Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information
Nonlinear Light Absorption in Many-Electron Systems Excited by an Instantaneous Electric Field: A Non-Perturbative Approach

Alberto Guandalini,[a,d] Caterina Cocchi,[b,c] Stefano Pittalis,[a] Alice Ruini,[d], and Carlo Andrea Rozzi[a]

[a] CNR – Istituto Nanoscienze, Via Campi 213A, I-41125 Modena, Italy

[b] Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, D-12489 Berlin, Germany

[c] Physics Department, Carl von Ossietzky Universität Oldenburg, Carl-von-Ossietzky-Straße 9, 26129 Oldenburg, Germany

[d] Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, Via Campi 213A, I-41125 Modena, Italy

S1 Absorption cross section in the dipole approximation

In the interaction between matter and an external transverse electric field, the absorption cross section at each frequency ω is defined as the ratio between the energy exchanged with the field during the interaction, E_{exc}, and the total field energy per unit area, I_{in},

$$\sigma(\omega) = \frac{E_{exc}(\omega)}{I_{in}(\omega)} \ . \tag{S1.1}$$

In the dipole approximation, with no magnetic field applied, the light-matter interaction Hamiltonian is $\hat{H}(t) = \hat{d}_\mu \mathscr{E}_\mu(t)$, where $\hat{d}_\mu$ is the dipole operator. The total amount of energy exchanged during the interaction is

$$\Delta E = \int_{-\infty}^{+\infty} \frac{dE(t)}{dt}\, dt = \int_{-\infty}^{+\infty} \frac{d}{dt} \langle \Psi(t)|\hat{H}(t)|\Psi(t)\rangle \ dt \ , \tag{S1.2}$$

where $E(t) = \langle \Psi(t)|\hat{H}(t)|\Psi(t)\rangle$ is the total energy at time t. By applying the Ehrenfest theorem to the integrand of Eq. (S1.2), we obtain

$$\frac{d}{dt} \langle \Psi(t)|\hat{H}(t)|\Psi(t)\rangle = \left\langle \Psi(t) \left| \frac{\partial \hat{H}(t)}{\partial t} \right| \Psi(t) \right\rangle = -d_\mu(t) \frac{d\mathscr{E}_\mu(t)}{dt} \ . \tag{S1.3}$$

Substituting Eq. (S1.3) into Eq. (S1.2), we have

$$\Delta E = -\int_{-\infty}^{+\infty} dt \ d_\mu(t) \frac{d\mathscr{E}_\mu(t)}{dt}. \tag{S1.4}$$

By using the Plancherel theorem, we change from time to the frequency domain

$$\Delta E = -\frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \ \omega \tilde{d}_\mu(\omega) \tilde{\mathscr{E}}^*_\mu(\omega), \tag{S1.5}$$

where $\tilde{d}_\mu(\omega)$ and $\tilde{\mathscr{E}}_\mu(\omega)$ are the Fourier transforms of $d_\mu(t)$ and $\mathscr{E}^\mu(t)$, respectively. In writing Eq. (S1.5), we have also used the property of Fourier transform: $\mathscr{F}[df(t)/dt] = -i\omega \tilde{f}(\omega)$ (where $\mathscr{F}[\ldots]$ is the Fourier transform operator).

Since both $d_\mu(t)$ and $\mathscr{E}_\mu(t)$ are real quantities, their complex conjugates fulfill the relations $\tilde{d}_\mu(-\omega) = \tilde{d}^*_\mu(\omega)$ and $\tilde{\mathscr{E}}_\mu(-\omega) = \tilde{\mathscr{E}}^*_\mu(\omega)$. Thus, we get

$$\Delta E = \int_0^\infty E_{exc}(\omega) \ d\omega \tag{S1.6}$$

where

$$E_{exc}(\omega) = \frac{1}{\pi}\omega\,\mathrm{Im}\left[\tilde{d}_\mu(\omega)\tilde{\mathscr{E}}^*_\mu(\omega)\right] \tag{S1.7}$$

may be regarded as the energy absorbed at each frequency ω — a quantity which is defined for $\omega > 0$. Inserting Eq. (S1.7) and using $I_{in}(\omega) = \frac{c}{4\pi^2}|\tilde{\mathscr{E}}(\omega)|^2$ [1] into Eq. (S1.1) leads to

$$\sigma(\omega) = \frac{4\pi\omega}{c}\frac{\mathrm{Im}\left[\tilde{d}_\mu(\omega)\tilde{\mathscr{E}}^*_\mu(\omega)\right]}{|\tilde{\mathscr{E}}(\omega)|^2} \tag{S1.8}$$

for which, we stress, a restriction to the linear regime is not invoked.

S2 Spectral resolution of the absorption cross section

Here, we derive the expression of Eq. (S1.1) for centrosymmetric systems under an incoming impulsive electric field of the form $\mathscr{E}_\mu(t) = \kappa_\mu\delta(t)$.

Let us start with the calculation of the Fourier transform of the time-dependent dipole moment

$$d_\mu(t) = \theta(t)\sum_{i,j=0}^{+\infty} c_i^* c_j d_\mu^{ij} e^{-i\omega_{ji}t} + \theta(-t)d_\mu^{00}. \tag{S2.1}$$

For this purpose, it is useful to consider the spectral representation of the Heaviside theta function:

$$\theta(t) = \frac{i}{2\pi}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{+\infty} d\omega\frac{e^{-i\omega t}}{\omega + i\varepsilon}. \tag{S2.2}$$

Straightforward but tedious steps lead us to

$$\tilde{d}_\mu(\omega) = i\lim_{\varepsilon\to 0^+}\sum_{i,j=0}^{+\infty} c_i^* c_j d_\mu^{ij}\left(\frac{1}{\omega - \omega_{ji} + i\varepsilon} - \frac{1}{\omega - i\varepsilon}\right). \tag{S2.3}$$

Next, let us evaluate $E_{exc}(\omega)$ as defined in Eq. (S1.7), using Eq. (S2.3) together with $\tilde{\mathscr{E}}_\mu(\omega) = \kappa_\mu$. By means of additional straightforward steps, we arrive at

$$E_{exc}(\omega) = \lim_{\varepsilon\to 0^+}\frac{1}{\pi}\sum_{i,j>i}^{+\infty}\mathrm{Re}\left[c_i^* c_j d_\mu^{ij}\kappa_\mu\frac{\omega_{ji}}{\omega - \omega_{ji} + i\varepsilon} - c_i c_j^* d_\mu^{ij}\kappa_\mu\frac{\omega_{ji}}{\omega + \omega_{ji} + i\varepsilon}\right]. \tag{S2.4}$$

We note that $\mathrm{Re}(c_i c_j^*) = \mathrm{Re}(c_i^* c_j)$, $\mathrm{Im}(c_i c_j^*) = -\mathrm{Im}(c_i^* c_j)$,

$$\mathrm{Re}\left(\frac{1}{\omega \pm \omega_{ji} + i\varepsilon}\right) = \frac{(\omega \pm \omega_{ji})}{(\omega \pm \omega_{ji})^2 + \varepsilon^2}, \tag{S2.5}$$

and

$$\mathrm{Im}\left(\frac{1}{\omega \pm \omega_{ji} + i\varepsilon}\right) = -\frac{\varepsilon}{(\omega \pm \omega_{ji})^2 + \varepsilon^2}. \tag{S2.6}$$

As a result, we get

$$E_{exc}(\omega) = \frac{1}{\pi}\lim_{\varepsilon\to 0^+}\sum_{i,j>i}\left[\mathrm{Re}(c_i^* c_j)d_\mu^{ij}\kappa_\mu\omega_{ji}\left(\frac{\omega - \omega_{ji}}{(\omega - \omega_{ji})^2 + \varepsilon^2} - \frac{\omega + \omega_{ji}}{(\omega + \omega_{ji})^2 + \varepsilon^2}\right)\right.$$
$$\left. + \,\mathrm{Im}(c_i^* c_j)d_\mu^{ij}\kappa_\mu\omega_{ji}\left(\frac{\varepsilon}{(\omega - \omega_{ji})^2 + \varepsilon^2} - \frac{\varepsilon}{(\omega + \omega_{ji})^2 + \varepsilon^2}\right)\right]. \tag{S2.7}$$

In Eq. (S2.7), we can use

$$\lim_{\varepsilon\to 0^+}\frac{1}{\pi}\frac{\varepsilon}{(\omega_{ji} \pm \omega)^2 + \varepsilon^2} = \delta(\omega_{ji} \pm \omega), \tag{S2.8}$$

where $\omega_{ji} > 0$ for $j > i$. Thus, we end up with

$$E_{exc}(\omega) = \sum_{i,j>i}\left[\lim_{\varepsilon\to 0^+}\mathrm{Re}(c_i^* c_j)d_\mu^{ij}\kappa_\mu\left(\frac{\omega_{ji}(\omega - \omega_{ji})}{(\omega - \omega_{ji})^2 + \varepsilon^2} - \frac{\omega_{ji}(\omega + \omega_{ji})}{(\omega + \omega_{ji})^2 + \varepsilon^2}\right)\right.$$
$$\left. + \,\mathrm{Im}(c_i^* c_j)d_\mu^{ij}\kappa_\mu\omega_{ji}\delta(\omega_{ji} - \omega)\right], \tag{S2.9}$$

where, as clarified in the derivation of Eq. (S1.7), we restrict ourselves to $\omega > 0$.

Next, let us consider the case of centrosymmetric systems. In this case, the eigenstates are either of *gerade* or *ungerade* parity under inversion of the coordinates. Solely on the based of symmetry considerations, we readily conclude that $\mathrm{Re}(c_i^* c_j) = 0$. Using the expression of the c_i coefficients in Eq. (3) in the main text, we find that

$$\mathrm{Im}(c_i^* c_j) = \langle \Psi_0 | \cos(\hat{d}_\mu \kappa_\mu) | \Psi_i \rangle \langle \Psi_j | \sin(\hat{d}_\mu \kappa_\mu) | \Psi_0 \rangle - \langle \Psi_0 | \sin(\hat{d}_\mu \kappa_\mu) | \Psi_i \rangle \langle \Psi_j | \cos(\hat{d}_\mu \kappa_\mu) | \Psi_0 \rangle . \quad \text{(S2.10)}$$

Finally, using Eq. (S2.9), Eq. (S2.10), and $I_{in}(\omega) = c/4\pi^2 |\kappa|^2$ in Eq. (S1.7), we arrive at

$$\sigma(\omega) = \frac{E_{exc}(\omega)}{I_{in}(\omega)} = \frac{4\pi^2}{c|\kappa|^2} \sum_{i,j>i} \left[\langle \Psi_0 | \cos(\hat{d}_\mu \kappa_\mu) | \Psi_i \rangle \langle \Psi_j | \sin(\hat{d}_\mu \kappa_\mu) | \Psi_0 \rangle - \langle \Psi_0 | \sin(\hat{d}_\mu \kappa_\mu) | \Psi_i \rangle \langle \Psi_j | \cos(\hat{d}_\mu \kappa_\mu) | \Psi_0 \rangle \right] (\hat{d}_\mu \kappa_\mu)_{ij} \omega_{ji} \delta(\omega_{ji} - \omega). \quad \text{(S2.11)}$$

S3 Fifth order correction to the cross section

Adopting the notation $d_\mu^{ij} = \langle \Psi_i | \hat{d}_\mu | \Psi_j \rangle$ and introducing $(\hat{d}_\mu \kappa_\mu)^n_{ij} = \langle \Psi_i | (\hat{d}_\mu \kappa_\mu)^n | \Psi_j \rangle$, the fifth order correction to the cross section is obtained by power expansion of Eq. (6) in the main text as

$$\sigma^{(5)}(\omega) = \frac{4\pi^2}{c\kappa^2} \Bigg\{ \frac{1}{120} \sum_j (\hat{d}_\mu \kappa_\mu)^5_{j0} (\hat{d}_\mu \kappa_\mu)_{0j} \omega_{j0} \delta(\omega - \omega_{j0}) + \frac{1}{12} \sum_{j>i} \left[(\hat{d}_\mu \kappa_\mu)^2_{0i} (\hat{d}_\mu \kappa_\mu)^3_{j0} - (\hat{d}_\mu \kappa_\mu)^3_{0i} (\hat{d}_\mu \kappa_\mu)^2_{j0} \right] (\hat{d}_\mu \kappa_\mu)_{ij} \omega_{ji} \delta(\omega - \omega_{ji}) + \frac{1}{24} \sum_{j>i} \left[(\hat{d}_\mu \kappa_\mu)^4_{0i} (\hat{d}_\mu \kappa_\mu)_{j0} - (\hat{d}_\mu \kappa_\mu)_{0i} (\hat{d}_\mu \kappa_\mu)^4_{j0} \right] (\hat{d}_\mu \kappa_\mu)_{ij} \omega_{ji} \delta(\omega - \omega_{ji}) \Bigg\} , \quad \text{(S3.1)}$$

which can be expressed as the sum of ground and excited state absorption as

$$\sigma^{(5)}(\omega) = \frac{4\pi^2}{c\kappa^2} \left[\sigma^{(5)}_{\mathrm{GSA}}(\omega) + \sigma^{(5)}_{\mathrm{ESA}}(\omega) \right] , \quad \text{(S3.2)}$$

where

$$\sigma^{(5)}_{\mathrm{GSA}}(\omega) = \frac{1}{120} \sum_j \left[(\hat{d}_\mu \kappa_\mu)_{0j} (\hat{d}_\mu \kappa_\mu)^5_{j0} + 10 (\hat{d}_\mu \kappa_\mu)^2_{00} (\hat{d}_\mu \kappa_\mu)_{0j} (\hat{d}_\mu \kappa_\mu)^3_{j0} - 10 (\hat{d}_\mu \kappa_\mu)^3_{00} (\hat{d}_\mu \kappa_\mu)_{0j} (\hat{d}_\mu \kappa_\mu)^2_{j0} + 5 (\hat{d}_\mu \kappa_\mu)^4_{00} |(\hat{d}_\mu \kappa_\mu)_{j0}|^2 \right] \omega_{j0} \delta(\omega - \omega_{j0}) \quad \text{(S3.3)}$$

and

$$\sigma^{(5)}_{\mathrm{ESA}}(\omega) = \frac{1}{24} \sum_{\substack{i>0 \\ j>i}} \left\{ 2 \left[(\hat{d}_\mu \kappa_\mu)^2_{0i} (\hat{d}_\mu \kappa_\mu)^3_{j0} - (\hat{d}_\mu \kappa_\mu)^3_{0i} (\hat{d}_\mu \kappa_\mu)^2_{j0} \right] + \left[(\hat{d}_\mu \kappa_\mu)^4_{0i} (\hat{d}_\mu \kappa_\mu)_{j0} - (\hat{d}_\mu \kappa_\mu)_{0i} (\hat{d}_\mu \kappa_\mu)^4_{j0} \right] \right\} (\hat{d}_\mu \kappa_\mu)_{ij} \omega_{ji} \delta(\omega - \omega_{ji}) . \quad \text{(S3.4)}$$

Notes and references

[1] J. D. Jackson, *Classical electrodynamics*, Wiley, New York, NY, 3rd edn., 1999.