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# Two-photon processes based on quantum commutators

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(Dated: January 23, 2018)

We developed a new method to calculate two-photon processes in quantum mechanics that replaces the infinite summation over the intermediate states by a perturbation expansion. This latter consists of a series of commutators that involve position, momentum and hamiltonian quantum operators. We analyzed several single- and many-particle cases for which a closed form solution to the perturbation expansion exists, as well as more complicated cases for which a solution is found by convergence. Throughout the article, Rayleigh and Raman scattering are taken as examples of two-photon processes. The present method provides a clear distinction between the Thomson scattering, regarded as classical scattering, and quantum contributions. Such a distinction let us derive general results concerning light scattering. Finally, possible extensions to the developed formalism are discussed.

## I. INTRODUCTION

Two-photon processes are of utmost importance for a variety of applications and techniques in chemistry and biology [1–4], including two-photon excited fluorescence microscopy [5–7], optical imaging [8, 9], three dimensional optical data storage [10, 11], two-photon induced biological caging studies [12, 13], and also analysis of mesoscopic systems [14]. In all the mention techniques, accurate theoretical predictions of both two-photon absorption and light scattering cross-sections are highly demanded for the search of molecules and specimens with the largest cross-sections, and thus with highest contrast.

The main full quantum mechanical approaches to calculate two-photon cross-sections are either third-order polarizabilities [15–17], or the dispersion theory of Kramers-Heisenberg [18, 19], as well as its relativistic analogous - the S-matrix approach [20, 21]. All of these approaches contain a summation over the infinite intermediate states of the target bound system. In case of one-electron atomic systems, such intermediate-state summation has been evaluated for a variety of second-order processes, leading to high accurate values of cross-sections and emissions rates [22–30], as well as its dependence upon photon polarizations [31–34] and geometry [35, 36]. Nevertheless, in case of many-body systems or complex potentials, such a summation over the infinite intermediate states is often difficult, or impossible to be evaluated accurately [37–42]. When considering molecules, this summation is even harder to perform due to either the complexity of obtaining states for complex potentials or the summation requiring a huge amount of vibrational and rotational states for a reliable evaluation, even for harmonic potentials [19]. Because of these reasons, simpler methods - such as the Thomson or the Form Factor (FF) approximations [43, 44] - are very much used when calculating, for instance, light scattering by many-electron atoms or crystallographic specimens [8, 9, 45],

although they are unable to capture quantum mechanical effects that are given by the target bound spectrum, such as quantum interference [46, 47] or resonance effects [29], among others.

Here, we propose a new method to calculate two-photon processes that replaces the infinite summation over the intermediate states by a perturbation expansion. This latter consists of a series of commutators that involve position, momentum and hamiltonian quantum operators. Thus, the problem of describing two-photon processes is moved from solving complex Schrödinger equations and Green functions - so to find the intermediate states to be summed - to computing a series of commutators. We show several cases for which a closed form solution to the perturbation expansion exists, as well as cases for which the solution is found by convergence. Moreover, our analytical method will allow us to make statements in the form of rules that the two-photon process must obey.

For simplicity and brevity, we shall restrict our analysis to light (Rayleigh or Raman) scattering, which is one of the most interesting two-photon processes due to its interdisciplinarity. In fact, Rayleigh and Raman scattering, besides being the main tools used to analyze molecular specimens in diverse areas of science [45, 48, 49], are also the basic processes in quantum communication for upcoming technologies based on light propagation at the single photon level [50–52]. The reader will notice that the formalism here developed is general and can be applied to any two-photon process, such as two-photon decay or two-photon absorption. Finally, conclusions and possible extensions to the developed formalism are discussed at the end of the article.

SI units are used throughout the article, unless differently specified.

## II. LIGHT SCATTERING OFF BOUND STATES

We shall work within the dipole approximation. Such an approximation is justified if the light wavelength is much larger than the size of the target. An extension of the present work to higher multipoles is possible, for which details are provided in Sec. VII.

Light scattering is described in non-relativistic quantum mechanics by the Kramer-Heisenberg formula. The (polarization dependent) differential cross section for such a process reads [53]

$$\frac{d\sigma^{\epsilon_1\epsilon_2}}{d\Omega} = r_e^2 \frac{E_2}{E_1} |\mathcal{M}|^2, \quad (1)$$

where  $r_e$  is a constant,  $E_{1(2)}$  and  $\epsilon_{1(2)}$  are the energy and polarization vector of the incoming (outgoing) photon, respectively. For atomic targets,  $r_e$  is equal to the classical electron radius. Considering a target composed by  $N$  charged compounds with mass  $m$ , the scattering amplitude  $\mathcal{M}$  is defined as

$$\mathcal{M} = N \langle f | \epsilon_1 \cdot \epsilon_2^* | i \rangle - \frac{1}{m} (\mathcal{A}_{12} + \mathcal{A}_{21}). \quad (2)$$

The term  $\mathcal{A}_{12}$  reads

$$\mathcal{A}_{12} = \sum_{\nu} \sum_{j,t=1}^N \frac{\langle f | \hat{\mathbf{p}}_j \cdot \epsilon_2^* | \nu \rangle \langle \nu | \hat{\mathbf{p}}_t \cdot \epsilon_1 | i \rangle}{E_{\nu} - E_i - E_1}, \quad (3)$$

while  $\mathcal{A}_{21}$  is obtained from  $\mathcal{A}_{12}$  by replacing  $E_1 \rightarrow -E_2$  and  $\epsilon_1 \leftrightarrow \epsilon_2$ .  $\hat{\mathbf{p}}$  is the momentum operator. We denote by  $E_{i,f}$  the energies of initial and final states of the target. On the other hand,  $E_{\nu}$  are the energies of the intermediate states to be summed for the computation of the am-

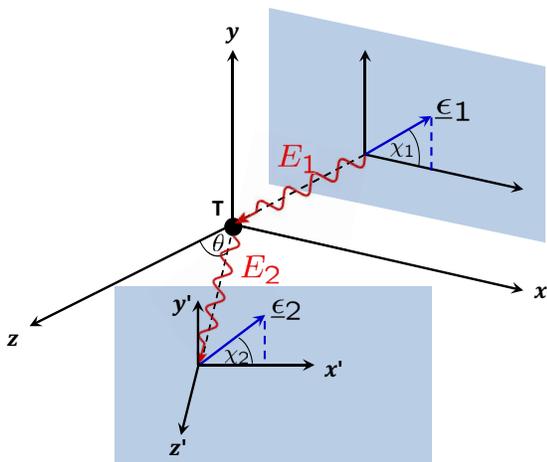


FIG. 1. (Color online) The light scattering process. An incident photon with energy  $E_1$  and linear polarization vector  $\epsilon_1$  scatters off a target T. The scattered photon has energy  $E_2$  and linear polarization vector  $\epsilon_2$ .  $\theta$  is the scattering angle, while  $xz$  plane is the scattering plane.

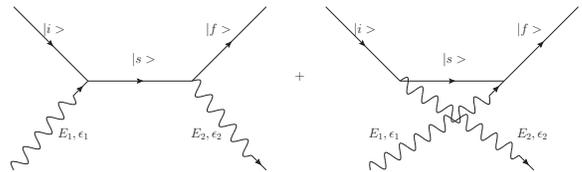


FIG. 2. Graphical representation of the scattering amplitudes  $\mathcal{A}_{12}$  and  $\mathcal{A}_{21}$ . The state  $|s\rangle$  is the target intermediate state during the scattering process.

plitude. As in [31, 32], we shall consider light scattering as depicted in Fig. 1. Without restriction of generality and unless differently specified, we consider linearly polarized photons, with  $\chi_{1(2)}$  being the azimuthal angle that defines the incoming (outgoing) photon polarization. The polar angle  $\theta$  uniquely defines the direction of the scattered photon in the  $xz$  plane (scattering plane). The target T is placed at the origin of the coordinate axes  $xyz$ .

Each of the amplitudes  $\mathcal{A}_{12,21}$  describes one graph in Fig. 2. The amplitude  $\mathcal{A} \equiv \mathcal{A}_{12} + \mathcal{A}_{21}$  is the coherent sum of the two graphs. Both terms are in general challenging to compute, since both contain a summation over the infinite spectrum of the target bound system. Within the Thomson approximation,  $\mathcal{A}_{12,21}$  are approximated to zero, which is evidently justified from Eq. (3) if the photon energies ( $E_{1,2}$ ) are much larger than the target binding energy. The first term of the right member in Eq. (2) thus represents the Thomson scattering amplitude. It must be therefore clear that any correction coming from the  $\mathcal{A}$  term is to be regarded as a correction to the Thomson approximation. Note that the Thomson scattering amplitude is vanishing in the case of inelastic scattering (Raman scattering).

With the aim to avoid the summation over the (infinite) intermediate target states, we shall propose an alternative method that is based on a perturbation expansion.

## III. PERTURBATION EXPANSION

### A. Basic theory

Let us focus on the term  $\mathcal{A}_{12}$  and rewrite it as

$$\mathcal{A}_{12} = \sum_{j,t=1}^N \langle f | \hat{\mathbf{p}}_j \cdot \epsilon_2^* \frac{1}{\hat{H}_0 - E_i - E_1} \hat{\mathbf{p}}_t \cdot \epsilon_1 | i \rangle, \quad (4)$$

where  $\hat{H}_0$  is the target hamiltonian, and we used the eigenvalues equation  $\hat{H}_0 | \nu \rangle = E_{\nu} | \nu \rangle$  as well as the completeness of the states  $| \nu \rangle$ . Now, let us define the state

$|s\rangle$  as

$$|s\rangle \equiv \frac{c}{\hat{H}_0 - E_i - E_1} \sum_{t=1}^N \hat{\mathbf{p}}_t \cdot \boldsymbol{\epsilon}_1 |i\rangle, \quad (5)$$

where  $c$  is the speed of light. Once the state  $|s\rangle$  is known, the term  $\mathcal{A}_{12}$  can be simply calculated as

$$\mathcal{A}_{12} = \frac{1}{c} \sum_{j=1}^N \langle f | \hat{\mathbf{p}}_j \cdot \boldsymbol{\epsilon}_2^* |s\rangle. \quad (6)$$

The equation above resembles the amplitude for a single photon process, and can be calculated with high accuracy, provided that  $|s\rangle$  is known. Our task is then to find a solution for the state  $|s\rangle$ . In the literature, there have been other studies that used a similar starting point to get inhomogeneous equations of the Green's function to be solved numerically [25, 54]. In contrast, we here seek an analytical solution of the problem via a perturbation expansion.

From Eq. (6), one sees that the state  $|s\rangle$  evidently represents the quantum intermediate state of the target during the scattering process, as depicted in Fig. 2. With the aim to find such a state, we cast equation (5) as

$$|s\rangle = - \sum_{t=1}^N \frac{c \boldsymbol{\epsilon}_1 \cdot \hat{\mathbf{p}}_t}{E_1} |i\rangle + \frac{\hat{H}_0 - E_i}{E_1} |s\rangle. \quad (7)$$

Equation (7) can be regarded as a perturbation expansion of the state  $|s\rangle$  on  $(\hat{H}_0 - E_i)/E_1$ . The term on which the expansion is made is easily interpretable: The numerator  $(\hat{H}_0 - E_i)$  describes the energy shift caused by the scattering photon, while the denominator  $(E_1)$  is the incident photon energy. The expansion coefficient is thus a measure of how much energy shift is brought to the target by the scattering photon in units of the incident photon energy.

In the following, we shall explicitly calculate some perturbation orders. Note that the state  $|s\rangle$  need not be normalized to one, since it does not represent a physical state. Close to resonances, from Eq. (4) it can be easily seen that  $\langle s | s \rangle \sim +\infty$ .

### B. $0^{th}$ order

At the  $0^{th}$  order, it is assumed  $1/E_1 = 0$ , which entails  $E_1 \rightarrow +\infty$ . From Eq. (7), this implies

$$|s\rangle_0 = 0, \quad (8)$$

where the subscript indicates the expansion order. In turn, this implies that the amplitudes  $\mathcal{A}_{12,21}$  are identically zero at this expansion order, that is  $\mathcal{A}_{12,21}^{(0)} = 0$ . The total scattering amplitude then turns out to be

$$\mathcal{M} = N \langle f | \boldsymbol{\epsilon}_1 \cdot \boldsymbol{\epsilon}_2^* |i\rangle = N \boldsymbol{\epsilon}_1 \cdot \boldsymbol{\epsilon}_2^* \delta_{i,f}, \quad (9)$$

where we used  $\langle f | i \rangle = \delta_{i,f}$ . This expansion order evidently corresponds to the Thomson approximation.

One may notice from Eq. (2) that the same result can be accomplished by approximating  $m \rightarrow +\infty$  and if the photon energy is far from the target spectrum. In other words, this is the case if the target can be considered classical. We may therefore conclude that approximating the intermediate state  $|s\rangle$  at the  $0^{th}$  order, i.e.  $|s\rangle \approx |s\rangle_0$ , is effectively like considering the target as classical. Because of this, we shall hereinafter call the  $0^{th}$  order term in the perturbation expansion as the ‘‘classical term’’.

### C. $1^{st}$ order

In order to compute the  $1^{st}$  order of the perturbed state, we insert  $|s\rangle_0$  into the right hand side of Eq. (7). We are thus approaching the exact scattering solution from the Thomson approximation, i.e. from photon energies above the spectrum. By doing so we get:

$$|s\rangle_1 = - \sum_{t=1}^N \frac{c \boldsymbol{\epsilon}_1 \cdot \hat{\mathbf{p}}_t}{E_1} |i\rangle. \quad (10)$$

It can be easily seen from Eq. (7) that this approximation corresponds to considering  $\hat{H}_0 |s\rangle \approx E_i |s\rangle$ . Within this approximation, we are therefore considering as if the energy of the perturbed state  $|s\rangle$  were approximately unperturbed, i.e.  $E_s \approx E_i$ .

By using (10), we can explicitly calculate the first order correction to the scattering amplitude:  $\mathcal{A}_{12}^{(1)} = -\frac{1}{E_1} \sum_{j,t} \langle f | \hat{\mathbf{p}}_j \cdot \boldsymbol{\epsilon}_2^* \hat{\mathbf{p}}_t \cdot \boldsymbol{\epsilon}_1 |i\rangle$ . Analogously, the term  $\mathcal{A}_{21}^{(1)}$  takes the form  $\mathcal{A}_{21}^{(1)} = +\frac{1}{E_2} \sum_{j,t} \langle f | \hat{\mathbf{p}}_j \cdot \boldsymbol{\epsilon}_1 \hat{\mathbf{p}}_t \cdot \boldsymbol{\epsilon}_2^* |i\rangle$ . Without restriction of generality and for simplicity, let us consider the case for which photon polarizations are measured in the linear basis, for which  $\boldsymbol{\epsilon}_{1(2)}^* = \boldsymbol{\epsilon}_{1(2)}$ . By using  $[\hat{\mathbf{p}}_j \cdot \boldsymbol{\epsilon}_2, \hat{\mathbf{p}}_t \cdot \boldsymbol{\epsilon}_1] = 0$  for any  $j, t$ , we obtain

$$\begin{aligned} \mathcal{A}^{(1)} &= \mathcal{A}_{12}^{(1)} + \mathcal{A}_{21}^{(1)} \\ &= \sum_{j,t=1}^N \langle f | \hat{\mathbf{p}}_j \cdot \boldsymbol{\epsilon}_1 \hat{\mathbf{p}}_t \cdot \boldsymbol{\epsilon}_2 |i\rangle \left( \frac{1}{E_2} - \frac{1}{E_1} \right). \end{aligned} \quad (11)$$

This is a fundamental correction to the Thomson amplitude that depends only on initial and final states. The scattering operator is in fact independent of the target binding potential. Given that the Thomson amplitude is vanishing for Raman scattering, equation (11) is actually the first non-vanishing quantum mechanical term related to Raman processes.

A first remark from Eq. (11) is that such equation could be also directly obtained from Eq. (3) by considering  $E_{1,2} \gg E_{i,f,\nu}$  and by then using the completeness of the intermediate states,  $\sum_{\nu} |\nu\rangle \langle \nu| = 1$ . A second remark is that the amplitude goes to zero as  $E_1 \rightarrow E_2$ . That demonstrates that the first order correction is al-

ways zero in Rayleigh scattering, independently of the binding potential. This rule is a consequence of the coherence between incoming and outgoing light in Rayleigh scattering.

#### D. $n^{\text{th}}$ order

To find the  $2^{\text{nd}}$  order of the perturbed state, we insert the  $1^{\text{st}}$  order solution into the right hand side of Eq. (7):

$$|s\rangle_2 = |s\rangle_1 - \frac{1}{E_1^2} \left[ \hat{H}_0, \sum_{t=1}^N c_{\xi_1} \cdot \hat{\mathbf{p}}_t \right] |i\rangle, \quad (12)$$

where we used  $(\hat{H}_0 - E_i) |i\rangle = 0$  and the fact that  $E_i$  commutes with any quantum operator. By  $n$  replacements, the state at order  $n$  is found to be

$$|s\rangle_n = \begin{cases} 0 & \text{for } n = 0 \\ |s\rangle_{n-1} + \frac{\hat{O}_n}{(E_1)^n} |i\rangle & \text{for } n > 0 \end{cases} \quad (13)$$

or equivalently

$$|s\rangle_n = \begin{cases} 0 & \text{for } n = 0 \\ \sum_{k=1}^n \frac{\hat{O}_k}{(E_1)^k} |i\rangle & \text{for } n > 0 \end{cases} \quad (14)$$

where

$$\begin{aligned} \hat{O}_k &= -\frac{im}{\hbar} \sum_t c_{\xi_1} \cdot \overbrace{\left[ \hat{H}_0, [\hat{H}_0, [\dots, [\hat{H}_0, \hat{\mathbf{r}}_t] \dots]] \right]}^{\hat{H}_0 \text{ repeated for } k \text{ times}} \\ &= \left[ \hat{H}_0, \hat{O}_{k-1} \right], \end{aligned} \quad (15)$$

while  $\hat{O}_0 = -\frac{im}{\hbar} \sum_t c_{\xi_1} \cdot \hat{\mathbf{r}}_t$  and  $\hat{O}_1 = -c_{\xi_1} \cdot \sum_t \hat{\mathbf{p}}_t$ . To write Eq. (15), we used the equivalence  $\hat{\mathbf{p}}_t = \frac{im}{\hbar} \left[ \hat{H}_0, \hat{\mathbf{r}}_t \right]$ , which holds as long as the target binding potential commutes with the position operator. From Eq. (15), one sees that, if  $\hat{O}_{k-1}$  is vanishing, then also  $\hat{O}_k$  is vanishing, as well as all operators  $\hat{O}_j$  with  $j \geq k$ .

We define  $\hat{T}$  as the *transition operator*, that is the operator that transforms the initial state into the intermediate state, viz.

$$|s\rangle \equiv \hat{T} |i\rangle. \quad (16)$$

From Eqs. (13), (14), it immediately follows

$$\hat{T} = \frac{\hat{O}_1}{E_1} + \frac{\hat{O}_2}{E_1^2} + \frac{\hat{O}_3}{E_1^3} + \dots, \quad (17)$$

Therefore, the transition operator at order  $n$  is given by  $\hat{T}_n = \sum_{k=1}^n \frac{\hat{O}_k}{(E_1)^k}$ . Equations (13)-(17) can be used jointly with Eqs. (6) and (2) to find the total two-photon

scattering amplitude, given the target hamiltonian  $\hat{H}_0$ . We shall explicitly do this in Secs. V and VI.

## IV. GENERAL THEORETICAL RESULTS AND REMARKS

By using the theory presented in the previous sections, we here derive several general results in the form of statements and formulas, which are potentially useful when analyzing Rayleigh and Raman scattering. We shall also use them later in Secs. V and VI.

### A. Scattering cross section formula

The dependence of the scattering amplitude on the photon energies  $E_{1,2}$  is wholly within the denominators of the kind  $\sim 1/E_{1,2}$  that are contained in the transition operator  $\hat{T}$  (see Eq. (17)). This means that, without any assumption on the target binding potential, we may predict the cross section dependence on the photon energy. For example, let us take Raman scattering, for which  $\langle f|i\rangle = 0$  and  $E_i \neq E_f$ . While the energy of the incident photon  $E_1 \equiv E$  is freely adjustable, the energy of the scattered photon is bound by energy conservation to be  $E_2 = E - E_{res}$ , where we defined the resonance energy  $E_{res} = E_f - E_i$ . The cross section at the leading order of the series expansion is thus proportional to (see Eq. (11))

$$\sigma^{(1)} \propto \left| \mathcal{M}^{(1)} \right|^2 \propto \left| \frac{1}{E_2} - \frac{1}{E_1} \right|^2 = \frac{E_{res}^2}{E^2} \frac{1}{(E - E_{res})^2}. \quad (18)$$

Deviations from this formula come from higher orders in  $1/E_{1,2}$ . For example, from Eq. (17) the cross section at the second order can be written as

$$\begin{aligned} \sigma^{(2)} &\propto \left| \mathcal{M}^{(2)} \right|^2 \propto \left| c_1 \left( \frac{1}{E_2} - \frac{1}{E_1} \right) + c_2 \left( \frac{1}{E_2^2} + \frac{1}{E_1^2} \right) \right|^2 \\ &\approx \left( \frac{E_{res}^2}{E^2} \frac{|c_1|^2}{(E - E_{res})^2} + \frac{E_{res}}{E} \frac{4\Re(c_1 c_2^*)}{(E - E_{res})^3} \right), \end{aligned} \quad (19)$$

where we assumed  $|c_2| \ll |c_1|$ , and we kept terms of lowest order in  $1/E$ . The coefficients  $c_{1,2}$  are scaling factors that depend on the matrix elements of the transition operator (and therefore they depend in general on the target potential). The second term in the right hand side of Eq. (19) represents the first correction to the leading order term. One may therefore measure the energy dependence of the scattering cross section and parametrize it as in Eq. (19) (and subsequent orders), by using the coefficients  $c_{1,2,3,\dots}$ . This will help isolating the quantum contributions to the scattering cross section, and would also provide an empirical cross section formula whose terms have physical meaning. From the fitted coefficients, one

would then be able to retrieve the (dipole) matrix elements for the target specimen.

### B. Cancellation of quantum contributions for targets composed by identical particles

Let us suppose the target to be composed by just two particles of equal mass and charge, which we denote by particle  $A$  and  $B$ . Suppose also that such two particles experience a two-body potential that depends on the reciprocal distance, that is of the type  $V(\mathbf{r}_A - \mathbf{r}_B)$ , as it is mostly the case in nature, e.g. the Coulomb potential. Calculating the second order contribution of the operator  $\hat{O}$  we obtain

$$\begin{aligned} \hat{O}_2 &= \left[ \sum_{j=A,B} \frac{\hat{\mathbf{p}}_j^2}{2m} + V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B), \hat{O}_1 \right] \\ &= -c\epsilon_1 \cdot \sum_{j=A,B} \left[ V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B), \hat{\mathbf{p}}_j \right] \\ &= -i\hbar c\epsilon_1 \cdot \sum_{j=A,B} \nabla_{\mathbf{r}_j} V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B). \end{aligned} \quad (20)$$

However, since  $\nabla_{\mathbf{r}_B} V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B) = -\nabla_{\mathbf{r}_A} V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B)$ , then  $\hat{O}_2 = 0$ . Consequently,  $\hat{O}_{k \geq 2} = 0$ , as seen from Eq. (15). Therefore the only two non-vanishing terms of the perturbation expansion are the classical term (9) and the first quantum correction (11). If light is scattered elastically (as it is mostly the case), then also the quantum correction is vanishing. Therefore the target behaves as a classical scatterer, since all quantum contributions are identically zero. This result can be trivially extended to a target composed by any number of identical particles, as long as the inter-particle potentials are reciprocal.

Summarizing, this finding shows that when the target is composed by identical particles that interact with light, the quantum contributions to the scattering amplitude are either zero or significantly reduced. More specifically, the dependence of the inter-particle potential on the reciprocal distance generates coherent scattered waves that interacts destructively with each other, in pair, thus resulting in a cancellation of the quantum contribution to the scattering amplitude. In case of elastic scattering (Rayleigh scattering), the cancellation of quantum contributions is complete. The resulting scattered wave is thus the same as if it were scattered by a classical target. Hence, the process of elastic scattering does not retrieve any information about the quantum nature of the scatterer. On the other hand, in the case of inelastic scattering (Raman scattering) the cancellation of quantum terms is almost complete, since only one term is left out of the perturbation expansion, beside the classical term.

One could use this result in different areas, ranging

from fundamental to applied physics. For example, one could build quantum information carriers made of identical bound particles that interact with light, such as BCS pairs [55]. The quanta of information could be embedded into a quantum feature of the bound system that is not retrievable by the classical term. Thus, any attempt to steal the information from the system with elastic light scattering would fail, provided that dipole approximation is valid. Moreover, this result has also impact on the coherence time of the quantum carriers, which is an ongoing research field [56, 57], since it predicts a suppression of electromagnetic noise for carriers made of identical particles.

Potentials that depend on the reciprocal distance are typical in atoms and nuclei. In atoms, however, electrons experience also interaction with the nucleus, other than with themselves. Similarly, in nuclei protons experience interactions with neutrons, other than with themselves. The resulting overall potential is thus not only among particles of equal mass and charge, but also among particles with different mass and charge. Because of this, the quantum cancellation does not fully apply, and consequently the scattered light does possess information about the quantum nature of the target. Nevertheless, we can show that there is anyways a suppression of the contribution of reciprocal potentials among identical particles, such as electron-electron or proton-proton repulsion, at high energies. To this aim, let us call  $\hat{V}_R \equiv \sum_{\mu > \nu} V(\hat{\mathbf{r}}_\mu - \hat{\mathbf{r}}_\nu)$  the reciprocal potential of the identical compounds within the target, where  $\mu, \nu = (1, \dots, N)$  indexes the compound. One may straightforwardly compute the scattering operators  $\hat{O}_1, \hat{O}_2, \hat{O}_3$ , and find out that they are linear in the momentum operator. They therefore commute with the reciprocal potential, as showed above. The fourth order is the lowest order where the scattering operator presents non-linear terms in the momentum operator. As a matter of fact,  $\hat{O}_4$  presents terms of the type  $\sim \hat{\mathbf{p}}_{\mu i} \hat{\mathbf{p}}_{\nu j}$ , where  $i, j = (x, y, z)$  are the cartesian coordinates. At the fifth order, the scattering operator gets non-zero contributions from the reciprocal potential since in general  $\hat{O}_5 \propto [\hat{V}_R, \hat{O}_4] \neq 0$ . Therefore, the fifth order is the lowest scattering order in which the reciprocal potential within identical particles in the target, such as electron-electron or proton-proton repulsion, contributes to the scattering cross section. This entails that the contribution of reciprocal potentials to the scattering cross section is reduced in those cases, as long as the photon energy is high enough to lead to convergency in Eq. (13). In addition to this argument, we shall demonstrate in Sec. VI that reciprocal potentials do not contribute at all to the Rayleigh scattering amplitude, as long as a) the binding potential can be approximated to harmonic, and b) the target wavefunction can be separated into relative and center-of-mass coordinates.

### C. Information retrieved by linearly polarized light

Let us suppose that the target binding potential is of the form  $V(x, y, z) = V(x) + V(y) + V(z)$ , and that the incident light is linearly polarized along the  $x$ -direction. From Eq. (15), we can easily calculate that the perturbation equation for the scattering operator  $\hat{O}$  depends only upon the potential along the  $x$ -axis:

$$\begin{aligned} \hat{O}_k &= \left[ \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{x}, \hat{y}, \hat{z}), \left[ \dots, \left[ \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{x}, \hat{y}, \hat{z}), -c\hat{p}_x \right] \dots \right] \right] \\ &= \left[ \frac{\hat{p}_x^2}{2m} + V(\hat{x}), \left[ \dots, \left[ \frac{\hat{p}_x^2}{2m} + V(\hat{x}), -c\hat{p}_x \right] \dots \right] \right]. \quad (21) \end{aligned}$$

This entails that the total cross section will only depend on the potential along the  $x$ -axis. Generalizing, if the target binding potentials along different cartesian axes are fully decoupled (i.e. they are different terms in the hamiltonian), linearly polarized light will *only* probe the binding potential along the polarization axis.

This result is particularly useful if one wants to individually probe the target binding potential along a given axis, as it might be the case, for example, in ion traps [58], especially in array-based approaches where the transport of ions along the trap axis is sought, to be eventually used for quantum communication purposes [59]. Alternatively, this result can be used to polarize light, by inducing asymmetric target potentials, where the asymmetry needs to be in the polarization plane. Conversely, one could retrieve asymmetries in the target binding potential by analyzing the polarization of the scattered light.

### D. Further considerations

Thanks to the commutators, at the  $n^{\text{th}}$  order we get a correction proportional to  $\hbar^n$ . This feature resembles typical semiclassical expansions which are also in powers of  $\hbar$ , such as the WKB approximation [60]. Here, however, the inverse dependence on the photon energy contributes to the convergence of the series in addition to the dependence on  $\hbar$ . If the target binding potential and all its derivatives are not singular anywhere, the convergence of the series in Eqs. (13)-(17) will be attained, at least for energies significantly above the target spectrum. To this regard, one must be careful when considering Coulomb binding potentials since they present singularities given by terms  $\propto 1/|\mathbf{r}_i|$  or  $\propto 1/|\mathbf{r}_i - \mathbf{r}_j|$ .

As last remark, we point out that an exact solution of the series expansion in Eq. (15) is in general difficult to find. Even so, below we shall show a few cases for which a closed solution can be found. Moreover, we shall show that convergence for any (arbitrarily complex, not singular) binding potential is guaranteed provided that the photon energy is high enough with respect to the binding energy. This endows the formulas (13)-(15) with a funda-

mental value that paves the way to compute two-photon processes within a full second-order quantum mechanical framework for complex quantum systems where the infinite sum of intermediate states is difficult or unfeasible to calculate.

## V. APPLICATION TO A FEW SINGLE-PARTICLE CASES

As practical examples, in this section we shall apply the technique we developed above to some specific (single-particle) cases that are easily found in literature for modeling quantum phenomena. We shall proceed in order of complexity with regard to the target binding potential. We will analyze Raman or Rayleigh light scattering, depending on the case study.

### A. Potential box

The simplest binding potential is a potential box, where the potential is zero (or any constant) within the box, while it is infinite outside. Notwithstanding its simplicity, such a potential is used to model bound states in nuclear physics [61], subnuclear physics [62], and semi-conductor physics [63], among others. Eigenstates and eigenenergies can be found in standard textbooks [64]. Specifically, the combination of quantum numbers  $(n_x, n_y, n_z)$  defines the eigenstates, with  $n_j = 1, 2, 3, \dots$  for any  $j = x, y, z$ . Quantum states are characterized by the energy  $E_n = \xi_a n^2$ , where  $n^2 = n_x^2 + n_y^2 + n_z^2$  and  $\xi_a = \frac{\pi^2 \hbar^2}{2ma^2}$ . Given that all eigenfunctions are vanishing at the edge of the potential box and beyond, we can restrict the integrals in Eq. (3) within the domain  $|x| < a/2$ ,  $|y| < a/2$ ,  $|z| < a/2$ , where  $a$  is the size of the potential box. Within such domain, the potential is constant and therefore  $\hat{O}_{k \geq 2} = 0$ . By using the theory developed in the previous sections, the total (exact) scattering amplitude  $\mathcal{M}$  is calculated as

$$\mathcal{M} = \boldsymbol{\varepsilon}_1 \cdot \boldsymbol{\varepsilon}_2 \delta_{i,f} - \frac{1}{m} \left( \frac{1}{E_2} - \frac{1}{E_1} \right) \underbrace{\langle f | \hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_1 \hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_2 | i \rangle}_{C_{f,i}} \quad (22)$$

where  $E_2 = E_1 - E_f + E_i$  by energy conservation, and where we considered (without restriction of generality) linear photon polarizations. The matrix elements  $C_{f,i}$  can be calculated by using standard techniques.

Let us investigate Raman scattering off one particle trapped in the potential box. Provided that the matrix element  $C_{f,i}$  is not zero, the Raman cross section will peak at photon energy  $E_1 \simeq E_f - E_i$ , as can be seen from Eq. (22). Since  $\xi_a$  depends on  $a$ , the relative position of the energy peaks will also depend on  $a$  (the box size). For example, the first peak is located at energy  $E_1 = 3\xi_a = 3\pi^2 \hbar^2 / (2ma^2) \approx 15/a^2$  (atomic units). By scanning through the incident photon energy and by

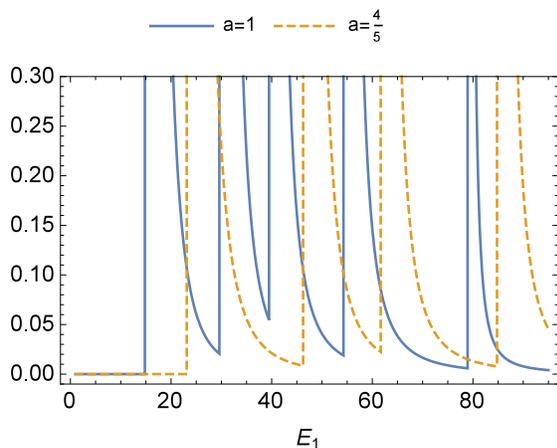


FIG. 3. The probability density,  $|\mathcal{M}|^2$ , for Raman scattering off one particle trapped by a potential box (see Sec. VA). Atomic units are used. The potential parameters can be retrieved by analyzing the relative positions of the resonance peaks.

thus investigating the distance between peaks, one can retrieve the size of the potential box. See Fig. 3 for this purpose, where  $|\mathcal{M}|^2$  is plotted after having summed over the final target states, integrated over the scattering angle, as well as summed (averaged) over the final (initial) photon polarizations. Furthermore, the dependence of the energy peaks on the box size  $a$  can be used to roughly estimate the range of the target binding potential, as long as it can be approximated to a potential box.

A similar analysis can be performed for a semi-infinite potential well or for a delta potential, which are potentials that can be used to model nucleon-nucleon and short-range interactions, respectively [65].

### B. Symmetric linear potential

Besides box potentials, linear potentials are also a class of potential models that are used in different areas of physics [66–69]. Let us therefore consider light scattering off one-particle bound by a potential of the form  $V = b_x|x| + b_y|y| + b_z|z|$ , where  $b_{x,y,z}$  are constants. Eigenstates and eigenenergies are well known and can be found in literature [70]. By using linear photon polarizations (without restriction of generality), from Eq. (15) we can solve for the operator  $\hat{O}$  of the amplitude  $\mathcal{A}_{12}$ :

$$\hat{O}_2 = -i\hbar c_{\epsilon_1} \cdot \hat{\mathbf{b}}, \quad \hat{O}_{k \geq 3} = 0, \quad (23)$$

where  $\hat{\mathbf{b}} = (\hat{x}b_x/|\hat{x}|, \hat{y}b_y/|\hat{y}|, \hat{z}b_z/|\hat{z}|)$ , while  $\hat{O}_1$  has been defined in Eq. (15). Equations (23) are valid only for  $x \neq 0$ ,  $y \neq 0$ ,  $z \neq 0$ . On the other hand, if  $x = 0$  or  $y = 0$  or  $z = 0$ , the operators  $\hat{O}_{k \geq 2}$  cannot be calculated since the first derivative of the potential is not defined. Nevertheless, this problem can be circumvented by either

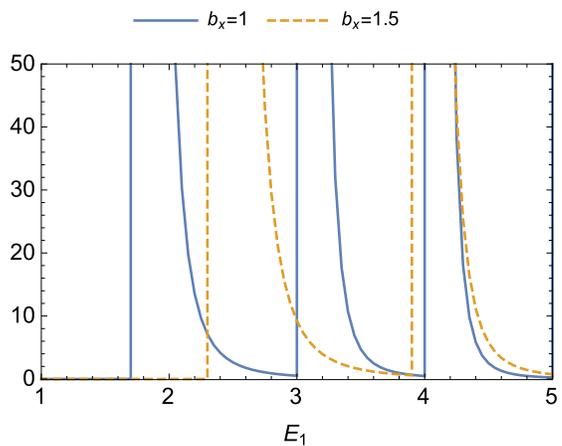


FIG. 4. Same as Fig. 3, but relative to the case-study presented in Sec. VB.

taking the principal value of the integral in Eq. (6), or by working with antisymmetric target wavefunctions, which are vanishing in those points.

By coherently summing the amplitudes  $A_{12}$  and  $A_{21}$  as in Eq. (2), the total (exact) scattering amplitude  $\mathcal{M}$  is found as

$$\begin{aligned} \mathcal{M} = & \epsilon_1 \cdot \epsilon_2 \delta_{i,f} - \frac{1}{m} \left( \frac{1}{E_2} - \frac{1}{E_1} \right) \langle f | \hat{\mathbf{p}} \cdot \epsilon_1 \hat{\mathbf{p}} \cdot \epsilon_2 | i \rangle \\ & - \frac{i\hbar}{m} \langle f | \left( \frac{\epsilon_2 \cdot \hat{\mathbf{p}} \epsilon_1 \cdot \hat{\mathbf{b}}}{E_1^2} + \frac{\epsilon_1 \cdot \hat{\mathbf{p}} \epsilon_2 \cdot \hat{\mathbf{b}}}{E_2^2} \right) | i \rangle, \end{aligned} \quad (24)$$

where  $E_2 = E_1 - E_f + E_i$  by energy conservation.

Let us consider Raman scattering, where the initial state is the (symmetric) ground state, while the incident photon linear polarization is along the  $x$ -axis ( $\chi_1 = 0$ ). Let us further consider for simplicity the case of a) scattering in the backward direction ( $\theta = \pi$ ), and b) no linear polarization flip, which implies  $\chi_2 = 0$ . Figure 4 displays  $|\mathcal{M}|^2$ , after having summed over the final target states. As for the previous case, the relative distance between peaks can be used to retrieve the potential parameter  $b_x$ . On the other hand, by virtue of the chosen settings, the scattering amplitude does not depend on the other two parameters  $b_y$ ,  $b_z$ , which is also a consequence of our findings in Sec. IV C.

### C. Harmonic potential

Here we consider the target being characterized by one charged particle bound by a harmonic potential. Such a model is extensively used in quantum optics [71, 72] as well as in nuclear physics (shell model) [73], among others. The target hamiltonian is

$$\hat{H}_0 = \hat{H}_{ho} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{m\omega^2}{2} (\hat{\mathbf{r}} - \mathbf{r}_0)^2, \quad (25)$$

where  $\omega$  is the oscillator constant, and  $\mathbf{r}_0$  the displacement vector. Let us further consider an incident photon that is linearly polarized along the  $x$ -direction, which entails  $\underline{\epsilon}_1 = (1, 0, 0)$ . Consequently, we

have  $\hat{O}_1 = -c\hat{p}_x$ . By straightforward calculation, one can see that  $[\hat{H}_0, \hat{O}_1] = -c\omega^2(\hat{x} - x_0)i\hbar m$ , as well as  $[\hat{H}_0, [\hat{H}_0, \hat{O}_1]] = \hbar^2\omega^2\hat{O}_1$ . This can be replaced in the definition of  $\hat{T}$  to find

$$\begin{aligned} \hat{T} &= \frac{\hat{O}_1}{E_1} + \frac{[\hat{H}_0, \hat{O}_1]}{E_1^2} + \frac{[\hat{H}_0, [\hat{H}_0, \hat{O}_1]]}{E_1^3} + \frac{[\hat{H}_0, [\hat{H}_0, [\hat{H}_0, \hat{O}_1]]]}{E_1^4} + \dots \\ &= \frac{\hat{O}_1}{E_1} + \frac{[\hat{H}_0, \hat{O}_1]}{E_1^2} + \frac{\hbar^2\omega^2}{E_1^2} \left( \frac{\hat{O}_1}{E_1} + \frac{[\hat{H}_0, \hat{O}_1]}{E_1^2} + \frac{[\hat{H}_0, [\hat{H}_0, \hat{O}_1]]}{E_1^3} + \dots \right) \\ &= \frac{\hat{O}_1}{E_1} + \frac{[\hat{H}_0, \hat{O}_1]}{E_1^2} + \frac{\hbar^2\omega^2}{E_1^2} \hat{T}. \end{aligned} \quad (26)$$

This leads to a closed solution:

$$\left(1 - \frac{\hbar^2\omega^2}{E_1^2}\right) \hat{T} = \frac{\hat{O}_1}{E_1} + \frac{[\hat{H}_0, \hat{O}_1]}{E_1^2}. \quad (27)$$

In the case of zero displacement ( $|\mathbf{r}_0| = 0$ ), the equation above can be recast as

$$\hat{T} = -i \frac{\hbar^2\omega^2}{E_1^2 - \hbar^2\omega^2} \sqrt{\frac{2mc^2}{\hbar\omega}} \hat{a}_{x,\gamma}^\dagger, \quad (28)$$

where  $\hat{a}_{x,\gamma}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega}\gamma\hat{p}_x\right) = \frac{1}{2}(\hat{a}_x^\dagger(1+\gamma) + \hat{a}_x(1-\gamma))$  and  $\gamma = E_1/(\hbar\omega)$ . Here,  $\hat{a}_x$  and  $\hat{a}_x^\dagger$  represent the standard annihilation and creation operator for the quantum harmonic oscillator along the  $x$ -direction [60]. While  $\gamma$  denotes the ratio between the photon energy and the oscillator energy,  $\hat{a}_{x,\gamma}^\dagger$  can be considered the ‘perturbed’ creation operator along the polarization direction. This leads us to an additional result: when linearly polarized photons with energy  $E_1$  are scattered by a harmonic oscillator with angular frequency  $\omega$ , the intermediate scattering state of the harmonic oscillator is equal to  $|s\rangle = \hat{T}|i\rangle = K\hat{a}_{j,\gamma}^\dagger|i\rangle$ , where  $j$  is the photon polarization direction and  $K$  is a numerical factor defined from Eq. (28). We may notice here again that, if the photon hits the resonance ( $E_1 \rightarrow \hbar\omega$ ), then  $K \rightarrow +\infty$ , and therefore  $\langle s|s\rangle \sim +\infty$ .

From Eqs. (28) and (6), the term  $\mathcal{A}_{12}$  can be calculated. Considering a general linear polarization for the incident photon, one has

$$\mathcal{A}_{12} = m \left( \frac{\hbar^2\omega^2}{E_1^2 - \hbar^2\omega^2} \right) \sum_{\substack{j,k= \\ x,y,z}} \epsilon_{2j}\epsilon_{1k} \langle f | (\hat{a}_j^\dagger - \hat{a}_j) \hat{a}_{k,\gamma}^\dagger | i \rangle. \quad (29)$$

Finally, with the help of Eq. (2), in the case of Rayleigh scattering (i.e. for  $E_1 = E_2 \equiv E$ , which implies  $|i\rangle = |f\rangle$ ), the total amplitude  $\mathcal{M}$  (exact) can be evaluated analytically:

$$\mathcal{M} = \underline{\epsilon}_1 \cdot \underline{\epsilon}_2^* \left( 1 + \frac{\hbar^2\omega^2}{E^2 - \hbar^2\omega^2} \right). \quad (30)$$

It can be easily noticed that the second term (which is the quantum term) represents a Lorentzian peak, with zero resonance width, the probability density being proportional to  $\frac{\hbar^4\omega^4}{(E+\hbar\omega)^2(E-\hbar\omega)^2}$ . The fact that the resonance width is zero is not unexpected, since we have not inserted the widths of bound states into the formalism. Moreover, we may notice that the amplitude peaks at the resonance  $E = \hbar\omega$ , which is the energy gap between neighboring states in a harmonic potential spectrum. This is easily understandable, since within the dipole approximation the transition operator is proportional to  $\underline{\epsilon} \cdot \hat{\mathbf{p}}$ , and thus proportional to  $\underline{\epsilon} \cdot (\hat{\mathbf{a}}^\dagger - \hat{\mathbf{a}})$ . Therefore, such operator has non-vanishing matrix elements only between states whose energy difference is  $\hbar\omega$ . One could also use this feature to retrieve Eq. (30) directly from Eqs. (3) and (2), by restricting the summation over intermediate states to neighboring states. In Fig. 5 we show the probability density for Rayleigh scattering off a harmonic oscillator with angular frequency  $\omega$ , as obtained from (30).

We see from Eq. (30) and from Fig. 5 that the amplitude  $\mathcal{M}$  asymptotically vanishes as  $E \rightarrow 0$ . At low photon energies, the contribution of higher terms (the quantum terms, which are represented by the second addend in Eq. (30)), fully destructively interferes with the contribution of the zero order term (the classical term, which is represented by the first addend in Eq. (30)). Overall, this results in a vanishing cross section. At low

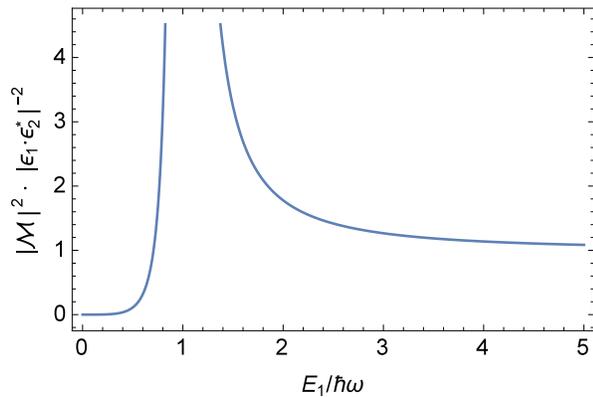


FIG. 5. Probability density for elastic light scattering (Rayleigh scattering) off a particle bound by a harmonic potential.

light frequency, also Raman scattering is zero, since the light does not carry enough energy to excite the target. Thus, a harmonic oscillator does not scatter light when the light frequency is much lower than the oscillator frequency. This is in line with the Rayleigh scattering formula, which states that the scattering cross section for low energetic light is proportional to the fourth power of the light frequency [74].

#### D. Morse potential

The Morse potential is typically used in molecular physics to model vibrations [75, 76]. In this section we consider the target having one charged particle that is vibrating along the  $x$ -axis, the vibration being modeled by a Morse potential

$$V(x) = V_0(e^{-2a(x-x_0)} - 2e^{-a(x-x_0)}), \quad (31)$$

where  $x$  and  $x_0$  are respectively the position with respect to the core potential and the position at the equilibrium, while  $a$ ,  $V_0$  are parameters. The eigenstates of this potential are known [75]. Let us denote by  $\mathcal{V}(y, z)$  the binding potential along directions different than  $x$ . Let us also suppose that the incident light is linearly polarized along the  $x$ -direction. In this situation,  $\mathcal{V}(y, z)$  does not contribute to the scattering amplitude, as showed in Sec. IV C. We are thus selectively probing the Morse potential axis with light [77].

We shall consider Rayleigh scattering off the ground state. The calculated components of the scattering operator  $\hat{O}$ , at orders 0 to 6, are showed in Appendix. Convergence of the series (13) is attained at sufficiently high energies. We explicitly show such a convergence in Fig. 6, where the scattering probability density is plotted for different perturbation orders, for the specific case of a) scattering in the backward direction ( $\theta = \pi$ ), and b) no linear polarization flip, which implies  $\chi_2 = 0$ .

The elastic resonance peak does not appear in Fig. 6,

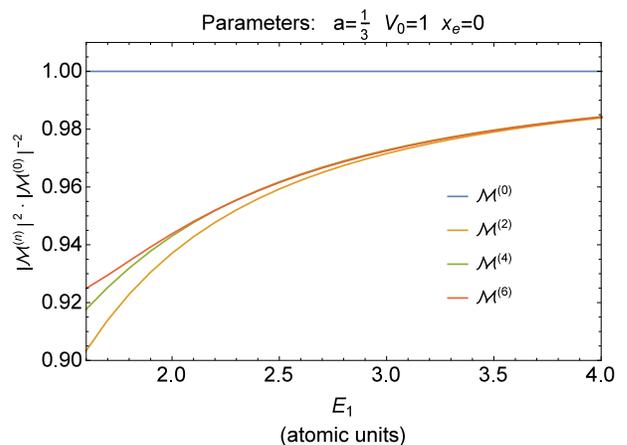


FIG. 6. Probability density of elastic light scattering (Rayleigh scattering) off a particle vibrating along the  $x$ -direction, the vibration being modeled by a Morse potential. Light is polarized along the  $x$ -direction. Parameters are set as showed.  $\mathcal{M}^{(n)}$  means scattering amplitude evaluated at the  $n^{\text{th}}$  order, with  $\mathcal{M}^{(0)} = \underline{\epsilon}_1 \cdot \underline{\epsilon}_2^*$ . Convergence of the series expansion can be noticed.

since it is located at lower energies. In the energy range related to the resonance peak, convergence of the perturbation expansion is difficult to attain, since it requires computing many expansion orders. Generally, convergence of the perturbation expansion is attained within few expansion orders if the photon energy is sufficiently above the resonance energies.

## VI. APPLICATION TO MULTI-PARTICLE CASES: COUPLED HARMONIC OSCILLATORS AND HOOKE'S ATOM

In this section we analyze two-photon scattering off multi-particle targets. For this purpose, we consider the target being a set of two coupled harmonic oscillators, as displayed in Fig. 7. The hamiltonian of such a system is:

$$\hat{H}_0 = \sum_{i=A,B} \left( \frac{\hat{\mathbf{p}}_i^2}{2m} + \frac{m\omega^2}{2} \hat{\mathbf{r}}_i^2 \right) + V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B), \quad (32)$$

where  $V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B)$  is *any* coupling potential between the oscillators. Let us consider, for simplicity, an incident photon that is linearly polarized along the  $x$ -direction. As showed in Sec. IV B, we may use  $[V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B), \hat{O}_1] = 0$ . Therefore  $[\hat{H}_0, \hat{O}_1] = -i\hbar cm\omega^2(x_A + x_B)$  and  $[\hat{H}_0, [\hat{H}_0, \hat{O}_1]] = \hbar^2\omega^2\hat{O}_1$ . As a consequence, equations (26) and (27) hold also in this multi-particle case. Then, similarly to Eq. (28), the transition operator  $\hat{T}$  turns out

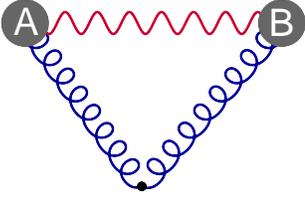


FIG. 7. (color online) A set of two coupled harmonic oscillators. The binding potential (blue line) is harmonic, while the A-B coupling (red line) can be differently defined.

to be

$$\hat{T} = -i \frac{\hbar^2 \omega^2}{E_1^2 - \hbar^2 \omega^2} \sqrt{\frac{2Mc^2}{\hbar\omega}} \hat{A}_{1x,\gamma}^\dagger, \quad (33)$$

where  $\hat{A}_{1x,\gamma}^\dagger = \sqrt{\frac{M\omega}{2\hbar}} \left( \hat{R}_x - \frac{i}{M\omega} \gamma \hat{P}_x \right)$ , and  $M = 2m$ .  $\hat{R}_x$  and  $\hat{P}_x$  are the projections along the  $x$ -axis of the operators related to the center-of-mass coordinates; these are defined as  $\hat{\mathbf{R}} = (\hat{\mathbf{r}}_A + \hat{\mathbf{r}}_B)/2$  and  $\hat{\mathbf{P}} = \hat{\mathbf{p}}_A + \hat{\mathbf{p}}_B$ .

To further proceed, one needs to define the interaction that yields the coupling potential  $V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B)$ , so to define the states  $|i\rangle$  and  $|f\rangle$ . As first example, let us choose the coupling potential to be harmonic. Harmonic coupling is mostly considered in crystals (classic phonon theory) [78], but also in many other physics fields, such as astrophysics [79] or quantum many-body systems [80]. With this choice, the target eigenstates  $|\Psi\rangle$  are factorized into the three cartesian coordinates,  $|\Psi\rangle = |\phi_x\rangle |\phi_y\rangle |\phi_z\rangle$ , where the vector state for each axis is itself factorized into center-of-mass and relative (inter-particle) coordinates as [81]

$$|\phi_j\rangle = \frac{(\hat{A}_{1j}^\dagger)^{n_{1j}} (\hat{A}_{2j}^\dagger)^{n_{2j}}}{\sqrt{n_{1j}! n_{2j}!}} |00\rangle \quad (34)$$

for any  $j = x, y, z$ , while  $n_{ij} = 0, 1, 2, \dots$  is the excitation number. The ladder operator related to the center-of-mass coordinates is defined as  $\hat{A}_{1j}^\dagger = \sqrt{\frac{M\omega}{2\hbar}} \left( \hat{R}_j - \frac{i}{M\omega} \hat{P}_j \right) = \hat{A}_{1j,\gamma=1}^\dagger$ . On the other hand,  $\hat{A}_{2j}^\dagger$  is the ladder operator related to the relative coordinates, and is not important for our analysis. Since the transition operator (33) does not contain operators related to relative coordinates, it follows that the Rayleigh scattering amplitude is the same as in Eq. (29) with  $a_j \rightarrow \hat{A}_{1j}$  and  $a_{j,\gamma} \rightarrow \hat{A}_{1j,\gamma}$ . The final form of the total amplitude is thus the one showed in Eq. (30) and displayed in Fig. 5. In conclusion, although the target bound structure in this multi-particle case is richer than in the single-particle case, the Rayleigh scattering amplitudes are the same, due to the fact that the transition operator only contains operators related to the center-of-mass coordinates, and that the wavefunction is factorized into center-of-mass and relative coordinates.

As a second example, we consider the coupling poten-

tial to be of Coulomb type:  $V(\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B) = \alpha/|\hat{\mathbf{r}}_A - \hat{\mathbf{r}}_B|$ , where  $\alpha$  is the coupling constant. With this choice, the set of coupled harmonic oscillators in Fig. 7 is known as Hooke's atom [82]. The Hooke's atom is an atomic model for helium that approximates the Coulomb interaction between atomic electrons and nucleus with a harmonic interaction, while retaining the full electron-electron repulsion term in the hamiltonian. For this reason, it is considered important in quantum chemistry and physics for the study of electron-electron correlations and quantum entanglement [83, 84]. The ground state wavefunction of the Hooke's atom is known analytically for many values of  $\omega$ . Such a wavefunction can be written in a factorized form as  $\Psi(\mathbf{R}, \mathbf{u}) = \chi(\mathbf{R}) \phi(\mathbf{u})$ , where  $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$  is the relative coordinate and  $\mathbf{R}$  (defined above) is the center-of-mass coordinate. While the function  $\phi(\mathbf{u})$  is specific to the Hooke's hamiltonian, the function  $\chi(\mathbf{R})$  turns out to be the wavefunction of a quantum harmonic oscillator.  $\chi(\mathbf{R})$  describes the movement of the center of mass of the coupled harmonic oscillators in Fig. 7. Let us now come back to the calculation of the Rayleigh scattering amplitude off the Hooke's atom. Since the transition operator (33) does not contain operators related to relative coordinates, it will only act on the wavefunction  $\chi(\mathbf{R})$ , and will consequently lead, once again, to the same transition amplitude we calculated for the single-particle harmonic oscillator in Sec. V C.

The calculations above lead us to another interesting result, which can be formulated as follows: Irrespectively of the choice of the coupling potential, the Rayleigh scattering off coupled- and uncoupled- harmonic oscillators is characterized by the same transition amplitude, as long as the wavefunction can be separated into center-of-mass and relative coordinates. In other words, the Rayleigh scattering is not sensible to the inter-particle coupling potential, provided that the mentioned hypotheses are satisfied. The same result would be obtained for  $N$  coupled harmonic oscillators.

## VII. FURTHER STUDIES AND EXTENSIONS

Similarly to what showed in Secs. V and VI, one could compute light scattering (as well as any two-photon processes) off other kinds of potential. The computation of the transition amplitude could be algebraically more complicated but certainly feasible. In other words, with the formalism developed in this paper one can calculate (dipole) two-photon transitions irrespectively of the complexity of the potential. If a closed form solution for the transition amplitude cannot be found, a solution given by convergence can be sought, provided that a) the potential is not singular anywhere in the Real space, and that b) the photons have sufficiently high energy.

The present study can be extended to higher multipoles. In order to consider all multipoles one needs to replace  $\underline{\epsilon}_{1,2} \cdot \hat{\mathbf{p}} \rightarrow \underline{\epsilon}_{1,2} \cdot \hat{\mathbf{p}} e^{\pm i \mathbf{k}_{1,2} \hat{\mathbf{r}}/\hbar}$  in Eq. (6), as well as in  $\hat{O}_1$  in Eq. (15), where  $k_{1,2}$  are the photon momenta.

Furthermore, one needs to adjust also the classical term (9), so to replace the Thomson term with the so-called Form Factor term [44]. The resulting computation for the matrix amplitude would be more difficult but certainly feasible, at least if one looks for convergence at high photon energies. A closed form solution might be in fact not be available when high multipoles are considered, even for the simpler cases described in Secs. V and VI.

An extension to relativistic quantum mechanics is analogously possible since the relativistic two-photon transition amplitude has a structure similar to the non-relativistic one. Even so, the commutators would be more challenging to compute, since the Dirac matrices do not commute with each other.

We so far considered the interaction potential to be that one given by (non-relativistic) quantum electrodynamics. If the interaction potential were different, equations (13) and (15) would still hold, as long as second order perturbation theory can be applied. The whole formalism here developed would be therefore unchanged. What would need an amendment is the definition of the operator  $\hat{O}_n$ , of equation (6), and of the classical term (9). The amendment would be the replacement of the potential operators.

### VIII. SUMMARY AND CONCLUSIONS

We developed a new method for evaluating two-photon processes that replaces the (well-know) summation over the intermediate states by a series of commutator operators. By focusing on Raman and Rayleigh scattering as examples of two-photon processes, we showed how this method gives a clear distinction between the Thomson scattering, regarded as the classical term, and the next terms of powers of  $\hbar$ , regarded as quantum contributions. We applied this new method to study light scattering off several target hamiltonians, and we thereby obtained closed form solutions of the commutator series for the simpler potential cases, while we looked for convergence in the case of more complex potentials.

In the course of our analysis, we derived several results. First, we derived a general correction to the Thomson approximation, as well as an energy-dependence law for the cross section, which is valid for any target potential within the dipole approximation. Furthermore, we found an analytical transformation from the ground state to the perturbed state of a harmonic oscillator immersed into radiation. We also showed that quantum contributions are vanishing (or significantly reduced) for targets composed by identical particles that are interacting with light. Moreover, we showed that linearly polarized

light only probes the target binding potential along the polarization axis, under the assumption that such a potential is decoupled in cartesian coordinates. Finally, we demonstrated that as long as a) the target binding potential can be approximated to harmonic, and b) the target wavefunction can be separated into relative and center-of-mass coordinates, then the elastic scattering amplitude is independent of inter-particle potentials.

As mentioned in previous sections, two-photon processes are applied in many scientific areas. The present work can be therefore potentially useful for forthcoming studies - in quantum chemistry, biology, crystals, mesoscopic systems, many-body physics, quantum optics and fundamental physics - that aim at analyzing two-photon processes beyond the Thomson or single resonance approximations [85], for which the infinite summation over the target intermediate states is difficult or unfeasible to calculate, or where a clear distinction between classical and quantum contributions is sought.

### IX. ACKNOWLEDGMENTS

P. A. acknowledges the support of the FCT, under Contracts No. SFRH/BPD/92329/2013. This work was funded by the Portuguese Fundação para a Ciência e a Tecnologia (FCT/MCTES/PIDDAC) under grant UID/FIS/04559/2013 (LIBPhys).

L. S. acknowledges financial support from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA Grant Agreement No. [291734].

F. F acknowledges partial support from the University of Applied Sciences BFI, Vienna.

### X. APPENDIX

Here we explicitly write the scattering operator  $\hat{O}$  for the case investigated in Sec. VD, that is Rayleigh scattering off a particle vibrating along the  $x$ -axis, the vibration being modeled by a Morse potential. For simplicity let us set units such that  $(V_0, a, x_0, m, \hbar, c) = (1, 1/3, 0, 1, 1, 1)$ . The ground state of the Morse potential is

$$\varphi_0 = 2^{\frac{9}{\sqrt{2}} - \frac{3}{4}} 3^{3\sqrt{2}-1} e^{\frac{\pi}{3} - 3\sqrt{2}e^{-x/3}} e^{-\frac{\pi}{3}(\frac{1}{2} + 3\sqrt{2})} \sqrt{\frac{6\sqrt{2}-1}{\Gamma(6\sqrt{2})}}. \quad (35)$$

The component of the operator  $\hat{O}$  up to the 6<sup>th</sup> order are found to be as follows:

$$\hat{O}_1 = -\hat{p}_x, \quad \hat{O}_2 = \frac{2}{3}ie^{-2\hat{x}/3} - \frac{2}{3}ie^{-\hat{x}/3}, \quad \hat{O}_3 = -\frac{2}{9}\left(\hat{p}_xe^{-2\hat{x}/3}\right) + \frac{1}{9}\left(\hat{p}_xe^{-\hat{x}/3}\right) - \frac{2}{9}\left(e^{-2\hat{x}/3}\hat{p}_x\right) + \frac{1}{9}\left(e^{-\hat{x}/3}\hat{p}_x\right),$$

$$\begin{aligned}
\hat{O}_4 &= -\frac{2}{27}i \left( \hat{p}_x^2 e^{-2\hat{x}/3} \right) + \frac{1}{54}i \left( \hat{p}_x^2 e^{-\hat{x}/3} \right) - \frac{2}{27}i \left( e^{-2\hat{x}/3} \hat{p}_x^2 \right) + \frac{1}{54}i \left( e^{-\hat{x}/3} \hat{p}_x^2 \right) - \frac{4}{27}i \left( \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x \right) + \frac{1}{27}i \left( \hat{p}_x e^{-\hat{x}/3} \hat{p}_x \right) \\
&\quad - \frac{2}{9}i \left( e^{-\hat{x}/3} e^{-2\hat{x}/3} \right) - \frac{2}{9}i \left( e^{-2\hat{x}/3} e^{-\hat{x}/3} \right) + \frac{8}{27}i e^{-4\hat{x}/3} + \frac{4}{27}i e^{-2\hat{x}/3} , \\
\hat{O}_5 &= \frac{2}{81} \left( \hat{p}_x^3 e^{-2\hat{x}/3} \right) - \frac{1}{324} \left( \hat{p}_x^3 e^{-\hat{x}/3} \right) + \frac{2}{81} \left( e^{-2\hat{x}/3} \hat{p}_x^3 \right) - \frac{1}{324} \left( e^{-\hat{x}/3} \hat{p}_x^3 \right) + \frac{2}{27} \left( \hat{p}_x^2 e^{-2\hat{x}/3} \hat{p}_x \right) - \frac{1}{108} \left( \hat{p}_x^2 e^{-\hat{x}/3} \hat{p}_x \right) \\
&\quad + \frac{2}{27} \left( \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x^2 \right) - \frac{1}{108} \left( \hat{p}_x e^{-\hat{x}/3} \hat{p}_x^2 \right) - \frac{28}{81} \left( \hat{p}_x e^{-4\hat{x}/3} \right) - \frac{7}{81} \left( \hat{p}_x e^{-2\hat{x}/3} \right) - \frac{28}{81} \left( e^{-4\hat{x}/3} \hat{p}_x \right) - \frac{7}{81} \left( e^{-2\hat{x}/3} \hat{p}_x \right) \\
&\quad + \frac{1}{9} \left( \hat{p}_x e^{-\hat{x}/3} e^{-2\hat{x}/3} \right) - \frac{8}{81} \left( e^{-2\hat{x}/3} \hat{p}_x e^{-2\hat{x}/3} \right) + \frac{14}{81} \left( e^{-\hat{x}/3} \hat{p}_x e^{-2\hat{x}/3} \right) + \frac{5}{27} \left( \hat{p}_x e^{-2\hat{x}/3} e^{-\hat{x}/3} \right) + \frac{14}{81} \left( e^{-2\hat{x}/3} \hat{p}_x e^{-\hat{x}/3} \right) \\
&\quad - \frac{2}{81} \left( e^{-\hat{x}/3} \hat{p}_x e^{-\hat{x}/3} \right) + \frac{5}{27} \left( e^{-\hat{x}/3} e^{-2\hat{x}/3} \hat{p}_x \right) + \frac{1}{9} \left( e^{-2\hat{x}/3} e^{-\hat{x}/3} \hat{p}_x \right) , \\
\hat{O}_6 &= \frac{56}{243}i \left( e^{-2\hat{x}/3} e^{-4\hat{x}/3} \right) + \frac{40}{81}i e^{-4\hat{x}/3} - \frac{38}{81}i \left( e^{-\hat{x}/3} e^{-4\hat{x}/3} \right) - \frac{8}{27}i \left( \hat{p}_x^2 e^{-4\hat{x}/3} \right) + \frac{8}{27}i \left( e^{-4\hat{x}/3} e^{-2\hat{x}/3} \right) - \frac{14}{243}i \left( e^{-\hat{x}/3} e^{-2\hat{x}/3} \right) \\
&\quad - \frac{1}{27}i \left( \hat{p}_x^2 e^{-2\hat{x}/3} \right) + \frac{2}{243}i \left( \hat{p}_x^4 e^{-2\hat{x}/3} \right) - \frac{38}{81}i \left( e^{-4\hat{x}/3} e^{-\hat{x}/3} \right) - \frac{2}{27}i \left( e^{-2\hat{x}/3} e^{-\hat{x}/3} \right) - \frac{i \left( \hat{p}_x^4 e^{-\hat{x}/3} \right)}{1944} - \frac{8}{27}i \left( e^{-4\hat{x}/3} \hat{p}_x^2 \right) \\
&\quad - \frac{1}{27}i \left( e^{-2\hat{x}/3} \hat{p}_x^2 \right) + \frac{2}{243}i \left( e^{-2\hat{x}/3} \hat{p}_x^4 \right) - \frac{i \left( e^{-\hat{x}/3} \hat{p}_x^4 \right)}{1944} - \frac{52}{243}i \left( e^{-2\hat{x}/3} e^{-\hat{x}/3} e^{-2\hat{x}/3} \right) + \frac{10}{243}i \left( \hat{p}_x^2 e^{-\hat{x}/3} e^{-2\hat{x}/3} \right) \\
&\quad - \frac{8}{81}i \left( e^{-2\hat{x}/3} \hat{p}_x^2 e^{-2\hat{x}/3} \right) + \frac{17}{162}i \left( e^{-\hat{x}/3} \hat{p}_x^2 e^{-2\hat{x}/3} \right) + \frac{64}{243}i \left( e^{-\hat{x}/3} e^{-2\hat{x}/3} e^{-\hat{x}/3} \right) + \frac{55}{486}i \left( \hat{p}_x^2 e^{-2\hat{x}/3} e^{-\hat{x}/3} \right) \\
&\quad + \frac{17}{162}i \left( e^{-2\hat{x}/3} \hat{p}_x^2 e^{-\hat{x}/3} \right) - \frac{1}{81}i \left( e^{-\hat{x}/3} \hat{p}_x^2 e^{-\hat{x}/3} \right) - \frac{136}{243}i \left( \hat{p}_x e^{-4\hat{x}/3} \hat{p}_x \right) - \frac{17}{243}i \left( \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x \right) + \frac{8}{243}i \left( \hat{p}_x^3 e^{-2\hat{x}/3} \hat{p}_x \right) \\
&\quad - \frac{1}{486}i \left( \hat{p}_x^3 e^{-\hat{x}/3} \hat{p}_x \right) + \frac{55}{486}i \left( e^{-\hat{x}/3} e^{-2\hat{x}/3} \hat{p}_x^2 \right) + \frac{4}{81}i \left( \hat{p}_x^2 e^{-2\hat{x}/3} \hat{p}_x^2 \right) + \frac{10}{243}i \left( e^{-2\hat{x}/3} e^{-\hat{x}/3} \hat{p}_x^2 \right) - \frac{1}{324}i \left( \hat{p}_x^2 e^{-\hat{x}/3} \hat{p}_x^2 \right) + \\
&\quad \frac{8}{243}i \left( \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x^3 \right) - \frac{1}{486}i \left( \hat{p}_x e^{-\hat{x}/3} \hat{p}_x^3 \right) - \frac{8}{81}i \left( \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x e^{-2\hat{x}/3} \right) + \frac{26}{243}i \left( \hat{p}_x e^{-\hat{x}/3} \hat{p}_x e^{-2\hat{x}/3} \right) \\
&\quad + \frac{49}{243}i \left( \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x e^{-\hat{x}/3} \right) - \frac{1}{81}i \left( \hat{p}_x e^{-\hat{x}/3} \hat{p}_x e^{-\hat{x}/3} \right) + \frac{10}{81}i \left( \hat{p}_x e^{-\hat{x}/3} e^{-2\hat{x}/3} \hat{p}_x \right) - \frac{8}{81}i \left( e^{-2\hat{x}/3} \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x \right) \\
&\quad + \frac{49}{243}i \left( e^{-\hat{x}/3} \hat{p}_x e^{-2\hat{x}/3} \hat{p}_x \right) + \frac{10}{81}i \left( \hat{p}_x e^{-2\hat{x}/3} e^{-\hat{x}/3} \hat{p}_x \right) + \frac{26}{243}i \left( e^{-2\hat{x}/3} \hat{p}_x e^{-\hat{x}/3} \hat{p}_x \right) - \frac{1}{81}i \left( e^{-\hat{x}/3} \hat{p}_x e^{-\hat{x}/3} \hat{p}_x \right) .
\end{aligned}$$

To compute the above elements we used the *Quantum* Mathematica package [86].

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- [1] S. L. Jacques, “Optical properties of biological tissues: a review,” *Physics in medicine and biology*, vol. 58, no. 11, p. R37, 2013.
- [2] R. Cesareo, A. Hanson, G. Gigante, L. Pedraza, and S. Mathaboally, “Interaction of kev photons with matter and new applications,” *Physics reports*, vol. 213, no. 3,

pp. 117–178, 1992.

- [3] A. K. Singh, D. Senapati, S. Wang, J. Griffin, A. Neely, P. Candice, K. M. Naylor, B. Varisli, J. R. Kalluri, and P. C. Ray, “Gold nanorod based selective identification of escherichia coli bacteria using two-photon rayleigh scattering spectroscopy,” *ACS Nano*, vol. 3, no. 7, pp. 1906–

- 1912, 2009.
- [4] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, and M. S. Feld, "Single molecule detection using surface-enhanced raman scattering (sers)," Phys. Rev. Lett., vol. 78, no. 9, pp. 1667–1670, 1997.
- [5] J. Mertz, C. Xu, and W. W. Webb, "Single-molecule detection by two-photon-excited fluorescence," Opt. Lett., vol. 20, no. 24, pp. 2532–2534, 1995.
- [6] M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, and C. Xu, "Design of organic molecules with large two-photon absorption cross sections," Science, vol. 281, no. 5383, p. 1653, 1998.
- [7] D. R. Larson, W. R. Zipfel, R. M. Williams, S. W. Clark, M. P. Bruchez, F. W. Wise, and W. W. Webb, "Water-soluble quantum dots for multiphoton fluorescence imaging in vivo," Science, vol. 300, no. 5624, p. 1434, 2003.
- [8] J. E. Ehrlich, X. L. Wu, I. Y. S. Lee, Z. Y. Hu, H. Röckel, S. R. Marder, and J. W. Perry, "Two-photon absorption and broadband optical limiting with bis-donor stilbenes," Opt. Lett., vol. 22, no. 24, pp. 1843–1845, 1997.
- [9] M. Pawlicki, H. A. Collins, R. G. Denning, and H. L. Anderson, "Two-photon absorption and the design of two-photon dyes," Angewandte Chemie International Edition, vol. 48, no. 18, pp. 3244–3266, 2009.
- [10] J. H. Strickler and W. W. Webb, "Three-dimensional optical data storage in refractive media by two-photon point excitation," Opt. Lett., vol. 16, no. 22, pp. 1780–1782, 1991.
- [11] S. Kawata and Y. Kawata, "Three-dimensional optical data storage using photochromic materials," Chem. Rev., vol. 100, no. 5, pp. 1777–1788, 2000.
- [12] W. Denk, "Two-photon scanning photochemical microscopy: mapping ligand-gated ion channel distributions," Proc. Natl. Acad. Sci., vol. 91, no. 14, pp. 6629–6633, 1994.
- [13] D. Warther, S. Gug, A. Specht, F. Bolze, J. F. Nicoud, A. Mourou, and M. Goeldner, "Two-photon uncaging: New prospects in neuroscience and cellular biology," Bioorganic & Medicinal Chemistry, vol. 18, no. 22, pp. 7753–7758, 2010.
- [14] E. Bartsch, M. Antonietti, W. Schupp, and H. Sillescu, "Dynamic light scattering study of concentrated microgel solutions as mesoscopic model of the glass transition in quasiautomatic fluids," The Journal of chemical physics, vol. 97, no. 6, pp. 3950–3963, 1992.
- [15] F. Terenziani, C. Katan, E. Badaeva, S. Tretiak, and M. Blanchard-Desce, "Enhanced two-photon absorption of organic chromophores: Theoretical and experimental assessments," Advanced Materials, vol. 20, no. 24, pp. 4641–4678, 2008.
- [16] A. e. m. Masunov and S. Tretiak, "Prediction of two-photon absorption properties for organic chromophores using time-dependent density-functional theory," The Journal of Physical Chemistry B, vol. 108, no. 3, pp. 899–907, 2004.
- [17] B. J. Orr and J. F. Ward, "Perturbation theory of the non-linear optical polarization of an isolated system," Mol. Phys., vol. 20, no. 3, pp. 513–526, 1971.
- [18] S. Mukamel and S. Rahav, Advances In Atomic, Molecular, and Optical Physics. Academic Press, 2010.
- Chapter 6 - Ultrafast Nonlinear Optical Signals Viewed from the Molecules Perspective: KramersHeisenberg Transition-Amplitudes versus Susceptibilities.
- [19] D. J. Tannor and E. J. Heller, "Polyatomic raman scattering for general harmonic potentials," J. Chem Phys., vol. 77, no. 1, pp. 202–218, 1982.
- [20] A. I. Akhiezer and V. B. Berestetskii, Quantum Electrodynamics. New York: Interscience Publishers, 1965.
- [21] S. C. Roy, "Elastic scattering of photons: perspectives and present status," X-Ray Spectrom., vol. 28, no. 5, pp. 376–378, 1999.
- [22] M. Gavrilu, "Elastic scattering of photons by a hydrogen atom," Phys. Rev., vol. 163, no. 1, pp. 147–155, 1967.
- [23] V. Florescu, M. Marinescu, and R. H. Pratt, "Relativistic effects on low-frequency rayleigh scattering including spin flip for hydrogenic atoms," Phys. Rev. A, vol. 42, no. 7, pp. 3844–3851, 1990.
- [24] H.-W. Lee and H. I. Kim, "Rayleigh scattering cross-section redward of  $1\gamma\alpha$  by atomic hydrogen," Mon. Not. R. Astron. Soc., vol. 347, no. 3, pp. 802–806, 2004.
- [25] H. R. Sadeghpour and A. Dalgarno, "Rayleigh and raman scattering by hydrogen and caesium," J. Phys. B, vol. 25, no. 22, p. 4801, 1992.
- [26] A. I. Miller, "Resonant photon-hydrogen-atom scattering," Phys. Rev. A, vol. 1, no. 5, pp. 1552–1553, 1970.
- [27] A. Surzhykov, P. Indelicato, J. P. Santos, P. Amaro, and S. Fritzsche, "Two-photon absorption of few-electron heavy ions," Phys. Rev. A, vol. 84, no. 2, p. 022511, 2011.
- [28] J. P. Santos, F. Parente, and P. Indelicato, "Application of b-splines finite basis sets to relativistic two-photon decay rates of  $2s$  level in hydrogenic ions," Eur. Phys. J. D, vol. 3, no. 1, pp. 43–52, 1998.
- [29] P. Amaro, J. P. Santos, F. Parente, A. Surzhykov, and P. Indelicato, "Resonance effects on the two-photon emission from hydrogenic ions," Physical Review A, vol. 79, no. 6, p. 062504, 2009.
- [30] S. P. Goldman and G. W. F. Drake, "Relativistic two-photon decay rates of  $2s_{1/2}$  hydrogenic ions," Phys. Rev. A, vol. 24, no. 1, pp. 183–191, 1981.
- [31] L. Safari, P. Amaro, S. Fritzsche, J. P. Santos, S. Tashenov, and F. Fratini, "Relativistic polarization analysis of rayleigh scattering by atomic hydrogen," Phys. Rev. A, vol. 86, no. 4, p. 043405, 2012.
- [32] L. Safari, P. Amaro, J. P. Santos, and F. Fratini, "Spin effects probed by rayleigh x-ray scattering off hydrogenic ions," Radiation Physics and Chemistry, vol. 106, no. 0, pp. 271–277, 2015.
- [33] F. Fratini and A. Surzhykov, "Polarization correlations in the twophoton decay of hydrogenlike ions," Hyp. Int., vol. 199, no. 1, pp. 85–92, 2011.
- [34] S. C. Roy, B. Sarkar, L. D. Kissel, and R. H. Pratt, "Polarization effects in elastic photon-atom scattering," Phys. Rev. A, vol. 34, no. 2, pp. 1178–1187, 1986.
- [35] L. Safari, P. Amaro, S. Fritzsche, J. P. Santos, and F. Fratini, "Relativistic total cross section and angular distribution for rayleigh scattering by atomic hydrogen," Phys. Rev. A, vol. 85, no. 4, p. 043406, 2012.
- [36] Z. W. Wu, A. V. Volotka, A. Surzhykov, and S. Fritzsche, "Angle-resolved x-ray spectroscopic scheme to determine overlapping hyperfine splittings in highly charged heliumlike ions," Phys. Rev. A, vol. 96, no. 1, p. 012503, 2017.
- [37] G. W. F. Drake, "Energy level calculations and **E1M1**

- two photon transition rates in two electron  $u^{90+}$ ,” Nucl. Instrum. and Meth. Phys. B, vol. 9, pp. 465–470, 1985.
- [38] C. Laughlin, “Radiative decay of the  $2\ ^3P_0^o$  level of beryllium-like ions,” Phys. Lett. A, vol. 75, no. 3, pp. 199–200, 1980.
- [39] R. W. Schmieder, “Double- and triple-photon decay of metastable  $^3P_0$  atomic states,” Phys. Rev. A, vol. 7, no. 5, pp. 1458–1468, 1973.
- [40] A. Surzhykov, A. Volotka, F. Fratini, J. P. Santos, P. Indelicato, G. Plunien, T. Stöhlker, and S. Fritzsche, “Angular correlations in the two-photon decay of heliumlike heavy ions,” Phys. Rev. A, vol. 81, no. 4, p. 042510, 2010.
- [41] A. V. Volotka, V. A. Yerokhin, A. Surzhykov, T. Stöhlker, and S. Fritzsche, “Many-electron effects on x-ray rayleigh scattering by highly charged he-like ions,” Phys. Rev. A, vol. 93, no. 2, p. 023418, 2016.
- [42] P. Amaro, F. Fratini, L. Safari, J. Machado, M. Guerra, P. Indelicato, and J. P. Santos, “Relativistic evaluation of the two-photon decay of the metastable  $1s^2 2s 2p\ ^3P_0$  state in berylliumlike ions with an effective-potential model,” Phys. Rev. A, vol. 93, no. 3, p. 032502, 2016.
- [43] S. Roy, R. Pratt, and L. Kissel, “Rayleigh scattering by energetic photons: Development of theory and current status,” Radiation Physics and Chemistry, vol. 41, p. 725738, Apr 1993.
- [44] L. Safari, J. P. Santos, P. Amaro, K. Jänkälä, and F. Fratini, “Analytical evaluation of atomic form factors: Application to Rayleigh scattering,” J. Math. Phys., vol. 56, no. 5, p. 052105, 2015.
- [45] C. Giacovazzo, Fundamentals of crystallography, vol. 7. Oxford university press, USA, 2002.
- [46] P. Amaro, B. Franke, J. J. Krauth, M. Diepold, F. Fratini, L. Safari, J. Machado, A. Antognini, F. Kottmann, P. Indelicato, et al., “Quantum interference effects in laser spectroscopy of muonic hydrogen, deuterium, and helium-3,” Physical Review A, vol. 92, no. 2, p. 022514, 2015.
- [47] P. Amaro, F. Fratini, L. Safari, A. Antognini, P. Indelicato, R. Pohl, and J. P. Santos, “Quantum interference shifts in laser spectroscopy with elliptical polarization,” Physical Review A, vol. 92, no. 6, p. 062506, 2015.
- [48] Z. Movasaghi, S. Rehman, and D. I. U. Rehman, “Raman spectroscopy of biological tissues,” Applied Spectroscopy Reviews, vol. 42, no. 5, pp. 493–541, 2007.
- [49] J. H. Hubbell, “Review of photon interaction cross section data in the medical and biological context,” Physics in Medicine & Biology, vol. 44, no. 1, p. R1, 1999.
- [50] H. J. Kimble, “The quantum internet,” Nature, vol. 453, no. 7198, pp. 1023–1030, 2008.
- [51] R. J. Warburton, “Electronics lightens up,” Nat. Phys., vol. 4, p. 676, 2008.
- [52] F. Fratini and R. Ghobadi, “Full quantum treatment of a light diode,” Physical Review A, vol. 93, no. 2, p. 023818, 2016.
- [53] J. Tulkki and T. Aberg, “Behaviour of raman resonance scattering across the k x-ray absorption edge,” Journal of Physics B: Atomic and Molecular Physics, vol. 15, no. 13, p. L435, 1982.
- [54] A. Derevianko and W. R. Johnson, “Two-photon decay of  $2\ ^1S_0$  and  $2\ ^3S_1$  states of heliumlike ions,” Phys. Rev. A, vol. 56, no. 2, pp. 1288–1294, 1997.
- [55] M. H. Devoret and R. J. Schoelkopf, “Superconducting circuits for quantum information: an outlook,” Science, vol. 339, no. 6124, pp. 1169–1174, 2013.
- [56] H. Paik, D. Schuster, L. S. Bishop, G. Kirchmair, G. Catelani, A. Sears, B. Johnson, M. Reagor, L. Frunzio, L. Glazman, et al., “Observation of high coherence in josephson junction qubits measured in a three-dimensional circuit qed architecture,” Physical Review Letters, vol. 107, no. 24, p. 240501, 2011.
- [57] R. Barends, J. Kelly, A. Megrant, D. Sank, E. Jeffrey, Y. Chen, Y. Yin, B. Chiaro, J. Mutus, C. Neill, et al., “Coherent josephson qubit suitable for scalable quantum integrated circuits,” Physical review letters, vol. 111, no. 8, p. 080502, 2013.
- [58] D. Leibfried, R. Blatt, C. Monroe, and D. Wineland, “Quantum dynamics of single trapped ions,” Reviews of Modern Physics, vol. 75, no. 1, p. 281, 2003.
- [59] D. Kielpinski, C. Monroe, and D. J. Wineland, “Architecture for a large-scale ion-trap quantum computer,” Nature, vol. 417, no. 6890, pp. 709–711, 2002.
- [60] J. J. Sakurai and J. J. Napolitano, Modern quantum mechanics. Pearson Higher Ed, 2014.
- [61] L. Wilets, “Theories of the nuclear surface,” Reviews of Modern Physics, vol. 30, no. 2, p. 542, 1958.
- [62] A. Chodos, R. Jaffe, K. Johnson, C. B. Thorn, and V. Weisskopf, “New extended model of hadrons,” Physical Review D, vol. 9, no. 12, p. 3471, 1974.
- [63] R. Kolbas and N. Holonyak Jr, “Man-made quantum wells: A new perspective on the finite square-well problem,” American Journal of Physics, vol. 52, no. 5, pp. 431–437, 1984.
- [64] B. H. Bransden and C. J. Joachain, Physics of Atoms and Molecules, p. 82. Longman Scientific and Technical, 1983.
- [65] K. Abdullah, Fundamentals in Nuclear Physics, pp. 259, 260. Saarbrücken: Noor Publishing, 2017.
- [66] H.-C. Pauli, “The hadronic potential at short distance,” arXiv preprint hep-ph/0312198, 2003.
- [67] R. Colella, A. W. Overhauser, and S. A. Werner, “Observation of gravitationally induced quantum interference,” Physical Review Letters, vol. 34, no. 23, p. 1472, 1975.
- [68] F. Han, G. Meng, F. Zhou, L. Song, X. Li, X. Hu, X. Zhu, B. Wu, and B. Wei, “Dielectric capacitors with three-dimensional nanoscale interdigital electrodes for energy storage,” Science advances, vol. 1, no. 9, p. e1500605, 2015.
- [69] F. Fratini and L. Safari, “Quantum mechanical evolution operator in the presence of a scalar linear potential: discussion on the evolved state, phase shift generator and tunneling,” Physica Scripta, vol. 89, no. 8, p. 085004, 2014.
- [70] M. Glasser and L. Nieto, “The energy level structure of a variety of one-dimensional confining potentials and the effects of a local singular perturbation,” Canadian Journal of Physics, vol. 93, no. 12, pp. 1588–1596, 2015. See also <https://www.physics.wisc.edu/~tgwalker/NumerovExamples/Line>
- [71] J. You and F. Nori, “Atomic physics and quantum optics using superconducting circuits,” Nature, vol. 474, no. 7353, pp. 589–597, 2011.
- [72] J. D. Moras, B. Strandberg, D. Suc, and K. Wilson, “Semiconductor clusters, nanocrystals, and quantum dots,” science, vol. 271, p. 933, 1996.
- [73] E. Caurier, G. Martinez-Pinedo, F. Nowacki, A. Poves, and A. Zuker, “The shell model as a unified view of nuclear structure,” Reviews of Modern Physics, vol. 77, no. 2, p. 427, 2005.

- [74] E. Hecht et al., Optics Fourth Edition, p. 86. Addison Wesley, 2003.
- [75] S.-H. Dong, MORSE POTENTIAL, p. 7394. Springer Netherlands, 2007.
- [76] M. S. A. E. Kader, “The depolarized interaction-induced light scattering spectrum and ground state potential curve of gaseous argon,” Journal of Physics B: Atomic, Molecular and Optical Physics, vol. 35, p. 40214032, Sep 2002.
- [77] S. Dixneuf, F. Ratchet, and M. Chrysos, “Collision-induced raman scattering and the peculiar case of neon: Anisotropic spectrum, anisotropy, and the inverse scattering problem,” The Journal of Chemical Physics, vol. 142, p. 84302, Feb 2015.
- [78] V. G. Tsirelson and R. P. Ozerov, Electron density and bonding in crystals: Principles, theory and X-ray diffraction experiments in solid state physics and chemistry, p. 261. CRC Press, 1996.
- [79] M. Srednicki, “Entropy and area,” Physical Review Letters, vol. 71, no. 5, p. 666, 1993.
- [80] K. Saito and A. Dhar, “Fluctuation theorem in quantum heat conduction,” Physical Review Letters, vol. 99, no. 18, p. 180601, 2007.
- [81] M. Jonker, “Entanglement entropy of coupled harmonic oscillators: an approach in fock space,” Master’s thesis, 2016. Institute for Theoretical Physics, Utrecht University.
- [82] D. P. O’Neill and P. M. W. Gill, “Wave functions and two-electron probability distributions of the hookes-law atom and helium,” Physical Review A, vol. 68, no. 2, p. 022505, 2003.
- [83] P. Gori-Giorgi and A. Savin, “Study of the discontinuity of the exchange-correlation potential in an exactly soluble case,” International Journal of Quantum Chemistry, vol. 109, no. 11, pp. 2410–2415, 2009.
- [84] D. Manzano, A. Plastino, J. Dehesa, and T. Koga, “Quantum entanglement in two-electron atomic models,” Journal of Physics A: Mathematical and Theoretical, vol. 43, no. 27, p. 275301, 2010.
- [85] F. Neese, T. Petrenko, D. Ganyushin, and G. Olbrich, “Advanced aspects of ab initio theoretical optical spectroscopy of transition metal complexes: Multiplets, spin-orbit coupling and resonance raman intensities,” Coordination Chemistry Reviews, vol. 251, no. 3, pp. 288–327, 2007.
- [86] J. L. Gomez-Muoz and F. Delgado, QUANTUM: a Dirac notation Add-on of Mathematica. 2013. <http://homepage.cem.itesm.mx/jose.luis.gomez>.