Normalizing $\chi(-2\omega;\omega,\omega)$ for Specific Cases

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First Case: Bulk Materials

Let us first consider the case of a bulk material, that is conformed entirely of a supercell with no vacuum region. A unit cell is repeated indefinitely in every direction, thus creating a three-dimensional reproduction of an infinite material. From Fig. 1, we can see that the volume of each unit cell is $V = L^3$. We calculate $\chi(-2\omega;\omega,\omega)$ using the TINIBA [1] software suite; for ease of notation, $\chi(-2\omega;\omega,\omega) = \chi_T$ (T for TINIBA).

For the bulk calculation, χ_T must be normalized over the volume of the unit cell (i.e. $1/V$); this normalization happens automatically in TINIBA. Thus, no further action is necessary and the susceptibility can be used as is. Finally, we establish that $\chi_T = \chi_b$, where χ_b is the desired susceptibility for our bulk system. Calculated in this fashion, χ_b has the appropriate MKS units of m/V.

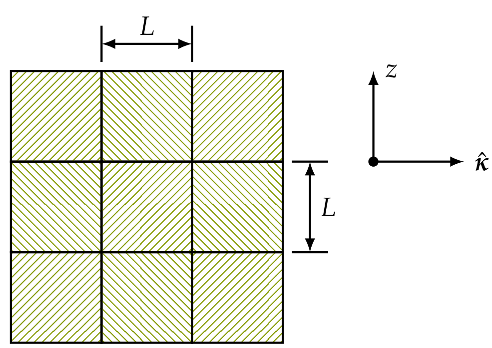
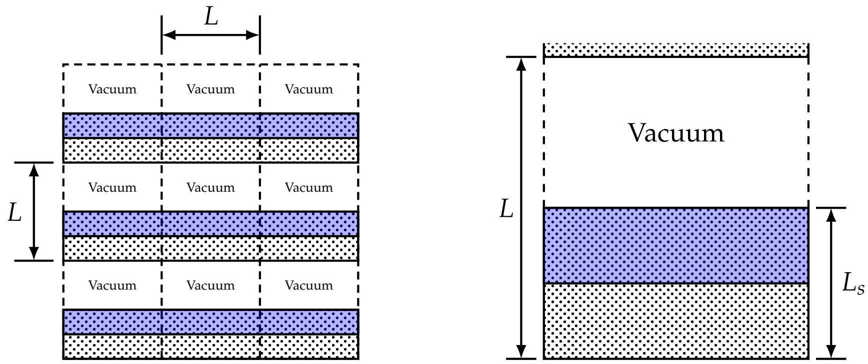


Figure 1: The bulk supercell is repeated indefinitely along the z and $\hat{\kappa}$ axes. There is only material present, with no vacuum region between each repeat.



(a) Repeated supercells for a surface material. Each individual supercell is repeated in every direction, just like the bulk case. Vacuum regions must be included, seperating each supercell.

(b) An individual supercell, which consists of a slab (with upper and bottom surfaces) and a vacuum region. The total height will be the combined height of the vacuum region and the slab (L_s).

Figure 2: Just like for the bulk case, we use the supercell scheme for calculating $\chi(-2\omega;\omega,\omega)$ for surfaces.

Second Case: Surfaces

Now, we will consider calculating $\chi(-2\omega;\omega,\omega)$ for surfaces. This is done following the theoretical framework established in Ref. [2]. Just as for the bulk case, we use the supercell method that repeats each cell across all directions (see Fig. 2). However, we represent the surface by using a slab of material with finite height; this necessarily implies that there are regions of empty space between each repeat. The slab has both upper and lower surfaces, and we can extract the response for each by use of the cut function.

Fig. 2b depicts a representative supercell for a surface material. As mentioned above, it is necessary to include the cut-function to extract the surface response. For instance, a centrosymmetric material will always yield $\chi(-2\omega;\omega,\omega) = 0$, except at the surface where the symmetry is broken. If we calculate the response from the entire slab, the contribution from the bottom half will cancel out the top half; thus, we use the cut function to only calculate over the desired region. Therefore, the surface calculation is simply done over the *half-slab* region, with is the blue shaded region in Fig. 2. Therefore, the proper normalization is as follows,

$$\frac{L}{L_s}\left(\frac{1}{V}\right) = \frac{L}{L_s}\left(\frac{1}{AL}\right) = \frac{1}{AL_s} \equiv \frac{1}{V_s}, \tag{1}$$

where L_s is the thickness of the material slab without the vacuum layer, and V_s is the volume of the material slab.

These same considerations apply for the linear response, $\chi(\omega)$. In Fig. 3, we show Im$[\chi(\omega)]$ for the `si_as_6` slab where three different values of the supercell thickness (L) were chosen. As the response is normalized with the volume $V = AL$ of the supercell, the intensity of $\mathrm{Im}[\chi(\omega)]$ decreases as L is increased. When the results are multiplied by L, and since the area A of the unit cell is fixed, we see that the results converge nicely.

WARNING: Note that if you compare the full- vs. the half-slab responses, there will be a factor of exactly 2 between them once the full-slab is properly normalized as explained above. Therefore, $\chi_{\mathrm{full-slab}}(\omega) = 2\chi_{\mathrm{half-slab}}(\omega)$.

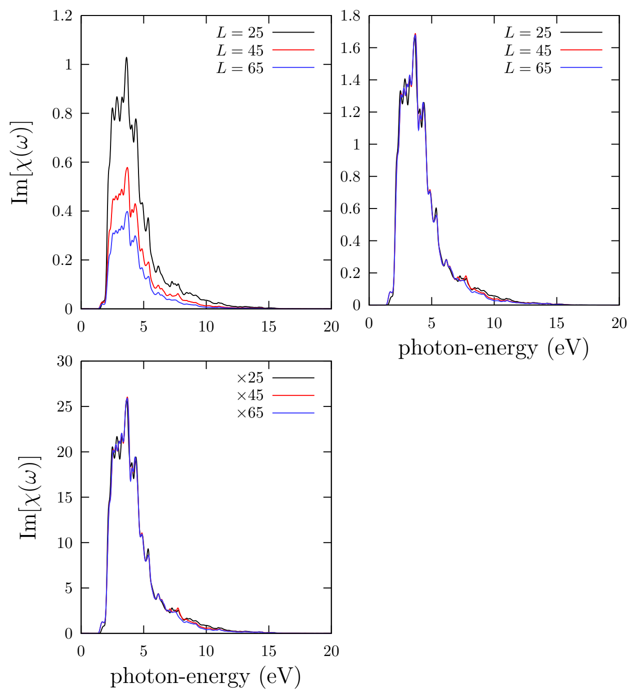
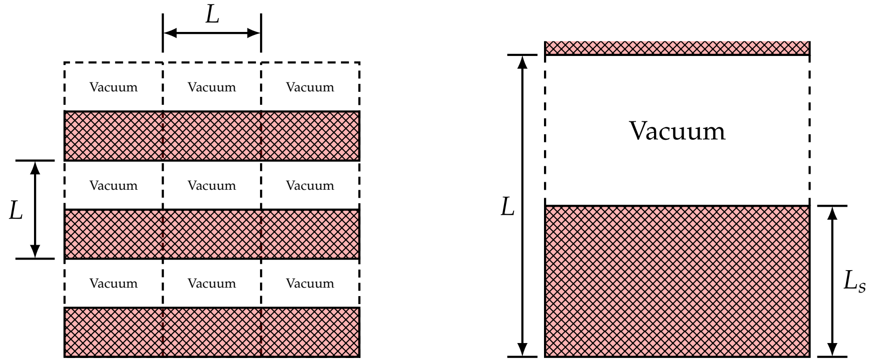


Figure 3: $\mathrm{Im}[\chi(\omega)]$ for three different supercells thickness L. Top-left panel: without the normalization; bottom-left panel: multiplied by L; and top-right panel: scaled according to Eq. (1).

Therefore, for a surface calculation, χ_T must be normalized over the volume of the unit cell (i.e. $1/V$) and multiplied by L; this normalization happens automatically in TINIBA in the `all_response.sh` shell for responses 21 and 24. Thus, no further action is necessary and the susceptibility can be used as is. Finally, we establish that $\chi_T = \chi_s$, where χ_s is the desired susceptibility for our surface system. Calculated in this fashion, χ_s has the appropriate MKS units of m^2/V.



(a) Repeated supercells for a 2D material. Again, each individual supercell is repeated in every direction. Vacuum regions seperate each slab of material.

(b) An individual supercell, with slab and vacuum region. We calculate the response from the entire slab, disregarding any layers.

Figure 4: The supercell scheme for calculating $\chi(-2\omega;\omega,\omega)$ for 2D materials is very similar to the surface case.

Third Case: Two-dimensional Materials

Lastly, let us consider the case for two-dimensional materials, as depicted in Fig. 4. These types of materials are essentially a combination of the two previous cases; namely, they must have a vacuum region included, but do not require restricting the calculated response to the just the half-slab region.

Since we don't need to calculate for the half-slab, we can simply effectuate a bulk calculation. However, as mentioned above, this does not include the appropriate normalization to compensate for the inclusion of the vacuum region. Therefore, χ_T must be normalized over the volume of the unit cell (i.e. $1/V$) and multiplied by L. Since we carry out the bulk calculation and $\chi_T = \chi_b$, we must multiply by L manually, since this normalization *does not* happen automatically in TINIBA. This is a necessary step in order to obtain the correct susceptibility. Calculated in this fashion, χ_{2D} has the appropriate MKS units of m^2/V.

References

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