Surface Enhanced Raman Spectroscopy as a High Order Raman Process dealt within Time-Dependent Perturbation Theory

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1 Introduction

The Raman effect is the inelastic scattering of photons when they interact with matter. Surface-enhanced Raman scattering (SERS) is a commonly used sensing technique in which the Raman effect of molecules is greatly enhanced by factors up to 10^8 or even larger (enabling single-molecule (SM) detection in some cases) by placing them near the surface of suitably nanostructured substrates [1]. Two competing mechanisms have been proposed so far to describe SERS, namely: electromagnetic (EM) enhancement and chemical (CT) enhancement [1][2][3]. However, the search for a unified theory of SERS is an open topic [2]. In this work the most recent theories, relying on time-dependent perturbation theory (TDPT) for the treatment of both EM and CT effects will be presented. In order to do it in a comprehensive and self-contained way, the work is organized as follows: first the reader will be introduced to the interaction picture in non relativistic quantum mechanics, then the TDPT will be presented in this formalism making use of the perturbative expansion of the unitary time evolution operator. Next the fundamentals of the quantization of the radiation field will be presented in order to gain insights into the molecular quantum electrodynamics mechanisms underlying the Raman effect and the time ordered terms of the Dyson series will be expressed in terms of Feynman diagrams, in order to simplify the treatment of high order effects. Then the well-known theory for the Raman scattering will be presented and will be recast in a useful framework, making use of Feynman diagrams of third order inelastic processes. After this, the theories for EM and CT enhancement will be presented making use of TDPT to high orders. Eventually, a personal suggestion on how the theories of the two effects can be merged into a unique framework to treat SERS will be presented. The quantities that need to be computed and the possible theoretical and technical problems that might arise will be then briefly analyzed.

2 Theoretical Background

2.1 Time Evolution: the Interaction Picture

The interaction picture of quantum mechanics is an alternative picture with respect to the usual Schrödinger's or Heisenberg's. It becomes particularly useful when dealing with time-dependent Hamiltonians. Let's consider:

$$H = H_0 + V(t) \qquad \text{with} \quad H_0|n\rangle = \varepsilon_n|n\rangle \tag{2.1}$$

Where H_0 is time independent and thus $V(t)$ leads to transitions between states $|n\rangle$. The idea behind the interaction picture is to separate the time evolution due to H_0 from the one caused by the time dependent perturbing potential $V(t)$. This is obtained by performing the following unitary transformation:

$$|\Psi(t)\rangle_I = e^{iH(t-t_0)/\hbar}|\Psi(t)\rangle \qquad ; \qquad V_I(t) = e^{iH(t-t_0)/\hbar}V(t)e^{-iH(t-t_0)/\hbar} \tag{2.2}$$

The state vector $|\Psi(t)\rangle$ in the Scrödinger's picture is expressed as:

$$|\Psi(t)\rangle = \sum_m c_{mn}(t)e^{-i\omega_m(t-t_0)}|m\rangle \tag{2.3}$$

Where $\omega_m = \varepsilon_m/\hbar$. This means that the interaction picture state vector $|\Psi(t)\rangle_I$ will have dropped the time-dependency on H_0 which was endowed in the $e^{-i\omega_m(t-t_0)}$ term , indeed:

$$|\Psi(t)\rangle_I = \sum_m c_{mn}(t)|m\rangle \tag{2.4}$$

By performing the time derivative on $|\Psi(t)\rangle_I$ one obtains the following time dependent Schrödinger equation (TDSE) in the interaction picture:

$$i\hbar\partial_t|\Psi(t)\rangle_I = V_I(t)|\Psi(t)\rangle_I \tag{2.5}$$

The evolution of the wavefunction can be expressed through an appropriate unitary time evolution operator, i.e. :

$$|\Psi(t)\rangle_I = \hat{U}_I(t, t_0)|\Psi(t_0)\rangle_I \tag{2.6}$$

By substituting this into Eq.2.5 and dropping out the ket, since the equation is valid irrespective of the particular initial state, one obtains:

$$i\hbar\partial_t \hat{U}_I(t, t_0) = V_I(t)\hat{U}_I(t, t_0) \tag{2.7}$$

The solution to Eq.2.7 is the path ordered exponential, which expanded leads to the well known Dyson series [4]:

$$\begin{aligned}\hat{U}_I(t, t_0) &= 1 + \sum_{m=1}^{\infty}\left(-\frac{i}{\hbar}\right)^m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \cdots \int_{t_0}^{t^m} dt^m V(t')V(t'')\dots V(t^m) \\ &= 1 - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')dt' - \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'} V_I(t')V_I(t'')dt'dt'' + \dots\end{aligned} \tag{2.8}$$

Where $t > t' > t'' > \cdots > t^m > t_0$.

2.2 Time Evolution: Time Dependent Perturbation Theory (TDPT)

If we assume that $|\Psi(t_0)\rangle_I = |n\rangle$, the coefficients $c_m(t)$ of the expansion 2.4 can be obtained in orders of the perturbative expansion of $\hat{U}_I(t, t_0)$ represented by Eq.2.8:

$$\begin{aligned}c_{mn}(t) &= \langle m|\Psi(t)\rangle_I = \langle m|\hat{U}_I(t, t_0)|n\rangle \\ &= \langle m|\hat{U}_I^{(0)}(t, t_0)|n\rangle + \langle m|\hat{U}_I^{(1)}(t, t_0)|n\rangle + \langle m|\hat{U}_I^{(2)}(t, t_0)|n\rangle + \dots \\ &= c_{mn}^{(0)} + c_{mn}^{(1)} + c_{mn}^{(2)} + \dots\end{aligned} \tag{2.9}$$

Where:

$$c_{mn}^{(0)} = \delta_{mn} \tag{2.10}$$

$$c_{mn}^{(1)} = -\frac{i}{\hbar}\int_{t_0}^{t}\langle m|V_I(t_1)|n\rangle dt_1 = -\frac{i}{\hbar}\langle m|V|n\rangle\int_{t_0}^{t} e^{i\omega_{mn}(t_1 - t_0)}dt_1 \tag{2.11}$$

$$\begin{aligned}c_{mn}^{(2)} &= -\frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t^1}\langle m|V_I(t_1)V_I(t_2)|n\rangle dt_1 dt_2 = -\frac{1}{\hbar^2}\sum_j\int_{t_0}^{t}\int_{t_0}^{t_1}\langle m|V_I(t_1)|j\rangle\langle j|V_I(t_2)|n\rangle dt_1 dt_2 \\ &= -\frac{1}{\hbar^2}\sum_j\langle m|V|j\rangle\langle j|V|n\rangle\int_{t_0}^{t} e^{i\omega_{mj}(t_1 - t_0)}\int_{t_0}^{t_1} e^{i\omega_{jn}(t_2 - t_0)}dt_1 dt_2\end{aligned} \tag{2.12}$$

In the derivation of this formulae, we have used the resolution of the identiy, i.e. $I = \sum_k |k\rangle\langle k|$. Moreover, we implicitly considered the perturbing potential to be time independent. This might seem counterintuitive based on the whole development we have done so far, which was based on a time dependent perturbing potential $V(t)$ e.g. the electromagnetic radiation (e.m.) of a laser source. However, as we shall see in the next section, this is in agreement with a quantum electrodynamical treatement of the light-matter interaction, and doesn't undermine the developement of the time dependent perturbation theory based on the expansion of the unitary time evolution operator $\hat{U}_I(t, t_0)$ carried out until now. In order to calculate the coefficients, we now need to evaluate the integrals involving the complex exponentials, together with evaluating the $V_{jn} = \langle j|V|n\rangle$ matrix elements. For sake of simplyifing the notation, in the following discussion we will call no-TDPT the n-th order time-dependent contribution.

2.3 Quick Overview: Molecular Quantum Electrodynamics Theory in Chemical Physics

When treating light-matter interaction, two theories are commonly applied: *Semiclassical theory* and *Quantum Electrodynamics*. *Semiclassical theory* (SCT) is a framework where matter is treated with methods that pertain quantum mechanics, whereas light is treated in a classical fashion. In *Quantum Electrodynamics* (QED) both light and matter obey the laws of quantum mechanics, and together they make up a closed system. Thus, if a molecule is excited, a photon is withdrawn from the radiation field and vice versa satisfying energy conservation within this closed system. In the framework of optics, QED usually treats space and time nonrelativistically [5], and in the following we shall briefly present the description that arises in this formulation. In particular, (without making all the derivation) the freely propagating radiation field is associated to an Hamiltonian which decomposes into a sum of modes (see Eq.2.15) each of which is identified by two quantum numbers: a wave-vector $\mathbf{k}$, which points in the direction of the propagation of the photon with angular frequency $\omega = ck$, and two possible polarization directions λ. Each term in the Hamiltonian has the structure of an harmonic oscillator.

The overall state of the radiation field is generally specified by occupation number vectors in the Fock space, generally written as:

$$|n_1(\mathbf{k_1}, \lambda_1), n_2(\mathbf{k_2}, \lambda_2), \dots\rangle \tag{2.13}$$

The ket $|n_1(\mathbf{k_1}, \lambda_1)\rangle$ indicates a state with the energy of n photons occupying the mode $(\mathbf{k}, \lambda)$. In this description, only modes with $n \neq 0$ are considered. The quantum electrodynamical Hamiltonian for an ensemble of molecules interacting with radiation can then be expressed as follows [6]:

$$H = H_{rad} + \sum_{\zeta} H_{mol}(\zeta) + \sum_{\zeta} H_{int}(\zeta) \tag{2.14}$$

Where:

$$H_{rad} = \sum_{\mathbf{k},\lambda} \left(a^{\dagger}_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} + \frac{1}{2} \right) \hbar k c \tag{2.15}$$

$$H_{mol} = \sum_{\alpha} \frac{\mathbf{p}_{\alpha}^2}{2m_{\alpha}} + V(\zeta) \tag{2.16}$$

$$\begin{aligned} H_{int} = & -\varepsilon_0^{-1} \boldsymbol{\mu}(\zeta) \cdot \mathbf{d}^{\perp}(\mathbf{R}_{\zeta}) - \varepsilon_0^{-1} Q_{ij}(\zeta) \nabla_i d_j^{\perp}(\mathbf{R}_{\zeta}) - \mathbf{m}(\zeta) \cdot \mathbf{b}(\mathbf{R}_{\zeta}) + \cdots + \\ & + \frac{e^2}{8m} \sum_{\alpha} [(\mathbf{q}_{\alpha}(\zeta) - \mathbf{R}_{\zeta}) \times \mathbf{b}(\mathbf{R}_{\zeta})]^2 + \frac{1}{2\varepsilon_0} \int |\mathbf{p}^{\perp}(\mathbf{r})|^2 d\mathbf{r} \end{aligned} \tag{2.17}$$

Where $H_{mol}(\zeta)$ is the Hamiltonian of an isolated atom or molecule with center of mass in ζ. $H_{int}(\zeta)$ will be the interaction energy between the molecular system and the radiation field. In the equations, $\mathbf{d}^{\perp}(\mathbf{r})$ and $\mathbf{b}(\mathbf{r})$ are the transverse electric displacement field operator and magnetic filed operator respectively. The operators $\mathbf{q}_{\alpha}$ and $\mathbf{p}_{\alpha}$ are the position vector and the canonical momentum of the α-th charged particle and V(ζ) is the total intramolecular energy. The interaction between the radiation field and matter is expressed in terms of the multipole operators: $\boldsymbol{\mu}$ (electric dipole), $\mathbf{m}$ (magnetic dipole), $\mathbf{Q}$ (electric quadrupole), etc. The last two terms in Eq.2.17 represent the leading contribution to an additional diamagnetic interaction energy and a field-independent contribution only significant for self energy calculations; $\mathbf{p}^{\perp}$ is the transverse component of the electric polarization. Moreover, we assumed that the Coulombic interactions within each atom or molecule can be separated out [6].

The form of the quantum electrodynamical field operator is expressible as a sum over radiation modes, and in the case of the transverse electric displacement it reads:

$$\mathbf{d}^{\perp}(\mathbf{r}) = i \sum_{\mathbf{k},\lambda} \left(\frac{\hbar c k \varepsilon_0}{2V} \right)^{\frac{1}{2}} \left[\mathbf{e}_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} - \bar{\mathbf{e}}_{\mathbf{k}\lambda} a^{\dagger}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} \right] \tag{2.18}$$

Where $\mathbf{e}_{\mathbf{k}\lambda}$ is the polarization unit vector for the electric field and $\bar{\mathbf{e}}_{\mathbf{k}\lambda}$ is its adjoint. For our purposes we can assume them to be real, thus $\bar{\mathbf{e}}_{\mathbf{k}\lambda} = \mathbf{e}_{\mathbf{k}\lambda}$. Moreover V is a quantization volume.

Let's now consider:

$$H_{mol}|j\rangle = \varepsilon_j |j\rangle = \varepsilon_{j,mol}|j\rangle \tag{2.19}$$

$$H_{rad}|\Theta\rangle = \varepsilon_{\Theta}|\Theta\rangle = \varepsilon_{\Theta,field}|\Theta\rangle \tag{2.20}$$

Then the eigenstates to the non-interacting Hamiltonian will be:

$$(H_{mol} + H_{field})|j\rangle|\Theta\rangle = (\varepsilon_{j,mol} + \varepsilon_{\Theta,field})|j\rangle|\Theta\rangle \tag{2.21}$$

The definition of a basis for the unperturbed molecule-radiation field space, allows us to define a more practical formulation of the electric-dipole interaction operator:

$$\begin{aligned} \boldsymbol{\mu} &= \sum_{ij\Theta\Gamma} |i, \Theta\rangle\langle i, \Theta|\boldsymbol{\mu}|j, \Gamma\rangle\langle j, \Gamma| \\ &= \sum_{ij} \boldsymbol{\mu}_{ij} |i\rangle\langle j| = \sum_{ij} \boldsymbol{\mu}_{ij} C_i^{\dagger} C_j \end{aligned} \tag{2.22}$$

Where $C_i^{\dagger}$, C_j are creation and annihilation operators for the molecular states. Note that i and j are a shorthand notation for all relevant quantum numbers regarding the molecular state. Moreover the resolution of the identity in the joint molecule-field space, the orthonormality of the Fock $|\Theta\rangle$ eigenstates and the resolution of the identity in the photonic space have been used. This formulation allows us to rewrite the interaction Hamiltonian to the first order in the multipolar expansion in a convenient form:

$$\begin{aligned} H_{int,1} &= -\varepsilon_0^{-1} \boldsymbol{\mu} \cdot \mathbf{d}^{\perp}(\mathbf{R}_{\zeta}) \\ &= -\sum_{\mathbf{k}\lambda} \sum_{ij} \left(\frac{\hbar c k}{2V\varepsilon_0} \right)^{\frac{1}{2}} \mathbf{e}_{\mathbf{k}\lambda} \cdot \boldsymbol{\mu}_{ij} \left[a_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{R}_{\zeta}} - a^{\dagger}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{R}_{\zeta}} \right] C_i^{\dagger} C_j \end{aligned} \tag{2.23}$$

If we now assume that the wavelength of the radiation $\eta = 2\pi/k$ is much bigger than the dimension of the molecule (Electric Dipole Approximation), then $e^{-i\mathbf{k}\cdot\mathbf{R}_\varsigma} = 1 = e^{i\mathbf{k}\cdot\mathbf{R}_\varsigma}$. Thus, the approximate interaction Hamiltonian reads:

$$H_{int,1} = -\sum_{\mathbf{k}\lambda}\sum_{ij} G^{ij}_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} C^\dagger_i C_j - G^{ij}_{\mathbf{k}\lambda} a^\dagger_{\mathbf{k}\lambda} C^\dagger_i C_j \tag{2.24}$$

Where $G^{ij}_{\mathbf{k}\lambda} = \left(\frac{\hbar ck}{2V\varepsilon_0}\right)^{\frac{1}{2}} \mathbf{e}_{\mathbf{k}\lambda} \cdot \boldsymbol{\mu}_{ij}$. As we can see, the interaction Hamiltonian is built in such a way that a change in the molecular state $|j\rangle$ to the state $|i\rangle$ is accompained either by the annhiliation or the creation of a photon. For sake of simplicity we will just consider the first part of this interaction Hamiltonian, i.e. where $a_{\mathbf{k}\lambda}$ is contained. If we now assume to consider this to be the perturbing potential V for which we developed the TDPT in the previous section, and we assume the unperturbed state of the overall molecule + field system to be in $|N\rangle = |n, \Gamma\rangle$, then to the first order in the perturbative expansion:

$$\begin{aligned}
c^{(1)}_{MN} = c^{(1)}_{(m,\Theta),(n,\Gamma)} &= \frac{i}{\hbar}\int_{t_0}^{t} \langle m, \Theta| e^{i\frac{H_0}{\hbar}(t_1-t_0)} \sum_{\mathbf{k}\lambda}\sum_{ij} G^{ij}_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} |i\rangle\langle j| e^{-i\frac{H_0}{\hbar}(t_1-t_0)} |n,\Gamma\rangle dt_1 \\
&= \frac{i}{\hbar}\sum_{\mathbf{k}\lambda}\sum_{ij} G^{ij}_{\mathbf{k}\lambda} \int_{t_0}^{t} e^{i(\omega_{mn}-\omega_{\mathbf{k}\lambda})(t_1-t_0)} \langle m|i\rangle\langle j|n\rangle\langle\theta|a_{\mathbf{k}\lambda}|\Gamma\rangle dt_1 \\
&= \frac{i}{\hbar}\sqrt{n_{\mathbf{x},\xi}} \sum_{ij} G^{ij}_{\mathbf{x},\xi} \frac{e^{i(\omega_{MN})(t-t_0)} - 1}{\omega_{MN}} = \frac{i}{\hbar}\sqrt{n_{\mathbf{x},\xi}} \sum_{ij} G^{ij}_{\mathbf{x},\xi} \delta(E_M - E_N)
\end{aligned} \tag{2.25}$$

Where $\omega_{MN} = (E_M - E_N)/\hbar = (\Delta E_{mol} + \Delta E_{field})/\hbar$ takes into account the overall energy balance of the closed molecule + field system. The Dirac's delta function $\delta(E_M - E_N)$ is introduced because energy conservation is required, usually this term can be substituted by the normalized lineshape function of the transition $g(\omega_{MN})$ [7]. Moreover $(\mathbf{x}, \xi)$ is the label of the photonic mode in which a photon is annhilated and $n_{\mathbf{x},\xi}$ is the number of photons of this mode in $|\Gamma\rangle$. The spectral distribution of the incoming radiation is recovered considering all the possible final photonic states $|\Theta\rangle$ that have at most one photon of difference with respect to the initial state. This result is obtained by exploiting the equation of motion of the creation and annhilation operators [1]. This has allowed us to justify the usage of the TDPT for a time-independent perturbing potential H_{int}. Before proceeding to analyze the Raman effect, it is interesting to present the Feynman Diagrams method for the evaluation of the perturbative coefficients as those just calculated.

2.4 A Brief Detour in the World of Feynman Diagrams

As we pointed out in section 2.1, the unitary time evolution operator $\hat{U}_I(t, t_0)$ can be expanded in a series Eq.2.8 in orders of the interaction. These subsequent terms are built taking into account the time ordering of the interaction processes, indeed $t > t' > t'' > \cdots > t^m > t_0$. This means that the time evolution of the wavefunction can be expressed as well in orders of the interaction. Moreover, the k-th term of this expansion, expresses the time evolution of the wavefunction, caused by k subsequent interaction with the perturbing potential. Thus, to this order, the perturbative expansion of the electronic wavefunction of a molecule interacting with the electromagnetic field (e.m.) will contain strings of k e.m. field operators. Their ordering in the string will express the time ordering of these processes, e.g. strings of the type $a_\nu a^\dagger_\mu a_\eta$ will represent a third order process in which a photon with energy ε_η is absorbed, then a photon with energy ε_μ is emitted, and then the molecule is excited again by absorbing a photon with energy ε_ν. Each process contributes to the perturbative expansion of the wavefunction with a matrix elements V_{MN} and with a nested (in time) integral of the form $\int_{t_0}^{t'} e^{i(\omega_{MN})(t''-t_0)}dt''$. If we are not interested in evaluating the specific form of the perturbed wavefunction, but rather we are interested just

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[1] In particular, if we consider the form of the creation and annhilation operators in the interaction picture:

$$a_I = e^{i\frac{H_0}{\hbar}(t-t_0)} a e^{-i\frac{H_0}{\hbar}(t-t_0)} \tag{2.26}$$

$$a^\dagger_I = e^{i\frac{H_0}{\hbar}(t-t_0)} a^\dagger e^{-i\frac{H_0}{\hbar}(t-t_0)} \tag{2.27}$$

. We are allowed to write their equation of motion as:

$$\dot{A}_I = i\Big[H_0, A_I\Big] + e^{i\frac{H_0}{\hbar}(t-t_0)} \Big(\partial_t A\Big) e^{-i\frac{H_0}{\hbar}(t-t_0)} \tag{2.28}$$

Since $H_0 = H_{mol} + H_{rad}$ but H_{mol} doesn't act on the $|\Theta\rangle$ photonic states, given the form of H_{rad} in Eq.2.15, it is easy to obtain the explicit time-dependency of the interaction picture creation and annhilation operators acting on the unperturbed radiation states:

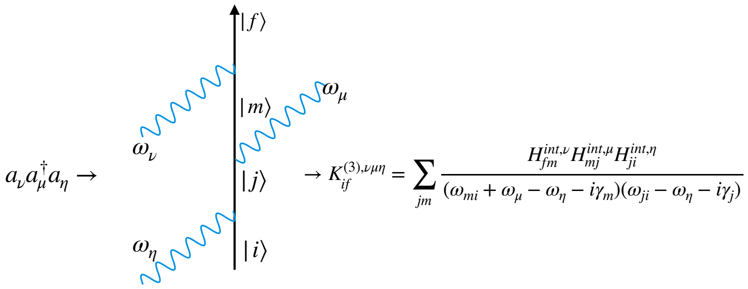
$$a_{I,\nu} = e^{-i\varepsilon_\nu} a_\nu \tag{2.29}$$

$$a^\dagger_{I,\nu} = e^{i\varepsilon_\nu} a^\dagger_\nu \tag{2.30}$$

in evaluating transition rates, then the contribution of each process can be simplified in $\frac{V_{MN}}{\omega_{MN}-i\gamma}$, where γ takes into account the finite lifetime for the virtual transitions in the molecule. A quick and intuitive way to evaluate the perturbative $c_{MN}^{(k)}$ coefficients, to any order k of the perturbation is by using Feynman diagrams. The rules for drawing a Feynman diagram are the following [8]:

1. Excitations such as photon, phonons and electron–hole pairs in Raman scattering are represented by lines (or propagators). These propagators can be labeled with properties of the excitations such as their wavevectors, frequencies, and polarizations.
2. The interaction between two excitations is represented by an intersection of their propagators. This intersection is known as a vertex.
3. Propagators can be drawn with an arrow to indicate whether the corresponding excitations (quasiparticles) are created or annihilated in an interaction. Arrows pointing towards a vertex represent excitations which are annihilated. Those pointing away from the vertex are created.
4. When several interactions are involved they are always assumed to proceed sequentially from bottom to top as a function of time.
5. Once a diagram has been drawn for a certain process, other possible processes are derived by permuting the time order in which the vertices occur in this diagram.
6. Each vertex, i.e. each scattering event contibutes to the perturbative coefficient with a term $\frac{V_{MN}}{\omega_{MN}\pm i\gamma}$.

Following these rules it is straightforward to draw the Feynamn diagram related to the third order process described before of absorption-emission-absorption:



$$a_\nu a_\mu^\dagger a_\eta \rightarrow \quad \rightarrow K_{if}^{(3),\nu\mu\eta} = \sum_{jm} \frac{H_{fm}^{int,\nu} H_{mj}^{int,\mu} H_{ji}^{int,\eta}}{(\omega_{mi}+\omega_\mu-\omega_\eta-i\gamma_m)(\omega_{ji}-\omega_\eta-i\gamma_j)}$$

Figure 1: Example of a third order process with it's Feynman diagram and the related scattering amplitude K. In the formula $H_{ij}^{int,\beta} = \mathbf{e}_\beta \cdot \boldsymbol{\mu}_{ij} = \sum_a \mu_{ij}^a = \mu_{ij}^\beta$, with $a = x, y, z$. The kets represent molecular states.

At this point we have at our disposal both the theory (time-dependent perturbation theory in non-relativistic QED framework) and a practical tool (Feynamn diagrams), which are needed to understand and handle practically the theory and equations underlying the surface enhanced Raman effect. However it is still useful to draw a quick review over the classical Raman effect.

3 The Classical Raman Effect

The Raman effect is the inelastic scattering of a photon by matter, the classical theory to describe it, is developed within the framework of the second-order time dependent perturbation theory (2o-TDPT). The processes involved can be represented by two Feynman diagrams, see Fig. 2. Where $K_{1,IF}^{\nu\mu}$, $K_{2,IF}^{\nu\mu}$ indicate the scattering amplitude

$$K_{1,IF}^{\nu\mu} = \sum_r \frac{\mu_{FR}^\mu \mu_{RI}^\nu}{(\omega_{RI}-\omega_\nu-i\gamma)} \qquad K_{2,IF}^{\nu\mu} = \sum_r \frac{\mu_{FR}^\nu \mu_{RI}^\mu}{(\omega_{RI}+\omega_\mu-i\gamma)}$$

Figure 2: Feynman diagrams and scattering amplitudes for 2o-TDPT Raman processes. Kets represent molecular states.

of the first and of the second process respectively. According to Fermi's Golden rule, the total Raman intensity will therefore be proportional to:

$$I^{Raman} \;\; \alpha \;\; \left| K^{\nu\mu}_{1,IF} + K^{\nu\mu}_{2,IF} \right|^2 = \left| \sum_{a,b} \tilde{\alpha}^{ab}_{IF} \right|^2 \tag{3.1}$$

Where $a = x, y, z$ and $b = x, y, z$ which independently refer to the molecule fixed coordinate system. Moreover, we introduced the transition dynamic polarizability as:

$$\tilde{\alpha}^{ab}_{IF} = \frac{1}{\hbar} \sum_{R \neq I,F} \left(\frac{\mu^a_{FR}\mu^b_{RI}}{(\omega_{RI} - \omega_\nu - i\gamma_{RI})} + \frac{\mu^b_{FR}\mu^a_{RI}}{(\omega_{RF} + \omega_\nu + i\gamma_{RF})} \right) \tag{3.2}$$

Key is now to consider explicitly the molecular transition dipole moments $\mu^a_{FR} = \langle F|\mu^a|R\rangle$. In particular it is necessary to explicit the form of the molecular wavefunction $|M\rangle$:

$$H^{mol}|M\rangle = E_M|M\rangle \tag{3.3}$$

If we now assume that we can separate the molecular Hamiltonian into a vibrational, rotational and an electronic part, then:

$$\text{if } \; H^{mol} = \left[H^{vib} + H^{rot} + H^{el}\right] \tag{3.4}$$

$$\text{then } \; |M\rangle = |e_m v_m r_m\rangle = |e_m\rangle|v_m\rangle|r_m\rangle \tag{3.5}$$

$$\left[H^{vib} + H^{rot} + H^{el}\right]|M\rangle = \left(\varepsilon_{e_m} + \varepsilon_{v_m} + \varepsilon_{r_m}\right)|e_m\rangle|v_m\rangle|r_m\rangle = \hbar\omega_M|M\rangle \tag{3.6}$$

Where we have assumed that the translational motion of the molecule has already been separated. At this point we can write the Raman transition polarizability Eq.3.2 as:

$$\tilde{\alpha}^{ab}_{IF} = \langle r_f v_f e_f|\hat{\alpha}^{ab}_{IF}|e_i v_i r_i\rangle \tag{3.7}$$

Where we introduced the polarizability operator:

$$\hat{\alpha}^{ab}_{IF} = \frac{1}{\hbar} \sum_{M \neq I,F} \left(\frac{\mu^a|e_j v_j r_j\rangle\langle r_j v_j e_j|\mu^b}{(\omega_{MI} - \omega_\nu - i\gamma_{MI})} + \frac{\mu^b|e_j v_j r_j\rangle\langle r_j v_j e_j|\mu^a}{(\omega_{MF} + \omega_\nu + i\gamma_{MF})} \right) \tag{3.8}$$

Several simplifications are furthermore usually carried out. If the temperature is not too high, then the initial electronic state is considered to be the ground state which is moreover in general considered to be nondegenerate. In conventional Raman scattering, the radiation lies well below any electronic transition frequency, implying that the final state $|F\rangle$ will be an excited rotovibrational state of the ground electronic state, i.e. $|F\rangle = |e_i v_f r_f\rangle$ with $|I\rangle = |e_i v_i r_i\rangle$. Moreover, for usual exciting frequencies, the range of the spectrum $\omega_{r_m r_i}$ and $\omega_{r_m r_f}$ will be negligible, unless ω_ν is resonant with some vibronic transitions. The usual approach is thus to drop the dependency upon the rotational spectrum at the denominator of Eq.3.8, employing the closure relation $\sum_j |r_j\rangle\langle r_j|$ and integrate Eq.3.2 over the rotational degrees of freedom. Thus:

$$\hat{\alpha}^{ab}_{IF} \rightarrow \frac{1}{\hbar} \sum_{J \neq I,F} \left(\frac{\mu^a|e_j v_j\rangle\langle v_j e_j|\mu^b}{(\omega_{JI} - \omega_\nu - i\gamma_{JI})} + \frac{\mu^b|e_j v_j\rangle\langle v_j e_j|\mu^a}{(\omega_{JF} + \omega_\nu + i\gamma_{JF})} \right) \tag{3.9}$$

$$\tilde{\alpha}^{ab}_{IF} \rightarrow \langle v_f e_f|\hat{\alpha}^{ab}_{if}|e_i v_i\rangle \tag{3.10}$$

Where here $\omega_{JI} = \hbar(\varepsilon_{e_j} + \varepsilon_{v_j} - \varepsilon_{e_i} - \varepsilon_{v_i})$. It is now common practice to integrate the transition dipole moments over the electron coordinates and then expand them in a Taylor series over the normal modes (Q_α) at the equilibrium geometry [9], i.e.:

$$\langle e_n|\mu^a|e_m\rangle = \mu^a_{nm}(0) + \sum_\alpha \mu^a_{nm}(\alpha)Q_\alpha; \qquad \mu^a_{nm}(\alpha) = \left(\frac{\partial\mu^a_{nm}}{\partial Q_\alpha}\right)_0 \tag{3.11}$$

A somewhat different approach which brings to the same expression but allows us to have a good starting point for our treatment of SERS is that followed by *Lombardi et al.*[10]. Indeed, they exploit the key concept in Herzberg-Teller theory that even small vibrations may cause mixing of zero order Born-Oppenheimer states $|e_j, 0\rangle$, allowing them to write:

$$|e_j\rangle = |e_j, 0\rangle + \sum_{e_m \neq e_j} \sum_\alpha \lambda_{mj}(Q_\alpha)|e_m, 0\rangle \tag{3.12}$$

$$\lambda_{mj}(Q_\alpha) = \frac{h_{mj}(Q_\alpha)Q_\alpha}{(E^0_m - E^0_j)} \tag{3.13}$$

$$h_{mj}(Q_\alpha) = \langle e_m, 0|\frac{\partial H}{\partial Q_\alpha}|e_j, 0\rangle \tag{3.14}$$

Substituting this into the Raman transition polarizability expression Eq.3.8 and recalling that $|F\rangle = |e_i v_f\rangle$, $|I\rangle = |e_i v_i\rangle$ and $|K\rangle = |e_k v_k\rangle$; one obtains at the first order in the normal modes Q_α:

$$\widetilde{\alpha_{IF}}^{ab} = A + B + C \tag{3.15}$$

$$A = \frac{1}{\hbar}\sum_{K\neq I}\sum_{v_k}\left[\frac{\mu^a_{e_ie_k}\mu^b_{e_ke_i}}{(\omega_{KI}-\omega-i\gamma_{KI})}+\frac{\mu^b_{e_ie_k}\mu^a_{e_ke_i}}{(\omega_{KF}+\omega+i\gamma_{KF})}\right]\langle v_i|v_k\rangle\langle v_k|v_f\rangle \tag{3.16}$$

$$\begin{aligned} B = \frac{1}{\hbar}\sum_{\alpha}\sum_{K\neq I}\sum_{v_k}\sum_{e_m\neq e_k}&\left[\frac{\mu^a_{e_ie_k}h_{km}\mu^b_{e_me_i}}{(\omega_{KI}-\omega-i\gamma_{KI})}+\frac{\mu^b_{e_ie_k}h_{km}\mu^a_{e_me_i}}{(\omega_{KF}+\omega+i\gamma_{KF})}\right]\frac{\langle v_i|v_k\rangle\langle v_k|Q_\alpha|v_f\rangle}{\hbar\omega_{MK}} \\ &+\left[\frac{\mu^a_{e_ie_m}h_{mk}\mu^b_{e_ke_i}}{(\omega_{KI}-\omega-i\gamma_{KI})}+\frac{\mu^b_{e_ie_m}h_{mk}\mu^a_{e_ke_i}}{(\omega_{KF}+\omega+i\gamma_{KF})}\right]\frac{\langle v_i|Q_\alpha|v_k\rangle\langle v_k|v_f\rangle}{\hbar\omega_{MK}} \end{aligned} \tag{3.17}$$

$$\begin{aligned} C = \frac{1}{\hbar}\sum_{\alpha}\sum_{K\neq I}\sum_{v_k}\sum_{e_m\neq e_i}&\left[\frac{\mu^a_{e_me_k}h_{im}\mu^b_{e_ke_i}}{(\omega_{KI}-\omega-i\gamma_{KI})}+\frac{\mu^b_{e_me_k}h_{im}\mu^a_{e_ke_i}}{(\omega_{KF}+\omega+i\gamma_{KF})}\right]\frac{\langle v_i|v_k\rangle\langle v_k|Q_\alpha|v_f\rangle}{\hbar\omega_{IM}} \\ &+\left[\frac{\mu^a_{e_ie_k}h_{mi}\mu^b_{e_ke_m}}{(\omega_{KI}-\omega-i\gamma_{KI})}+\frac{\mu^b_{e_ie_k}h_{mi}\mu^a_{e_ke_m}}{(\omega_{KF}+\omega+i\gamma_{KF})}\right]\frac{\langle v_i|Q_\alpha|v_k\rangle\langle v_k|v_f\rangle}{\hbar\omega_{IM}} \end{aligned} \tag{3.18}$$

Further considerations and approximations can can be carried out depending on the conditions under which the Raman process is occurring. For example, in the case when $\omega_{KI} >> \omega$ then expression A, B and C can be simplified further, leading to:

$$A = \tilde{\alpha}^{ab}_{IF}\langle v_i|v_f\rangle \qquad\qquad B + C = \sum_{\alpha}\left(\frac{\partial\tilde{\alpha}^{ab}_{IF}}{\partial Q_\alpha}\right)_0\langle v_i|Q_\alpha|v_f\rangle \tag{3.19}$$

In vibrational Raman scattering $v_f \neq v_i$. Thus, the allowed transitions are those along normal modes that cause a change in polarizability, and in the nuclear harmonic approximation one obtains the usual vibrational Raman selection rule, for which $v_f = v_i \pm 1$. It makes sense for our discussion to notice that the Herzberg-Teller expansion of the molecular electronic states (Eq.3.12) is introducing a further approximation, making in practice our Raman theory a third order theory. A perhaprs more consistent approach would be that of considering immediately the 3o-TDPT coefficients over an Hamiltonian which includes non adiabatic effect, i.e. what translates into the mixing of zero order Born-Oppenheimer states. In doing so, we follow the theory of the linear-vibronic coupling [11] [12]. In particular we can consider the molecular Hamiltonian to have the following form [13]:

$$H_{mol} = H_{el}(\mathbf{Q}) + H_{nuc} \tag{3.20}$$

Where $\mathbf{Q}$ provides the nuclear coordinates in terms of displacements in normal modes, computed at a reference geometry, $\mathbf{Q} = 0$. We now approximate the nuclear kinetic energy operator, disregarding the rotational and the vibro-rotational part. Moreover we treat the nuclear-nuclear repulsion term in the harmonic approximation. Doing so allows us to write [14]:

$$H_{nuc} \cong H^{harm}_{nuc} = \sum_{\alpha}\omega_\alpha\left(\frac{1}{2} + b^\dagger_\alpha b_\alpha\right) \tag{3.21}$$

Where $b^\dagger_\alpha$, b_α are the creation and annihilation operators in the vibrational normal mode $Q_\alpha = (2\omega_\alpha)^{-1/2}(b^\dagger_\alpha + b_\alpha)$ with energy ω_α. Expanding the electronic Hamiltonian in Taylor series with respect to the normal coordinates $\mathbf{Q}$ we obtain:

$$H_{mol} = H_{el}(\mathbf{0}) + \mathbf{Q}\cdot\nabla_Q\big[H_{el}\big](\mathbf{0}) + H^{ham}_{nuc} \tag{3.22}$$

This equation is the basis for the linear-vibronic coupling theory. In particular the first term is the usual Born-Oppenheimer (BO) electronic Hamiltonian. The last term is the vibrational harmonic Hamiltonian, whereas the term $\mathbf{Q}\cdot\nabla\big[H_{el}\big](\mathbf{0}) = H_{ep}$ is the so called electron-phonon coupling. In the language of second quantization, this can be rewritten as [15]:

$$H_{ep} = \sum_{jj'\alpha} M^{ep}_{jj'\alpha} C^\dagger_{j'} C_j (b^\dagger_\alpha + b_\alpha) \tag{3.23}$$

Where $C^\dagger_{j'}$ (C_j) are creation (annihilation) operators for the electronic states. Note that j is a shorthand notation for all relevant quantum numbers regarding the electronic state, including momentum and spin. Moreover the electron phonon interaction matrix terms are given by:

$$M^{ep}_{\alpha jj'} = \sum_{s}\sqrt{\frac{\hbar}{2NM_s\omega_\alpha}}\,\mathbf{e}_{\alpha s}\cdot\int d^3r\,\psi^*_{j'}(\mathbf{r})\psi_j(\mathbf{r})\nabla_s U(\mathbf{r})e^{i\mathbf{Q}_\alpha\cdot\mathbf{r}} \tag{3.24}$$

Where N is the number of atoms in the system, M_s is mass of the atom s, $\mathbf{Q}_\alpha$ is the phonon wave vector, ω_α is the phonon frequency, and and $\mathbf{e}_{\alpha s}$ represents the unit movement of atom s for the vibrational mode defined by the quantum number α. Again, we are, in principle, assuming that both j and α represent, respectively, all the quantum numbers of the electronic and vibrational states of the whole system. The function $\nabla_s U(\mathbf{r})$ is the change in potential energy at position $\mathbf{r}$ due to an infinitesimal movement of atom s. Let's now consider the following Hamiltonian:

$$H = H_0 + H_{er} + H_{ep} \tag{3.25}$$

Where $H_0 = H_{el}(\mathbf{0}) + H^{harm}_{nuc}$ and H_{er} and H_{ep} are the electron-photon (Eq. 2.24) and electron-phonon (Eq. 3.23) interaction Hamiltonians. By performing third order TDPT over them, the Raman scattering processes (for simplicity we consider only Stokes processes, i.e. a phonon is emitted) are obtained from the following Feynman diagrams (excluding the time-permutation of the photonic processes):

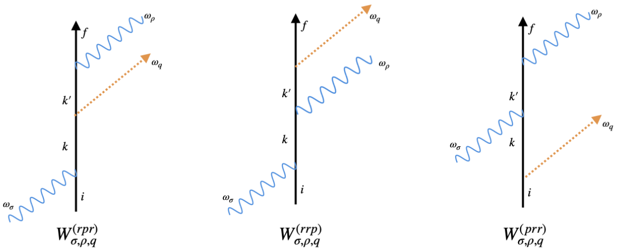


Figure 3: Some of the processes involved in the Stokes Raman scattering. In blue the photons and in orange the phonon. The molecular system is represented by the line and time proceed from bottom to the top of the figure.

Which leads to the following total scattering amplitude $W_{\sigma,\rho,q} = W^{(rpr)}_{\sigma,\rho,q} + W^{(rrp)}_{\sigma,\rho,q} + W^{(prr)}_{\sigma,\rho,q}$, where:

$$W^{(rpr)}_{\sigma,\rho,q} = \sum_{ik'k} \chi^{iq}_{k'k} \frac{M^{er,\rho}_{ik'} M^{ep,q}_{k'k} M^{er,\sigma}_{ki}}{(E_{k'} - E_i + \hbar\omega_q - \hbar\omega_0)\,(E_k - E_i - \hbar\omega_0)} \tag{3.26}$$

$$W^{(rrp)}_{\sigma,\rho,q} = \sum_{ik'k} \chi^{iq}_{k'k} \frac{M^{ep,q}_{ik'} M^{er,\rho}_{k'k} M^{er,\sigma}_{ki}}{(E_k - E_i - \hbar\omega_0)\,(E_{k'} - E_i - \hbar\omega_q)} \tag{3.27}$$

$$W^{(prr)}_{\sigma,\rho,q} = \sum_{ik'k} \chi^{iq}_{k'k} \frac{M^{er,\rho}_{ik'} M^{er,\sigma}_{k'k} M^{ep,q}_{ki}}{(E_{k'} - E_i + \hbar\omega_q - \hbar\omega_0)\,(E_k - E_i + \hbar\omega_q)} \tag{3.28}$$

Where i, k and k' zero-order Born Oppenheimer states evaluated at the equilibrium geometry and χ are some selection-rules functions, the from of which is not important now. If the time-permutation of the processes is taken into account, the summation will lead to terms identical to those in Eqs.3.17 - 3.18. Although the results are the same, this has allowed us to introduce the non-adiabatic terms right at the beginning of our treatment, separating the Hamiltonian into terms with a very clear physical picture and allowing us to use a unique tool (namely TDPT) to reach the expressions needed to calculate the Raman intensity. The advantage of this will become evident in the next sections.

4 Surface Enhanced Raman Effect

Suface-enhanced Raman scattering (SERS) is the giant enhancement of the Raman scattering cross section for a molecule in proximity of a suitably nanostructured substrate, in general a metal [16]. It is widely accepted [1][2][3] that the enhancement arises as a combination of an electromagnetic (EM) enhancement associated with plasmon excitation in metal particles serving as the SERS substrate and a chemical (CHEM or CT) enhancement due to the target molecules being able to transfer electrons to/from the metal particles in both ground and excited states, often in the process of forming the metal molecule bond [1]. The theory of EM enhancement is a classical theory. It describes the plasmon as an external antenna for the standard Raman process. This implicitly separates a coupled quantum mechanical system (plasmon and Raman scatterer) into two distinct parts. Although this separation might be useful to have a pictorial representation of the processes occurring, the physics underlying the SERS is utterly different. As we learned from section 2.3 radiation and molecular systems have to be treated as part of a single, closed system, where enegy is conserved. This leads to the idea that SERS should be treated as one quantum-mechanical process that must not be separated into distinct subsystems [17]. The chemical mechanism of SERS refers to contributions to the Raman scattering that do not rely on the EM environment (e.g., plasmon excitation), often because they are associated with the transfer of electrons between adsorbed molecules and the NP substrate [1]. The most recent theories developed to explain these different enhancement mechanisms [15],[17],[18] rely in considering SERS as a higher-order Raman scattering (HORa) and thus are treated within the framework of time-dependent perturbation theory. In particular, foundamental papers from *Niclas S. Mueller et al.* [17][18] allow us to gain a theroetical perspective in the processes involved in the EM enhancement, whereas a paper from *E.B.Barros and M.S. Dresselhaus* [15] study the processes of charge transfer. The next sections are meant to provide a brief description of the models developed by the authors of the different papers. The derivation of the formulae can be found in the papers. It will be the purpose of the last section to suggest a way to merge these two effects in a comprehensive treatement of the SERS within the theory of HORa.

4.1 SERS as HORa Process: EM Enhancement

Following the ideas of *Niclas S. Mueller et al.* [17] we consider a general SERS experiment where a plasmonic nanostructure is coupled to a molecule as a Raman scattering probe (Fig.4). Let's now consider the following SERS-type scattering event: an incoming photon ω_L excites a localized surface plasmon (LSP) mode w with energy ω_w. The LSP couples via its near field to the molecule and excites a transition from the molecular ground state with energy ε_g^{vib} into an intermediate vibronic state with energy ε_i^{vib}. This intermediate state can be a virtual state. The molecule relaxes into a final vibronic state with energy ε_f^{vib} exciting again the LSP. Finally, the Raman scattered light ω_S is emitted by the LSP. This process corresponds to a fourth-order process in TDPT and is depicted as a Feynman diagram in Fig.4B with a scattering amplitude $K^{w,w',j}_{\mathrm{pl-pl}}(\omega_{\mathrm{L}})$. In addition to this process, there are other three processes that have the same initial (incoming photon ω_L, molecule in vibronic ground state g) and final state (Raman scattered photon ω_S, molecule in vibronic excited state f). These scattering pathways interfere, leading to the selective increase or decrease of plasmonic enhancement at a given excitation wavelength.

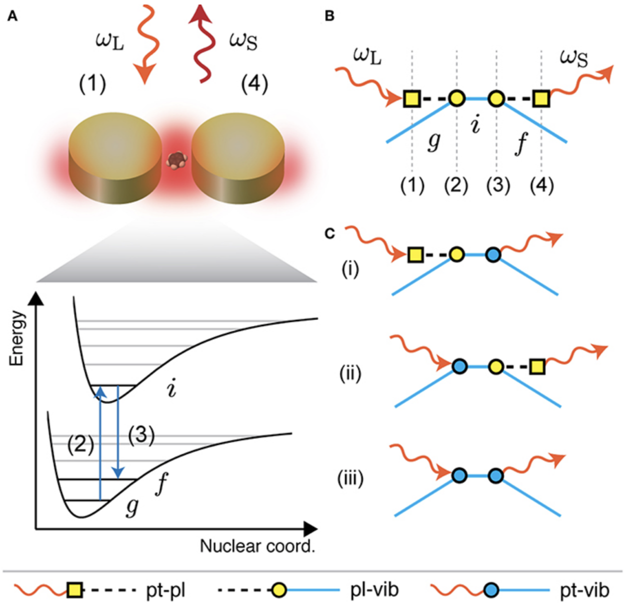


Figure 4: EM enhancement as a higher-order Raman process. (A) Sketch of a plasmon-enhanced Raman process relevant for SERS. The steps are: (1) excitation of a plasmon by the incoming light ω_L; (2) molecular transition from ground state g to intermediate state i by coupling to the plasmonic near field; (3) molecular relaxation to final state f and excitation of the plasmon; (4) emission of Raman-scattered light ω_S by the plasmon. (B) Plasmon-enhanced Raman process in (A) illustrated as a Feynman diagram which corresponds to fourth-order perturbation theory. (C) Feynman diagrams of three other scattering processes that are relevant for SERS, i.e., (i) only the incoming light $K^{w,j}_{\mathrm{pl-pt}}$ or (ii) only the Raman-scattered light couples to the plasmon $K^{w,j}_{\mathrm{pt-pl}}$ and (iii) the Raman process without plasmonic enhancement $K^{j}_{\mathrm{pt-pt}}$.[18]

The Raman scattering amplitudes associated with each process can be calculated in the framework of TDPT and are reported below:

$$K^{w,w',j}_{\mathrm{pl-pl}}(\omega_{\mathrm{L}}) = \frac{\mathcal{M}^{w_{\mathrm{L}}}_{\mathrm{pt-pl}}\mathcal{M}^{w',j}_{\mathrm{pl-vib}}\mathcal{M}^{w,j}_{\mathrm{vib-pl}}\mathcal{M}^{w}_{\mathrm{pl-pt}}}{\left(\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \epsilon^{\mathrm{vib}}_{f} - \hbar\omega_{w'} - i\gamma_{w'}\right)\left(\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \epsilon^{\mathrm{vib}}_{j} - i\gamma^{\mathrm{vib}}_{j}\right)\left(\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \hbar\omega_{w} - i\gamma_{w}\right)} \tag{4.1}$$

$$K^{w,j}_{\mathrm{pl-pt}}(\omega_{\mathrm{L}}) = \frac{\mathcal{M}^{j}_{\mathrm{pt-vib}}\mathcal{M}^{w,j}_{\mathrm{vib-pl}}\mathcal{M}^{w}_{\mathrm{pl-pt}}}{\left(\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \epsilon^{\mathrm{vib}}_{j} - i\gamma^{\mathrm{vib}}_{j}\right)\left(\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \hbar\omega_{w} - i\gamma_{w}\right)} \tag{4.2}$$

$$K^{w,j}_{\mathrm{pt-pl}}(\omega_{\mathrm{L}}) = \frac{\mathcal{M}^{w}_{\mathrm{pt-pl}}\mathcal{M}^{w,j}_{\mathrm{pl-vib}}\mathcal{M}^{j}_{\mathrm{vib-pt}}}{\left(\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \epsilon^{\mathrm{vib}}_{f} - \hbar\omega_{w} - i\gamma_{w}\right)\left(\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \epsilon^{\mathrm{vib}}_{j} - i\gamma^{\mathrm{vib}}_{j}\right)} \tag{4.3}$$

$$K^{j}_{\mathrm{pt-pt}}(\omega_{\mathrm{L}}) = \frac{\mathcal{M}^{j}_{\mathrm{pt-vib}}\mathcal{M}^{j}_{\mathrm{vib-pt}}}{\hbar\omega_{\mathrm{L}} + \epsilon^{\mathrm{vib}}_{g} - \epsilon^{\mathrm{vib}}_{j} - i\gamma^{\mathrm{vib}}_{j}} \tag{4.4}$$

Where "vib" stands for vibronic. Key is now to evaluate the coupling matrix elements $\mathcal{M}_{\mathrm{k-l}} = \langle k|H^{int}|l\rangle$. To do so, we need to make explicit the form of the interaction Hamiltonians.

4.1.1 Quantization of the LSP and Interaction Hamiltonians

In order to make a coherent treatment of all the phyiscal enetities coming into play (e.m. field, vibration field, electronic states, etc.), the localized surface plasmons of the metallic nanoparticles needs to be quantized. This is done by using the jellium model [18], which assumes a density of $\mathcal{N}$ free electrons that move in the presence of a uniform positively charged background [19]. In this case the plasmonic Hamiltonian can be written as:

$$H_{pl} = \sum_w \hbar\omega_w (b_w^\dagger b_w + \frac{1}{2}) \tag{4.5}$$

Where $b_w^\dagger$ and b_w create and annhilate respecitively a quantum of energy in the plasmon mode $\mathbf{q}_w$[2].
The **Plasmon-Photon** interaction Hamiltonian can then be written as [18][19]:

$$H_{pl-pt} = ie\hbar\sqrt{\frac{\mathcal{N}V_p}{4mV_R\epsilon_0\epsilon_m}} \sum_w \left(\varepsilon_w^{pt} a_{pt} b_w^\dagger - (\varepsilon_w^{pt})^* a_{pt}^\dagger b_w\right) \tag{4.6}$$

Where V_p is the volume of the metallic nanoparticle, V_R the normalizing volume of the electromagnetic field and

$$\varepsilon_w^{pt} = C_{LF} \int_{V_p} d\mathbf{r}' \mathbf{e}^{pt} \cdot \mathbf{q}_w(\mathbf{r}') e^{i\mathbf{k}_{\mathbf{pt}}\cdot\mathbf{r}'} \tag{4.7}$$

is a factor that gives the selection rules for the interaction of light with the plasmonic mode w. Moreover C_{LF} is a local field correction factor which accounts for the difference between the microscopic light field that couples to the plasmonic mode $\mathbf{q}_w(\mathbf{r})$ and the incident macroscopic field $\mathbf{A}_{pt}$ [18].
The Plasmon-Photon coupling matrix elements are thus:

$$\mathcal{M}_{\mathrm{pl-pt}}^{w} = \left\langle 1_w^{\mathrm{pl}}, 0^{\mathrm{pt}} \middle| H_{\mathrm{pl-pt}} \middle| 0_w^{\mathrm{pl}}, 1_{\mathbf{k}_{\mathrm{pt}},\mathbf{e}_{\mathrm{pt}}}^{\mathrm{pt}} \right\rangle = ie\hbar\sqrt{\frac{\mathcal{N}V_{\mathrm{p}}}{4mV_{\mathrm{R}}\epsilon_0\epsilon_m}} \varepsilon_w^{\mathrm{pt}} \tag{4.8}$$

The **Plasmon-Molecule** interaction Hamiltonian can be written as [17] [18]:

$$H_{pl-vib} = -\boldsymbol{\mu} \cdot \mathbf{E}_{LSP}(\mathbf{r}) = \sum_w \frac{e}{\epsilon_0\epsilon_m} \sqrt{\frac{\hbar\mathcal{N}V_p}{2m\omega_w}} \left(b_w^\dagger + b_w\right) \boldsymbol{\mu} \cdot \mathbf{G}_w(\mathbf{r}) \tag{4.9}$$

Where $\mathbf{E}_{LSP}(\mathbf{r})$ is the electric field generated by the plasmonic nanostructure and

$$\mathbf{G}_w(\mathbf{r}) = C_{\mathrm{LF}} \nabla_{\mathbf{r}} \int_{V_{\mathbf{p}}} \mathrm{d}\mathbf{r}' \mathbf{q}_w\left(\mathbf{r}'\right) \cdot \nabla_{\mathbf{r}'} G_0\left(\mathbf{r}, \mathbf{r}'\right) \tag{4.10}$$

Where $G_0\left(\mathbf{r}, \mathbf{r}'\right)$ is a Green function that gives the field distribution outside the plasmonic nanoparticle [3].
The Plasmon-Molecule coupling matrix elements are:

$$\mathcal{M}_{\mathrm{vib-pl}}^{w,i} = \left\langle 0_w^{\mathrm{pl}}, i^{\mathrm{vib}} \middle| H_{\mathrm{pl-vib}} \middle| 1_w^{\mathrm{pl}}, g^{\mathrm{vib}} \right\rangle = \mu_0 e\sqrt{\frac{\hbar\mathcal{N}V_{\mathrm{p}}\omega_w^3}{2m}} \boldsymbol{\mu}_{gj} \cdot \mathbf{G}_w(\mathbf{r}) \tag{4.12}$$

The **Light-Molecule** coupling matrix elements are

$$\mathcal{M}_{\mathrm{vib-pt}}^{j} = \left\langle 0^{\mathrm{pt}}, j^{\mathrm{vib}} \middle| H_{\mathrm{pt-vib}} \middle| 1_{\mathbf{k}_{\mathrm{pt}},\mathbf{e}_{\mathrm{pt}}}^{\mathrm{pt}}, g^{\mathrm{vib}} \right\rangle = -i\sqrt{\frac{\hbar\omega_{\mathrm{pt}}}{2V_{\mathrm{R}}\epsilon_0\epsilon_m}} e^{i\mathbf{k}_{\mathrm{pt}}\cdot\mathbf{r}} \mathbf{e}_{\mathrm{pt}} \cdot \boldsymbol{\mu}_{gj} \tag{4.13}$$

Moreover, it is interesting to notice that this theory considers the standard Raman processes within 2o-TDPT. This means that Herzberg-Teller contributions still need to be introduced to further simplify the electron-photon interaction terms.

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[2] These $\mathbf{q}_w$ vectors can be viewed as the amplitude of an harmonic displacement. Indeed these are the eigenmodes associated to the current distribution generated by the collective free oscillations at each resonance frequency ω_w of the particle electron gas.

[3] Indeed the electric near field of the plasmonic nanostructure is calculated within the electrostatic approximation as the gradient of the scalar potential $\mathbf{E}_{LSP}(\mathbf{r}) = -\nabla_{\mathbf{r}}\phi_{pl}(\mathbf{r})$, where

$$\phi_{\mathrm{pl}}(\mathbf{r}) = -\frac{1}{\epsilon_0\epsilon_m} \int_{V_{\mathrm{p}}} \mathrm{d}\mathbf{r}' \rho\left(\mathbf{r}'\right) G_0\left(\mathbf{r}, \mathbf{r}'\right) \tag{4.11}$$

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4.2 SERS as HORa Process: CT Enhancement

In this section I will analyze the theory from *Barros and Dresselhaus* [15] for the description of the Raman-enhancement effect by 2D materials. Due to the geometry of 2D materials, EM-SERS should be negligible, making the following theory useful to describe CT-SERS effects. This theory is based on considering the following Hamiltonian:

$$H = H_0 + H_{er} + H_{ep} \tag{4.14}$$

Where H_0 is the equilibrium Hamiltonian for the system, which includes a molecular (H_M) part, a surface (H_S) part and a coupling (H_{SM}) term. The coupling term is assumed here to be evaluated at the equilibrium position for both the surface atoms and the atoms within the interacting molecule. Let's also assume that the eigenstates of the equilibrium Hamiltonian H_0 can be described as a combination of eigenstates localized at the molecule and eigenstates localized at the surface atoms. The remaining tems in Eq. 4.14, namely H_{er} and H_{ep}, correspond to the electron-radiation and electron-phonon interactions, respectively, and are treated using perturbation theory. Up to now, no differences are present with respect to the 3o-TDPT treatment for Raman we developed in the previous section. It is now important to introduce a few considerations about the possible many-body states. First, we will assume that when the molecule is not in contact with the surface, the main spectroscopic properties of the molecule can be described in terms of its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO). Also, in the absence of molecules, the surface electronic states are described by an electronic band (or a set of electronic bands in the case of a semiconducting surface) in which the Fermi energy (EF) is defined as the energy of the highest occupied electronic state of the surface. As we will see in the following, the relationship between the HOMO and LUMO energies of the molecule and the Fermi energy of the metal will be one of the determining factors governing the intensity of the Raman enhancement. When the molecule is in contact with the substrate, the surface-molecule interaction can be classified in terms of two broad classes: interaction without charge transfer and with charge transfer. In the first situation, the occupancy of the HOMO and/or the LUMO states will not be modified by the interaction. This is usually the case when the HOMO state is positioned well below the Fermi level of the surface and the LUMO state is above it. In the second case (with charge transfer), the distribution of electronic states is not so trivial and the HOMO state of the molecule can become partially or totally unoccupied, or the LUMO state can be occupied by electrons coming from the surface. Considering the Stokes Raman processes, where a phonon is generated in the molecule, the scattring processes ivolved in the Raman process are the same as in Fig.3. Thus, the total scattering amplitude is given by $W_{\sigma,\rho,q} = W^{(rpr)}_{\sigma,\rho,q} + W^{(rrp)}_{\sigma,\rho,q} + W^{(prr)}_{\sigma,\rho,q}$, where:

$$\begin{aligned} W^{(rpr)}_{\sigma,\rho,q} = & \sum_{ik'k} \chi^{iq}_{k'k} \frac{M^{er,\rho}_{ik'} M^{ep,q}_{k'k} M^{er,\sigma}_{ki}}{\left(E_{k'} - E_i + \hbar\omega_q - \hbar\omega_0\right)\left(E_k - E_i - \hbar\omega_0\right)} \\ & + \xi^{iq}_{k'k} \frac{M^{er,\rho}_{kk'} M^{ep,q}_{ik} M^{er,\sigma}_{k'i}}{\left(E_{k'} - E_k + \hbar\omega_q - \hbar\omega_0\right)\left(E_{k'} - E_i - \hbar\omega_0\right)} \end{aligned} \tag{4.15}$$

$$\begin{aligned} W^{(rrp)}_{\sigma,\rho,q} = & \sum_{ik'k} \chi^{iq}_{k'k} \frac{M^{ep,q}_{ik'} M^{er,\rho}_{k'k} M^{er,\sigma}_{ki}}{\left(E_k - E_i - \hbar\omega_0\right)\left(E_{k'} - E_i - \hbar\omega_q\right)} \\ & + \xi^{iq}_{k'k} \frac{M^{ep,q}_{kk'} M^{er,\rho}_{ik} M^{er,\sigma}_{k'i}}{\left(E_{k'} - E_i - \hbar\omega_0\right)\left(E_{k'} - E_k - \hbar\omega_q\right)} \end{aligned} \tag{4.16}$$

$$\begin{aligned} W^{(prr)}_{\sigma,\rho,q} = & \sum_{ik'k} \chi^{iq}_{k'k} \frac{M^{er,\rho}_{ik'} M^{er,\sigma}_{k'k} M^{ep,q}_{ki}}{\left(E_{k'} - E_i + \hbar\omega_q - \hbar\omega_0\right)\left(E_k - E_i + \hbar\omega_q\right)} \\ & + \xi^{iq}_{k'k} \frac{M^{er,\rho}_{kk'} M^{er,\sigma}_{ik} M^{ep,q}_{k'i}}{\left(E_{k'} - E_k + \hbar\omega_q - \hbar\omega_0\right)\left(E_{k'} - E_i + \hbar\omega_q\right)} \end{aligned} \tag{4.17}$$

Where i, k and k' are single electron states of the system. Moreover

$$\chi^{iq}_{k'k} = \begin{cases} \sqrt{n_q + 1} f_i \left(1 - f_k\right)\left(1 - f_{k'}\right), & \text{if } i \neq k \neq k' \\ \sqrt{n_q + 1} f_i \left(1 - f_k\right), & \text{if } k' = k \text{ or } i = k \text{ or } k' \end{cases} \tag{4.18}$$

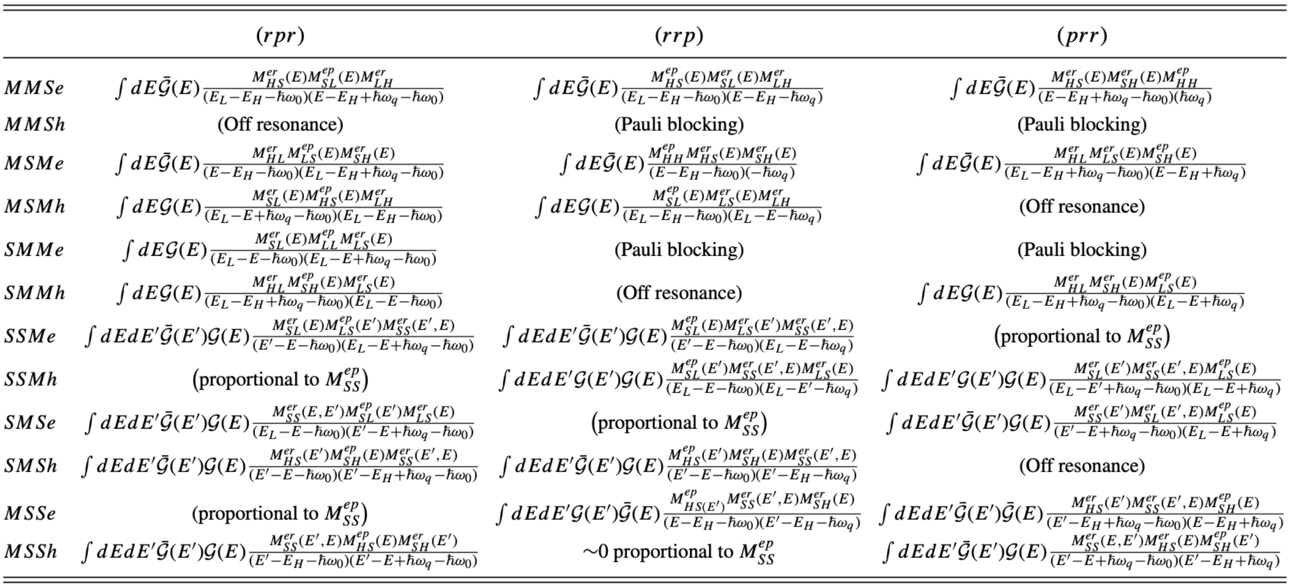
and

$$\xi^{iq}_{k'k} = \begin{cases} \sqrt{n_q + 1} f_i f_k \left(1 - f_{k'}\right), & \text{if } i \neq k \neq k' \\ 0, & \text{if } k' = k \text{ or } k' = i \end{cases} \tag{4.19}$$

where f_i , $f_{k'}$, and f_k are the occupancies (1 or 0) for each of these states in the initial state $|I\rangle$. Note that for each process there are two terms, one proportional to $\chi^{iq}_{k'k}$ and one proportional to $\xi^{iq}_{k'k}$. The first term can be interpreted in terms of electron-phonon scattering and the second in terms of hole-phonon scattering. The main difference with respect to the usual Raman spectroscopy is that now, the electronic states take into account both surface and molecular states.

4.2.1 Rensonance Processes

Let's assume a weak interaction regime, thus a negligible charge transfer between the molecule and the surface is assumed, meaning that the HOMO state of the molecule is fully occupied whereas the LUMO is unoccupied. Processes involving only states of the molecule or of the surface are not of our interest. Thus, the possible initial state can be either of the surface or of the molecule (the HOMO). For each sequence of scattering events (rpr, rrp, prr) there are six processes for the electrons and six for the holes, depending on the sequence of states involved. For example a process such as the (rrp)-SMM involve a photon mediated transition from initial state S to the LUMO state in the molecule, a transition from the LUMO to the HOMO due to the emission of a photon and the transition from the HOMO to the initial state S due to the scattering of a phonon. It has to be noticed that due to the weak interaction regime, this process should have a vanishing contibution due to the transition from the LUMO to the occupied HOMO (Pauli blocking). Moreover in this discussion *Barros and Dresselhaus* are interested in the vibrational modes of the molecule, and thus the phonon mediated processes involve the excitation of phonons within the molecule. Thus, the possible scattering of phonons in the surface is disregarded. For this reason, those processes proportional to M^{ep}_{SS}, i.e. that involve the scattering of a phonon in the molecule due to the transition between two electronic surface states, are considered to be rather weak. In any case, the surface-molecule Raman process will be given by a sum of 36 different processes, each one having a different set of resonance conditions and a different dependence on the position of the Fermi level. The whole set of matrix elements can be found in the following Fig. 5. In deriving these, it has been used the fact that the summation over the surface states can be transformed into an integral over the possible electronic energies by defining the density of electronic states $g(E) = \sum_{k'} \int dE\delta(E - E_{k'})$ where k' covers all the possible electronic surface states, meaning for example that:



	(rpr)	(rrp)	(prr)
$MMSe$	$\int dE\bar{\mathcal{G}}(E)\frac{M^{er}_{HS}(E)M^{ep}_{SL}(E)M^{er}_{LH}}{(E_L-E_H-\hbar\omega_0)(E-E_H+\hbar\omega_q-\hbar\omega_0)}$	$\int dE\bar{\mathcal{G}}(E)\frac{M^{ep}_{HS}(E)M^{er}_{SL}(E)M^{er}_{LH}}{(E_L-E_H-\hbar\omega_0)(E-E_H-\hbar\omega_q)}$	$\int dE\bar{\mathcal{G}}(E)\frac{M^{er}_{HS}(E)M^{er}_{SH}(E)M^{ep}_{HH}}{(E-E_H+\hbar\omega_q-\hbar\omega_0)(\hbar\omega_q)}$
$MMSh$	(Off resonance)	(Pauli blocking)	(Pauli blocking)
$MSMe$	$\int dE\bar{\mathcal{G}}(E)\frac{M^{er}_{HL}M^{ep}_{LS}(E)M^{er}_{SH}(E)}{(E-E_H-\hbar\omega_0)(E_L-E_H+\hbar\omega_q-\hbar\omega_0)}$	$\int dE\bar{\mathcal{G}}(E)\frac{M^{ep}_{HH}M^{er}_{HS}(E)M^{er}_{SH}(E)}{(E-E_H-\hbar\omega_0)(-\hbar\omega_q)}$	$\int dE\bar{\mathcal{G}}(E)\frac{M^{er}_{HL}M^{er}_{LS}(E)M^{ep}_{SH}(E)}{(E_L-E_H+\hbar\omega_q-\hbar\omega_0)(E-E_H+\hbar\omega_q)}$
$MSMh$	$\int dE\mathcal{G}(E)\frac{M^{er}_{SL}(E)M^{ep}_{HS}(E)M^{er}_{LH}}{(E_L-E+\hbar\omega_q-\hbar\omega_0)(E_L-E_H-\hbar\omega_0)}$	$\int dE\mathcal{G}(E)\frac{M^{ep}_{SL}(E)M^{er}_{LS}(E)M^{er}_{LH}}{(E_L-E_H-\hbar\omega_0)(E_L-E-\hbar\omega_q)}$	(Off resonance)
$SMMe$	$\int dE\mathcal{G}(E)\frac{M^{er}_{SL}(E)M^{ep}_{LL}M^{er}_{LS}(E)}{(E_L-E-\hbar\omega_0)(E_L-E+\hbar\omega_q-\hbar\omega_0)}$	(Pauli blocking)	(Pauli blocking)
$SMMh$	$\int dE\mathcal{G}(E)\frac{M^{er}_{HL}M^{ep}_{SH}(E)M^{er}_{LS}(E)}{(E_L-E_H+\hbar\omega_q-\hbar\omega_0)(E_L-E-\hbar\omega_0)}$	(Off resonance)	$\int dE\mathcal{G}(E)\frac{M^{er}_{HL}M^{er}_{SH}(E)M^{ep}_{LS}(E)}{(E_L-E_H+\hbar\omega_q-\hbar\omega_0)(E_L-E+\hbar\omega_q)}$
$SSMe$	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{er}_{SL}(E)M^{ep}_{LS}(E')M^{er}_{SS}(E',E)}{(E'-E-\hbar\omega_0)(E_L-E+\hbar\omega_q-\hbar\omega_0)}$	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{ep}_{SL}(E)M^{er}_{LS}(E')M^{er}_{SS}(E',E)}{(E'-E-\hbar\omega_0)(E_L-E-\hbar\omega_q)}$	(proportional to M^{ep}_{SS})
$SSMh$	(proportional to M^{ep}_{SS})	$\int dEdE'\mathcal{G}(E')\mathcal{G}(E)\frac{M^{ep}_{SL}(E')M^{er}_{SS}(E',E)M^{er}_{LS}(E)}{(E_L-E-\hbar\omega_0)(E_L-E'-\hbar\omega_q)}$	$\int dEdE'\mathcal{G}(E')\mathcal{G}(E)\frac{M^{er}_{SL}(E')M^{er}_{SS}(E',E)M^{ep}_{LS}(E)}{(E_L-E'+\hbar\omega_q-\hbar\omega_0)(E_L-E+\hbar\omega_q)}$
$SMSe$	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{er}_{SS}(E,E')M^{ep}_{SL}(E')M^{er}_{LS}(E)}{(E_L-E-\hbar\omega_0)(E'-E+\hbar\omega_q-\hbar\omega_0)}$	(proportional to M^{ep}_{SS})	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{er}_{SS}(E')M^{er}_{SL}(E',E)M^{ep}_{LS}(E)}{(E'-E+\hbar\omega_q-\hbar\omega_0)(E_L-E+\hbar\omega_q)}$
$SMSh$	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{er}_{HS}(E')M^{ep}_{SH}(E)M^{er}_{SS}(E',E)}{(E'-E-\hbar\omega_0)(E'-E_H+\hbar\omega_q-\hbar\omega_0)}$	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{ep}_{HS}(E')M^{er}_{SH}(E)M^{er}_{SS}(E',E)}{(E'-E-\hbar\omega_0)(E'-E_H-\hbar\omega_q)}$	(Off resonance)
$MSSe$	(proportional to M^{ep}_{SS})	$\int dEdE'\mathcal{G}(E')\bar{\mathcal{G}}(E)\frac{M^{ep}_{HS(E')}M^{er}_{SS}(E',E)M^{er}_{SH}(E)}{(E-E_H-\hbar\omega_0)(E'-E_H-\hbar\omega_q)}$	$\int dEdE'\bar{\mathcal{G}}(E')\bar{\mathcal{G}}(E)\frac{M^{er}_{HS}(E')M^{er}_{SS}(E',E)M^{ep}_{SH}(E)}{(E'-E_H+\hbar\omega_q-\hbar\omega_0)(E-E_H+\hbar\omega_q)}$
$MSSh$	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{er}_{SS}(E',E)M^{ep}_{HS}(E)M^{er}_{SH}(E')}{(E'-E_H-\hbar\omega_0)(E'-E+\hbar\omega_q-\hbar\omega_0)}$	~0 proportional to M^{ep}_{SS}	$\int dEdE'\bar{\mathcal{G}}(E')\mathcal{G}(E)\frac{M^{er}_{SS}(E,E')M^{er}_{HS}(E)M^{ep}_{SH}(E')}{(E'-E+\hbar\omega_q-\hbar\omega_0)(E'-E_H+\hbar\omega_q)}$

Figure 5: Expressions for all relevant surface-enhanced Raman processes considering a two-state molecule interacting with a general 2D surface. The values E_L,E_H, ω_0,and ω_q are the energies for the LUMO and HOMO states of the molecule,the incident laser and the phonon involved with the Raman process respectively.[15]

$$W_{(rpr)-MMSe} = \int dE\bar{\mathcal{G}}(E)\frac{M^{er}_{HS}(E)M^{ep}_{SL}(E)M^{er}_{LH}}{(E_L - E_H - \hbar\omega_0)\,(E - E_H + \hbar\omega_q - \hbar\omega_0)} \tag{4.20}$$

Where the density of occupied states $\mathcal{G}(E) = f(E - E_F)g(E)$, and density of unoccupied states $\bar{\mathcal{G}}(E) = [1 - f(E - E_F)]g(E)$ have been defined considering $f(E - E_F)$ the Fermi-Dirac distribution. The last note is that this theory would be in principle applicable to a variety of materials, however for insulators or semiconductors, excitonic effects might become relevant and open new scattering channels.

4.3 Merging the Theories: a Personal Suggestion

Up to now, the model presented treats situations in which the two enhancement effects i.e. EM and CT can be easily separated. In a generic SERS experiment, however this might not be the case, for example if the analyte is adsorbed onto a surface but it also feels the effect of a plasmon field [1]. The goal of this section will be first of all to reformulate the EM-HORa (Sec.4.1) approximating the molecular Hamiltonian according to the vibronic coupling theory Eq. 3.22. Then a common theory to treat both EM and CT SERS will be presented. Thus, the quantities that have to be calculated in order to develop a computational tool able to simulate SERS spectra will be analyzed, highlighting the possible theoretical and computational issues that might arise.

4.3.1 EM+CT SERS as HORa Processes

Let's condsider the following Hamiltonian:

$$H = H_0^r + H_0^{el} + H_0^p + H_0^{pl} + H^{ep} + H^{er} + H^{epl} + H^{rpl} \tag{4.21}$$

Where H_0^r,H_0^{el},H_0^p and H_0^{pl} are the radiation field (Eq. 2.15), the equilibrium electronic Hamiltonian, the molecule phonon (Eq. 3.21) and the metal plasmon (Eq. 4.5) unperturbed Hamiltonians respectively. Moreover, H^{ep}, H^{er}, H^{epl} and H^{rpl} are the electon-phonon (Eq. 3.23), electron-radiation (Eq. 2.24), electron-plasmon (Eq. 4.9) and photon-plasmon (Eq. 4.6) interaction Hamiltonians. Starting from this, the perturbative time-dependent treatment of the plasmon-mediated Raman scattering of the analyte needs to be expanded up to the fifth-order. Let's now consider the possible molecule to surface interaction effects. In particular, let's assume that H_0^{el} can be split into a molecular (H_0^M) part, a surface (H_0^S) part and a coupling (H_0^{SM}) term between the molecule and the surface. Moreover, let us assume that H_0^p can be split in a phononic Hamiltonian for the surface $H_0^{p,S}$ and a phononic Hamiltonian for the molecule $H_0^{p,M}$ (this approximation can be reasonable in the weak-coupling regime). The discussion has nothing different with respect to that in Sec. 4.2. However, due to the fact that the plasmon-mediated processes reach the fifth-order in PT, also 2-phonon and 3-phonon processes need to be accounted. In the following figure (Fig.6) the set of Feynman diagrams related to the possible plasmon-molecule-surface scattering processes up to fifth order are reported:

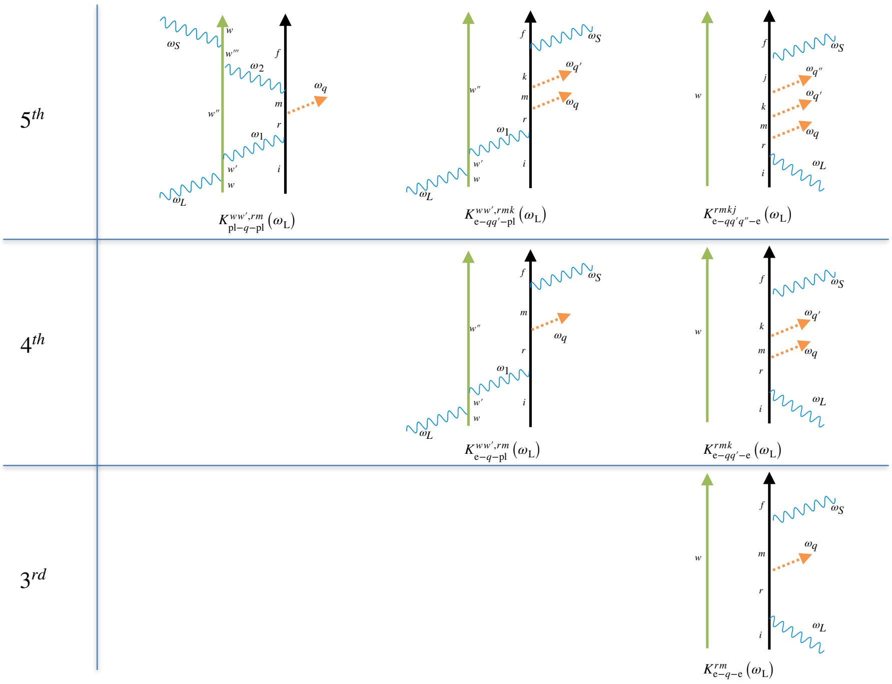


Figure 6: Representation of the possible processes involved in a SERS experiment under the approximations of the model presented so far. The processes are reordered according to the order they appear in the perturbative expansion. Time evolves from bottom to the top. The green line represents the plasmonic field and w, w', ... represent plasmonic states with excitation energy $\hbar\omega_{w'}$, $\hbar\omega_{w''}$ and so on. The black line represents the electronic system (molecule + surface) and r, k, m, j are zero-order Born-Oppenheimer states. The time permutation of the processes is not taken into account. Moreover 5^{th} order processes where phonons are both absorbed and emitted by the electronic system are not considered for simplicity, but their Feynman diagrams and scattering amplitudes are rather straightforward.

Where the scattering amplitudes will take the following form (only two amplitudes are reported):

$$K^{ww',rm}_{\text{pl}-q-\text{pl}}(\omega_\text{L}) = \frac{1}{\hbar^5}\frac{M^{ph-pl}_{w'w} M^{pl-e}_{ri,w''w'} M^{p-e}_{mr,q} M^{e-pl}_{fr,w'''w''} M^{pl-ph}_{ww'''}}{(\omega_{w'w}-\omega_L)(\omega_{ri}-\omega_1)(\omega_{mi}-\omega_L+\omega_q)(\omega_{fi}-\omega_L+\omega_q+\omega_2)} \tag{4.22}$$

$$K^{ww',rmk}_{\text{e}-qq'-\text{pl}}(\omega_\text{L}) = \frac{1}{\hbar^5}\frac{M^{e-ph}_{ri} M^{e-p}_{mr,q} M^{e-p}_{km,q'} M^{e-pl}_{fk,w'w} M^{pl-r}_{w''w'}}{(\omega_{ri}-\omega_L)(\omega_{mi}+\omega_q-\omega_L)(\omega_{km}+\omega_q+\omega_{q'}-\omega_L)(\omega_{fi}-\omega_L+\omega_q+\omega_{q'}+\omega_1)} \tag{4.23}$$

The term $K_{\text{e}-qq'-\text{pl}}$ indicates a process where the electronic system (surface + molecule) absorbs the radiation field photon, then two phonons q and q' are subsequently scattered and then the plasmon emits light (meaning that a virtual photon is exchanged between the electronic system and the metal-plasmon system).

4.3.2 Computational Feasibility and Complications

In order to develop a computational tool able to simulate such spectra we need to careful analyze the different quantities that need to be calculated. In order to evaluate the resonance conditions (the complex part of the denominator, i.e. the transition linewidths, were not taken into account for sake of simplifying the notation) the phonon energies, plasmon energies and electronic excitation energies need to be known. Ideally first principle calculations could be performed in order to determine the vibrational and electronic properties of the molecule-surface hybrid system. However, computational limitations arise immediately as the system of interest grows, tending to more realistic structures. Focused models such as QM/MM [20][21] can be used for estimating the electronic properties of the analyte, treating the surface as an embedding environment within the framework of molecular mechanics (MM). This approach disregards the electronic structure of the surface, leading to severe problems related to the estimation of the surface-molecule interaction matrix elements (Eq.3.23, Eq.2.24) and in the evaluation of the alignment of the molecule-surface energy levels. Regarding the plasmon, the $\mathbf{q}_w$ LSP eigenvectors need to be calculated. Many approaches such as modal-expansion discrete-dipole approximation [22] and boundary-elements method eigenmode expansion [23] may be used to obtain these eigenvectors. Another possible approach might make use of approximate molecular mechanics models such as the recently developed frequency-dependent fluctuating charges (ωFQ) [24] to reproduce the plasmonic response of complex nanostructures. This approach would fit perfectly in a focused treatment of the analyte within a QM/MM methodology, where the emebedding of the analyte takes into account both the surface and the plasmonic-metal. Within our model, the fact that the plasmonic material is not treated within an *ab-initio* methodology, shouldn't be such of a problem when evaluating interaction matrix elements (in contrast to the surface-molecule coupling terms), as far as the $\mathbf{q}_w$ eigenvectors are known and the quantity $\mathbf{G}_w(\mathbf{r})$ in Eq.4.10 can be calculated. However, it has to be considered that the Jellium model used by *Finazzi and Ciccacci* [19] to determine the quantized expression for the unperturbed plasmon Hamiltonian Eq.4.5, has its roots in the Drude model for metals and therefore it disregards possible interband transitions, i.e. the promotion of electrons from low lying bands to the conduction band. This effect should be more evident for laser frequencies in the visible to UV range. Unfortunately, the UV-Vis range is also the range in which electronic resonances usually fall and thus where CT-SERS effect might give a substantial contribution to the signal. Thus the model itself might show some deficiencies when the laser frequency is high enough to match band to band transitions. In addition to all of this, if the molecule and the surface interact in a stronger way, possible spilling of charge between the molecule and the surface might happen. This was not considered so far. Moreover, other complications might appear if the plasmonic-metal is also the surface on which the molecule is adsorbed and thus its electronic states contribute to the CT-SERS. In this case, indeed, a coupling between the plasmons and the normal mode of the surface is present, allowing the plasmon to decay [25]. A possible coupling with the normal modes of the molecule might therefore be present, opening different scattering channels. Another issue is the approximation of the nuclear Hamiltonian as a collection of harmonic oscillators. Although for classical Raman this can be an acceptable approximation, in HORa-SERS theory, where the perturbative terms reach the fifth-order and two and three phonon scattering events need to be considered (see Fig.6), this approximation can become rather crude and underestimate the intensity of certain scattering channels. A possible solution can be that of expanding the nuclear Hamiltonian to higher orders in the normal modes, thus including higher-order force constants (see for example Ref. [14] for a possible form of the Hamiltonian). Another problem with this model arises when the CT-substrate is a semiconductor. In this case excitonic effects can become relevant. Although a possible solution to this problem have been presented by *Lombardi et Al.* [26], up to my knowledge no effort has been done to include this effect within the HORa theory of SERS.

5 Conclusions

In conclusion, surface enhanced Raman spectroscopy (SERS) is a widely used experimental technique. Classically, the mechanisms for the enhancement are recognized to be a combination of electromagnetic (EM) and chemical (CT) mechanisms. Most recent theoretical models describe these processes as high-order Raman processes (HORa) within the framework of time-dependent perturbation theory (TDPT). Quantization of the radiation field is mandatory whereas the quantization of the localized surface plasmon and of the vibrational nuclear Hamiltonian result to be useful approximations in order to develop the theory. The possible scattering channels for both the EM and CT effects are highlighted and they involve a sequence of scattering events involving different particles/quasi-particles and electronic states owing either to the molecule or to the enhancing surface. The enhancement mechanisms are identified as resonance transitions among one of the scattering processes involved in a certain scattering channel. In this work, I tried to give a self-contained discussion of SERS as an HORa process within TDPT, trying moreover to suggest a way to unify the EM and CT theory within the same framework. The advantages of this modelling rely in the clarity of the physical processes involved and in the possibility of adding extra terms to the Hamiltonian (e.g. electron-2-phonons interaction terms) without compromising the theoretical framework (there is only the need of drawing extra Feynman diagrams and calculating extra quantities). However, many complications are present due to the intrinsic complexity of the physics of SERS but their possible solution go beyond the scope of this work.

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