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Full Quantum Theory of Molecular Hot-Electroluminescence in Scanning Tunneling Microscope Tunnel Junctions

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The pursuit of nanoscale photonics and molecular optoelectronics has stimulated a lot of interests in scanning tunneling microscope (STM) induced molecular emission. In this work, we have introduced a full quantum mechanical approach instead of the previous semiclassical theory to consider the quantized surface plasmon modes in this system. By considering the mutual interactions between a single molecule and the quantized surface plasmon, we have studied the molecular electroluminescence from STM tunnel junctions. Due to the coupling to the surface plasmons, the spontaneous emission rate and the fluorescence intensity of the molecule are both enormously enhanced. In particular, we show that when the radiative decay rate becomes comparable to the vibrational damping rate, hot-electroluminescence can be observed. All these findings are believed to be instructive for further developments of both molecular electronics and photonics.

Key words: Scanning tunneling microscope induced luminescence, Master equation, Surface plasmon, Hot-electroluminescence

I. INTRODUCTION

Due to its potential to offer insights into the transport and optical properties of the nanoscale system, much attention has been paid to the light emission from the tunnel junction of a scanning tunneling microscope (STM) over the last two decades. Ever since the first experimental report of the STM induced luminescence (STML) [1], extensive research has been carried out on the electroluminescence on metal surfaces [2, 3], nanoparticles [4], metallic quantum wells [5], *etc.*, and STM induced plasmon emission has now been well understood [6–10].

On the other hand, the pursuit of nanoscale molecular optoelectronics has stimulated a lot of interests in applying the STML technique to the study of molecular electroluminescence [11–15]. It's argued that if both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) lie inside the bias voltage window of the junction, the molecule can be effectively excited by the simultaneous tunneling of one electron into LUMO and the other out of HOMO [13].

The optical property of the molecular junction is

found to depend not only on the intrinsic electronic structure of the molecule, but also on its local nanocavity environment [16–18], and the mutual interaction between the single molecule and surface plasmon in STM induced molecular electroluminescence can never be overestimated. Essentially, in STM induced molecular emission, the plasmon, which acts as an efficient optical antenna [19], helps to transmit the light emission from the tunnel junction to far field. Besides fluorescence enhancement [20], plasmon also plays an important role in mode selection in the molecular electroluminescence [21, 22]. We have recently demonstrated experimentally that such profound modulation of molecular emission profiles by resonant plasmonic nanocavity can even generate the relaxationless hot luminescence (HL) from highly excited vibrational levels [22]. In a later theoretical treatment, molecular hot-luminescence has been explained based on Purcell effect [23], which states that the spontaneous emission rate of an electric dipole could be greatly enhanced in a resonant plasmonic nanocavity with high photon density of states, thus generating the anomalous HL without vibrational relaxation [21].

In our previous study the molecule is treated quantum mechanically using density matrix theory, while the contribution of the surface plasmon is calculated using classical electrodynamics [21]. However, it remains to be verified whether the results obtained by such semiclassical treatment is still valid in the full quantum me-

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chanical regime, *i.e.*, when the surface plasmon is also treated quantum mechanically. In this work, we have developed a full quantum theory to study the STM induced molecular emission and the peculiar HL phenomenon.

In this work, we introduce the theoretical framework of quantum master equation, taking into account of electron tunneling, electron-phonon interaction, plasmon-molecule coupling and various damping processes. Compared with previous study, surface plasmon is treated quantum mechanically, *i.e.*, in second-quantized form. Based on the numerical results of above theory, we mainly discuss the luminescence in STM induced molecular emission and the HL phenomenon.

II. THEORETICAL MODEL

The model molecule, represented by two electronic levels, *i.e.*, the HOMO and LUMO molecular states, is located in the electron tunnel junction with two metal leads. The model Hamiltonian for the system is composed of five parts corresponding to the leads, the molecule, surface plasmons, vacuum photons, and the interaction part.

$$\hat{H} = \hat{H}_{\text{lead}} + \hat{H}_{\text{mol}} + \hat{H}_{\text{sp}} + \hat{H}_{\text{ph}} + \hat{V} \quad (1)$$

The left and right leads are considered to be each in its own equilibrium, modeled with two free electron reservoirs which are characterized by corresponding electronic chemical potential μ_L and μ_R , $\mu_L - \mu_R = eV_b$ with V_b being the imposed bias voltage across the junction

$$\hat{H}_{\text{lead}} = \sum_{ik} \xi_{ik} \hat{c}_{ik}^\dagger \hat{c}_{ik} \quad (2)$$

here \hat{c}_{ik}^\dagger (\hat{c}_{ik}) corresponds to the creation (annihilation) operators for the electrons in lead i ($i=L, R$) with momentum k .

When both HOMO and LUMO lie within the bias window, the molecule can be electrically excited. The molecular states are composed of the electronic $|m\rangle$ and vibrational $|\nu\rangle$ part. As to the electronic wave function $|m\rangle$, it's sufficient to consider the ground state $|g\rangle$ and lowest excited state $|e\rangle$ for the molecule, the molecular Hamiltonian is

$$\hat{H}_{\text{mol}} = \sum_M \varepsilon_M |M\rangle \langle M| \quad (3)$$

where $|M\rangle = |m\rangle |\nu\rangle$ is the molecular state and $\varepsilon_M = \varepsilon_m + \nu \hbar \Omega_0$ is its corresponding energy, $\hbar \Omega_0$ and ν are respectively the vibrational energy and vibrational quantum numbers.

The Hamiltonian of the radiation field is

$$\hat{H}_{\text{ph}} = \sum_q \hbar \omega_q \hat{b}_q^\dagger \hat{b}_q \quad (4)$$

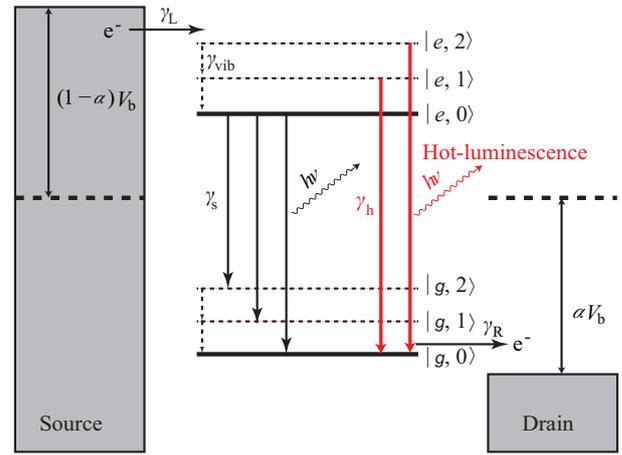


FIG. 1 Schematic diagram of the energy levels and various transition processes within the system formed by a molecule in a tunnel junction. $|g, \nu\rangle$ and $|e, \nu\rangle$ stands for the ground and excited electronic states respectively, with ν denoting the vibrational quantum number. γ_L (γ_R) is the bare tunneling rate of electrons between the molecule and the left (right) lead; γ_{vib} , γ_s , and γ_h are the vibrational damping, spontaneous emission, and hot-luminescence rate, respectively. In our simulations, we set $\gamma_L = \gamma_R = 10^{10} \text{ s}^{-1}$ and $\gamma_{\text{vib}} = 10^{12} \text{ s}^{-1}$, based on physically realistic tunneling currents ($\sim 100 \text{ pA}$) and picosecond vibrational lifetime for porphyrin molecules. The coupling coefficient is chosen to be $\alpha = 1/2$ [21].

where \hat{b}_q^\dagger (\hat{b}_q) corresponds to the creation (annihilation) operators for the vacuum photons.

Figure 1 is the schematic diagram of the energy levels and various transition processes within the system formed by a molecule in a tunnel junction. The interaction Hamiltonian can be further decomposed into three parts, *i.e.*, electron tunneling between the leads and the molecule \hat{V}_{tun} , plasmon-molecule interaction \hat{V}_{pm} , and the damping of the plasmon-molecule coupled system \hat{V}_{damp} . The tunneling Hamiltonian is trivially $\hat{V}_{\text{tun}} = \sum_{ikn} [t_{nk}^i \hat{d}_n^\dagger \hat{c}_{ik} + h.c.]$, where \hat{d}_n^\dagger (\hat{d}_n) is the creation (annihilation) operator for the electron in the n th ($n=1, 2$) molecular level with energy ε_n .

The interaction between the single molecule and the localized surface plasmon of the STM tunnel junction is calculated in the dipole approximation, $\hat{V}_{\text{pm}} = \hat{\mu}_m \cdot \hat{\mathbf{E}}_{\text{sp}}$, where $\hat{\mu}_m$ is the transition dipole momentum for the molecule and $\hat{\mathbf{E}}_{\text{sp}}$ is the plasmon local field operator. Define \hat{p}_0 as the bosonic operator corresponding to the single plasmon mode of the junction interacting with the molecular dipole, thus the plasmon-molecule interaction in the rotating wave approximation is

$$\hat{V}_{\text{pm}} = V_0(r) \hat{D}^\dagger \hat{p}_0 + h.c. \quad (5)$$

When the molecule is not very close to the metal surface, the plasmon excitations of the spherical metal nano-particles (MNP) can be restricted to dipole excitations, where the coupling ma-

trix is $V_0(r) = -2\mu_m \sqrt{\frac{\hbar\omega_{sp}}{2\epsilon_0 V_m}} \frac{R^3}{(R+d)^3}$ [20, 24], here $V_m = \frac{4}{3} \frac{2\epsilon_b + 1}{\epsilon_b + 1} \pi R^3$ is the mode volume of the quantized plasmon field, with R being the radius of the MNP, ϵ_b is the dielectric function of the surrounding environment, d is the distance between the MNP and the molecule. The interaction between the molecule and the multipole excitation of the spherical MNP can also be calculated straightforwardly if needed [25].

There are mainly two channels for the damping of the molecular and plasmonic excitation, *i.e.*, spontaneous emission and non-radiative decay with electron-hole pairs creation in the metal leads. The Hamiltonian for the damping is

$$\hat{V}_{\text{damp}} = \sum_q W_q \hat{D}^\dagger \hat{b}_q + \sum_{ikk'} V_{kk'}^i \hat{D}^\dagger \hat{c}_{ik}^\dagger \hat{c}_{ik'} + \sum_q \bar{W}_q \hat{p}_0^\dagger \hat{b}_q + \sum_{ikk'} \bar{V}_{kk'}^i \hat{p}_0^\dagger \hat{c}_{ik}^\dagger \hat{c}_{ik'} + h.c. \quad (6)$$

where $\hat{D}^\dagger = \hat{d}_2^\dagger \hat{d}_1$ is the creation operator for molecular excitation, W_q (\bar{W}_q) describes the coupling between the molecule (plasmon) and vacuum photon, $V_{kk'}^i$ ($\bar{V}_{kk'}^i$) describes the coupling between the molecule (plasmon) and electron-hole pair in the i th MNP, corresponding to the strength of the non-radiative decay.

The master equation describing the dynamics of the coupled plasmon-molecule system reads [21, 26–28],

$$\frac{d\rho}{dt} = \frac{1}{\hbar} [H_0 + V_{\text{pm}}, \rho] + (\mathcal{L}_{\text{tun}} + \mathcal{L}_{\text{damp}} + \mathcal{L}_{\text{deph}})\rho \quad (7)$$

where $H_0 = H_{\text{mol}} + H_{\text{sp}}$ is the free Hamiltonian for the molecule and the surface plasmon, $\rho = \rho_{\text{mol}} \otimes \rho_{\text{sp}}$ is the density operator for the plasmon-molecule coupled system. The eigenvector of the system is $|m, \nu, n\rangle$, with $m = g, e$ represents the ground and excited state of the molecule, ν is the vibrational number and n is the plasmon excitation number. Since the tunneling rate is much smaller compared with the various damping rates, for the plasmon-molecule coupled system, we will only consider the ground state $|g, \nu, 0\rangle$ and the singly excited state $|g, \nu, 1\rangle$ and $|e, \nu, 0\rangle$ [20]. The three Liouvillian operators describing different kinetic processes are detailed below.

The Liouvillian operator \mathcal{L}_{tun} accounts for the resonant electron tunneling between the molecule and the leads with the molecule excited or de-excited. Assuming this transition would only modify the population of the molecule, *i.e.*, the diagonal elements of the density matrix ρ_{mol} , while the population of the plasmon is unchanged, we thus have the rate equation form [21, 27, 28]

$$\mathcal{L}_{\text{tun}}\rho = - \sum_{ij} (\gamma_{i \rightarrow j}^{\text{tun}} \sigma_{ii} \rho \sigma_{ii} - \gamma_{j \rightarrow i}^{\text{tun}} \sigma_{ij} \rho \sigma_{ji}) \quad (8)$$

where $\gamma_{i \rightarrow j}^{\text{tun}}$ is the tunneling induced transition rate from the i th level of molecule to the j th level, σ_{ij} is a square

matrix of dimension $3N_{\text{vib}}$ with element (i, j) equals 1 while all other elements vanish; N_{vib} is the number of the vibrational levels for each electronic state.

The Liouvillian operator $\mathcal{L}_{\text{damp}}$ describing damping processes is decomposed into three parts: $\mathcal{L}_{\text{damp}} = \mathcal{L}_{\text{spon}} + \mathcal{L}_{\text{eh}} + \mathcal{L}_{\text{vib}}$, which accounts for spontaneous decay, non-radiative decay and vibrational relaxation, respectively. The damping of the electronic state has the Lindblad form [21, 26]

$$\mathcal{L}_{\text{spon,eh}}\rho = - \sum_{ij} \frac{1}{2} \gamma_{j \rightarrow i}^{\text{spon,eh}} (\sigma_{ji} \sigma_{ij} \rho - 2\sigma_{ij} \rho \sigma_{ji} + \rho \sigma_{ji} \sigma_{ij}) \quad (9)$$

where $\gamma_{j \rightarrow i}^{\text{spon,eh}}$ is the transition rate from j th to i th level for the spontaneous or non-radiative process for the molecule and plasmon. The damping of molecule and plasmon correspond to the transition $|e, \nu, 0\rangle \rightarrow |g, \nu', 0\rangle$ and $|g, \nu, 1\rangle \rightarrow |g, \nu, 0\rangle$ respectively.

The term \mathcal{L}_{vib} characterizing vibrational relaxations of the molecule can be written as [21, 29]

$$\mathcal{L}_{\text{vib}}\rho = -\gamma_{\text{vib}} \sum_i \left[\sigma_{ii} \rho \sigma_{ii} - \frac{e^{\left(\frac{-\hbar\omega_{\text{vib}}^i}{k_B T}\right)} \sum_j \sigma_{ij} \rho \sigma_{ji}}{\sum_k e^{\left(\frac{-\hbar\omega_{\text{vib}}^k}{k_B T}\right)}} \right] \quad (10)$$

where γ_{vib} is the vibrational relaxation rate, and the energy levels i, j and k should belong to the same electronic and plasmon state because the vibrational damping is an intraband transition.

The last Liouvillian term $\mathcal{L}_{\text{deph}}$ describes the dephasing of the interband coherence [26],

$$\mathcal{L}_{\text{deph}} = -\gamma_{\text{deph}} \sum_{ij} (\sigma_{ij} \rho_{ij} + \sigma_{ji} \rho_{ji}) \quad (11)$$

with $i = |g, \nu, 0\rangle$ and $j = |e, \nu', 0\rangle$ or $|g, \nu', 1\rangle$, corresponding respectively to the dephasing of the molecular or plasmonic density operator, γ_{deph} is the corresponding dephasing rate.

By solving Eq.(7) with the Liouvillian terms described above, we can obtain the steady state population of the molecule at dynamic equilibrium, then the spontaneous emission spectra can be simply described by Lorentzian function as [20, 21],

$$I(\omega) \propto \frac{\Gamma}{2\pi} \sum_{i \in g, j \in e} \frac{\gamma_{j \rightarrow i}^{\text{rad}} \rho_{jj}^s}{(\omega - \omega_{ji})^2 + (\Gamma/2)^2} \quad (12)$$

where Γ is the full width at half maximum of the molecular emission spectra, and ρ_{jj}^s is the steady state population of the molecular excited state. The effective radiative decay rate for the molecule

is $\gamma_{j \rightarrow i}^{\text{rad}} = \left[\gamma_{\text{m}}^{\text{spon}}(\omega_{ji}) + \frac{V_0^2 \gamma_{\text{sp}}^{\text{spon}}}{(\omega_{ji} - \omega_{\text{sp}})^2 + \gamma_{\text{sp}}^2/4} \right] |f_{\nu, \nu'}|^2$ with $f_{\nu, \nu'}$ the Franck-Condon factor between the ground and excited state of the molecule, $\gamma_{\text{m}}^{\text{spon}}$ and $\gamma_{\text{sp}}^{\text{spon}}$ the spontaneous emission rate of the molecule and plasmon in vacuum, γ_{sp} is the total damping (both radiative and non-radiative) rate of the surface plasmon.

III. RESULTS AND DISCUSSION

Near the metal surface, the electronic levels of the molecule are considerably broadened and the light emission is strongly quenched. Thus the STM induced molecular emission has been experimentally observed either from single molecule supported on an oxide film [12], or in a system with a multilayer of molecules with the bottom layers acting as a spacer [13, 22]. In this junction, the plasmon excitation induced by inelastic electron tunneling is largely suppressed due to increased distance between the two metal leads. We thus consider only the direct excitation of the molecule by the tunneling currents and have ignored the plasmon excitation by inelastic electron tunneling.

The transition dipole momentum of the molecule is typically $\mu_{\text{m}} \approx 1 \text{ e}\text{\AA}$ while the dipole momentum of the surface plasmon for a spherical MNP can be estimated as $\mu_{\text{sp}} = \sqrt{4\pi\epsilon_0 \hbar \omega_{\text{sp}} R^3}$ [9], which gives $\mu_{\text{sp}} \approx 1000 \text{ e}\text{\AA}$ for a MNP with radius $R \approx 30 \text{ nm}$. For an ideal point electric dipole μ_{m} in vacuum, the spontaneous decay rate is $\gamma_{\text{m}}^{\text{spon}}(\omega) = (\omega^3 \mu_{\text{m}}^2) / (3\pi \hbar \epsilon_0 c^3)$. To facilitate the comparison between different decay rates, we define the quantum efficiency as the ratio of the radiative decay rate to total decay rate $\eta(\omega) = \gamma_{\text{m}}^{\text{rad}}(\omega) / \gamma_{\text{m}}^{\text{tot}}(\omega)$. Close to the metal surface, the non-radiative decay rate of the molecule is many orders of magnitude larger than $\gamma_{\text{m}}^{\text{spon}}$, leading to very low quantum efficiency. However, the theory of cavity-QED shows that through coupling to plasmon, the spontaneous emission rate could be enhanced enormously [30]. The Purcell factor in the present system, defined as the ratio of the modified to unmodified spontaneous emission rate of the molecule, is $F_p = 1 + \frac{V_0^2 \gamma_{\text{sp}}^{\text{spon}}}{\gamma_{\text{m}}^{\text{spon}} [(\epsilon_0 - \omega_{\text{sp}})^2 + \gamma_{\text{sp}}^2/4]}$ [24]. Therefore

the surface plasmon plays a very important role in fluorescence intensity enhancement [20]. On resonance, the radiative decay rate can be enhanced by several orders of magnitude, estimated to be $\gamma_{\text{m}}^{\text{rad}} \approx 1.5 \times 10^{12} \text{ s}^{-1}$ according to the parameters used in this work, which enables the radiative process to occur on the timescale of picoseconds, thus becoming competitive to the vibrational relaxation. As have been shown using semi-classical theory in Ref.[21], such a large Purcell factor F_p may open up new emission channels to generate the hot luminescence that arises directly from higher vibronic levels of the molecular excited state. Here we show how this phenomenon can be explained using the

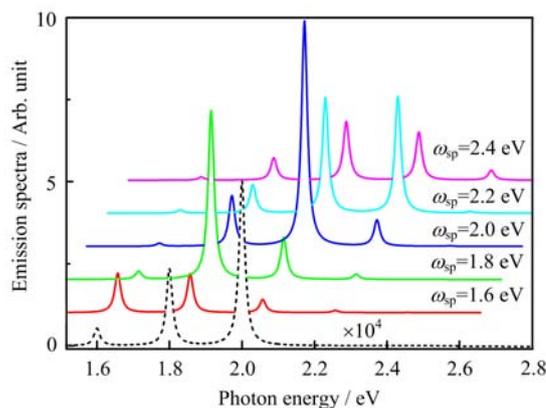


FIG. 2 Molecular electroluminescence spectra with variation of the surface plasmon energy. The solid curves from foreground to background correspond to plasmon energy $\omega_{\text{sp}} = 1.6, 1.8, 2.0, 2.2,$ and 2.4 eV , respectively. The foremost dashed curve shows the emission for a molecule decoupled from plasmon (amplified by a factor of 10^4). The molecular optical gap $\epsilon_0 = 2 \text{ eV}$, the vibrational energy $\Omega_0 = 0.2 \text{ eV}$, the plasmon-molecule interaction $V_0 = 0.02 \text{ eV}$, the bias voltage $V_b = 3.0 \text{ V}$, the nonradiative decay rate for the molecule and surface plasmon are set to be $\gamma_{\text{m}}^{\text{eh}} = 1 \text{ meV}$ and $\gamma_{\text{sp}}^{\text{eh}} = 0.2 \text{ eV}$ respectively.

full quantum theory developed in section II.

In addition to the enhancement of radiative decay rates, plasmon also plays an important role in mode selection in the molecular electroluminescence [21]. For a single molecule decoupled from plasmon, the relative intensities of the different emission channels are determined mainly by the bias voltage and Franck-Condon factors between the ground and excited state. In STM tunnel junctions, the relative intensities of molecular emission peaks can be further modified by the plasmon resonance conditions associated with the nanocavity configuration [21]. As shown in Fig.2, due to coupling to plasmon, the fluorescence intensity has been increased by some four orders of magnitude. We have thus clearly shown one of the critical role of surface plasmon in molecular electroluminescence, *i.e.*, fluorescence enhancement. Without coupling to surface plasmon the detection of the optical signal from a single molecule will be quite impractical if not impossible.

Besides large fluorescence intensity enhancement, the emission pattern of the molecule in the nanocavities deviates profoundly from that in vacuum [22]. Evidently, we can see that the relative intensities of these normal emission peaks are correlated with the quantum efficiencies, which are wavelength dependent, with the peak maximum corresponding to the plasmon frequency. More remarkably, when the surface plasmon is in resonance with the transition from higher vibrational excited states, some new peaks also appear with higher energies and can be identified as the HL. This is because their energies are higher than the zero-phonon line $(0, 0)$ and can only be obtained from the direct radiative

decay of the excited vibrational states $|e, \nu > 0, n\rangle$. In other words, the plasmon-molecule interaction will allow us to not only shape the spectral profile of molecular emissions, but also to generate the HL without vibrational relaxation. Thus we have shown that the previous explanations of the HL phenomenon based on semi-classical theory is also valid in the full quantum regime in which the surface plasmon is also treated quantum mechanically.

IV. CONCLUSION

We have used quantum master equation theory to study the light emission from the STM junction, in which the surface plasmon is also treated quantum mechanically. The effects of the surface plasmon on the molecular electroluminescence is discussed. Acting as an effective optical antenna, the plasmon can not only enhance the intensity of the molecular fluorescence, but also tune the emission pattern and generate the anomalous hot-electroluminescence via the Purcell effect. All these findings are believed to be instructive for further developments of both molecular electronics and photonics.

V. ACKNOWLEDGMENTS

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