Stochastic scattering theory for excitation induced dephasing: Comparison to the Anderson-Kubo lineshape

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In this paper we present a quantum stochastic model for spectroscopic line-shapes in the presence of a co-evolving and non-stationary background population of excitations. Starting from a field theory description for interacting bosonic excitons, we derive a reduced model whereby optical excitons are coupled to an incoherent background via scattering as mediated by their screened Coulomb coupling. The Heisenberg equations of motion for the optical excitons are then driven by an auxiliary stochastic population variable, which we take to be the solution of an Ornstein-Uhlenbeck process. Itô’s Lemma then allows us to easily construct and evaluate correlation functions and response functions. Focusing on the linear response, we compare our model to the classic Anderson-Kubo model. While similar in motivation, there are profound differences in the predicted lineshapes, notably in terms of asymmetry, and variation with increasing background population.

I. INTRODUCTION

One of the cornerstones of modern spectroscopy is that the lineshape of a spectral transition gives an indication of the underlying environment and background dynamics of the system being probed. According to the Anderson-Kubo model (AK)1–5 the energy levels of a molecule or atom are modulated by fluctuations within the surrounding environment. Such fluctuations can arise from nuclear and electronic motions of the surrounding environment which induce a noisy driving field. A suitable model for this is to write that a transition frequency has an intrinsic time dependence

\[ \omega(t) = \omega_0 + \delta \omega(t) \]

where \( \omega_0 \) is the central (mean) transition frequency and \( \delta \omega(t) \) is some time-dependent modulation with \( \langle \delta \omega(t) \rangle = 0 \). Lacking detailed knowledge of the environment, it is reasonable to write the frequency auto-correlation function in terms of the deviation about the mean, \( \Delta \) and a correlation time, \( \tau_c = \gamma^{-1}, \) \( \forall \varepsilon \).

\[ \langle \delta \omega(t) \delta \omega(0) \rangle = \Delta^2 e^{-\gamma |t|}. \]

From this we can go on to write the linear response for light absorption or emission between initial and final quantum states. The model has two important limits. First, if \( \Delta \gamma \ll 1 \) absorption line shape takes a Lorenzian functional form with a homogeneous width determined by the dephasing time \( T_{\gamma^{-1}} = \Delta^2 / \gamma \). On the other hand, if \( \Delta \gamma \gg 1 \), the absorption spectrum takes a Gaussian form with a line width independent of the correlation time. In this limit, fluctuations are slow and the system samples a broad distribution of environmental motions. Increasing the rate of the fluctuations (i.e. decreasing the correlation time) leads to the effect of motional narrowing where by the line width becomes increasingly narrow.

All of this assumes that the background dynamics are more or less due to fluctuations about a stationary state. This is certainly the case for isolated chromophores embedded in a condensed phase environment. However for a semiconductor system, one can have weak Coulomb interactions between excitations as well as a nonstationary ensemble of background excitations produced by broad-band excitation from an initial laser pulse. Such transient fluctuations in the number density of excitations, \( \delta n(r,t) \) induce space-charges and hence fluctuating potential6–11. This is effect is known as excitation induced dephasing (EID) and has been observed in a number of contexts12–18.

In this paper, we lay the groundwork for an accompanying paper concerning the observation of the phenomena of excitation induced dephasing (EID) in the coherent 2D spectroscopy of a hybrid perovskite semiconductor (PEA)\(_2\)PbI\(_4\) (PEA = phenylethylammonium) — a multiple-quantum-well-like single-layer metal-halide perovskite derivative. We choose this material to test the theoretical framework developed here because of its susceptibility to strong many-body effects12–15 and dynamic exciton-lattice coupling that drives their dynamics16–18. In this system, we reported that the homogeneous linewidth broadened with increasing pumping fluence, which is a hallmark of EID. Moreover, we reported that this line width progressively narrows as the exciton population evolves in time and we attributed this to the transient decay of background exciton population. In this paper, we start with a generalized field theory for interacting bosonic excitons.

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then reduce this to a quantum stochastic model whereby the background population evolves from a non-stationary initial population generated by the initial excitation. Here we focus upon the linear response and compare our approach to AK. In Ref. [19] we shall consider the non-linear responses and compare the predictions of our approach to experimental coherent 2D spectroscopic signals.

II. MANY-BODY MODEL

Here we consider the case where we have an ensemble of excitons which we will write first in terms of field operators \( \hat{\psi}^\dagger (r) \) and \( \hat{\psi} (r) \) which create and remove excitons at location \( r \). These are bosonic operators \([\hat{\psi} (r') , \hat{\psi}^\dagger (r) ] = \delta (r-r') \). 

\[
H = \int \frac{\hbar^2}{2m} (\nabla \hat{\psi}^\dagger)(\nabla \hat{\psi})dr + \frac{1}{2} \int dr dr' \hat{\psi}^\dagger (r') \hat{\psi}^\dagger (r) V (r-r') \hat{\psi} (r') \hat{\psi} (r) \tag{3}
\]

By Fourier transform we define

\[
\hat{\psi} (r) = \frac{1}{\sqrt{V}} \sum_k a_k e^{ikr} \tag{5}
\]

and recast the Hamiltonian as

\[
H = \sum_k \frac{\hbar^2 k^2}{2m} a_k^\dagger a_k + \frac{1}{2} \sum_{k q} V_q a_{k+q}^\dagger a_{k-q} \tag{6}
\]

where \( V = L^3 \) is the unit volume and

\[
V_q = \int V(r)e^{iqr} dr \tag{7}
\]

is the Fourier component of the many-body interaction potential. In general, \( V (r) \) always will include short and long-ranged contributions.

Here we have taken only the \( \ell = 0 \) (s-wave) term in the expansion. The interaction potential \( V (r) \) always will include short and long-ranged contributions. However, for any finite-ranged potential, we can express this interaction in terms of the s-wave scattering length, \( a \), according to the Born approximation \( V_o = 4 \pi \hbar^2 a / \mu \). Such an approximation is valid in the limit that the momentum exchange is small compared to the effective range of the potential. Under this approximation, we can replace the actual exciton/exciton interaction potential with an arbitrary, but smooth, fictitious potential that has the same value of \( V_o \). For the case at hand, we assume that the exciton/exciton interaction takes the form of a screened-Coulomb or Yukawa potential of the form \((r_c = 1/\alpha \) is the screening length) 

\[
V (r) = \frac{1}{4\pi} \frac{e^{-\alpha r}}{r}, \tag{8}
\]

the Fourier-transform of which reads

\[
V(q) = \frac{1}{q^2 + \alpha^2}. \tag{9}
\]

The full exciton \( H \) is then 

\[
H = \sum_k \frac{\hbar^2 k^2}{2m} a_k^\dagger a_k + \frac{1}{2} \sum_{k q} V_q a_{k+q}^\dagger a_{k-q} a_{k'}. \tag{10}
\]

We now split out the \( k = 0 \) excitons and treat the \( k \neq 0 \) excitons as a bath. First, one finds that Hamiltonian can be re-written as

\[
H = \hbar \omega_0 a_0^\dagger a_0 + \frac{V_0}{2} a_0^\dagger a_0 a_0 a_0 + \frac{V_0}{2} \sum_{q \neq 0} \left( 4a_q^\dagger a_q a_q + \frac{V_0}{2} \sum_{q \neq 0} a_q^\dagger a_q \right) \tag{11}
\]

where \( \hbar \omega_0 = \hbar^2 k^2 / 2m \) is the exciton dispersion and the second term is the \( k = 0 \) exciton self-interaction. The first \( q \neq 0 \) interaction term arises from direct and exchange interactions between the \( k = 0 \) excitons and the \( k \neq 0 \) excitons. The next two terms correspond to exciton pair creation/annihilation.

Within the Bogoliubov theory of an interacting Bose condensate, these terms give rise to a linearization of the energy dispersion around \( k = 0 \). Whereas in the Bogoliubov approach, one can assume that the \( k = 0 \) population is very large and use this to re-write the interaction in terms of the \( k = 0 \) population by writing \( \langle a_0 a_0 \rangle = \langle a_0^\dagger a_0 \rangle = n_0 \) and take \( n_o \) to approach macroscopic populations, in the case at hand we need to keep these as quantum operators and we will treat the \( q \neq 0 \) operators as sources of quantum noise and dissipation.

Rewriting the Hamiltonian once more, we collect all the \( k \neq 0 \) terms

\[
H = \hbar \omega_0 a_0^\dagger a_0 + \sum_{k \neq 0} \hbar \omega_k a_k^\dagger a_k + \frac{V_0}{2} a_0^\dagger a_0 \left[ 2V_0 \sum_{q \neq 0} (a_q^\dagger a_q) \right] + a_0^\dagger a_0 \left[ \frac{V_0}{2} \sum_{q \neq 0} a_q^\dagger a_q \right] \tag{12}
\]

We can use the form of this Hamiltonian to derive quantum stochastic equations of motion for the \( k = 0 \) operators treating the \( k \neq 0 \) terms as a Markov bath. First, define the \( k = 0 \) term as

\[
H_0 = \hbar \omega_0 a_0^\dagger a_0 + \frac{V_0}{2} a_0^\dagger a_0 a_0 a_0 + 2V_o a_0^\dagger a_0 A^\dagger \cdot A + \gamma_2 a_0^\dagger a_0 B^\dagger \cdot B + \gamma_2 a_0 a_0 B^\dagger \cdot B \tag{13}
\]

where the \( A \) and \( B \) operators are collective bath operators defined by inspection of Eq. [12]. The term involving \( A^\dagger \cdot A \) introduces an energy fluctuation/dissipation simply due to scattering of the \( k \neq 0 \) population from the \( k = 0 \) population. The other two terms give rise to fluctuations/dissipation due to exciton pair creation/annihilation. The constants \( 2V_o \) and \( \gamma_2 \) can be determined by inspection of Eq. [12].

To proceed, we shall drop the pair creation/annihilation terms and focus solely on the term involving \( A^\dagger \cdot A \), we shall also treat these as a collective variable and further assume that
they undergo rapid thermalization via contact with a dissipative bath due to non-optical degrees of freedom. That is to say that we define a reservoir Hamiltonian

\[ H_{\text{res}} = \hbar \Omega (A^\dagger A + 1/2) + \sum_i g_i (b_i^\dagger A + A^\dagger b_i) + \sum_i \hbar \omega_i (b_i^\dagger b_i + 1/2) \]  

(14)

Focusing solely upon the coupling to the reservoir, we define

\[ \hat{A}(t) = A(t) e^{i\Omega t} \quad \text{and} \quad \hat{b}_i(t) = b_i(t) e^{i\omega_i t} \]  

(15)

so that the newly defined operators evolve only with the interaction. One obtained equations of motion of the form

\[ i\hbar \partial_t \hat{A} = \sum_i g_i \hat{b}_i(t) e^{i(\Omega - \omega_i)t} \]  

(16)

\[ i\hbar \partial_t \hat{b}_i = g_i \hat{A}(t) e^{-i(\Omega - \omega_i)t} \]  

(17)

which can be integrated

\[ \hat{b}_i(t) = \hat{b}_i(t_0) - \frac{i}{\hbar} \sum_i g_i \int_{t_0}^{t} d\tau \hat{A}(\tau') e^{i(\omega_i - \Omega)\tau'} \]  

(19)

and inserted to the equations of motion for \( \hat{A}(t) \)

\[ \frac{d}{dt} \hat{A}(t) = - \int_{t_0}^{t} d\tau \kappa(\tau) (\hat{A}(t - \tau) + \hat{F}(t)) \]  

(20)

where \( \kappa(\tau) \) is given by

\[ \kappa(\tau) = \frac{1}{\hbar} \sum_i |g_i|^2 e^{i(\Omega - \omega_i)\tau} \]  

(21)

\( \hat{F}(t) \) is a quantum operator acting on the reservoir variables:

\[ \hat{F}(t) = - \frac{i}{\hbar} \sum_i g_i \hat{b}_i(t) e^{i(\Omega - \omega_i)t} \]  

(22)

Integrating \( \kappa(t) \) over all time

\[ \int_0^\infty \kappa(\tau) d\tau = \frac{1}{\hbar^2} \lim_{\eta \to 0^+} \sum_i |g_i|^2 \int_0^\infty e^{i(\Omega - \omega_i + i\eta)\tau} d\tau \]  

(23)

\[ = \frac{1}{\hbar^2} \sum_i |g_i|^2 \left( \pi \delta(\Omega - \omega_i) + i \frac{\eta}{2} + i\Delta \right) \]  

(24)

where \( \gamma \) is the spontaneous emission rate and \( \Delta \) is the energy shift. Thus, the equation of motion for the collective \( \hat{A} \) variables read

\[ \partial_t \hat{A} = - \left( \frac{\gamma}{2} + i\Delta \right) \hat{A} + \hat{F}(t) \]  

(26)

The \( \hat{F}(t) \) remains a quantum operator that depends upon the reservoir variables and it is straightforward to write correlation functions assuming the collective \( \hat{A} \) operators are connected to thermal reservoir.

\[ \langle \hat{F}(t') \hat{F}(t) \rangle = \langle \hat{F}^\dagger(t') \hat{F}^\dagger(t) \rangle = 0 \]  

(27)

\[ \langle \hat{F}^\dagger(t') \hat{F}(t) \rangle = \sum_i \frac{|g_i|^2}{\hbar^2} \langle \eta_i \rangle e^{i(\Omega - \omega_i)(t-t')} \]  

(28)

\[ \langle \hat{F}(t') \hat{F}^\dagger(t) \rangle = \sum_i \frac{|g_i|^2}{\hbar^2} \langle \eta_i \rangle e^{i(\Omega - \omega_i)(t-t')} \]  

(29)

We now can take the background density as stochastic variable and re-cast Eq. (13) as

\[ H_0(t) = \hbar \omega_0 a_0^\dagger a_0 + \frac{V_0}{2} a_0^\dagger a_0 a_0 a_0 + 2V_0 a_0^\dagger a_0 N(t) \]  

(30)

where \( \hbar = 1 \). Converting to the interaction representation, the exciton operators evolves as

\[ \hat{a}_0(t) = \exp \left( -i\omega_0 t - iV_0 \hat{n}_0 - i2V_0 \int_0^t N(\tau) d\tau \right) \hat{a}_0 = \hat{U}(t) \hat{a}_0, \]  

(31)

where \( \hat{n}_0 = \hat{a}_0^\dagger \hat{a}_0 \) is the number operator of \( k = 0 \) excitons.

In order to integrate this we need to specify the initial conditions for the bath. Generally, one takes it as being in a thermal state. However, in the case we consider here, the background excitations are generated by a laser pulse which creates a non-equilibrium non-stationary “bath”, characterized by an initial distribution related to the power spectrum of the excitation pulse. At this point we shall take the background to be an incoherent population characterized by an initial mean \( N_0 \) and variance \( \sigma_{N_0} \) that evolved according to the stochastic differential equation

\[ dN(t) = -\gamma N(t) dt + \sigma dW(t). \]  

(32)

the variance \( \sigma \) represents the equilibrium fluctuations (white noise) in the background population and \( dW(t) \) represents a Wiener process. The stochastic model is also called Ornstein-Uhlenbeck model or mean-reverting model that describes a noisy relaxation process[20,23] . The solution of the stochastic differential equation is

\[ N(t) = N(0) e^{-\gamma t} + \sigma \int_0^t e^{-\gamma(t-s)} dW_s, \]  

(33)

and the expectation value of the second term on the right hand side is zero due to the property of the Brownian motion \( W_t \). Setting \( N_0 = \langle N(0) \rangle \), the background population relaxes exponentially,

\[ \langle N(t) \rangle = e^{-\gamma t} N_0. \]  

(34)

Formally, the spectral density of the bath can be obtained by Laplace transform of the kernel in Eq. (33) which implies that one can introduce more complex and nuanced stochastic processes directly into the our model. Further, more complex kernels do not present any limitation to our approach. The
The second term reads $\sigma_A$. Optical responses $f$ for an arbitrary adaptive process where the first term on the right hand side can be simplified by the quadratic variation of Itô calculus. From this, the covariance of $N$ can be written as

$$\text{Cov}(N(t), N(\tau)) = \mathbb{E}[(N(t) - \mathbb{E}[N(t)])(N(\tau) - \mathbb{E}[N(\tau)])] = \mathbb{E}(N(t) - N_0) - N_0^2 e^{-\gamma(t+\tau)}$$

where $\mathbb{E}$ denotes the expected value (i.e. average over noise).

From this, the covariance of $N(s)$ and $N(t)$ can be computed as

$$\text{Cov}(N_s, N_t) = \mathbb{E}[(N(s) - \mathbb{E}[N(s)])(N(t) - \mathbb{E}[N(t)])] = \mathbb{E}(N(s)N_t) - N_0^2 e^{-\gamma(s+t)}$$

$$= \mathbb{E} \left[ \sigma^2 \int_0^s e^{-\gamma(x-y)} dW_u \int_0^t e^{-\gamma(t-v)} dW_v \right] + \mathbb{E} \left[ (N(0) - N_0)^2 e^{-\gamma(t+\tau)} \right]$$

$$+ \mathbb{E} \left[ \sigma (N(0) - N_0) \left( e^{-\gamma} \int_0^t e^{-\gamma(t-v)} dW_v + e^{-\gamma} \int_0^s e^{-\gamma(s-y)} dW_u \right) \right].$$

The first term on the right hand side can be simplified by the quadratic variation of Itô calculus, and the Wiener process $dW_t$ is statistically independent.

### A. Optical responses

We can now use these results to derive the response functions for optical excitation

$$S^{(1)}(t) = \frac{i}{h} \langle [\hat{\mu}(t), \hat{\mu}(0)] \rho(-\infty) \rangle$$

$$= \frac{\mu^2}{h} \langle [\hat{a}^2(t), \hat{a}(0)] \rho(-\infty) \rangle - c.c.$$

$$= -2 \frac{\mu^2}{h} S \left\{ \exp \left[ i(\omega_0 + i\nu_0 t) \hat{a}_0 + i2V_o \int_0^t \rho(N(d\tau)) \right] \left[ (e^{-\nu_0 t} - 1) \hat{a}_0 - 1 \right] \rho(-\infty) \right\}$$

$$\approx -2 \frac{\mu^2}{h} S \left\{ \left[ (e^{-\nu_0 t} - 1) \hat{a}_0 - 1 \right] \exp \left[ i(\omega_0 + V_0 \phi_0) t \right] \exp \left[ -\frac{2V_o}{\gamma} N_0 (1 - e^{-\gamma}) \right] \right. \times \exp \left[ -\frac{4V_o^2 \sigma^2}{4\gamma^3} (2\gamma + 4e^{-\gamma} - e^{-2\gamma} - 3) - \frac{4V_o^2 \sigma^2}{4\gamma^3} (1 - e^{-\gamma})^2 \right] \right\}.$$
where the initial background population averages \( \langle N(0) \rangle = N_0 \) and has the variance of \( \sigma_{N_0}^2 \). The expressions for \( g_1(t) \) and \( g_2(t) \) constitute the central results of this paper. For completion, we note that the double time integral in this last expression can also be obtain for when the two time limits are not equal.

\[
\int_0^t \int_0^{t'} \text{Cov} \left[ N(\tau), N(t') \right] d\tau' d\tau = \frac{\sigma^2}{2}\left[ 2\gamma \min(t, t') + 2e^{-\gamma t} + e^{-\gamma t'} - e^{-\gamma(t + |t'|)} - e^{-\gamma(t' + |t|)} - 2 \right] + \frac{\sigma_{N_0}^2}{\gamma} \left[ e^{-\gamma|t'|} - e^{-\gamma t} - e^{-\gamma t'} + 1 \right].
\]

This term will arise in the analysis of the non-linear responses as we discuss in Ref. [19].

### B. Comparison to Anderson-Kubo theory

The expressions we have above are exact insofar as the assumptions of our stochastic model is concerned. We now compare our approach to the more familiar Anderson-Kubo model in order to point out some key similarities and crucial differences. First, let us assume that the background population follows a stochastic process given by

\[
N(t) = N_s + \delta N(t)
\]

where \( N_s \) is the stationary background population and \( \delta N(t) \) corresponds to fluctuations about that stationary state. In principle, \( N_s \) can be set to zero, but we shall carry it through as non-zero until the end. Following AK, we can write the variance as

\[
\langle \delta N(t) \delta N(0) \rangle = \sigma_K^2 e^{-\gamma t}.
\]

Note, that we shall use \( \sigma_K \) to discriminate between the variance in the population in the AK model versus the variance \( \sigma^2 \) in Eq. [33]. The distinction is crucial since \( \sigma_K^2 \) is unitless while the \( \sigma^2 \) in the Ornstein-Uhlenbeck stochastic differential equation (Eq. [33]) carries units of \([t^{-1}]\). Within the context of AK.

The expression for \( g_2(t) \) in Eq. [43] can be rearranged to read

\[
g_2(t) = \left( \frac{\sigma_{N_0}^2}{\gamma^2} + \frac{3\sigma^2}{2\gamma^2} \right) + \frac{2}{\gamma^3} e^{-\gamma t} \left( \sigma^2 - \gamma \sigma_{N_0}^2 \right) - \frac{e^{-2\gamma t}}{2\gamma^3} \left( \sigma^2 - 2\gamma \sigma_{N_0}^2 \right) + \frac{\sigma^2}{\gamma^3}.
\]
which allows us to introduce $\kappa = \sigma^2 - 2\gamma\sigma^2_{\text{N}_0}$ as a important parameter in determining the overall spectral lineshape. When $\kappa \neq 0$, the dynamics are determined by magnitude of the Brownian noise that characterizes the steady-state of the background. This is equivalent to stating that the initial excitation is narrow ($\kappa > 0$) or broad ($\kappa < 0$) compared to the background fluctuations. When $\kappa = 0$, we obtain an important limiting case of our model. In this specific case, our model is exactly equivalent to the Anderson-Kubo model viz.

$$g_2(t) \rightarrow \frac{\sigma^2}{\gamma}(e^{-\gamma t} + \gamma - 1). \tag{51}$$

giving $\sigma^2_{\text{K}} = \sigma^2/\gamma$. This limit only holds when the initial excitation pulse produces $N_0 = 0$ and that the fluctuations are about the steady-state.

C. Non-stationary spectra.

When the excitation pulse produces a non-stationary background population ($N_0 > 0$), it is no longer consistent to compare against the Anderson-Kubo model, which is valid solely for a stationary background. Fig. 2(a) displays the effect of a non-stationary background on the linear absorption spectrum of a system. The character of this tail depends most strongly upon the initial choice of $N_0$ and is attributable to the $g_1(t)$ term in our response function which is the time-integral over the evolving background population. This term, as it appears in Eq. (40) produces an evolving frequency shift reflecting the dynamical relaxation of the background. In the $S^{(1)}$ response, this produces a tail extending out to the blue. Our model exhibits all the correct features observed in the absorption spectroscopy of typical 2D semiconductor systems and transition metal dichalcogenides.

1. **Blocking**: Increasing the initial background suppresses the peak absorption intensity.

2. **Energy shift**: The peak position shifts to the blue with increasing background population due to increased Coulombic interactions.

3. **Broadening**: The spectrum acquires a long tail extending to the blue due to the dynamical evolution of the background. This feature also appears in the 2D coherent spectroscopy as an asymmetry along the absorption axis and as phase scrambling in the rephasing and non-rephasing signals.

4. **Biexciton**: The peak is split by $V_0$ corresponding to the biexciton interaction.

In Ref. [19] where we compute the non-linear coherent responses, we find that this evolution produces both asymmetry as well as phase scrambling in the 2D spectroscopy of (PEA)$_2$PbI$_4$.

In Fig. 2 we compare the effect of decreasing the relaxation rate $\gamma$ for fixed values of $N_0 = 4$ which carries the system from the homogeneous limit ($\gamma = 50\text{meV}$) in which the background relaxation is very fast to the fully broadened inhomogeneous limit. Under this extreme, the exciton and bi-exciton splitting is clearly resolved and the lineshapes are Lorentzian about each peak. to the inhomogeneous limit. Decreasing the relaxation rate $\gamma$ produces a systematic shift towards the blue due to the mean-field interaction between the exciton and the background. This shift saturates when the peak is fully shifted by $2V_0N_0$ and acquires a Gaussian form reflecting mean $N_0$ and variance $\sigma^2_{\text{N}_0}$ of the initial background. Physically this corresponds to the the excitation pulse as projected onto the density of states of the system.

At this point it is worth comparing our results and model to the work recently presented by Katsch, et al. in Ref. [11]. In this the authors use a many-body/Heisenberg equations of motion approach to describe inter-valley electron/hole interactions in 2d semiconductors systems and use this approach to compute the response to a time-dependent electric field explicitly incorporated into the equations of motions. In principle, this is an exact calculation and provides a highly useful benchmark for the present theoretical analysis. Our analytical model produces all the important features found in the more detailed computational approach and offers additional insight into the underlying physics leading to these effects. Moreover, our analytical model provides an efficient avenue for computing higher-order coherent spectroscopies, which we present in Ref. [19].

III. DISCUSSION

We present here what appeared to be a straightforward extension of the Anderson-Kubo model in the sense that the external environment serves as a non-stationary source of noise which modulates the energy gap of a given transition. We
find that model produces non-linear spectral shifts and asymmetries that depend vary systematically with the initial background population and are consistent with the absorption characteristics of a wide range of semiconducting systems. In the most general sense, our model does not hinge upon a specific model for the the environmental noise, we only require that it follow from stochastic differential equation that can be integrated using Itô’s Lemma. In principle, one can implement more system-specific noise-sources, as well as correlated sources, directly into our approach.

In the accompanying paper (Ref. 19) we explore the implications of the model for higher-order non-linear coherent optical responses and apply the approach to study the excitation-induced dephasing (EID) observed in a hybrid perovskite semiconductor.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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