

Energy, Particle, and Photon Fluxes in Molecular Junctions

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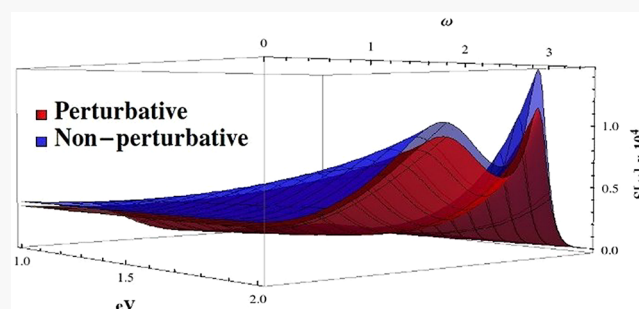
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ABSTRACT: Electroluminescence from a current-carrying molecular junction at steady state is simulated. (Charge) particle conservation and energy conservation are satisfied by a perturbative expansion in the radiation/matter coupling. Our approach makes it possible to adopt standard tools of traditional (equilibrium) spectroscopy to study signals from open systems such as molecular junctions. The nonperturbative analysis of spontaneous light emission signals coincides with the perturbative approach for weak molecule–field coupling.



Spectroscopy is undoubtedly the most widely used technique for probing the dynamics of atomic and molecular systems over a broad range of time scales.¹ With the recent development of attosecond (10^{-18} s) pulses, spectroscopic methods can probe elementary electron dynamics in atoms and molecules.^{2–5} Perturbative expansion in radiation–matter coupling provides order-by-order insight into the underlying physical processes. Nonequilibrium open quantum systems, such as current-carrying molecular junctions, have been extensively studied.^{6–8} A molecular junction is a quantum system which facilitates the transport of both particles (electrons) and energy across the two junction boundaries. At nonequilibrium steady state, the particle flux must be the same at the two boundaries and the energy flux into each (electronic and photonic) degree of freedom must be balanced. This is known as flux conservation.

The optical response of molecular junctions has been measured^{9,10} and studied theoretically with both perturbative^{11–13} and nonperturbative techniques.⁸ In particular, current-induced spontaneous emission from molecular junctions, known as electroluminescence, has been of interest^{14–21} due to its applications to optoelectronic devices and in understanding the fundamental physics of light–matter interaction in nonequilibrium systems.

A self-consistent nonperturbative expansion in the radiation–matter coupling has been proposed to maintain flux conservation.²² This requires solving self-consistently a set of coupled equations for the electronic and radiation field degrees of freedom. It has been argued that this is necessary to take care of the mutual back action of the molecule on the radiation field, especially in the case of spontaneous emission signals which represent coupled quantum systems. A flux-conserving perturbative scheme for optical signals should allow a simpler interpretation of optical processes. Flux conservation is related to the continuity relation connecting population and energy

change in the molecule to the particle and heat fluxes at the two boundaries, respectively. If the fluxes are analytic functions of the perturbation, then the continuity relation must hold order-by-order in the perturbative expansion. For strong radiation–matter coupling, this analytic nature of the fluxes may be lost, leading to a qualitative change in the response of the system as shown recently.²³

In this work, we show that a simple a perturbative expansion in the coupling to the radiation field keeps the radiation degrees of freedom unperturbed by coupling to the molecule. The analytic spontaneous light emission signal from a molecular junction calculated perturbatively satisfies flux conservation without using the more elaborate self-consistent scheme.⁸

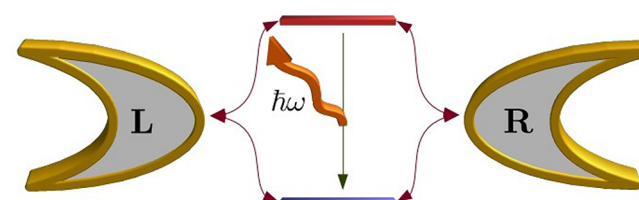


Figure 1. Schematic of a molecular junction with two metal leads at chemical potentials μ_L and μ_R . A photon of frequency ω is generated due to radiative relaxation of the molecule excited by tunneling electrons across the junction.

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We consider a molecular junction where a molecule is coupled to two metal leads and the radiation field as shown in Figure 1. The system is described by the Hamiltonian

$$H = \sum_{i \in M} \epsilon_i \hat{c}_i^\dagger \hat{c}_i + \sum_{\alpha=L,R} \sum_{k \in \alpha} \epsilon_{ak} \hat{a}_{ak}^\dagger \hat{a}_{ak} + \sum_{s \in V} \hbar \omega_s \hat{a}_s^\dagger \hat{a}_s + \sum_{\alpha=L,R} \sum_{k \in \alpha} \sum_{i \in M} [T_{aki} \hat{c}_i^\dagger \hat{a}_{ak} + T_{aki}^* \hat{a}_{ak}^\dagger \hat{c}_i] + \sum_{s \in V} [\hat{\mu}_s^\dagger \hat{a}_s + \hat{\mu}_s \hat{a}_s^\dagger] \quad (1)$$

where $\hat{\mu}_s = \sum_{i,j \in M, \epsilon_i > \epsilon_j} \mu_{ji}^s \hat{c}_j^\dagger \hat{c}_i$ represents the molecular dipole operator. Fermi operators \hat{c}_i (\hat{c}_i^\dagger) and \hat{a}_{ak} (\hat{a}_{ak}^\dagger) represent the destruction (creation) of an electron in the i th molecular (M) single-particle state and k th state in the α th lead, respectively. Boson operators \hat{a}_s (\hat{a}_s^\dagger) represent the destruction (creation) of a photon in the s th vacuum (V) field mode. The first three terms in eq 1 represent the isolated molecule, the leads ($\alpha = L$ for the left lead and $\alpha = R$ for the right lead), and the field modes. The last two terms represent the coupling of the molecule with the leads and the field, respectively.

We shall consider three fluxes: the particle (I_α) and energy (J_α) fluxes between the molecule and the two (left and right) leads

$$I_\alpha(t) = \sum_{k \in \alpha} \frac{d}{dt} \langle \hat{a}_{ak}^\dagger(t) \hat{a}_{ak}(t) \rangle$$

$$J_\alpha(t) = \sum_{k \in \alpha} \frac{d}{dt} \epsilon_{ak} \langle \hat{a}_{ak}^\dagger(t) \hat{a}_{ak}(t) \rangle \quad (2)$$

and the energy flux into the radiation field modes

$$S(t) = \sum_{s \in V} \hbar \omega_s \frac{d}{dt} \langle \hat{a}_s^\dagger(t) \hat{a}_s(t) \rangle \quad (3)$$

At steady state, these fluxes are time-independent and can be represented in terms of the Keldysh Green functions²⁵ for the molecule and the field subsystems. For the particle and energy currents in the leads, one obtains

$$I_\alpha(n) = \int \frac{d\omega}{2\pi} (\hbar\omega)^n \text{Tr}[\Sigma_\alpha^>(\omega) G^<(\omega) - \Sigma_\alpha^<(\omega) G^>(\omega)] \quad (4)$$

where $I_\alpha = I_\alpha(n=0)$ and $J_\alpha = I_\alpha(n=1)$. $G^>$ and $G^<$ are the greater and lesser matrix projections²⁵ of the molecular Green function $G_{ij}(\tau, \tau') = (-i/\hbar) \langle T \hat{c}_i(\tau) \hat{c}_j^\dagger(\tau') \rangle$ where times τ and τ' are defined on the Keldysh contour. $\Sigma^>$ and $\Sigma^<$ denote the corresponding projections of the self-energy due to interactions with the left/right lead, and Tr denotes a matrix trace in the molecular orbital basis. The molecular Green function contains interactions with the leads and the radiation field. These interactions are incorporated through the self-energies in the Dyson equations, which in the frequency domain at steady state are given by²⁵

$$G^{r/a}(\omega) = G_0^{r/a}(\omega) + G_0^{r/a}(\omega) \tilde{\Sigma}^{r/a} G^{r/a}(\omega) \quad (5)$$

$$G^<(\omega) = G^r(\omega) [\Sigma^<(\omega) + \tilde{\Sigma}^<(\omega)] G^a(\omega) \quad (6)$$

$$G^>(\omega) = G^r(\omega) [\Sigma^>(\omega) + \tilde{\Sigma}^>(\omega)] G^a(\omega) \quad (7)$$

where $\Sigma = \sum_\alpha \Sigma_\alpha$ and $G^{</>}$ and $G^{r/a}$ are lesser/greater and retarded/advanced Green functions. G_0 is defined without the field interaction, and thus $\tilde{\Sigma}$ is the self-energy due to interaction with the radiation field. In the lowest-order diagram,²⁴ we have

$$\tilde{\Sigma}^{</>}(t, t') = i\hbar \sum_{s, s' \in V} [D_{ss'}^{</>}(t, t') \mu^{s\dagger} G^{</>}(t, t') \mu^{s'} + D_{s's}^{>/<}(t', t) \mu^s G^{>/<}(t, t') \mu^{s\dagger}] \quad (8)$$

where $D_{ss'}(t, t')$ denotes the field propagator which satisfies its own Dyson equation on the Keldysh loop. Its projection to real time is given by equations similar to eqs 5–7 with $G(G_0)$ replaced by $D(D_0)$, $\Sigma = 0$, and $\tilde{\Sigma}$ by a self-energy representing back action of the molecule in the field mode. Since we are interested in perturbative results for the lowest-order interaction with the field (higher-order terms can be generated in a similar fashion as for the lowest order), we need only D_0 and ignore the back action in field mode.

An exact expression for the energy flux (S) can be recast in terms of greater and lesser projections of the dipole–dipole correlation, $\mathcal{G}_{ss'}(\tau, \tau') = (-i/\hbar) \langle T \hat{\mu}_s(\tau) \hat{\mu}_{s'}^\dagger(\tau') \rangle$, and the free-field propagator, $D_0(\tau, \tau')$. This gives

$$S = \sum_{s \in V} \hbar \omega_s \int \frac{d\omega}{2\pi} [\mathcal{G}_{ss}^>(\omega) D_{0s}^<(\omega) - \mathcal{G}_{ss}^<(\omega) D_{0s}^>(\omega)] \quad (9)$$

One can write a closed set of exact equations for $\mathcal{G}_{ss}(\omega)$ in terms of its self-energy which can be expressed in terms of the derivative of $\tilde{\Sigma}(\tau, \tau')$ with respect to $G(\tau, \tau')$ using a Bethe–Salpeter-type expansion.²⁶ However, for our purposes we retain the first term of the expansion, which allows us to replace

$$\mathcal{G}_{ss}^{</>}(t, t') = -i\hbar \sum_{i,j \in M} \sum_{i',j' \in M} \sum_{\epsilon_i > \epsilon_j} \sum_{\epsilon_{i'} > \epsilon_{j'}} G_{ii'}^{</>}(t, t') \mu_{ij'}^{s\dagger} G_{jj'}^{>/<}(t', t) \mu_{ij}^{ss*}$$

Substituting this into eq 9 and using $D_{0s}^<(\omega) = (-2\pi i/\hbar) n(\omega) \delta(\omega - \omega_s)$ and $D_{0s}^>(\omega) = (-2\pi i/\hbar) (1+n(\omega)) \delta(\omega - \omega_s)$, where $n(\omega) = (e^{\hbar\omega/(k_B T)} - 1)^{-1}$ is the boson occupation factor, we obtain for the energy flux into the field mode

$$S = \sum_{s \in V} \hbar \omega_s \int \frac{d\omega}{2\pi} \text{Tr}[(1+n(\omega_s)) G^>(\omega) \mu^s G^<(\omega + \omega_s) \mu^{s\dagger} - n(\omega_s) G^<(\omega) \mu^s G^>(\omega + \omega_s) \mu^{s\dagger}] \quad (10)$$

where $G^<$ and $G^>$ are the molecular Green functions which contain interactions with the leads and the field modes.

Equations 4 and 10 with eqs 5–8, together with similar equations for D , constitute a closed set of coupled equations which need to be solved self-consistently in order to compute the particle and energy fluxes. Below we show that a perturbative calculation of S in the molecule–field coupling is consistent with perturbative results for energy and particle currents and satisfies the flux conservation. To lowest order in the interaction with the radiation field, the energy flux S can be obtained by replacing G with G_0 , defined in eq 5, in eq 10. Furthermore, for spontaneous energy flux $n(\omega_s) = 0$ and to lowest order in the radiation/matter coupling, we obtain

$$S = \sum_{s \in V} \hbar \omega_s \int \frac{d\omega}{2\pi} \text{Tr}\{G_0^>(\omega) \mu^s G_0^<(\omega + \omega_s) \mu^{s\dagger}\} \quad (11)$$

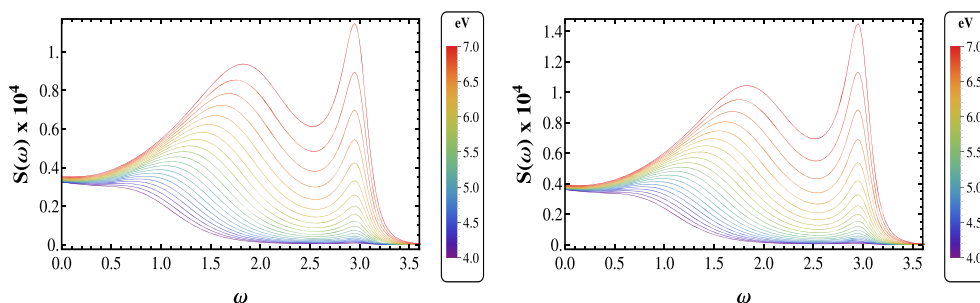


Figure 3. Optical signal $S(\omega)$ at inverse temperature $\beta = 5.0$ for different values of applied bias (eV). The left figure is the signal obtained using a perturbative approach, and the right figure is that obtained using a nonperturbative self-consistent approach.

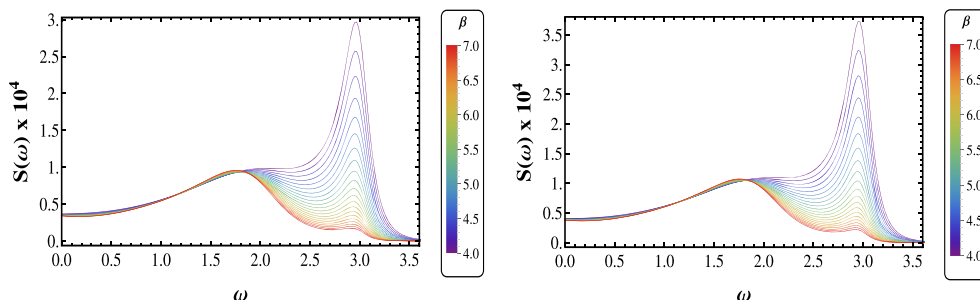


Figure 4. Optical signal $S(\omega)$ at applied bias eV = 2.0 for different values of the lead temperatures (β). The left figure shows the signal obtained using the perturbative approach, and the right figure is that obtained using the nonperturbative self-consistent approach.

where $S(\omega_s)$ is the photon flux in field mode ω_s , which is identified as the spontaneous spectroscopic signal intensity at frequency ω_s and was employed recently¹³ to compute the electroluminescence from a molecular junction.

Model Calculations. We consider a two-level system to compare the lowest-order perturbative results, as discussed above, with a fully self-consistent result where the molecular Green function is renormalized within the first-order Born approximation. Both levels are coupled to the two leads. The corresponding self-energy is given in eq 8. We solve eq 5 self-consistently and compute the left and the right particle and energy currents using eq 4 along with the energy flux into the field reservoir using eq 10.

On the left side of Figure 2, we show the particle current at the left interface with and without the self-consistent calculation for weak coupling to the field modes. The two results are in good agreement. On the right side of Figure 2, we show the energy fluxes, $J_{L/R}$, at the two interfaces of the junction. The results for the energy flux with and without perturbation are virtually the same and indistinguishable in the figure. Finally, in Figures 3 and 4, we show the energy-resolved photon flux (optical signal) with and without self-consistency in the coupling to the field. The two results agree well.

To conclude, we have shown that perturbation theory in the coupling between the molecule and the radiation field for computing energy and particle fluxes in molecular junctions satisfies both particle and energy conservation. Perturbative techniques are widely used to compute spectroscopic signals in closed systems at equilibrium. The present work generalizes it to compute spectroscopy signals in open nonequilibrium systems.

APPENDIX

Here we derive eq 15 starting from eq 14 for the general case in which Green functions are not diagonal. Using identity $G^r - G^a = G^> - G^<$ with eqs 6 and 7, we can write

$$G^> - G^< = G^r(\Sigma^> - \Sigma^<)G^a = G^a(\Sigma^> - \Sigma^<)G^r \quad (20)$$

Using the above identity, we can write

$$\begin{aligned} \text{Tr}[\Sigma^>G_0^r\tilde{\Sigma}_0^<G_0^a] &= \text{Tr}[(G_0^> - G_0^< + G_0^a\Sigma^<G_0^r)\tilde{\Sigma}_0^<] \\ \text{Tr}[\Sigma^<G_0^r\tilde{\Sigma}_0^>G_0^a] &= \text{Tr}[(G_0^< - G_0^> + G_0^a\Sigma^>G_0^r)\tilde{\Sigma}_0^>] \end{aligned} \quad (21)$$

Subtracting eqs 21 and using the identity (eq 20), we get

$$\begin{aligned} \text{Tr}[\Sigma^>G_0^r\tilde{\Sigma}_0^<G_0^a - \Sigma^<G_0^r\tilde{\Sigma}_0^>G_0^a] &= \text{Tr}[G_0^>\tilde{\Sigma}_0^< - G_0^<\tilde{\Sigma}_0^>] \\ &+ \text{Tr}[(G_0^a\Sigma^<G_0^r - G_0^<)(\tilde{\Sigma}_0^a - \tilde{\Sigma}_0^r)] \end{aligned} \quad (22)$$

Substituting eq 22 into eq 14, we obtain

$$\begin{aligned} I_L^1(n) + I_R^1(n) &= \int \frac{d\omega}{2\pi} (\hbar\omega)^n \text{Tr}[G_0^>\tilde{\Sigma}_0^< - G_0^<\tilde{\Sigma}_0^>] \\ &+ \int \frac{d\omega}{2\pi} (\hbar\omega)^n \text{Tr}[\{G_0^a\Sigma^<(G_0^a - G_0^<) - G_0^< \\ &+ G_0^a\Sigma^>G_0^<\}\tilde{\Sigma}_0^a] \\ &- \text{Tr}[\{(G_0^a + G_0^>)\Sigma^<G_0^r - G_0^< - G_0^<\Sigma^<G_0^r\}\tilde{\Sigma}_0^r] \end{aligned} \quad (23)$$

Consider the first trace in the second integral above. Using $G^< = G^r\Sigma^<G^a$, the quantity inside the trace can be rearranged as follows

$$\begin{aligned} &\{G_0^a\Sigma^<(G_0^a - G_0^<) - G_0^< + G_0^a\Sigma^>G_0^<\}\tilde{\Sigma}_0^a \\ &= \{G_0^< - G_0^> + G_0^a(\Sigma^> - \Sigma^<)G_0^r\}\Sigma^<G_0^a\tilde{\Sigma}_0^a \\ &= 0 \end{aligned} \quad (24)$$

where the last equality is due to eq 20. Similarly, for the second trace we have

$$\begin{aligned}
& \{(G_0^a + G_0^>) \Sigma^< G_0^r - G_0^< - G_0^< \Sigma^< G_0^r\} \tilde{\Sigma}_0^r \\
&= \{(G_0^r + G_0^<) \Sigma^< G_0^r - G_0^< - G_0^< \Sigma^< G_0^r\} \tilde{\Sigma}_0^r \\
&= \{G_0^r \Sigma^< G_0^r - G_0^< (\Sigma^> - \Sigma^<) G_0^r - G_0^< \} \tilde{\Sigma}_0^r \\
&= \{G_0^r \Sigma^< (G_0^> - G_0^<) - G_0^r \Sigma^< G_0^a (\Sigma^> - \Sigma^<) G_0^r\} \tilde{\Sigma}_0^r \\
&= G_0^r \Sigma^< \{G_0^> - G_0^< - G_0^a \Sigma^> G_0^r + G_0^a \Sigma^< G_0^r\} \tilde{\Sigma}_0^r \\
&= 0
\end{aligned} \tag{25}$$

where in going from the second to the third equality we have used $G_0^< = G_0^r \Sigma^< G_0^a$, and the last equality follows from eq 20.

Thus, the second integral in eq 23 vanishes identically, and we recover eq 15.

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Notes

The authors declare no competing financial interest.

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