

Brief introduction to Raman study of charged particles

Breve introducción al estudio Raman de partículas cargadas

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ABSTRACT

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Classic System,
Electromagnetic field,
Quantum system,
Raman spectroscopy

An analytical development is proposed to determine the solution of the motion equations of a charged particle under the influence of an electric field. In the proposal, the advantages and properties of Laplace's transformation are used to map a system of N second-order non-homogeneous differential equations into a system composed of N linear equations. From the most general solution for the dynamics of the system, some particular cases were studied to recover, in a simple way, the results present in the literature. To motivate the study, Ehrenfest's theorem is used and we discuss how the classical results can be interpreted in their quantum version.

RESUMEN

Palabras claves:

Sistemas
clásicos, Campos
electromagnéticos,
Sistemas cuánticos,
Espectroscopía Raman.

Se propone un desarrollo analítico para determinar la solución de las ecuaciones de movimiento de una partícula cargada bajo la influencia de un campo eléctrico. En la propuesta se utilizan las ventajas y propiedades de la transformación de Laplace, para mapear un sistema de N ecuaciones diferenciales no homogéneas de segundo orden en un sistema compuesto por N ecuaciones lineales. A partir de la solución más general para la dinámica del sistema, se estudian algunos casos particulares para recuperar, de manera sencilla, los resultados presentes en la literatura. Para motivar el estudio, se utiliza el teorema de Ehrenfest y se discute como los resultados clásicos pueden ser interpretados en su versión cuántica.

1. Introducción

A decade ago since the centenary Nobel Prize in Physics for the discovery of the Raman effect, awarded to Sir Chandrasekhara Venkata Raman [1]. It is still little known and perhaps for this reason little disseminated in academia. This work comes as an effort to introduce the subject to teachers and students of the various areas of exact sciences and enable the theoretical discussion of this important physical phenomenon.

The Raman effect can be considered a topic of contemporary physics of relative complexity in its mathematical formulation since for its correct understanding it is necessary to know specific concepts of quantum physics. On the other hand, a classical approach can be

adopted to introduce and understand the phenomenon. Such an approach starts from the understanding of oscillatory phenomena, which appear throughout academic life and become familiar in the most diverse applications. So, for example, second-year undergraduate students, in general, are already having contact with equations of motion, mechanical and electromagnetic waves, differential equations, differentiation, and anti-differentiation and in future periods they are becoming familiar with concepts of quantum physics. Unfortunately, the experimental requirement of the phenomenon can be a limiting factor when exposing the subject; since, from an experimental point of view, laboratories with a high financial investment are required to deal with the matter.

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Maybe that's why the topic is not approached very often or with due depth in the physics disciplines of physics, chemistry, or engineering courses of the vast majority of universities. We aim to show that there is a relatively straightforward way to introduce the Raman effect problem and obtain its main features, without falling back on experimental requirements or the deep formulations of advanced mathematics. From this perspective, an important starting point is based on knowing the generalization of the harmonic oscillator, thus making it possible to understand and describe the phenomenon classically, in a qualitative way, allowing the student to have a deeper contact with the oscillatory nature of the phenomenon. We hope that this text will serve as a basis for the teacher who wants to approach the topic of Raman spectroscopy in a certain depth, mathematically deducing important properties of the phenomenon, thus giving a reasonable theoretical basis to the student who wants to continue with research in the area. The only ones necessary prerequisites to understanding this development are that the student has already taken a course of waves, basic electromagnetism, and a foundation on differential equations.

In the following sections of our work, we have, in the second section, a brief presentation on what spectroscopy is. In Section 2, we will be concerned to present a brief history of the development of the Raman effect since 1928 and its implications in the scientific environment. In section 3 we will analyze the description of the classical formulation to explain the phenomenon. Finally, in the section 4, we show how the classical treatment can provide us with important information about the dynamics of a beam of charged particles.

2. Raman Espectroscopy

Raman spectroscopy is a technique associated with the electromagnetic scattering of atoms in a sample, whether liquid, gaseous or solid [1-5]. The phenomenon as it is known today was initially proposed in the early 1920s, being improved with Smekal's theoretical implications in 1923 [2]. Experimental verifications suggested that certain materials when irradiated with light were capable of scattering radiation in a diffuse way and such scattered radiation presented a classic change of the radiation incident on the sample (Fig.1) In 1928 the publications "A New Radiation" [3]. and "A New Type of Secondary Radiation" [4]. were responsible for understanding the phenomenon that soon became known as the Raman effect in tribute to your discover. Two years later, the experimental facts were beyond dispute, and in 1930, the Nobel Prize in Physics was awarded to Sir Chandrasekhara Venkata Raman for his work on scattering light and discovering the effect that bears his name.

Even after the visibility provided by a Nobel Prize, Raman spectroscopy presented major limitations in the following years, precisely because it was a technique that required obtaining a good and intense source of monochromatic light (In the Raman effect, the incident radiation is of monochromatic light, that is, light with a single wavelength.), something difficult to obtain before the advent of the laser in the 1960s. With the discovery of the laser and its proper use, Raman spectroscopy began to offer spectra of solid samples. with high quality and resolution, making it applicable in the most diverse areas and scientific fields [6].

Being a very powerful technique in the investigation of molecular counterparts, it has become one of the main non-destructive techniques in the physical-chemical analysis of organic and inorganic compounds, standing out in the investigation of biological systems. This highlight is due to the advantages that include the requirement of small samples, the possibility of analyzing gases and solids, and being easily applied to the analysis of aqueous solutions [7]. Among the various applications of Raman spectroscopy, we have: biomedical applications [8-13], pharmaceuticals [14,15]. Archaeometry [16,17], nanotechnology [18,19], ceramic materials [20], and polymers [21], extraterrestrial materials [22,23], forensic applications [24,25]. Currently, more than consolidated in the scientific environment, Raman spectroscopy is well-founded and for a deeper study, some authors can be consulted [26-30].

The observed scattering is nothing more than the scattering of light by the material. The Raman effect is only characterized for scatterings where there are changes in the frequency of the scattered radiation concerning the incident radiation, otherwise, the phenomenon is known as Rayleigh scattering. Rayleigh scattering is elastic scattering, while the Raman effect is defined by inelastic scattering (figure 1).

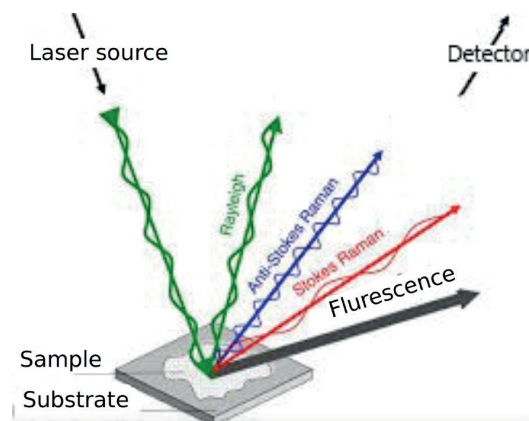


Figure 1. Representation of the monochromatic light scattering process. Raman scattering presents light scattered as different wavelengths (blue and red trace).

In general, when dealing with light spectroscopy, we are dealing with some experimental technique that uses a light source to obtain information on a particular material to be studied. Such techniques allow obtaining information about molecular structure, energy levels, atomic bonds, etc. The type of spectroscopy can be differentiated according to the range of electromagnetic radiation used in a given procedure. Thus, knowing the nature of the electromagnetic spectrum is of great importance when specifying contents in spectroscopy. In the figure 2, we have a representation for the visible spectrum in the ultraviolet region 400 nm to the infrared region 700 nm [31].

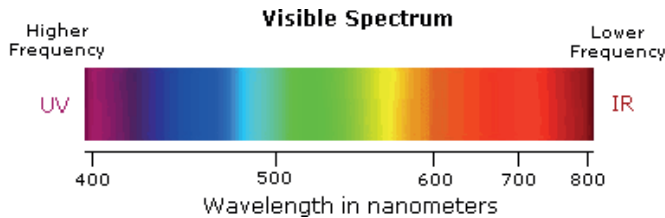


Figure 2. Electromagnetic spectrum in the visible region

In cases such as Infrared and Raman spectroscopy, monochromatic radiation is used in the visible. According to the spectral region, the transitions observed depend on the type of levels: electronic, vibrational, or rotational.

3. Classic treatment

In this section, we will describe the classical treatment of the main characteristic associated with the dynamics of a molecule subject to the incidence of monochromatic E electric fields. In this context, we deal directly with a forced oscillatory phenomenon, which can be started with the objections of the classical harmonic oscillator. For this to happen naturally and correctly, we must understand the concept of polarization **P** and molecular polarizability α [32] which arise naturally in the development of the equations. The important parameters are the wavelength λ and the frequency ν .

When a beam of light falls on a certain material, which contains a set of atoms linked to each other by forces of an electrical nature, the light particles (photons) interact with it, colliding with the molecules of the sample. From this interaction, a response to the given stimulus is produced, that is, the incident light will be part absorbed, partly transmitted and a small fraction of the light will be scattered in all directions [6]. Regarding scattered light, if it has the same wavelength as the incident light, there is no exchange of energy between the photon and the molecule, and consequently, it will have the same frequency $\nu(0)$ of incidence. This is elastic scattering or Rayleigh scattering (A tribute to Lord Rayleigh who studied this phenomenon and showed that he is responsible for the bluish color of the sky).

There is also the case where scattered light ν does not have the same frequency as incident light $\nu(0)$, i.e., some photons can excite one mode of vibration of the molecule (or several modes), losing or gaining energy in the process. This scattering is known as inelastic scattering, where the molecule starts to vibrate due to photon-matter interaction, changing the wavelength (and frequency) of the scattered light wave concerning the incident one. This simple modification of your energy is the foundation for the so-called Raman effect. In terms of energy, the described process can be presented as follows:

$$\Delta E = \hbar\omega_s = \hbar(\omega_0 - \omega) \quad (1)$$

Where $\omega = 2\pi\nu$. Thus, the frequency of scattered light can be lower or higher than the frequency of incident light, that is, when ν is less than $\nu(0)$, the scattered radiation is called Stokes radiation (equation 1), otherwise $\nu\nu_0$, the radiation is called anti-Stokes (equation 2):

$$\hbar\omega_{as} = \hbar(\omega_0 + \omega) \quad (2)$$

3.1 Oscillatory Motion Equations

It starts from the concept of the incident wave, characterized by a frequency ν and an oscillatory electric field E, when the electric field interacts with the electron cloud of atoms in the molecule, it induces a dipole moment (figure 3) given by: gy

$$\mathbf{P}_\omega = \alpha_\omega \mathbf{E} = \alpha_\omega \mathbf{E}_0 e^{-i\omega t} \quad (3)$$

Understand how the polarizability is a constant associated with the measurement of molecular bond deformation under incident electric field action (equation 3).

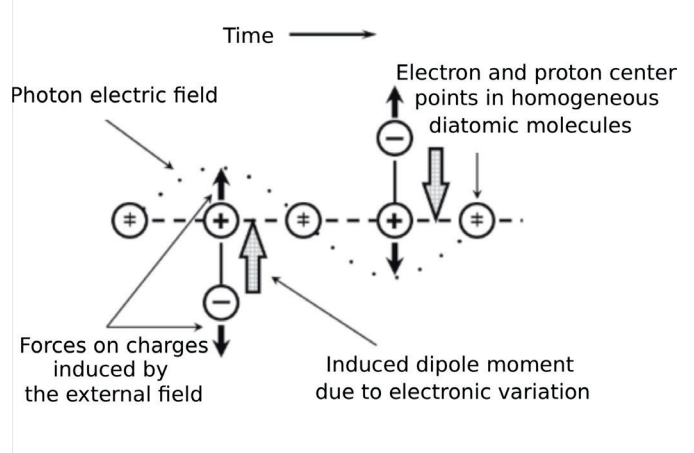


Figure 3. Action of the electric field in the formation of induced dipole moment. Source [11].

Since there is a variation of α concerning the distance r between atomic nuclei, we can suggest that a generalized coordinate q is the expansion of α in the form:

$$f(x) = f(0) + f'(1) + f'(2) + \dots \quad (4)$$

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial q}\right)_0 \quad (5)$$

Where α_0 is the polarizability of the bond in the distance between the equilibrium nuclei q_{eq} and the separation for any instant given by q . Thus, we have that the internuclear variation is given by the vibration frequency ν which is given by:

$$q = q_0 \cos((2\pi\nu t)) \quad (6)$$

Here q_0 is the maximum internuclear separation relative to the equilibrium position. Thus, gathering equations 4 to equation 6, making the possible distributions we will have:

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial q}\right)_0 \cos((2\pi\nu t)) \quad (7)$$

The equation 7, can be substituted into the equation 3, so we have

$$P = \alpha_0 E_0 \cos((2\pi\nu_0 t)) + \frac{q_0}{2} E_0 \left(\frac{\partial\alpha}{\partial q}\right)_0 [\cos\{2\pi t(\nu + \nu_0)\} + \cos\{2\pi t(\nu_0 - \nu)\}] \quad (8)$$

We have that the first term of the equation 8, represents the Rayleigh scattering, elapsed from the frequency ν_0

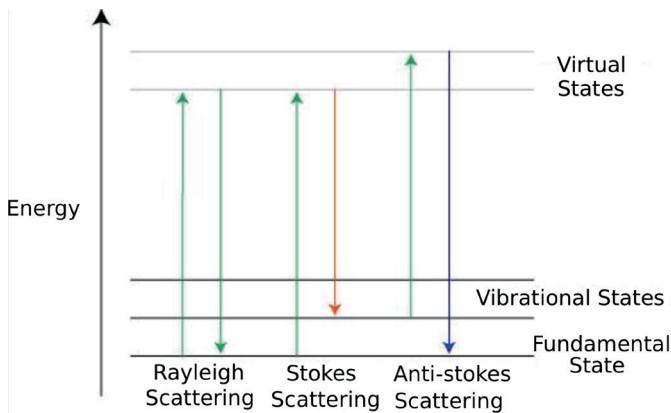


Figure 4. Configuration of energy transitions in Ramam scattering.

The second and third terms correspond to Raman scattering, being respectively the anti-Stokes and Stokes for frequencies $\nu+\nu_0$ and $\nu_0-\nu$. In the figure 4, there is a scattered frequency lower than the incident frequency (Stokes scattering) and another with a higher scattered frequency, called anti-Stokes [27] scattering. Note also that Raman scattering requires that the polarizability of a bond varies as a function of distance [31] - that is, $\left(\frac{\partial\alpha}{\partial q}\right)_0$ in the equation 9 must be on-zero for Raman lines to appear.

4. Quantum treatment

Our quantum system has a classical logo as a reference for the harmonic oscillatory system that was discussed earlier in the section 3. What we will do here is nothing more and than an approximation seeking to describe the dynamics of a bundle of particles whose dynamics thermic of each particle that constitutes the system given by the Schrodinger equation in the form:

$$-\frac{\hbar}{2\mu} \frac{d^2}{dq^2} \psi(q) + \frac{1}{2} (kq)^2 \psi(q) = E\psi(q) \quad (9)$$

Classically, the absorption of radiation by a system is due to the periodic variation of its electric dipole moment. This absorbed frequency is identical to the dipole oscillation frequency. We see that polarizability originates from the induced dipole moment. In a quantum system, transitions between two states are characterized by the wave functions ψ_m and ψ_n . These functions solve a classic obstacle in the solution that describes the Raman effect lines. Knowing the nature of the equation 4 for polarizability:

$$P_i = \alpha_{ij} E_j \quad (10)$$

The equation 10 shows us that α_{ij} , a Raman tensor, which is a matrix 3×3 correlating the electric vector $x_1 y_1 z_1$ of the exciting radiation with the electric vector $x_2 y_2 z_2$ of the scattered Raman radiation.

It is important to note that the polarizability tensor argument could arise naturally in a classic case of electrical systems involving molecular groups as developed in the section 3. In this case, as the solutions of the quantum model are closely linked to the effects of the Raman tensor, we chose to show it in this section. An example of this is the association between the Raman tensor and the functions ψ_m and ψ_n shown below.

$$(\alpha_{ij})_{mn} = \int \psi_m(\alpha_{ij})\psi_n d\tau \quad (11)$$

The components α_{ij} form a symmetrical tensor in the Raman effect [33], so:

$$(\alpha_{ij})_{mn} = (\alpha_{ij})_0 \int \psi_m \psi_n d\tau + \left(\frac{\partial\alpha_{ij}}{\partial q}\right)_0 \int \psi_m \psi_n d\tau \quad (12)$$

In Stokes and anti-Stokes scattering, the vibrational states m and n are different and the first integral of the second member is always equal to zero, due to the orthogonality between ψ_m and ψ_n .

The selection rule $\Delta V = \pm 1$ can be understood by checking the solution of the equation:

$$\frac{d^2\psi}{dq^2} + \frac{2\mu}{\hbar^2} \left(E - \frac{kq^2}{2} \right) \psi = 0 \quad (13)$$

Given the necessary physical conditions of $\psi(q)$ whose development suggests a solution of the type:

$$\psi(q) = Ae^{-\alpha q^2/2} \quad (14)$$

The solution 14 tested on equation 13 give us:

$$\frac{d^2H}{dq^2} - 2q \frac{dH}{dq} + (\delta - 1)H = 0 \quad (15)$$

which is called the Hermite equation. Your solutions must meet the $\psi(q)$ requirements. After the development of equation (15) we arrive at:

$$E = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} = \frac{1}{2} \hbar \nu \quad (16)$$

The equation 16 gives the eigenvalues E of the Quantum Harmonic Oscillator. In this case, if the energy has this value from equation 14 it satisfies the equation 15. In the equation 16 we have the energy of the so-called ground state ψ_0 . Energies for excited states ψ_ν (more energetic) can be admitted since $\psi(q) \rightarrow \psi_\nu(q)$, where ν is a quantum number.

$$\psi_\nu(q) = N_\nu \cdot H_\nu(\sqrt{\alpha q}) e^{-\alpha q^2/2} \quad (17)$$

It is important to note how naturally the Hermite polynomials. The H_ν appears, which is an added function to obtain solutions of second-order ordinary differential equations. The various energy levels are then defined by the quantum number V . This difference between energy levels is equally spaced by a difference ΔV . Figure 5 shows the wave functions of the harmonic oscillator described by the equation 16 already normalized.

In Stokes Raman scattering, the molecule in the ground state collides with the photon of energy $\hbar\nu_0$ passing to an

intermediate state. It then decays to an excited state of energy e_ν . In anti-Stokes Raman scattering the photon encounters the molecule in an excited state and after the interaction, the molecule decays to the ground state. This fact can be compared if we look at the figure 4.

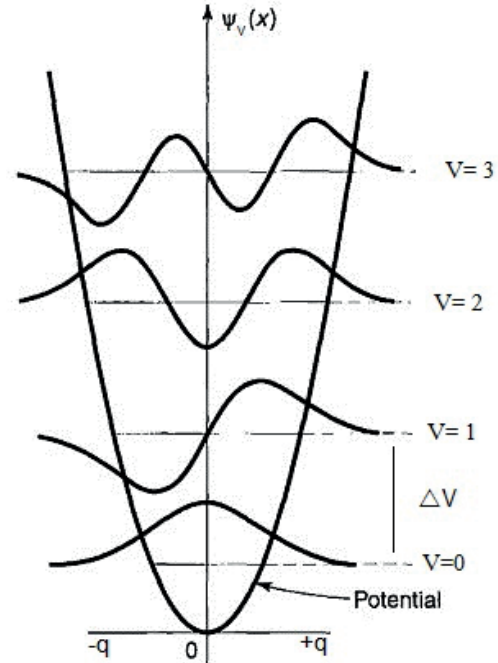


Figure 5. Potential function for different ψ_ν .

Finally, as example in another physics areas, non-linear ordinary and partial differential equations can be obtained for to explain quantum model, by example, expressed by the Ginzburg- Time-dependent Landau, obtained by computational simulation in two and three dimensions [34-37].

5. Conclusions

From the Laplace transform we study the more general case of the dynamics of a particle subject to interaction with static electric and magnetic fields. Using the definition and properties of the Laplace transform, we show how to map the problem of solving a system of ordinary differential equations to a problem of finding the solution of a system of first-degree linear equations. With this, we find the most general possible solution of the equation of motion that governs the dynamics of the system in terms of the components of the electromagnetic fields from the general solution, we show how to obtain the solution of three particular cases whose importance and applicability exceed the didactic point of view. Finally, we motivated our study by doing the quantum treatment of the studied system, where we consider a beam of charged particles

without spin. In this context, we show that the parameterized curve of the expected value (on average) of the position vector of a beam particle as a function of time corresponds to that curve associated with its classical analog.

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