

13.3: Semiclassical Approximation to the Dipole Correlation Function

In introducing the influence of dark degrees of freedom on the spectroscopy of a bright state, we made some approximations that are not always valid, such as the *Condon approximation* and the *Second Cumulant Approximation*. To develop tools that allow us to work outside of these approximations, it is worth revisiting the evaluation of the dipole correlation function and looking at this a bit more carefully. In particular, we will describe the semiclassical approximation, which is a useful representation of the dipole correlation function when one wants to describe the dark degrees of freedom (the bath) using classical molecular dynamics simulations.

For a quantum mechanical material system interacting with a light field, the full Hamiltonian is

$$H = H_0 + V(t) \quad (13.3.1)$$

$$V(t) = -\bar{m} \cdot \bar{E}(t) \quad (13.3.2)$$

$\bar{m} = \sum_i z_i \bar{r}_i$ is the quantum mechanical dipole operator, where z_i are charges. The absorption lineshape is given by the Fourier transformation of the dipole autocorrelation function $C_{\mu\mu}$:

$$C_{\mu\mu}(\tau) = \langle \bar{m}(t) \bar{m}(0) \rangle = \text{Tr}(\rho_{eq} \bar{m}(t) \bar{m}(0)) \quad (13.3.3)$$

and the time dependence in \bar{m} is expressed in terms of the usual time-propagator:

$$\bar{m}(t) = \hat{U}_0^\dagger \bar{m} \hat{U}_0 \quad (13.3.4)$$

$$\hat{U}_0 = e^{-\frac{i}{\hbar} \int_0^t H_0(t) dt} \quad (13.3.5)$$

In principle, the time development of the dipole moment for all degrees of freedom can be obtained directly from *ab initio* molecular dynamics simulations.

For a more practical expression in which we wish to focus on one or a few bright degrees of freedom, we next partition the Hamiltonian into system and bath

$$H_0 = H_S(Q) + H_B(q) + H_{sb}(Q, q) \quad (13.3.6)$$

For purposes of spectroscopy, the system H_S refers to those degrees of freedom (Q) with which the light will interact, and which will be those in which we calculate matrix elements. The bath H_B refers to all of the other degrees of freedom (q), and the interaction between the two is accounted for in H_{sb} . Although the interaction of the light depends on how \bar{m} varies with Q , the dipole operator remains a function of system and bath coordinates: $\bar{m}(Q, q)$.

We now use the interaction picture transformation to express the time propagator under the full material Hamiltonian \hat{U}_0 in terms of a product of propagators in the individual terms in H_0 :

$$\hat{U}_0 = U_S U_B U_{SB} \quad (13.3.7)$$

$$\mathbf{H}_{sB}(t) = e^{i(H_S+H_B)t} H_{SB} e^{-i(H_S+H_B)t} \quad (13.3.8)$$

$$\mathbf{H}_{sB}(t) = e^{i(H_S+H_B)t} H_{SB} e^{-i(H_S+H_B)t} \quad (13.3.9)$$

Then the **dipole autocorrelation function** becomes

$$C_{\mu\mu} = \sum_n p_n \left\langle n \left| U_{SB}^\dagger U_B^\dagger U_S^\dagger \bar{m} U_S U_B U_{SB} \bar{m} \right| n \right\rangle \quad (13.3.10)$$

where

$$p_n = \langle n | e^{-\beta H_0} | n \rangle / \text{Tr}(e^{-\beta H_0}) \quad (13.3.11)$$

Further, to make this practical, we make an adiabatic separation between the system and bath coordinates, and say that the interaction between the system and bath is weak. This allows us to write the state of the system as product states in the system (a) and bath (α): $|n\rangle = |a, \alpha\rangle$:

$$(H_S + H_B) |a, \alpha\rangle = (E_a + E_\alpha) |a, \alpha\rangle \quad (13.3.12)$$

With this we evaluate Equation 13.3.10 as

$$C_{\mu\mu} = \sum_{a,\alpha} p_a p_\alpha \left\langle a, \alpha \left| U_{SB}^\dagger U_B^\dagger U_S^\dagger \bar{m} U_B U_{BB} \bar{m} \right| a, \alpha \right\rangle \quad (13.3.13)$$

$$= \sum_{a,b} p_a p_\alpha \left\langle \alpha \left| \left\langle a \left| U_{SB}^\dagger U_S^\dagger U_B^\dagger \bar{m} U_B U_S U_{SB} \right| b \right\rangle \bar{m}_{ba} \right| \alpha \right\rangle \quad (13.3.14)$$

where $\bar{m}_{ba} = \langle b | \bar{m} | a \rangle$, and we have made use of the fact that H_S and H_B commute. Also,

$$p_a = e^{-E_j/kT} / Q_s. \quad (13.3.15)$$

Now, by recognizing that the time propagators in the system and system-bath Hamiltonians describe time evolution at the system eigenstate energy plus any modulations that the bath introduces to it

$$U_S U_{SB} |b\rangle = e^{-iH_s t} |b\rangle e^{-i \int_0^t dt' E_b(t')} = |b\rangle e^{-i \int_0^t dt' E_b(t')} \quad (13.3.16)$$

and we can write our correlation function as

$$C_{\mu\mu} = \sum_{a,b} p_a p_\alpha \left\langle \alpha \left| e^{i \int_0^t dt' E_a(t')} U_B^\dagger \bar{m}_{ab} U_B e^{-i \int_0^t dt' E_b(t')} \bar{m}_{ba} \right| \alpha \right\rangle \quad (13.3.17)$$

$$C_{\mu\mu} = \left\langle \bar{m}_{ab}(t) \bar{m}_{ba}(0) e^{-i \int_0^t dt' \omega_{ba}(t')} \right\rangle_B \quad (13.3.18)$$

$$\bar{m}_{ab}(t) = e^{-iH_B t} \bar{m}_{ab} e^{-iH_B t} \quad (13.3.19)$$

Equation 13.3.18 is the first important result. It describes a correlation function in the dipole operator expressed in terms of an average over the time-dependent transition moment, including its orientation, and the fluctuating energy gap. The time dependence is due to the bath and refers to a trace over the bath degrees of freedom.

Let's consider the matrix elements. These will reflect the strength of interaction of the electromagnetic field with the motion of the system coordinate, which may also be dependent on the bath coordinates. Since we have made an adiabatic approximation, to evaluate the matrix elements we would typically expand the dipole moment in the system degrees of freedom, Q . As an example for one system coordinate (Q) and many bath coordinates q , we can expand:

$$\bar{m}(Q, q) = \bar{m}_0 + \frac{\partial \bar{m}}{\partial Q} Q + \sum_\alpha \frac{\partial^2 \bar{m}}{\partial Q \partial q_\alpha} Q q_\alpha + \dots \quad (13.3.20)$$

\bar{m}_0 is the permanent dipole moment, which we can take as a constant. In the second term, $\partial \bar{m} / \partial Q$ is the magnitude of the transition dipole moment. The third term includes the dependence of the transition dipole moment on the bath degrees of freedom, i.e., non-Condon terms. So now we can evaluate

$$\begin{aligned} \bar{m}_{ab} &= \left\langle a \left| \bar{m}_0 + \frac{\partial \bar{m}}{\partial Q} Q + \sum_\alpha \frac{\partial^2 \bar{m}}{\partial Q \partial q_\alpha} Q q_\alpha \right| b \right\rangle \\ &= \frac{\partial \bar{m}}{\partial Q} \langle a | Q | b \rangle + \sum_\alpha \frac{\partial}{\partial q_\alpha} \frac{\partial \bar{m}}{\partial Q} \langle a | Q | b \rangle q_\alpha \end{aligned}$$

We have set $\langle a | \bar{m}_0 | b \rangle = 0$. Now defining the transition dipole matrix element,

$$\bar{\mu}_{ab} = \frac{\partial \bar{m}}{\partial Q} \langle a | Q | b \rangle \quad (13.3.21)$$

we can write

$$\bar{m}_{ab} = \bar{\mu}_{ab} \left(1 + \sum_\alpha \frac{\partial \bar{\mu}_{ab}}{\partial q_\alpha} q_\alpha \right) \quad (13.3.22)$$

Remember that $\bar{\mu}_{ab}$ is a vector. The bath can also change the orientation of the transition dipole moment. If we want to separate the orientational and remaining dynamics this we could split the matrix element into an orientational component specified by a unit vector along $\partial \bar{m} / \partial Q$ and a scalar that encompasses the amplitude factors: $\bar{\mu}_{ab} = \hat{u}_{ab} \mu_{ab}$. Then Equation 13.3.18 becomes

$$\bar{m}_{ab} = \bar{\mu}_{ab} \left(1 + \sum_{\alpha} \frac{\partial \bar{\mu}_{ab}}{\partial q_{\alpha}} q_{\alpha} \right) \quad (13.3.23)$$

Mixed quantum-classical spectroscopy models apply a semiclassical approximation to Equation 13.3.18. Employing the semiclassical approximation says that we will replace the quantum mechanical operator $\hat{m}_{ab}(t)$ with a classical $\bar{m}_{ab}(t)$, i.e., we replace the time propagator U_B with classical propagation of the dynamics. Also, the trace over the bath in the correlation function becomes an equilibrium ensemble average over phase space.

How do you implement the semiclassical approximation? Replacing the time propagator U_B with classical dynamics amounts to integrating Newton's equations for all of the bath degrees of freedom. Then you must establish how the bath degrees of freedom influence $\omega_{ba}(t)$ and $\bar{m}_{ab}(t)$. For the quantum operator $\hat{m}(Q, q, t)$, only the system coordinate Q remains quantized, and following Equation 13.3.22 we can express the orientation and magnitude of the dipole moment and the dynamics depends on the classical degrees of freedom \tilde{q}_{α} .

$$\bar{m}_{ab} = \bar{\mu}_{ab} \left(1 + \sum_{\alpha} a_{\alpha} \tilde{q}_{\alpha} \right) \quad (13.3.24)$$

a_{α} is a (linear) mapping coefficient

$$a_{\alpha} = \partial \bar{\mu}_{ab} / \partial \tilde{q}_{\alpha} \quad (13.3.25)$$

between the bath and the transition dipole moment.

In practice, use of this approximation has been handled in different ways, but practical considerations have dictated that $\omega_{ba}(t)$ and $\bar{m}_{ab}(t)$ are not separately calculated for each time step, but are obtained from a mapping of these variables to the bath coordinates q . This mapping may be to local or collective bath coordinates, and to as many degrees of freedom as are necessary to obtain a highly correlated single valued mapping of $\omega_{ba}(t)$ and $\bar{m}_{ab}(t)$. Examples of these mappings include correlating ω_{ba} with the electric field of the bath acting on the system coordinate.

Appendix

Let's evaluate the dipole correlation function for an arbitrary HSB and an arbitrary number of system eigenstates. From Equation 13.3.14 we have

$$C_{\mu\mu} = \sum_{\alpha} p_a p_{\alpha} \left\langle \alpha \left| \left\langle a \left| U_{SB}^{\dagger} \right| c \right\rangle U_B^{\dagger} \left\langle c \left| U_s^{\dagger} \bar{m} U_s \right| d \right\rangle U_B \left\langle d \left| U_{SB} \right| b \right\rangle \left\langle b \left| \bar{m} \right| a \right\rangle \right| \alpha \right\rangle \quad (13.3.26)$$

$$\left\langle c \left| U_s^{\dagger} \bar{m} U_s \right| d \right\rangle = e^{-i(E_d - E_c)t} \bar{m}_{cd} \quad (13.3.27)$$

$$\bar{m}_{cd}(t) = U_B^{\dagger} \bar{m}_{cd} U_B \quad (13.3.28)$$

$$\left\langle a \left| U_{SB}^{\dagger} \right| c \right\rangle = \left\langle a \left| e^{i \int_0^t dt' \mathbf{H}_{sb}(t')} \right| c \right\rangle = \exp \left[i \int_0^t dt' [\mathbf{H}_{sB}]_{ac}(t') \right] \quad (13.3.29)$$

$$C_{\mu\mu} = \sum_{\alpha} p_a \left\langle e^{-i\omega_{dc}t} e^{i \int_0^t dt' [H_{SB}]_{ac}} \bar{m}_{cd} e^{-i \int_0^t dt' [H_{SB}]_{db}(t')} \bar{m}_{ba} \right\rangle_B \quad (13.3.30)$$

$$= \left\langle \bar{m}_{cd}(t) \bar{m}_{ba}(0) \exp \left[-i\omega_{dc}t - i \int_0^t dt' [H_{SB}]_{db}(t') - [H_{SB}]_{ac}(t') \right] \right\rangle_B \quad (13.3.31)$$

Readings

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