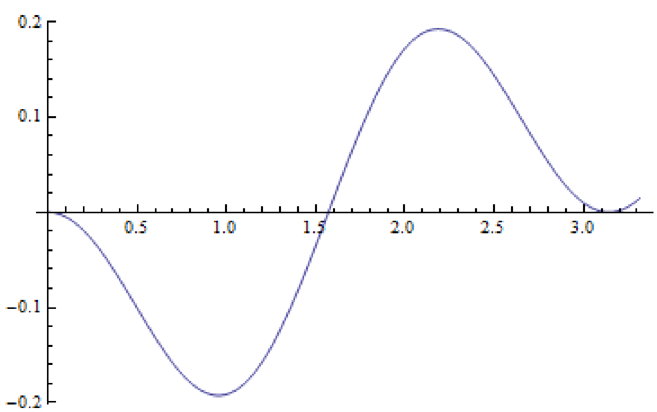
$$\boxed{\chi^{(2)\,as,B_1}_{Y,Y,Z}=-\frac{1}{2}N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

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

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



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

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

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

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

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

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

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

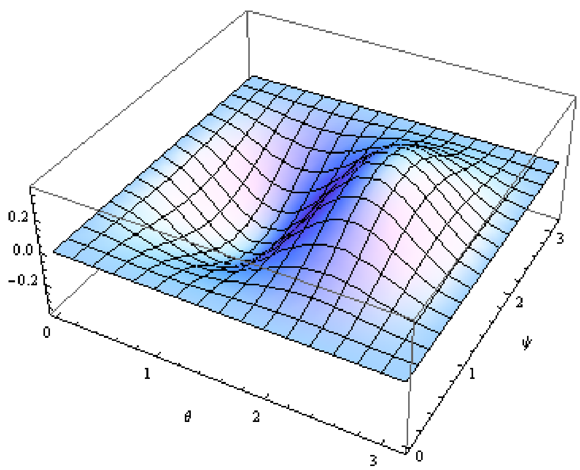
$$\boxed{\chi^{(2)\ as,B_2}_{Y,Y,z} = -N_s\, \beta_{b,c,b}\, Sin[\psi]^2\, (Cos[\theta] - Cos[\theta]^3)}$$

"Plot"

$N_s = 1$

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

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



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

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

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

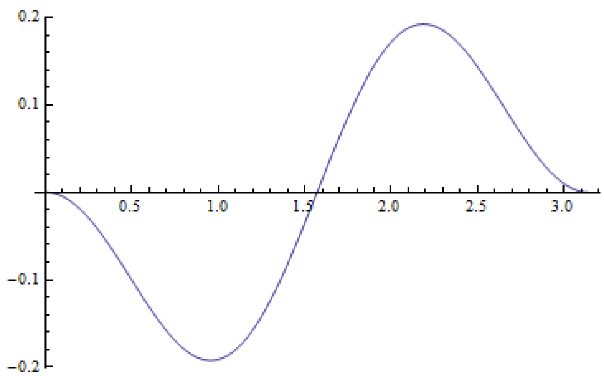
$$\boxed{\chi^{(2)\,as,B_2}_{Y,Y,Z} = -\frac{1}{2}N_s\,\beta_{b,c,b}\,\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

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

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



A.3.1.3. C∞v symmetry molecules

A.3.1.3.a. Symmetric stretching vibration

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

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

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

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

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

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

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

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

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

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

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

"Average Over Orientation (ϕ)"

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

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

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

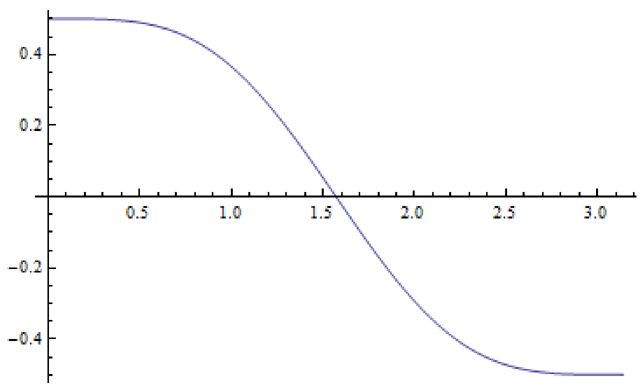
"Plot"

$N_s = 1$

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

$R = 0.5$

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



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

A.3.2.1. C_{3v} symmetry molecules

A.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)"

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

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

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

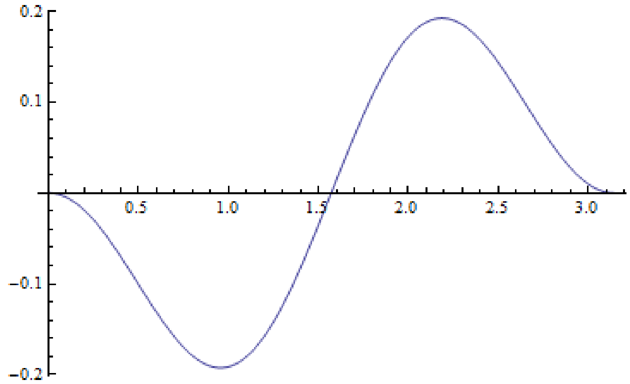
"Plot"

$N_s = 1$

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

$R = 2$

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



A.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--> $\beta_{c,a,a}=\beta_{a,c,a}$"

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

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

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

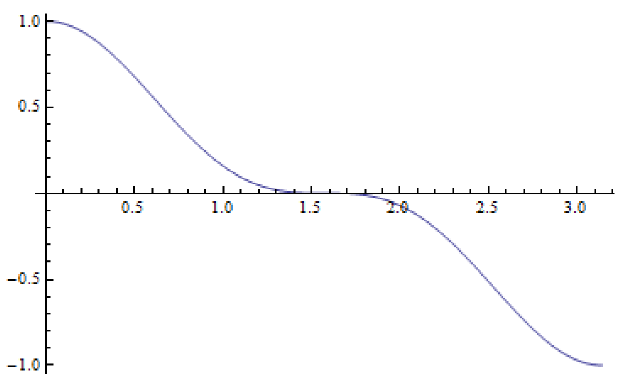
$\boxed{\chi^{(2)\,as}_{y,z,y} = N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$

"Plot"

$N_s = 1$

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

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



A.3.2.2. C_{2v} symmetry molecules

A.3.2.2.a. Symmetric stretching vibration

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

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

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

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

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

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

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

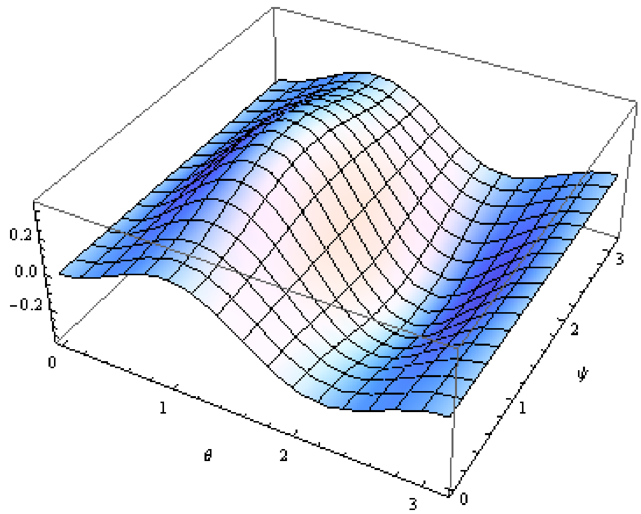
$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}(-\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,(\beta_{a,a,c}-\beta_{b,b,c}))\,d\phi\right)-$$
$$\frac{N_s}{2\pi}\mathrm{Cos}[\theta]\left(\int_0^{2\pi}\left(\mathrm{Cos}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,a,c}+\mathrm{Cos}[\phi]^2\,\mathrm{Cos}[\psi]^2\,\beta_{b,b,c}-\mathrm{Cos}[\phi]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

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

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

"Plot"

```
N_s = 1
β_{a,a,c} = 1
β_{b,b,c} = 2
β_{c,c,c} = 3
Plot3D[-1/2 N_s (Sin[ψ]^2 β_{a,a,c} + Cos[ψ]^2 β_{b,b,c} - β_{c,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"

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

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

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

"Plot"

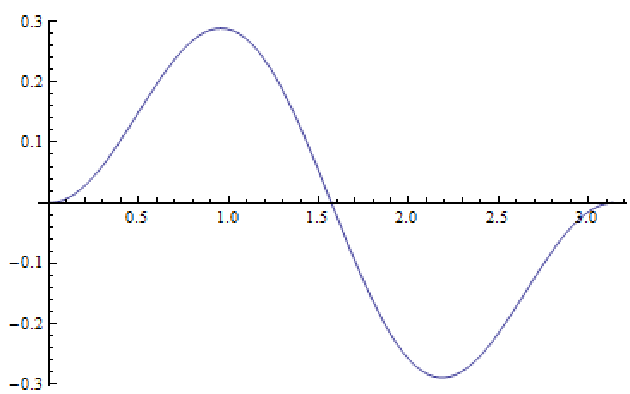
$N_s = 1$

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

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

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

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



A.3.2.2.b. Anti- symmetric stretching vibration

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

$\chi^{(2)\,as,B_1}_{Y,Z,Y}$ =
Expand[
-Cos[ϕ] Sin[θ]^2 Sin[ψ] (Cos[ψ] Sin[ϕ] + Cos[θ] Cos[ϕ] Sin[ψ]) $\beta_{a,c,a}$ +
Cos[θ] (Cos[ψ] Sin[ϕ] + Cos[θ] Cos[ϕ] Sin[ψ])^2 $\beta_{a,c,a}$]

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

= Cos[θ] Cos[ψ]^2 Sin[ϕ]^2 $\beta_{a,c,a}$ +
2 Cos[θ]^2 Cos[ϕ] Cos[ψ] Sin[ϕ] Sin[ψ] $\beta_{a,c,a}$ -
Cos[ϕ] Cos[ψ] (1 - Cos[θ]^2) Sin[ϕ] Sin[ψ] $\beta_{a,c,a}$ +
Cos[θ]^3 Cos[ϕ]^2 Sin[ψ]^2 $\beta_{a,c,a}$ -
Cos[θ] Cos[ϕ]^2 (1 - Cos[θ]^2) Sin[ψ]^2 $\beta_{a,c,a}$

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

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

= -Cos[ϕ] Cos[ψ] Sin[ϕ] Sin[ψ] $\beta_{a,c,a}$ +
Cos[θ] (Cos[ψ]^2 (1 - Cos[ϕ]^2) - (1 - Cos[ψ]^2) Cos[ϕ]^2) $\beta_{a,c,a}$ +
3 Cos[θ]^2 Cos[ϕ] Cos[ψ] Sin[ϕ] Sin[ψ] $\beta_{a,c,a}$ +
2 Cos[θ]^3 Cos[ϕ]^2 Sin[ψ]^2 $\beta_{a,c,a}$

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

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

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

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

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

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

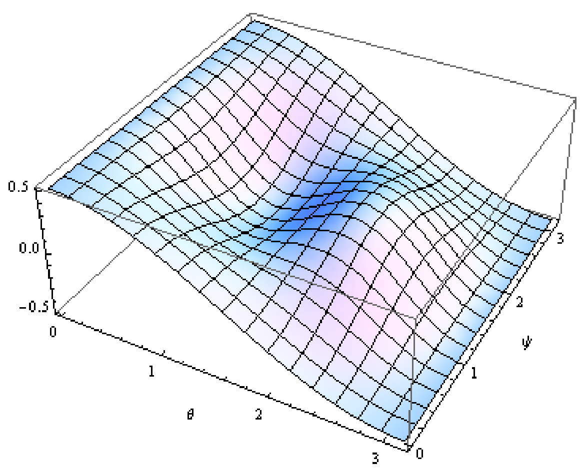
$$\boxed{\chi^{(2)\,as,B_1}_{Y,z,Y}=\frac{1}{2}N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



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

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

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

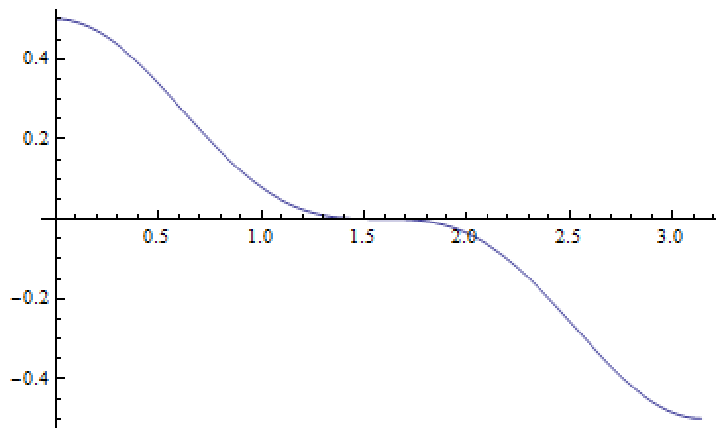
$$\boxed{\chi^{(2)\,as,B_1}_{Y,Z,Y}=\frac{1}{2}N_s\,\beta_{a,c,a}\,\mathrm{Cos}[\theta]^3}$$

"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"

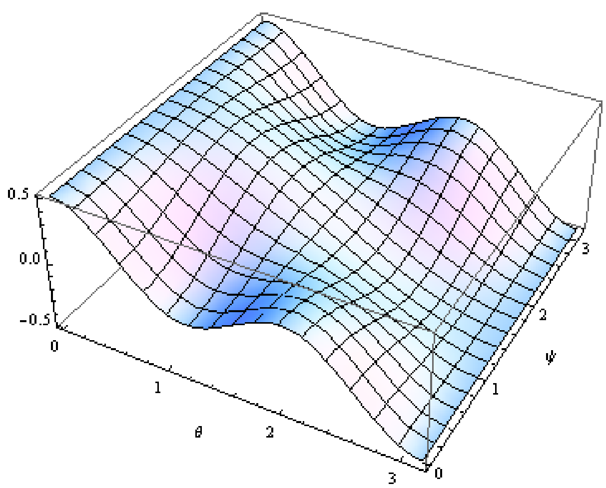
$$\boxed{\chi^{(2)\,as,B_2}_{Y,z,Y} = -\frac{1}{2}N_s\,\beta_{b,c,b}\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta]+N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3}$$

"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"

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

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

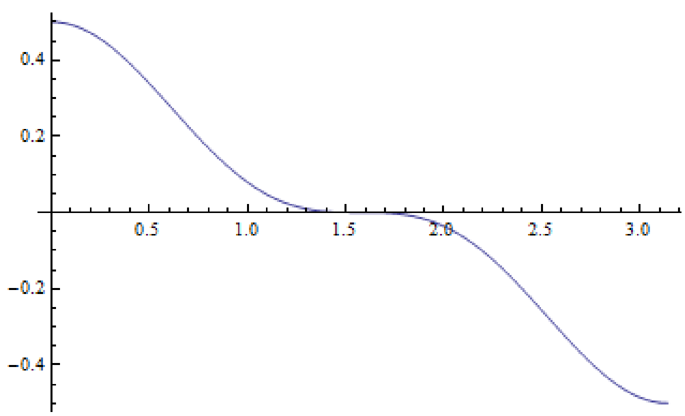
$$\boxed{\chi^{(2)\,as,B_2}_{Y,z,Y}=\frac{1}{2}N_s\,\beta_{b,c,b}\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



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

A.3.2.3.a. Symmetric stretching vibration

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

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

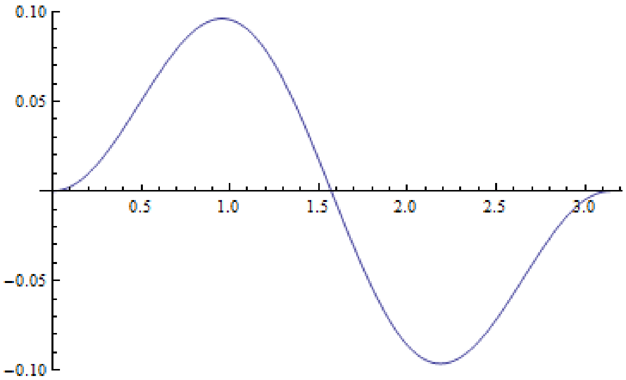
$$= -\frac{1}{2}\,(-1+R)\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\beta_{c,c,c}$$

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

"Plot"

```
N_s = 1
β_{c,c,c} = 1
R = 0.5
```

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



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

A.3.3.1. C_{3v} symmetry molecules

A.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)"

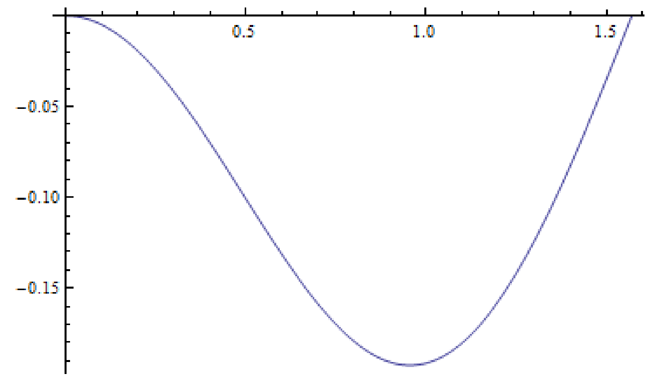
$$\frac{N_s}{(2\pi)^2}\left(\int_0^{2\pi}\int_0^{2\pi}\left(\beta_{c,c,c}\left(-\text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,R - \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\psi]^2\,R + \text{Cos}[\theta]\,\text{Cos}[\phi]^2\,\text{Sin}[\theta]^2\right)\right)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

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

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

"Plot"

```
Ns = 1
βc,c,c = 1
R = 2
Plot[1/2 Ns βc,c,c (1 - R) (Cos[θ] - Cos[θ]^3), {θ, 0 Degree, 90 Degree}]
```



A.3.3.1.b. Anti- symmetric stretching vibration

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

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

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

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

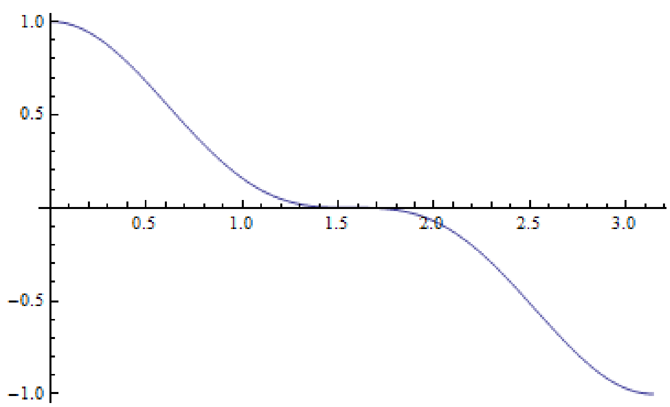
$$\boxed{\chi^{(2)\,as}_{z,y,y} = N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



A.3.3.2. C_{2v} symmetry molecules

A.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"

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

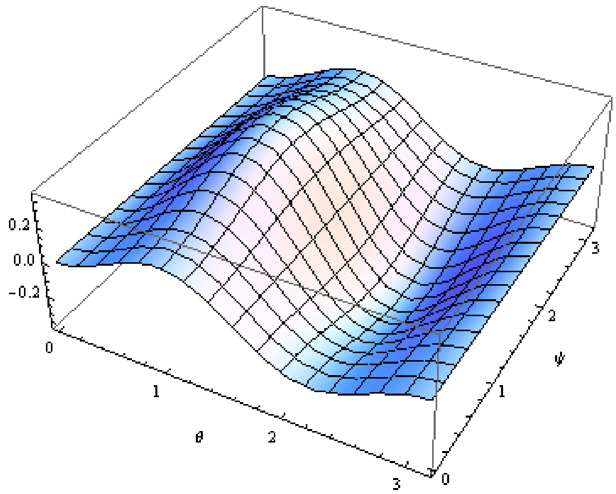
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\left(-\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\psi]^2\,\beta_{b,b,c} + \beta_{c,c,c}\right)$$

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

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

"Plot"

```
Nₛ = 1
β_{a,a,c} = 1
β_{b,b,c} = 2
β_{c,c,c} = 3
Plot3D[-1/2 Nₛ (Sin[ψ]^2 β_{a,a,c} + Cos[ψ]^2 β_{b,b,c} - β_{c,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"

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

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

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

"Plot"

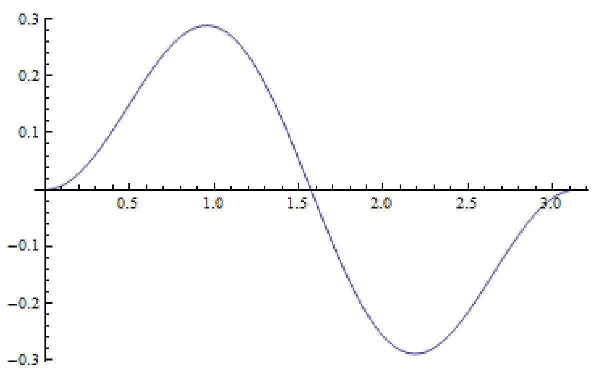
$N_s = 1$

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

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

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

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



A.3.3.2.b. Anti- symmetric stretching vibration

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

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

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

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

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

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

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

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

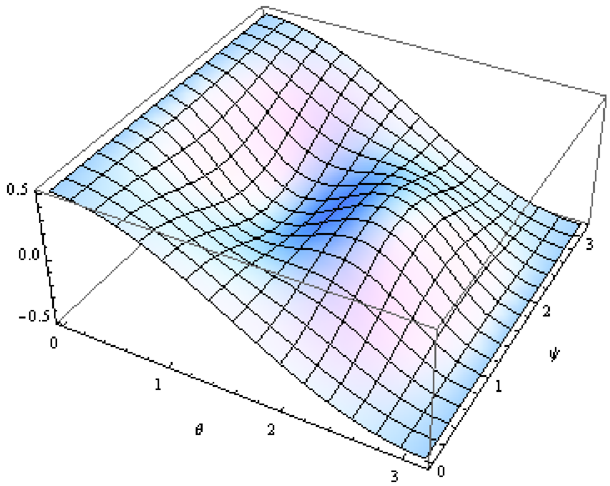
$$\boxed{\chi^{(2)\,as,B_1}_{z,y,y}=\frac{1}{2}\,N_s\,\beta_{a,c,a}\,\left(\text{Cos}[\psi]^2-\text{Sin}[\psi]^2\right)\text{Cos}[\theta]+N_s\,\beta_{a,c,a}\,\text{Sin}[\psi]^2\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



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

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

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

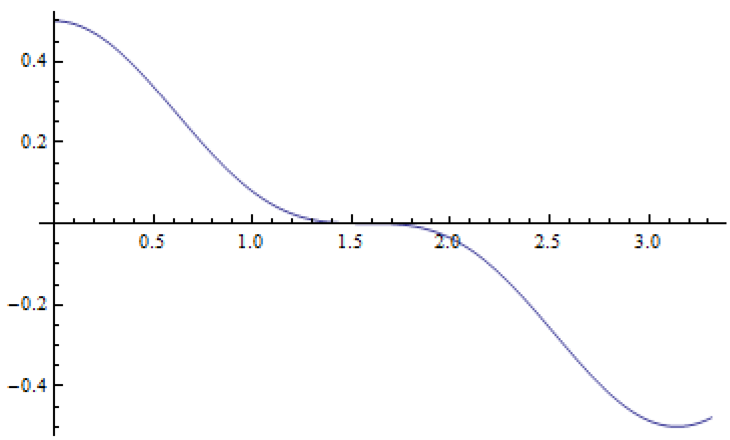
$$\boxed{\chi^{(2)\,as,B_1}_{z,Y,Y} = \frac{1}{2} N_s\, \beta_{a,c,a}\, \text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



"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"

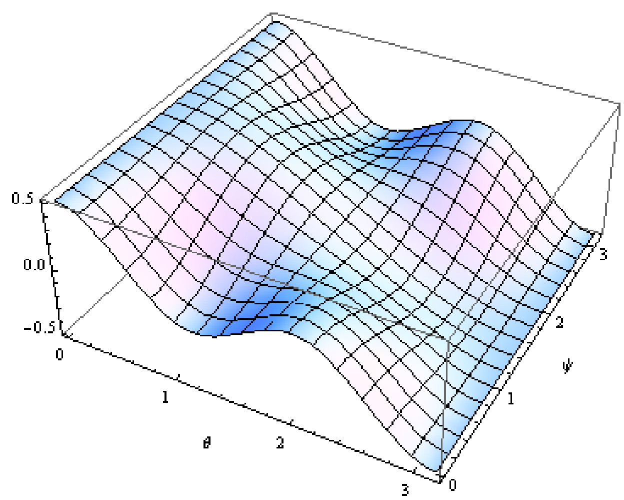
$$\boxed{\chi^{(2)\,as,B_2}_{Z,Y,Y} = -\frac{1}{2}\,N_s\,\beta_{b,c,b}\,\left(\mathrm{Cos}[\psi]^2-\mathrm{Sin}[\psi]^2\right)\mathrm{Cos}[\theta] + N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\psi]^2\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



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

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

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

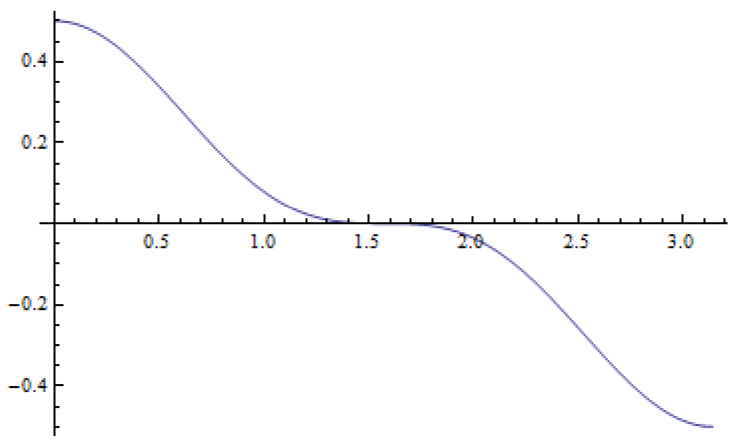
$$\boxed{\chi^{(2)\,as,B_2}_{z,y,y}=\frac{1}{2}N_s\,\beta_{b,c,b}\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



A.3.3.3. $C_{\infty v}$ symmetry molecules

A.3.3.3.a. Symmetric stretching vibration

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

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

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

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

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

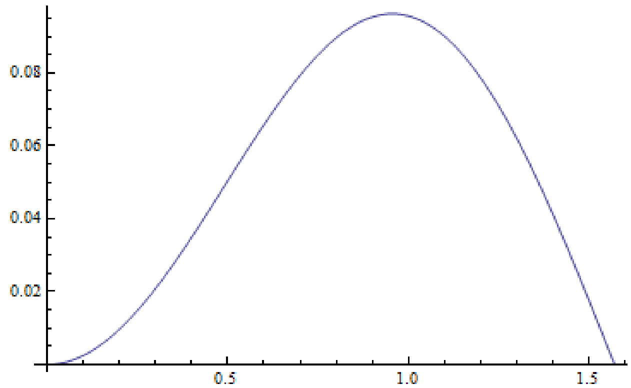
"Average Over Orientation (ϕ,ψ)"

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

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

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

```
"Plot"

N_s = 1
β_{c,c,c} = 1
R = 0.5
Plot[1/2 N_s β_{c,c,c} (1 - R) (Cos[θ] - Cos[θ]^3), {θ, 0 Degree, 90 Degree}]
```



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

A.3.4.1. C_{3v} symmetry molecules

A.3.4.1.a. Symmetric stretching vibration

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

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

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

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

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

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

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

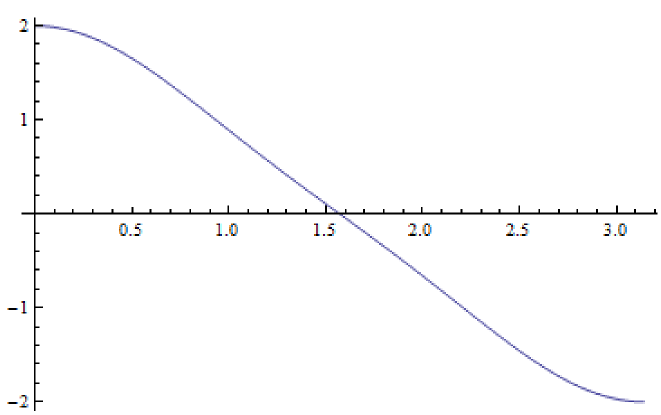
"Plot"

$N_s = 1$

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

$R = 2$

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



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

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

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

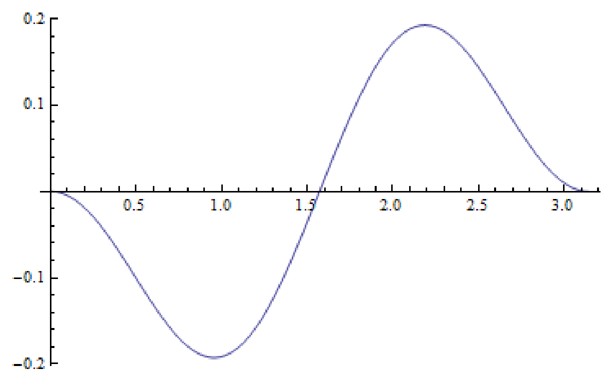
"Plot"

$N_s = 1$

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

$R = 2$

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



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

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

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

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

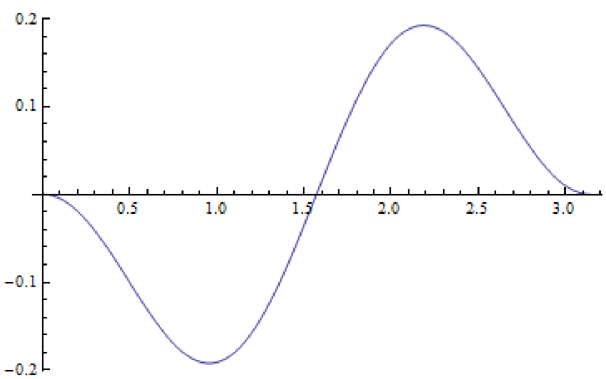
"Plot"

$N_s = 1$

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

$R = 2$

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



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

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

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

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

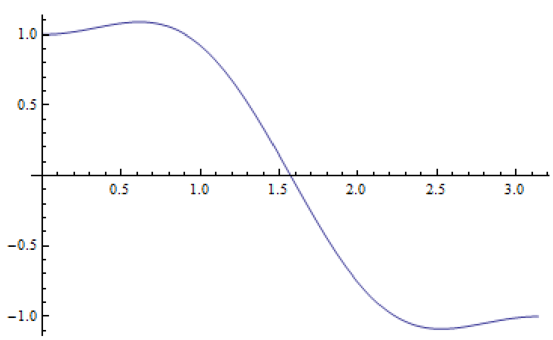
$= \left(\cos[\theta]^3 + R\cos[\theta] - R\cos[\theta]^3\right)N_s\,\beta_{c,c,c}$

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

"Plot"

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

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



A.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--> $\beta_{c,a,a}$=$\beta_{a,c,a}$"

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

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

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

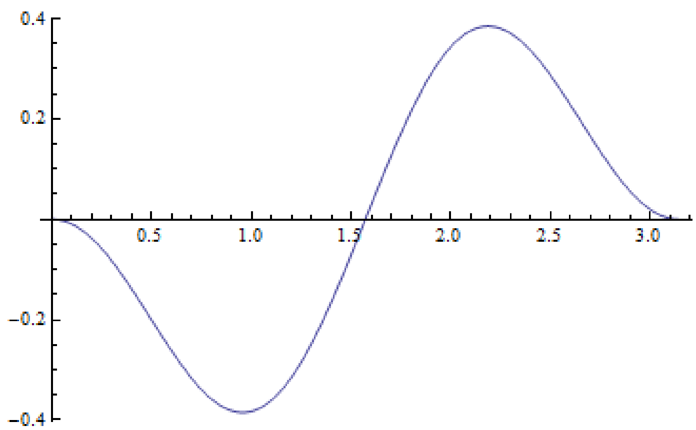
$\boxed{\chi^{(2)\,as}_{x,x,z} = -N_s\,\beta_{a,c,a}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$

"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-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

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

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

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

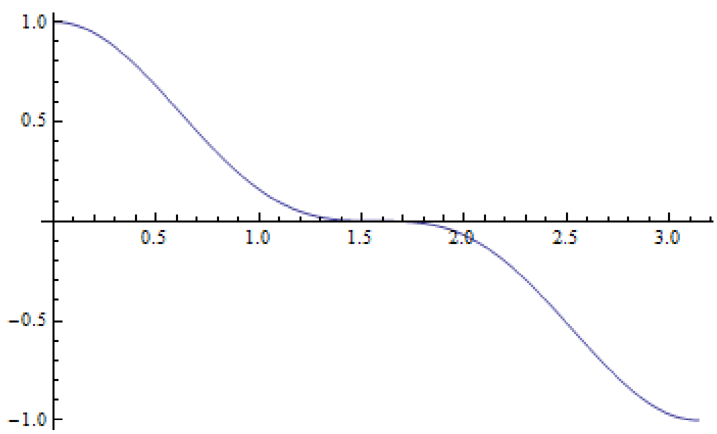
$$\boxed{\chi^{(2)\,as}_{x,z,x} = N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

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

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

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

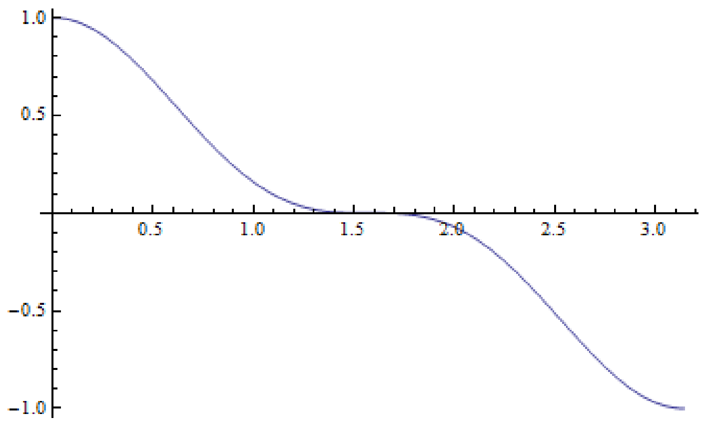
$$\boxed{\chi^{(2)\,as}_{z,x,x} = N_s\,\beta_{a,c,a}\,\text{Cos}[\theta]^3}$$

"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-->$\beta_{a,c,a}$, $\beta_{c,a,a}$, $\beta_{a,a,a}$"

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

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

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

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

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

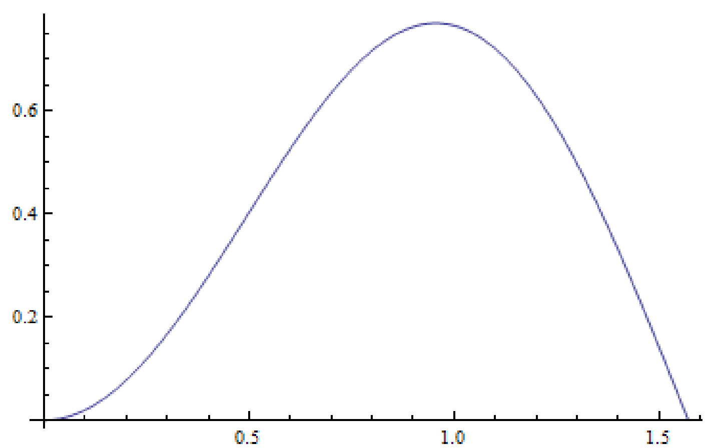
$$\boxed{\chi^{(2)\,as}_{z,z,z} = 2\, N_s\, \beta_{a,c,a} \left(\text{Cos}[\theta] - \text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

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

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



A.3.4.2. C_{2v} symmetry molecules

A.3.4.2.a. Symmetric stretching vibration

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

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

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

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

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

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

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

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

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

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

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

"Plot"

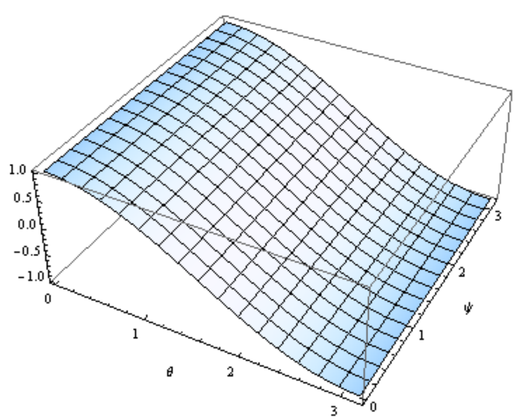
$N_s = 1$

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

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

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

```
Plot3D[1/2 Ns (Cos[ψ]^2 βa,a,c + Sin[ψ]^2 βb,b,c + βc,c,c) Cos[θ] +
  1/2 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"

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

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

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

"Plot"

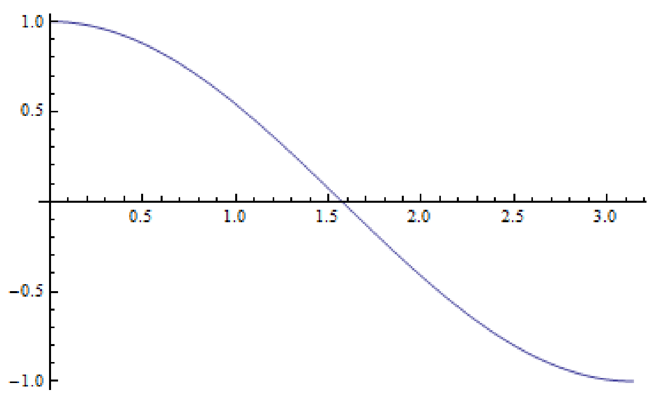
$N_s = 1$

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

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

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

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



"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"

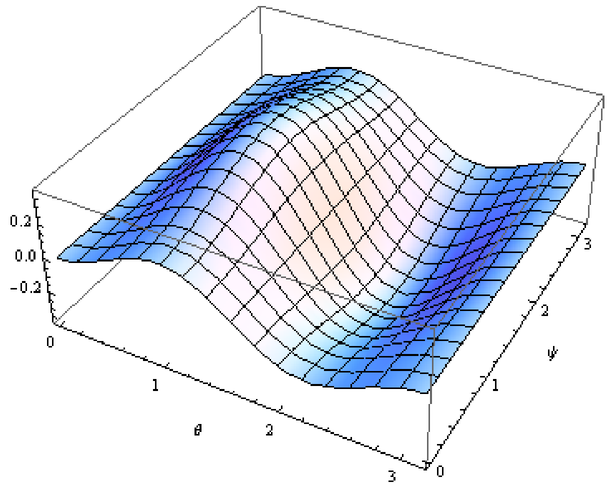
$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(\text{Cos}[\phi]\,\text{Cos}[\psi]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]\,\text{Sin}[\psi]\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\theta]\,\text{Cos}[\psi]^2\,\text{Sin}[\theta]^2\,\text{Sin}[\phi]^2\,\beta_{b,b,c}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

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

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

"Plot"

```
N_s = 1
β_{a,a,c} = 1
β_{b,b,c} = 2
β_{c,c,c} = 3
Plot3D[-1/2 N_s (Sin[ψ]^2 β_{a,a,c} + Cos[ψ]^2 β_{b,b,c} - β_{c,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"

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

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

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

"Plot"

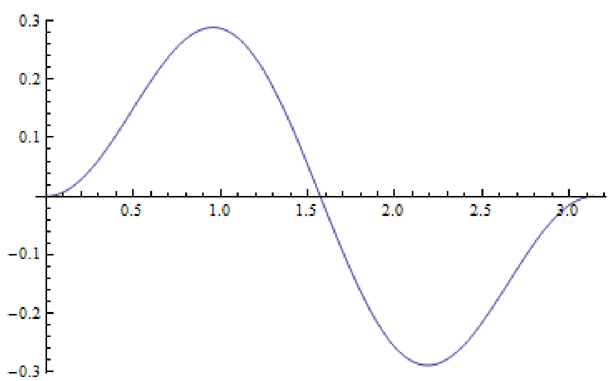
$N_s = 1$

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

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

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

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



"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"

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

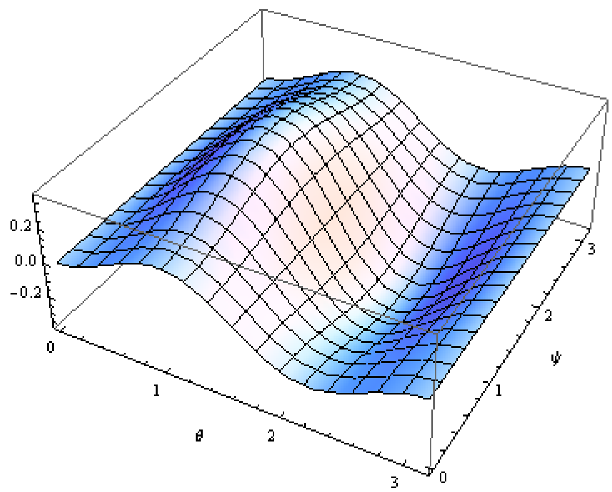
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\text{Sin}[\theta]^2\,N_s\,\left(-\text{Sin}[\psi]^2\,\beta_{a,a,c} - \text{Cos}[\psi]^2\,\beta_{b,b,c} + \beta_{c,c,c}\right)$$

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

"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"

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

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

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

"Plot"

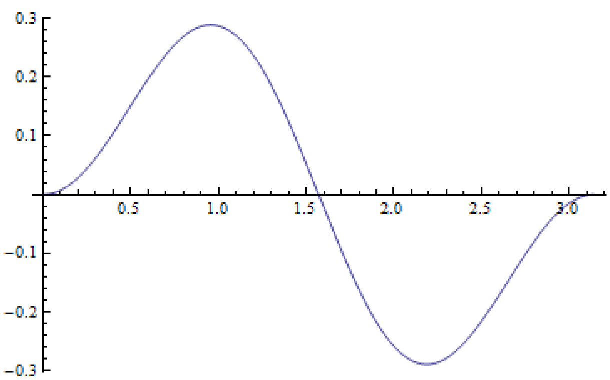
$N_s = 1$

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

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

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

```
Plot[-1/4 Ns (βa,a,c + βb,b,c - 2 βc,c,c) (Cos[θ] - Cos[θ]^3),
 {θ, 0 Degree, 180 Degree}]
```



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

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

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

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

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

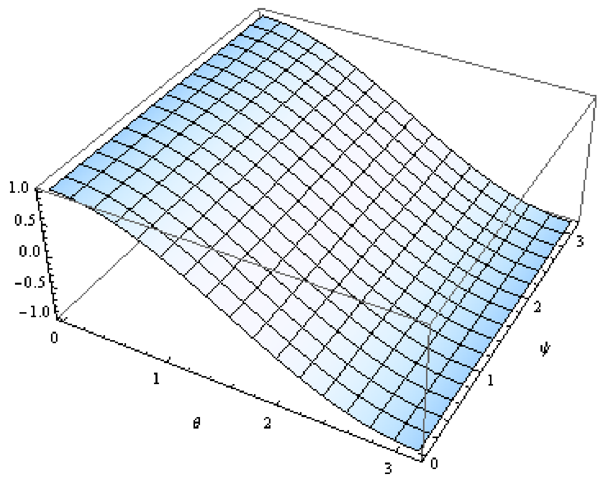
$$=N_s\left(\cos[\theta]\,\sin[\theta]^2\,\sin[\psi]^2\,\beta_{a,a,c}+\cos[\theta]\,\cos[\psi]^2\,\sin[\theta]^2\,\beta_{b,b,c}+\cos[\theta]^3\,\beta_{c,c,c}\right)$$

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

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

"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"

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

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

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

"Plot"

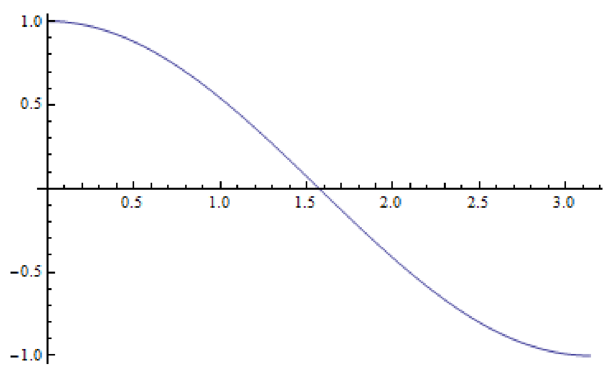
$N_s = 1$

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

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

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

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



A.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 Sin[θ]^2 Sin[ϕ] Sin[ψ] (Cos[ϕ] Cos[ψ] - Cos[θ] Sin[ϕ] Sin[ψ]) $\beta_{a,c,a}$]

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

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

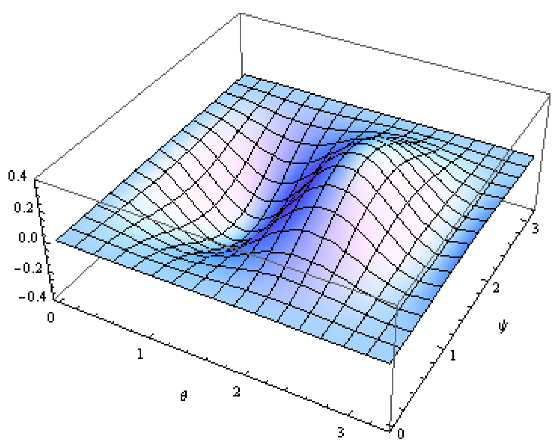
$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(2\,\mathrm{Cos}[\phi]\,\mathrm{Cos}[\psi]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]\,\mathrm{Sin}[\psi]\,\beta_{a,c,a} - 2\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]^2\,\mathrm{Sin}[\phi]^2\,\mathrm{Sin}[\psi]^2\,\beta_{a,c,a}\right)d\phi\right)$$

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

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

"Plot"

```
Ns = 1
βa,c,a = 1
Plot3D[-Ns βa,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"

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

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

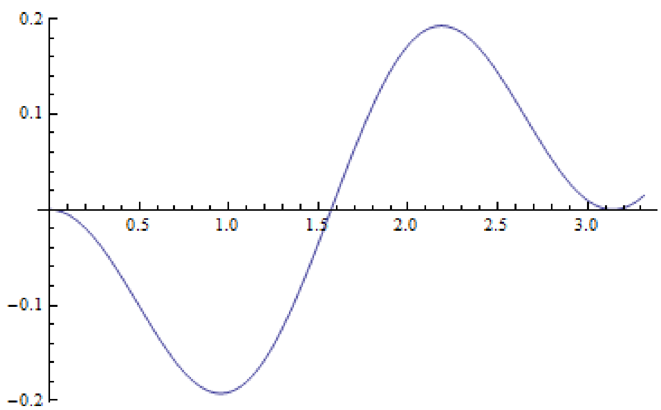
$$\boxed{\chi^{(2)\,as,B_1}_{x,x,z}=-\frac{1}{2}\,N_s\,\beta_{a,c,a}\,\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"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-->$\beta_{b,c,b}$"

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

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

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

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

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

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

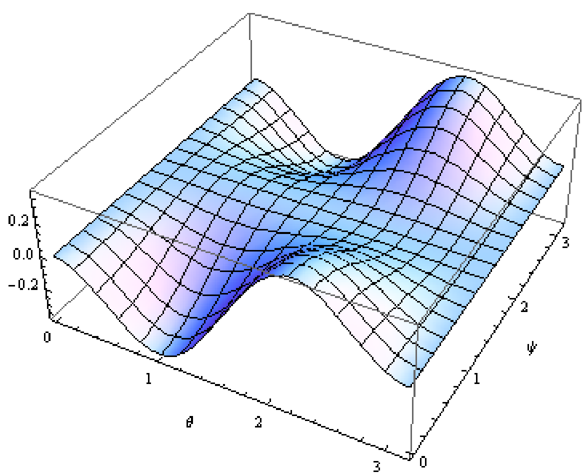
$$\boxed{\chi_{x,x,z}^{(2)\ as,B_2} = -N_s\,\beta_{b,c,b}\cos[\psi]^2\left(\cos[\theta]-\cos[\theta]^3\right)}$$

"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"

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

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

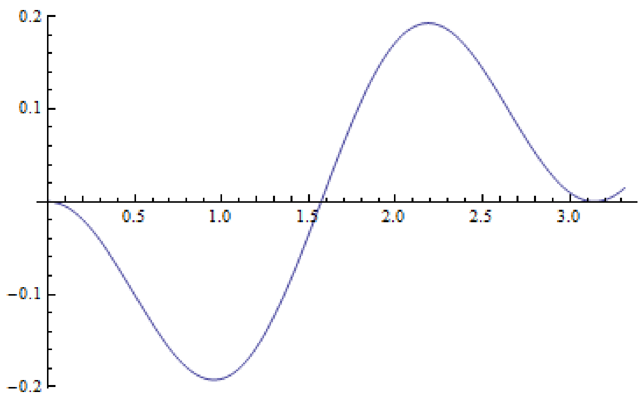
$$\boxed{\chi^{(2)\,as,B_2}_{x,x,z} = -\frac{1}{2}\,N_s\,\beta_{b,c,b}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"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]) $\beta_{a,c,a}$ +
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"

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

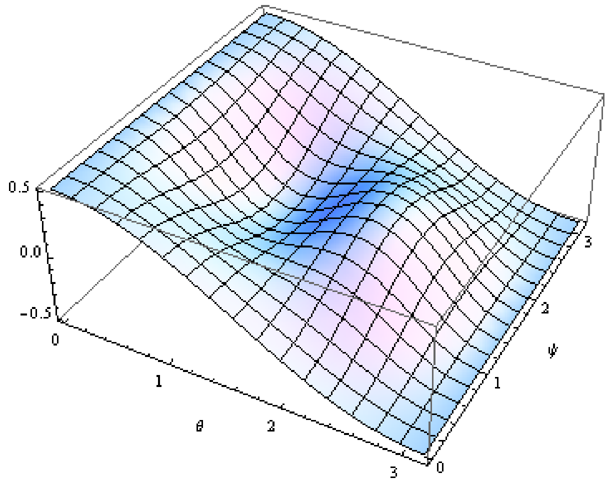
$$= \frac{1}{2}\cos[\theta]\left(\cos[\psi]^2 + \cos[2\theta]\sin[\psi]^2\right)\beta_{a,c,a}$$

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

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

"Plot"

```
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"

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

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

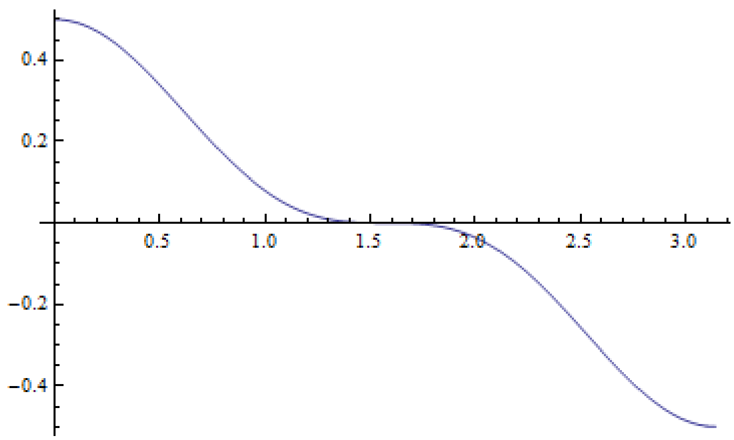
$$\boxed{\chi^{(2)\,as,B_1}_{x,z,x}=\frac{1}{2} N_s\, \beta_{a,c,a}\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



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

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

Expand[

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

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

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

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

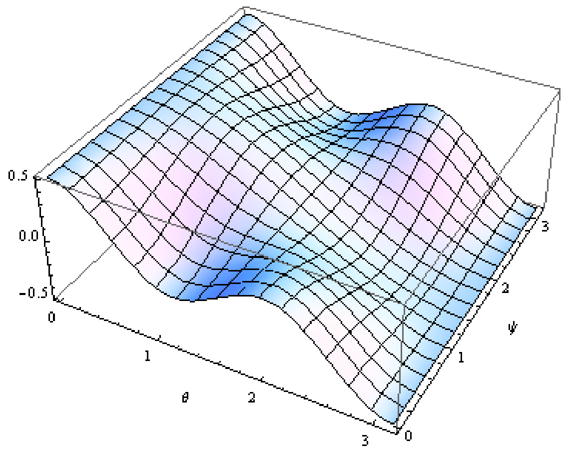
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\left(\text{Cos}[\theta]^2 - \left(\text{Cos}[\psi]^2 - \text{Sin}[\psi]^2\right)\text{Sin}[\theta]^2\right)N_s\,\beta_{b,c,b}$$

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

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

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

```
"Plot"

Nₛ = 1
β_{b,c,b} = 1
Plot3D[-1/2 Nₛ β_{b,c,b} (Cos[ψ]^2 - Sin[ψ]^2) Cos[θ] +
  Nₛ β_{b,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"

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

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

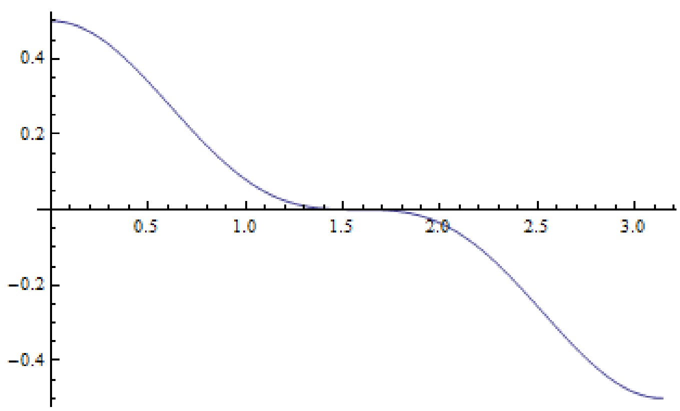
$$\boxed{\chi^{(2)\,as,B_2}_{x,z,x}=\frac{1}{2}N_s\,\beta_{b,c,b}\,\mathrm{Cos}[\theta]^3}$$

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

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

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

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

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

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

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

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

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

"Plot"

```
Nₛ = 1
β_{a,c,a} = 1
```

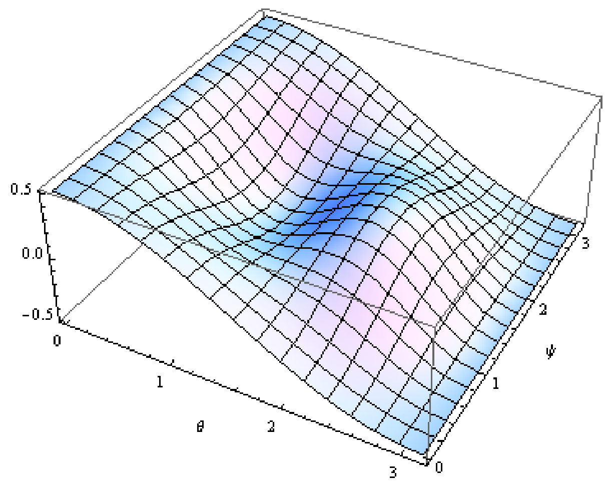
$N_s = 1$

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

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

$\{\theta, 0\,\text{Degree}, 180\,\text{Degree}\}, \{\psi, 0\,\text{Degree}, 180\,\text{Degree}\},$

$\left.\text{AxesLabel} \to \{\theta, \psi\}\right]$



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

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

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

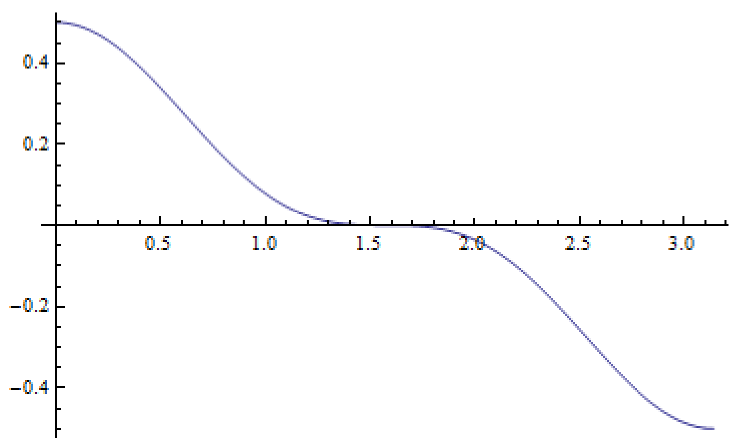
$$\boxed{\chi^{(2)\,as,B_1}_{z,x,x}=\frac{1}{2}N_s\,\beta_{a,c,a}\,\mathrm{Cos}[\theta]^3}$$

"Plot"

$N_s = 1$

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

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



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

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

Expand[

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

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

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

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

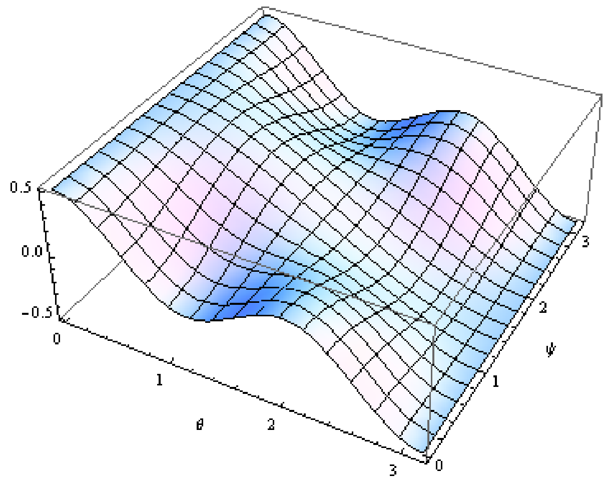
$$= \frac{1}{2}\,\text{Cos}[\theta]\,\left(\text{Cos}[\theta]^2 - \text{Cos}[2\,\psi]\,\text{Sin}[\theta]^2\right)\,N_s\,\beta_{b,c,b}$$

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

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

"Plot"

```
N_s = 1
β_{b,c,b} = 1
Plot3D[-1/2 N_s β_{b,c,b} (Cos[ψ]^2 - Sin[ψ]^2) Cos[θ] +
  N_s β_{b,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"

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

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

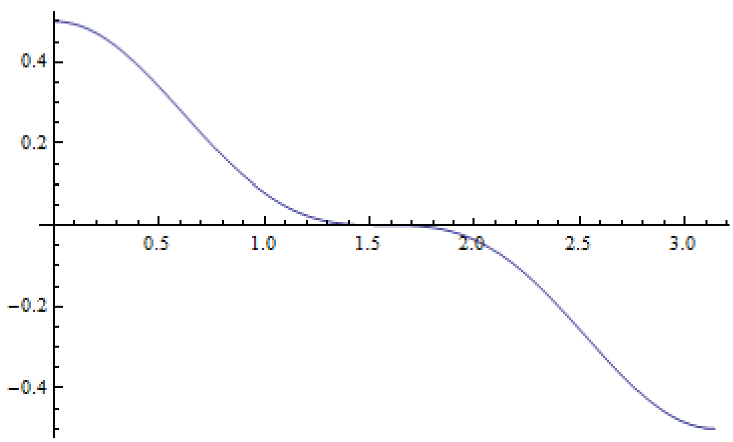
$$\boxed{\chi^{(2)\,as,B_2}_{s,x,x} = \frac{1}{2} N_s \beta_{b,c,b} \mathrm{Cos}[\theta]^3}$$

"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"

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

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

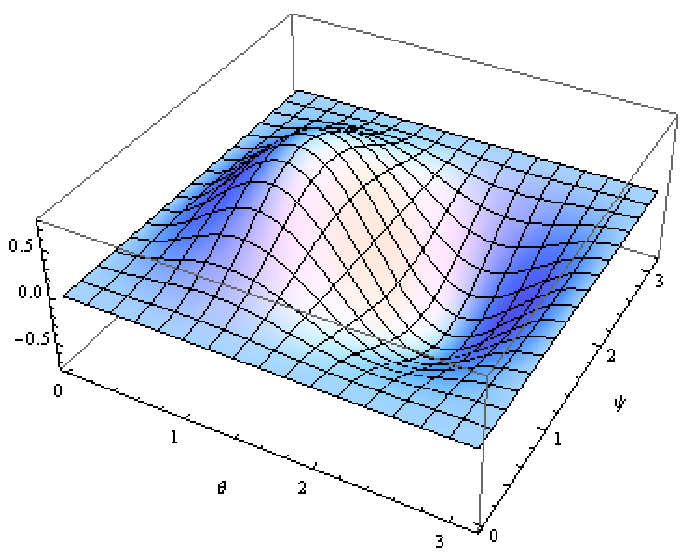
$$\boxed{\chi^{(2)\,as,B_1}_{z,z,z} = 2\,N_s\,\beta_{a,c,a}\,\mathrm{Sin}[\psi]^2\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"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"

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

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

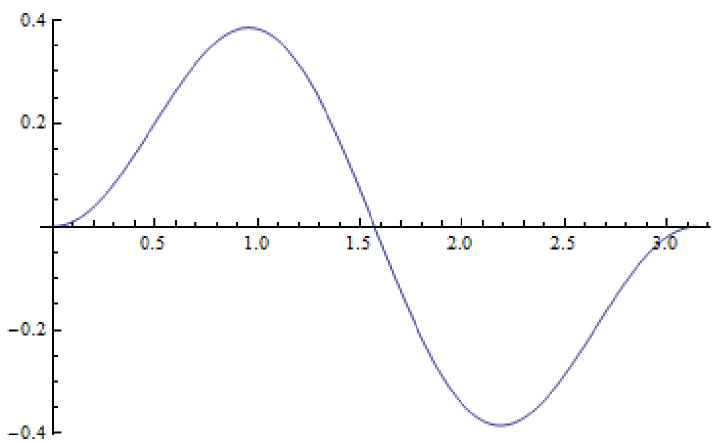
$$\boxed{\chi^{(2)\,as,B_1}_{z,z,z}=N_s\,\beta_{a,c,a}\left(\mathrm{Cos}[\theta]-\mathrm{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

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

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



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

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

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

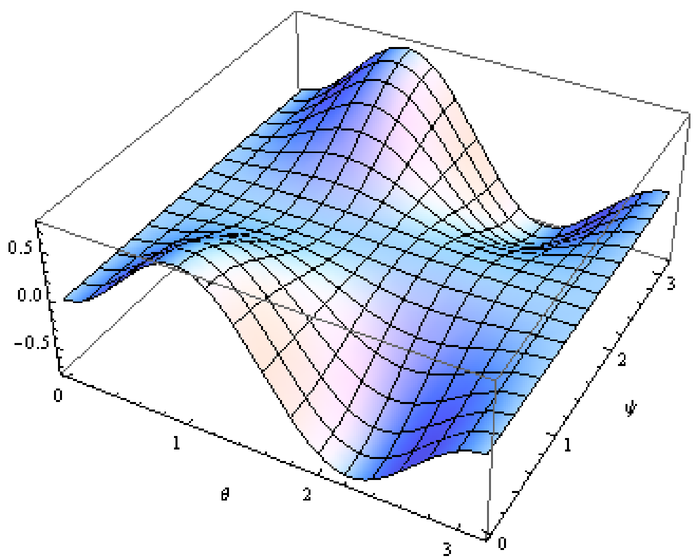
$$\frac{N_s}{2\pi}\left(\int_0^{2\pi}\left(2\,\mathrm{Cos}[\theta]\,\mathrm{Cos}[\psi]^2\,\mathrm{Sin}[\theta]^2\,\beta_{b,c,b}\right)d\phi\right)$$

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

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

"Plot"

```
Ns = 1
βb,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"

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

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

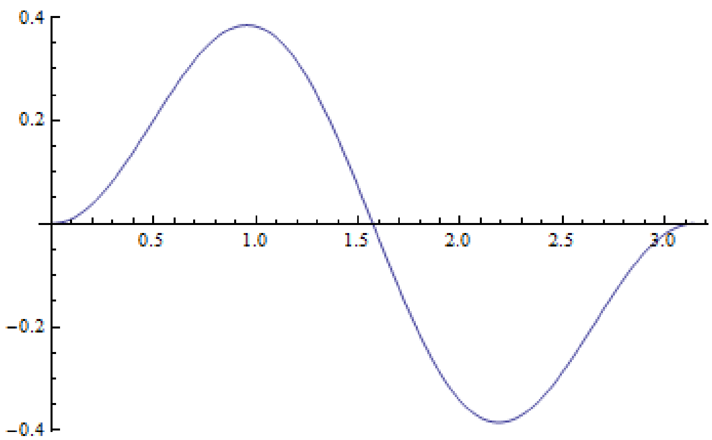
$$\boxed{\chi^{(2)\,as,B_2}_{z,z,z}=N_s\,\beta_{b,c,b}\left(\text{Cos}[\theta]-\text{Cos}[\theta]^3\right)}$$

"Plot"

$N_s = 1$

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

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



A.3.4.3. C∞v symmetry molecules

A.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)"

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

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

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

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

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

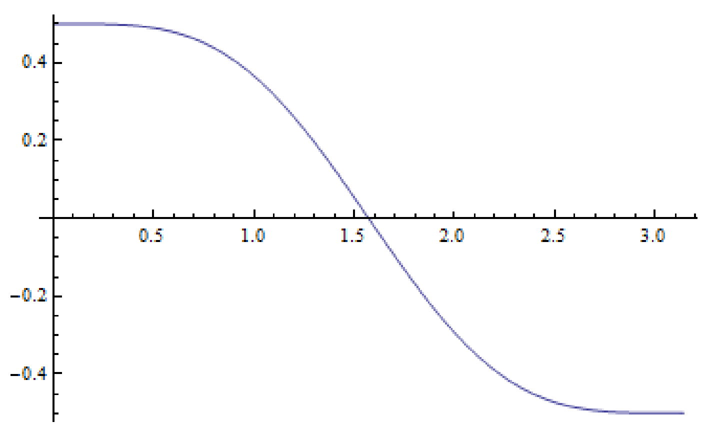
"Plot"

$N_s = 1$

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

$R = 0.5$

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



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

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

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

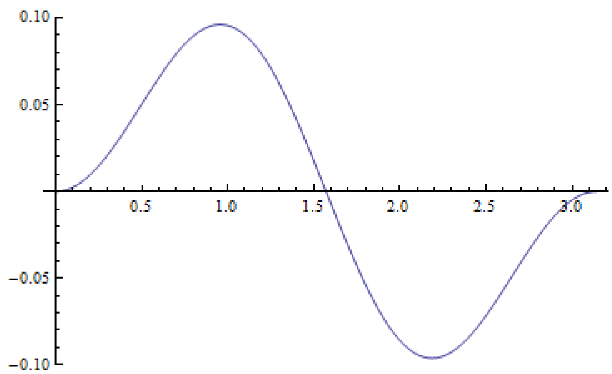
"Plot"

$N_s = 1$

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

$R = 0.5$

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



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

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

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

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

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

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

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

"Average Over Orientation (ϕ,ψ)"

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

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

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

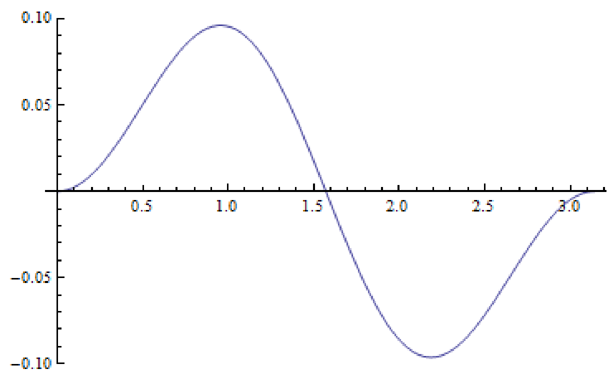
"Plot"

$N_s = 1$

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

$R = 0.5$

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



"PPP,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)"

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

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

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

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

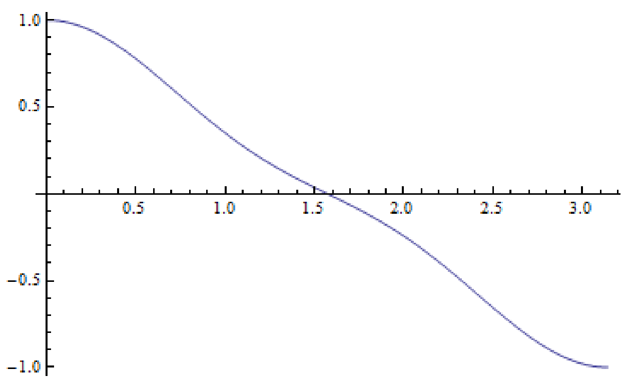
"Plot"

$N_s = 1$

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

$R = 0.5$

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
*)
```

$\beta_{sfg} = B_{sfg}\,°;$

$\beta_{vis} = B_{vis}\,°;$

$\beta_{ir} = B_{ir}\,°;$

$\gamma_{sfg} = \Gamma_{sfg}\,°;$

$\gamma_{vis} = \Gamma_{vis}\,°;$

$\gamma_{ir} = \Gamma_{ir}\,°;$

```
(*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
*)
```

$R = 3.4;$

$\beta_{a,c,a} = 3.4;$

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

$N_s = 1;$

```
(*Wavenumber
*)
```

$\omega_{vis} = 9400;$

$\omega_{ir} = 2900;$

$\omega_{sfg} = \omega_{vis} + \omega_{ir};$

```
(*Angles
*)
```

$B_{vis} = 60;$

$B_{ir} = 70;$

$$B_{sfg} = \mathrm{ArcSin}\left[\frac{\omega_{vis}\,\mathrm{Sin}[\beta_{vis}] + \omega_{ir}\,\mathrm{Sin}[\beta_{ir}]}{\omega_{sfg}}\right] \Big/ °;$$

```
(*Snell's Law
*)
```

$$\gamma_{sfg} = \mathrm{ArcSin}\left[\frac{\mathrm{Sin}[\beta_{sfg}]\,n_{1,sfg}}{n_{2,sfg}}\right];$$

$$\gamma_{vis} = \mathrm{ArcSin}\left[\frac{\mathrm{Sin}[\beta_{vis}]\,n_{1,vis}}{n_{2,vis}}\right];$$

$$\gamma_{ir} = \mathrm{ArcSin}\left[\frac{\mathrm{Sin}[\beta_{ir}]\,n_{1,ir}}{n_{2,ir}}\right];$$

```
(*Fresnel Factors
*)
```

$$L_{xx,sfg} = \frac{n_{1,sfg}\,2\,\mathrm{Cos}[\gamma_{sfg}]}{n_{1,sfg}\,\mathrm{Cos}[\gamma_{sfg}] + n_{2,sfg}\,\mathrm{Cos}[\beta_{sfg}]}\,\mathrm{Cos}[\beta_{sfg}];$$

$$L_{xx,vis} = \frac{n_{1,vis}\,2\,\mathrm{Cos}[\gamma_{vis}]}{n_{1,vis}\,\mathrm{Cos}[\gamma_{vis}] + n_{2,vis}\,\mathrm{Cos}[\beta_{vis}]}\,\mathrm{Cos}[\beta_{vis}];$$

$$L_{xx,ir} = \frac{n_{1,ir}\,2\,\mathrm{Cos}[\gamma_{ir}]}{n_{1,ir}\,\mathrm{Cos}[\gamma_{ir}] + n_{2,ir}\,\mathrm{Cos}[\beta_{ir}]}\,\mathrm{Cos}[\beta_{ir}];$$

$$L_{yy,sfg} = \frac{n_{1,sfg}\,2\,\mathrm{Cos}[\beta_{sfg}]}{n_{1,sfg}\,\mathrm{Cos}[\beta_{sfg}] + n_{2,sfg}\,\mathrm{Cos}[\gamma_{sfg}]};$$

$$L_{yy,vis} = \frac{n_{1,vis}\,2\,\mathrm{Cos}[\beta_{vis}]}{n_{1,vis}\,\mathrm{Cos}[\beta_{vis}] + n_{2,vis}\,\mathrm{Cos}[\gamma_{vis}]};$$

$$L_{yy,ir} = \frac{n_{1,ir}\,2\,\mathrm{Cos}[\beta_{ir}]}{n_{1,ir}\,\mathrm{Cos}[\beta_{ir}] + n_{2,ir}\,\mathrm{Cos}[\gamma_{ir}]};$$

$$L_{zz,sfg} = \frac{n_{2,sfg}\,2\,\mathrm{Cos}[\beta_{sfg}]}{n_{1,sfg}\,\mathrm{Cos}[\gamma_{sfg}] + n_{2,sfg}\,\mathrm{Cos}[\beta_{sfg}]}\left(\frac{n_{1,sfg}}{n_{m,sfg}}\right)^2 \mathrm{Sin}[\beta_{sfg}];$$

$$L_{zz,vis} = \frac{n_{2,vis}\,2\,\mathrm{Cos}[\beta_{vis}]}{n_{1,vis}\,\mathrm{Cos}[\gamma_{vis}] + n_{2,vis}\,\mathrm{Cos}[\beta_{vis}]}\left(\frac{n_{1,vis}}{n_{m,vis}}\right)^2 \mathrm{Sin}[\beta_{vis}];$$

$$L_{zz,ir} = \frac{n_{2,ir}\,2\,\mathrm{Cos}[\beta_{ir}]}{n_{1,ir}\,\mathrm{Cos}[\gamma_{ir}] + n_{2,ir}\,\mathrm{Cos}[\beta_{ir}]}\left(\frac{n_{1,ir}}{n_{m,ir}}\right)^2 \mathrm{Sin}[\beta_{ir}];$$

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
*)

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

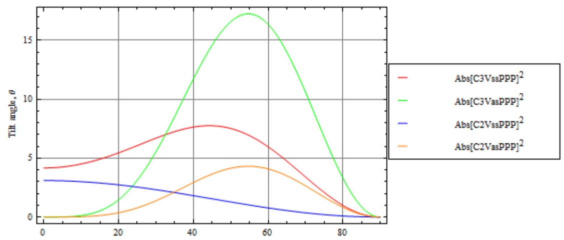
$$\mathrm{C\infty VssSPS} = L_{yy,sfg}\, L_{zz,vis}\, L_{yy,ir}\, \frac{1}{2}\, N_s\, \beta_{c,c,c}\, (1-R) \left(\mathrm{Cos}[\theta] - \mathrm{Cos}[\theta]^3\right);$$

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

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

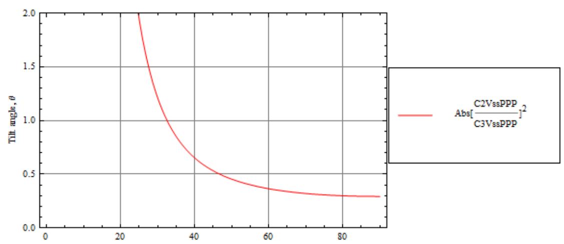
Delta Function Orientation Plot

```
(*Plot
*)
θ = th °;

Plot[{Abs[C3VssPPP]^2, Abs[C3VasPPP]^2, Abs[C2VssPPP]^2, Abs[C2VasPPP]^2},
 {th, 0, 90},
 PlotStyle → {Red, Green, Blue, Orange}, PlotRange → All, PlotStyle → Thick,
 PlotLegend → {"Abs[C3VssPPP]^2", "Abs[C3VasPPP]^2", "Abs[C2VssPPP]^2", "Abs[C2VasPPP]^2"},
 LegendPosition → {1.0, -0.2}, LegendSize → {0.9, 0.5}, LegendShadow → None,
 ImageSize → 600, GridLines → Automatic, Frame → True,
 FrameLabel → {"Tilt angle, θ"}]
```



Delta Function Orientation Ratio−CH2SS/CH3SS

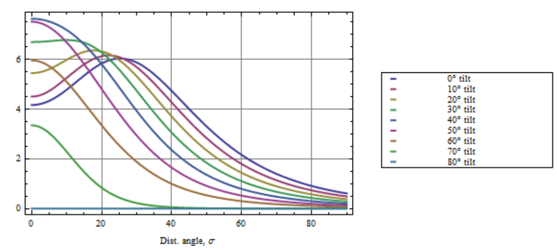
```
Plot[{Abs[C3VssPPP/C3VasPPP]^2},
 {th, 0, 90},
 PlotStyle → {Red}, PlotRange → {0, 2}, PlotStyle → Thick,
 PlotLegend → {"Abs[C2VssPPP/C3VssPPP]^2"},
 LegendPosition → {1.0, -0.2}, LegendSize → {0.9, 0.5}, LegendShadow → None,
 ImageSize → 600, GridLines → Automatic, Frame → True,
 FrameLabel → {"Tilt angle, θ"}]
```



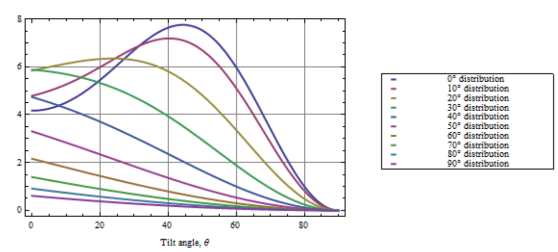
Gaussian Distribution Orientation Plot−CH3SS

```
(*Change rad to degree
*)
θ = π/180 θdeg;
θ0 = π/180 θ0deg;
σ = π/180 σdeg;

(*Gaussian distribution
*)
gauss = 1/(Sqrt[2 π] σdeg) e^(-(θ-θ0)^2/(2 σ^2));

(*CH3PPPss
*)
χeff = C3VssPPP;
Distribution[θ0deg_] = Abs[∫_0^180 (χeff Sin[θ] gauss) dθdeg / ∫_0^180 (Sin[θ] gauss) dθdeg]^2;
Orientatoin[σdeg_] = Abs[∫_0^180 (χeff Sin[θ] gauss) dθdeg / ∫_0^180 (Sin[θ] gauss) dθdeg]^2;
Quiet[{Plot[{
    Distribution[0], Distribution[10], Distribution[20], Distribution[30], Distribution[40], Distribution[50], Distribution[60], Distribution[70],
     Distribution[80], Distribution[90]}, {σdeg, 0, 90}, PlotRange → All,
   PlotLegend → {"0° tilt", "10° tilt", "20° tilt", "30° tilt", "40° tilt", "50° tilt", "60° tilt", "70° tilt", "80° tilt", "90° tilt"},
   LegendPosition → {1.0, -0.2}, LegendSize → {0.9, 0.5}, LegendShadow → None,
   ImageSize → 600, PlotStyle → Thick, FrameLabel → {"Dist. angle, σ", ""}, Frame → True, GridLines → Automatic],
  Plot[{
    Orientatoin[0.01], Orientatoin[10], Orientatoin[20], Orientatoin[30], Orientatoin[40], Orientatoin[50], Orientatoin[60],
    Orientatoin[70], Orientatoin[80], Orientatoin[90]}, {θ0deg, 0, 90}, PlotRange → All,
   PlotLegend → {"0° distribution", "10° distribution", "20° distribution", "30° distribution", "40° distribution",
     "50° distribution", "60° distribution", "70° distribution", "80° distribution", "90° distribution"},
   LegendPosition → {1.0, -0.2}, LegendSize → {0.9, 0.5}, LegendShadow → None,
   ImageSize → 600, PlotStyle → Thick, FrameLabel → {"Tilt angle, θ", ""}, Frame → True, GridLines → Automatic]
 }]
```

{



,



}