Correction terms for $\mathrm{Im}[\chi_{\mathrm{v}}^{abc}(-2\omega;\omega,\omega)]$ for different ABINIT versions

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Let us begin with equation (35) from [1] – the imaginary part of the nonlinear SHG susceptibility for the scissored Hamiltonian within the velocity-gauge formalism. I reproduce it here as follows.

$$
\begin{aligned}
&\mathrm{Im}[\chi_{\mathrm{v}}^{abc}(-2\omega;\omega,\omega)] = \\
&\frac{\pi|e|^3}{2\hbar^2}\int\frac{d^3k}{8\pi^3}\left[\sum_{vc}\frac{16}{(\omega_{vc}^S)^3}\left(\sum_{c'}\frac{\mathrm{Im}\left[v_{vc}^{\Sigma,a}\left\{v_{cc'}^{\Sigma,b}v_{c'c}^{\Sigma,c}\right\}\right]}{\omega_{cv}^S-2\omega_{c'v}^S}-\sum_{v'}\frac{\mathrm{Im}\left[v_{vc}^{\Sigma,a}\left\{v_{cv'}^{\Sigma,b}v_{v'c}^{\Sigma,c}\right\}\right]}{\omega_{cv}^S-2\omega_{cv'}^S}\right)\delta(\omega_{cv}^S-2\omega)\right.\\
&\qquad+\sum_{(vc)\neq\ell}\frac{1}{(\omega_{cv}^S)^3}\left(\frac{\mathrm{Im}\left[v_{\ell c}^{\Sigma,a}\left\{v_{cv}^{\Sigma,b}v_{v\ell}^{\Sigma,c}\right\}\right]}{\omega_{c\ell}^S-2\omega_{cv}^S}-\frac{\mathrm{Im}\left[v_{v\ell}^{\Sigma,a}\left\{v_{\ell c}^{\Sigma,b}v_{cv}^{\Sigma,c}\right\}\right]}{\omega_{\ell v}^S-2\omega_{cv}^S}\right)\delta(\omega_{cv}^S-\omega)\\
&\qquad\left.-\sum_{vc}\frac{1}{(\omega_{cv}^S)^3}\left(4\mathrm{Re}\left[v_{vc}^{\Sigma,a}\left\{\mathcal{F}_{cv}^{bc}\right\}\right]\delta(\omega_{cv}^S-2\omega)+\mathrm{Re}\left[\left\{\mathcal{F}_{vc}^{ab}v_{cv}^{\Sigma,c}\right\}\right]\delta(\omega_{cv}^S-\omega)\right)\right].
\end{aligned}
\tag{1}
$$

We want to derive this expression with a first-order correction accounting for discrepancies in the calculated energy. Let us assume that the frequency has been shifted,

$$\omega_n \to \omega_n + \Delta_n, \tag{2}$$

where Δ_n is the (small) difference between the old and new frequencies. This holds for both scissored and unscissored energy differences between states, thus

$$\omega_{nm} \to \omega_{nm} + \Delta_{nm} \quad \text{and} \quad \omega_{nm}^S \to \omega_{nm}^S + \Delta_{nm}. \tag{3}$$

It is convenient to express (3) as

$$\omega_{nm}^S + \Delta_{nm} = \omega_{nm}^S\left(1+\frac{\Delta_{nm}}{\omega_{nm}^S}\right) = \omega_{nm}^S(1+\delta_{nm}^S), \quad \text{where} \quad \delta_{nm}^S \equiv \frac{\Delta_{nm}}{\omega_{nm}^S} << 1. \tag{4}$$

We now want to separate the different terms in (1).

1 Denominators with ω_{nm}^S

All denominators have the same form and are dependent on ω. If we disregard the numerators, the denominators are

$$\frac{1}{(\omega_{nm}^S)^3} \cdot \frac{1}{\omega_{n\ell}^S - 2\omega_{nm}^S}. \tag{5}$$

Substituting the expression from (4) we obtain

$$\begin{aligned}
\frac{1}{(\omega_{nm}^S)^3(1+\delta_{nm}^S)^3} &\cdot \frac{1}{\omega_{n\ell}^S(1+\delta_{n\ell}^S) - 2\omega_{nm}^S(1+\delta_{nm}^S)},\\
\frac{(1+\delta_{nm}^S)^{-3}}{(\omega_{nm}^S)^3} &\cdot \frac{1}{\omega_{n\ell}^S - 2\omega_{nm}^S + \omega_{n\ell}^S\delta_{n\ell}^S + 2\omega_{nm}^S\delta_{nm}^S},\\
\frac{1}{(\omega_{nm}^S)^3} &\cdot \frac{(1+\delta_{nm}^S)^{-3}}{\omega_{n\ell}^S - 2\omega_{nm}^S + \Delta_{n\ell} + 2\Delta_{nm}},\\
\frac{1}{(\omega_{nm}^S)^3} \cdot \frac{1}{\omega_{n\ell}^S - 2\omega_{nm}^S} &\cdot (1+\delta_{nm}^S)^{-3}\left(1 + \frac{\Delta_{n\ell} + 2\Delta_{nm}}{\omega_{n\ell}^S - 2\omega_{nm}^S}\right)^{-1}.
\end{aligned} \tag{6}$$

The two terms on the left are equation (5). We can expand the terms on the right into their series representations. The first can be expanded to

$$(1+\delta_{nm}^S)^{-3} = 1 - 3\delta_{nm}^S + 6\delta_{nm}^{S^2} - 10\delta_{nm}^{S^3} + \cdots \approx (1 - 3\delta_{nm}^S), \tag{7}$$

taking into consideration that $\delta_{nm} << 1$. The second,

$$\left(1 + \frac{\Delta_{n\ell} + 2\Delta_{nm}}{\omega_{n\ell}^S - 2\omega_{nm}^S}\right)^{-1} \equiv (1+\gamma)^{-1}, \quad \text{where} \quad \gamma << 1,$$

which we can then expand into

$$(1+\gamma)^{-1} = 1 - \gamma + \gamma^2 - \gamma^3 + \gamma^4 + \cdots \approx (1-\gamma) = 1 - \frac{\Delta_{n\ell} + 2\Delta_{nm}}{\omega_{n\ell}^S - 2\omega_{nm}^S}. \tag{8}$$

Finally, substituting (7) and (8) into (5),

$$\begin{aligned}
\frac{1}{(\omega_{nm}^S)^3} \cdot \frac{1}{\omega_{n\ell}^S - 2\omega_{nm}^S} \to & \frac{1}{(\omega_{nm}^S)^3} \cdot \frac{1}{\omega_{n\ell}^S - 2\omega_{nm}^S} \cdot (1 - 3\delta_{nm}^S)\left(1 - \frac{\Delta_{n\ell} + 2\Delta_{nm}}{\omega_{n\ell}^S - 2\omega_{nm}^S}\right),\\
& \frac{1}{(\omega_{nm}^S)^3} \cdot \frac{1}{\omega_{n\ell}^S - 2\omega_{nm}^S} \cdot \left(1 - 3\delta_{nm}^S - \frac{\Delta_{n\ell} + 2\Delta_{nm}}{\omega_{n\ell}^S - 2\omega_{nm}^S}\right).
\end{aligned} \tag{9}$$

2 Scissored velocity operator

The next term that is dependent on ω is equation (23) from [1], the scissored velocity operator

$$\mathbf{v}_{nm}^{\Sigma} = \frac{\omega_{nm}^s}{\omega_{nm}} \mathbf{v}_{nm}. \tag{10}$$

We substitute our new ω from (4),

$$\begin{aligned}\mathbf{v}^{\Sigma}_{nm} \to & \frac{\omega^s_{nm}(1+\delta^S_{nm})}{\omega_{nm}(1+\delta_{nm})}\mathbf{v}_{nm}, \\ & \frac{\omega^s_{nm}}{\omega_{nm}}\mathbf{v}_{nm}(1+\delta^S_{nm})(1+\delta_{nm})^{-1}. \end{aligned} \tag{11}$$

We expand $(1+\delta_{nm})^{-1}$ into a series as we did before in (8)

$$(1+\delta_{nm})^{-1} = 1 - \delta_{nm} + \delta^2_{nm} - \delta^3_{nm} + \delta^4_{nm} + \cdots \approx (1-\delta_{nm}), \tag{12}$$

and we can also disregard all terms above first-order. Substituting (12) into (11),

$$(1+\delta^S_{nm})(1-\delta_{nm}) = 1 - \delta_{nm} + \delta^S_{nm} - \delta_{nm}\delta^S_{nm} \approx 1 - \delta_{nm} + \delta^S_{nm}, \tag{13}$$

where $\delta_{nm}\delta^S_{nm}$ can be disregarded for the same reason as above. Finally, our new scissored velocity operator can be expressed as

$$\mathbf{v}^{\Sigma}_{nm} \to \mathbf{v}^{\Sigma}_{nm}(1 - \delta_{nm} + \delta^S_{nm}). \tag{14}$$

We can express the components of $\mathbf{v}$ in (1) as

$$\begin{aligned} v^{\Sigma,a}_{\ell n}\left\{v^{\Sigma,b}_{nm}v^{\Sigma,c}_{m\ell}\right\} \to & \; v^{\Sigma,a}_{\ell n}\left\{v^{\Sigma,b}_{nm}v^{\Sigma,c}_{m\ell}\right\}(1-\delta_{\ell n}+\delta^S_{\ell n})(1-\delta_{nm}+\delta^S_{nm})(1-\delta_{m\ell}+\delta^S_{m\ell}), \\ & \; v^{\Sigma,a}_{\ell n}\left\{v^{\Sigma,b}_{nm}v^{\Sigma,c}_{m\ell}\right\}(1-\delta_{\ell n}-\delta_{nm}-\delta_{m\ell}+\delta^S_{\ell n}+\delta^S_{nm}+\delta^S_{m\ell}) \end{aligned} \tag{15}$$

3 Terms in $\mathcal{F}^{ab}_{nm}$

$$\mathcal{F}^{ab}_{nm} = i\Delta \sum_{n\neq m} f_{nm}\left(r^a_{nm}r^b_{mn} + r^b_{nm}r^a_{mn}\right), \quad \text{where} \quad f_n = f\left[\hbar\omega_n\right] \tag{16}$$

4 Correction Terms

We can now obtain the final correction terms from (9) and (15),

$$\begin{aligned} &\left(1 - 3\delta^S_{nm} - \frac{\Delta_{n\ell}+2\Delta_{nm}}{\omega^S_{n\ell}-2\omega^S_{nm}}\right)(1-\delta_{\ell n}-\delta_{nm}-\delta_{m\ell}+\delta^S_{\ell n}+\delta^S_{nm}+\delta^S_{m\ell}) \approx \\ &\qquad \left(1-\delta_{\ell n}-\delta_{nm}-\delta_{m\ell}-2\delta^S_{nm}+\delta^S_{\ell n}+\delta^S_{m\ell}-\frac{\Delta_{n\ell}+2\Delta_{nm}}{\omega^S_{n\ell}-2\omega^S_{nm}}\right). \end{aligned} \tag{17}$$

References

[1] J. Cabellos, B. Mendoza, M. Escobar, F. Nastos, and J. Sipe. Effects of nonlocality on second-harmonic generation in bulk semiconductors. *Physical Review B*, 80(15), Oct. 2009.