Supplementary Information for manuscript titled "Spontaneous light emission from molecular junctions: Theoretical analysis of up-conversion signal"

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The Liouville space algebraic expression for the current-induced fluorescence can be written down readily[1] from the double-sided diagram shown in Fig. (1a). We get,

$$S^{(1)}(\omega_s) = \frac{1}{\hbar^4}\text{Re}\sum_{i\alpha}|T_{i\alpha}|^2\int_{-\infty}^{t}d\tau\,\mathrm{e}^{-i\omega_s(t-\tau)}\int_{-\infty}^{\tau}d\tau_1\int_{-\infty}^{\tau}d\tau_2\mathrm{e}^{\frac{i}{\hbar}\epsilon_\alpha(\tau_2-\tau_1)}f_\alpha(\epsilon_\alpha)\langle\hat{T}\hat{\mu}_{sR}^\dagger(t)\hat{\mu}_{sL}(\tau)\hat{c}_{iL}^\dagger(\tau_1)\hat{c}_{iR}(\tau_2)\rangle \quad ($$

where the electron is created due to the interaction with αth lead. Note that the relative time-ordering in the first two operators at τ_1 and τ_2 is irrelevant as they act on different branches. It is straightforward to write down the corresponding Hilbert space expression. After inserting the molecular many-body states and performing the time integrals, we obtain,

$$S^{(1)}(\omega_s) = \frac{\gamma}{\hbar}\sum_{i\alpha}\sum_{a'e'}|T_{i\alpha}|^2\frac{|\langle a|c_i|e'\rangle\langle e'|\mu_s^\dagger|a'\rangle|^2 f_\alpha(\epsilon_\alpha)}{[(\hbar\omega_s - E_{e'a'})^2 + \gamma^2][(\epsilon_\alpha - \hbar\omega_s - E_{a'a})^2 + \Gamma^2]} \quad (2)$$

where Γ and γ are the life-times of the $a \to e'$ and $e' \to a'$ excitations, and $E_{e'a'} = E_{e'} - E_{a'}$ is the energy difference between the anionic excited and (lower energy) ground states, $|e'\rangle$ and $|a'\rangle$, respectively, and the first Lorentzian with width γ in (2) is to make sure that the correct a' and e' states are picked up from the sum. This fact has been used above to replace $E_{e'a'}$ by $\hbar\omega_s$ in the second Lorentzian. Sum over the lead states α can be converted to integration by introducing lead density of states $\rho_\alpha(\epsilon_\alpha)$. Taking small temperature limit such that $f_\alpha(\epsilon_\alpha) = \Theta(\epsilon_\alpha - E_F - eV)$ and performing the integral over the lead energies, ϵ_α, we obtain the results given in Eq. (5).

Similarly, for the EL process depicted in Fig. (1b), we obtain the following expression in terms of the Liouville space correlation function.

$$
\begin{aligned}
S^{(2)}(\omega_s) &= -\frac{1}{12\hbar^6} \mathrm{Re} \sum_{ii'} \sum_{\alpha\beta} |T_{i\alpha}|^2 |T_{i'\beta}|^2 \int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\tau_1 \int_{-\infty}^{\tau} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3 \int_{-\infty}^{\tau_1} d\tau_4 \\
&\quad \mathrm{e}^{i\omega_s(\tau-t)} \mathrm{e}^{\frac{i}{\hbar}\epsilon_\alpha(\tau_2-\tau_1)} \mathrm{e}^{\frac{i}{\hbar}\epsilon_\beta(\tau_4-\tau_3)} f_\alpha(\epsilon_\alpha)(1 - f_\beta(\epsilon_\beta)) \langle \hat{T} \hat{\mu}_{sR}^\dagger(t) \hat{\mu}_{sL}(\tau) \hat{c}_{iR}(\tau_2) \hat{c}_{iL}^\dagger(\tau_1) \hat{c}_{i'L}(\tau_4) \hat{c}_{i'R}^\dagger(\tau_3) \rangle
\end{aligned}
\tag{3}
$$

where $\alpha \neq \beta$. Again, it is straightforward to write down the corresponding Hilbert space expression and then inserting the molecular many-body states as depicted in the diagram and leads to

$$
\begin{aligned}
S^{(2)}(\omega_s) &= -\frac{1}{12\hbar^5} \mathrm{Re} \sum_{ii'} \sum_{\alpha\beta} |T_{i\alpha}|^2 |T_{i'\beta}|^2 f_\alpha(\epsilon_\alpha)(1 - f_\beta(\epsilon_\beta)) |\langle a|\hat{c}_{i'}^\dagger|e''\rangle \langle e''|\hat{c}_i|e\rangle \langle e|\hat{\mu}_s^\dagger|a\rangle|^2 \delta(\hbar\omega_s - E_{ea}) \\
&\quad \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \int_0^\infty d\tau_4 \mathrm{e}^{\frac{i}{\hbar}(\epsilon_\alpha-\epsilon_\beta-E_{ea})(\tau_1-\tau_2)} \mathrm{e}^{\frac{i}{\hbar}(\epsilon_\beta - E_{ae''})(\tau_3-\tau_4)}
\end{aligned}
\tag{4}
$$

Straightforward integration over times and replacing sum over lead energies we obtain,

$$
S^{(2)}(\omega_s) = \frac{\gamma}{12\hbar} \sum_{ii'ee''} \frac{\rho_\alpha\rho_\beta |T_{i\alpha}T_{i'\beta}|^2}{(\hbar\omega_s - E_{ea})^2 + \gamma^2} \int d\epsilon \int d\epsilon' \left| \frac{\langle a|c_{i'}|e''\rangle \langle e''|c_i|e\rangle \langle e|\mu^\dagger|a\rangle}{(\epsilon - \epsilon' - \hbar\omega_s - i\Gamma_{ae})(\epsilon' + E_{e''a} - i\Gamma_{e''a})} \right|^2 f_\alpha(\epsilon)(1 - f_\beta(\epsilon'
$$

In order to perform energy integrals, we assume small Γ_{ae} limit and then taking small temperature limit, such that the Fermi functions become heavy-side function and $\mu_\alpha = eV$

and $\mu_\beta = 0$, we obtain the result given in Eq. (6).

Green function result

When the self-energy matrix, Γ, is not diagonal, that is, when the coherences between the molecular orbitals induced by the leads are not negligible, Green functions are not diagonal in the molecular orbital basis. For this case, $G^{RL}(\omega)$ and $G^{LR}(\omega)$ for a non-interacting system at steady-state and within the wide band approximation can be expressed in matrix form as,

$$G^{RL}(\omega) = -i \sum_{\alpha=L,R} [1 - f_\alpha(\omega)] G^r(\omega) \mathcal{S}_\alpha G^a(\omega) \tag{6}$$

$$G^{LR}(\omega) = i \sum_{\alpha=L,R} f_\alpha(\omega) G^r(\omega) \mathcal{S}_\alpha G^a(\omega) \tag{7}$$

where $f_\alpha(\omega) = \left(e^{\beta(\omega - \mu_\alpha)} + 1 \right)^{-1}$ are the Fermi functions of the reservoirs and $\mathcal{S}_\alpha$ is the self-energy matrix due to coupling to the αth lead. $G^{r/a}(\omega)$ are the retarded/advanced Green functions of the molecule under the influence of the leads given as,

$$G^r(\omega) = G^a(\omega)^\dagger = \left[\omega \mathcal{I} - H_{sys} + \frac{i}{2} \sum_{\alpha=L,R} \mathcal{S}_\alpha \right]^{-1} \tag{8}$$

with $\left[H_{sys} \right]_{ij} = \xi_i \delta_{ij}$ and $[\mathcal{S}_\alpha]_{ij} = 2\pi \rho_\alpha T_{i\alpha}^* T_{j\alpha}$. $G^r(\omega)$ can be expressed in quasi-diagonal form using the right ($|R_n\rangle$) and the left ($\langle L_n|$) eigenstates corresponding to the nth eigenvalue, γ_n, of the non-hermitian operator $H_{sys} - \frac{i}{2} \sum_{\alpha=L,R} \mathcal{S}_\alpha$. This gives,

$$G^r(\omega) = \sum_n \frac{|R_n\rangle \langle L_n|}{\omega - \gamma_n}. \tag{9}$$

Substituting this in (6), we obtain,

$$G^{RL}(\omega) = -i \sum_{\alpha=L,R} \sum_{mn} (1 - f_\alpha(\omega)) |R_n\rangle \frac{\langle L_n|\mathcal{S}_\alpha|L_m\rangle}{(\omega - \gamma_n)(\omega - \gamma_m^*)} \langle R_m| \tag{10}$$

$$G^{LR}(\omega) = i \sum_{\alpha=L,R} \sum_{mn} f_\alpha(\omega) |R_n\rangle \frac{\langle L_n|\mathcal{S}_\alpha|L_m\rangle}{(\omega - \gamma_n)(\omega - \gamma_m^*)} \langle R_m| \tag{11}$$

Using the above expressions for $G^{LR}(\omega)$ and $G^{RL}(\omega)$ in the equation for signal given in Eq. (11) and performing ω integral using Cauchy's residue method[2] gives,

$$S(\omega_s) = \frac{2}{\pi} \sum_{\alpha,\beta=L,R} n_{\alpha\beta}(\omega_s) \Re \left\{ \sum_{n,m,k,l} \left[\frac{\langle L_n|\mathcal{S}_\alpha|L_m\rangle \langle R_m|\mu^\dagger|R_k\rangle \langle L_k|\mathcal{S}_\beta|L_l\rangle \langle R_l|\mu|R_n\rangle}{(\omega_s + \gamma_n - \gamma_k)} \right] \times \right.$$
$$\left. \left[\frac{\Psi\left[\frac{1}{2} + i\frac{\beta(\gamma_n - \mu_\alpha)}{2\pi}\right] - \Psi\left[\frac{1}{2} + i\frac{\beta(\gamma_n - \mu_\beta + \omega_s)}{2\pi}\right]}{(\gamma_n - \gamma_m^*)(\omega_s + \gamma_n - \gamma_l^*)} + \frac{\Psi\left[\frac{1}{2} + i\frac{\beta(\gamma_k - \mu_\alpha - \omega_s)}{2\pi}\right] - \Psi\left[\frac{1}{2} + i\frac{\beta(\gamma_k - \mu_\beta)}{2\pi}\right]}{(\gamma_k - \gamma_l^*)(\omega_s - \gamma_k + \gamma_m^*)} \right] \right\} \tag{12}$$

where $n_{\alpha\beta}(\omega_s) = \left(e^{\beta(\mu_\alpha - \mu_\beta + \hbar\omega)} - 1\right)^{-1}$ is the Bose-Einstein distribution function, $\Psi[Z]$ is the digamma function[3] and $[\mu]_{ij} = \Theta[\epsilon_i - \epsilon_j]V_{ij}$.

References

References

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