Absorption Spectra of Quantum Aggregates Interacting via Long-Range Forces

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We present a simple formula by which the shape of the absorption spectrum of an aggregate of quantum "monomers" (cold atoms, molecules, quantum dots, nanoparticles, etc.) interacting via dipole-dipole forces can be calculated from the averaged spectrum of the quantum monomer itself. Spectral broadening, due to a wide variety of causes, is included explicitly so that the formula is applicable not only to the idealization of a discrete spectrum but also to the practical situation of a continuously broadened spectrum. In simple cases, analytic results are obtained showing the strong dependence of the aggregate spectrum on the precise nature of the broadening of the quantum monomer spectrum. The formula is compared with results of exact diagonalization of model aggregate Hamiltonians and with experiment.

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Quantum aggregates (QA) in the form of loosely coupled assemblies of organic molecules interacting via dipole-dipole forces have been known for a very long time (see, e.g., [1]). They are typified, for example, by many dye molecules whose spectra undergo radical shifts and changes of shape on aggregation. Advance in technology in recent years has expanded considerably the range of tools available with which to manipulate small quantum objects, e.g., the techniques of trapping and cooling atoms and molecules [2], the force microscope, and the production of nanosized clusters on surfaces [3,4] or in helium droplets [5]. This has allowed new types of quantum aggregates to be studied in detail. Here the term quantum "monomer" (QM) will be used to refer to any object, atom, molecule, quantum dot, etc., which aggregates without essential loss of its identity. This limits the forces between QMs to be small compared to typical intra-QM forces. In turn, this will mostly limit discussion to QMs separated by distances somewhat larger than their size so that there is no wave function overlap and no essential transfer of electrons.

In addition to the traditional QA, i.e., assemblies of large organic molecules in chemistry [1,6], solid state physics [7] and biology [8,9], examples of such new types of aggregate are electronically excited atoms in optical lattices [10], "molecules" and "crystals" composed of quantum dots [11–13], assemblies of nanosize metallic particles [3,4], or molecules bound to DNA as a template [14]. On electronic excitation, the (transition) dipole-dipole interaction between such QMs leads to migration of dipole excitation through the aggregate. In ordered structures of identical QMs, this transfer of excitation arises from the formation of entangled cooperative states, known as excitons, in which electron excitation migrates freely through the whole aggregate.

As with all quantum objects, the simplest method of obtaining information on the QA energy spectrum and its structure is optical absorption. Indeed, the changes in the absorption spectra between QA and noninteracting QMs furnish key evidence as to the geometrical structure of the aggregate. The simplest theory of QA absorption is the exciton theory involving electronic degrees of freedom only. Unfortunately, the absorption spectrum of the noninteracting QM is rarely well-approximated by a single sharp electronic excitation line. Rather, the spectra are broadened. The broadening is due to a variety of effects. Often, the QMs have other internal degrees of freedom which couple to the electronic excitation, e.g., intramolecular vibrations in the case of large molecules. The excited electronic, or vibronic, state has often, apart from the natural radiation lifetime, a finite lifetime due to coupling to phonons of the substrate or solvent surroundings. Inhomogeneous broadening occurs where the QMs are not absolutely identical, either due to varying chemical shifts from the surroundings at different locations or simply due to nonuniformity in the manufacture of the QM (e.g., quantum dots). Similarly, a nonunique ground state may lead to temperature-broadening effects. All such broadening will be referred to as dynamic averaging, since it affects the effective QM Hamiltonian. In the dipole-dipole interaction between QMs and in the absorption spectrum, there occurs the transition dipole moment $\boldsymbol{\mu}_n$. A key assumption is that $\boldsymbol{\mu}_n$ is independent of dynamical averaging. However, fluctuations in its position about some mean value in the QA imply that quantities involving $\boldsymbol{\mu}_n$ are subject to a separate geometrical averaging in calculating the QM and QA absorption spectra.

These broadening effects have mostly been taken into account by assuming that the QM spectrum is discrete and folding the resulting QA "stick" spectrum with some assumed line shape function or by assuming that broadening is due to statistical fluctuations. The aim here is to present a rather general but, above all, simple formula by which the QA spectrum can be calculated directly from the average spectrum of the noninteracting QM. This formula is applicable not only when the QM spectrum is assumed to be discrete but, more importantly, can be applied also to continuous spectra. This leads to a semiempirical procedure in which the QM spectrum taken from experiment can be used as input.

The photon absorption cross section $\sigma_{\hat{x}}^A$, of the aggregate, for light of frequency ω and polarization vector $\hat{x}$, is expressed in terms of the frequency-dependent polarizability tensor $\boldsymbol{\alpha}^A$ as

$$\sigma_{\hat{x}}^A \propto -\mathrm{Im}\hat{x} \cdot \boldsymbol{\alpha}^A \cdot \hat{x}, \tag{1}$$

with

$$\boldsymbol{\alpha}^A = \sum_{nm} \{\langle \boldsymbol{\mu}_n G_{nm}(E_0 + \hbar\omega)\tilde{\boldsymbol{\mu}}_m \rangle\}. \tag{2}$$

Here angle brackets $\langle \cdots \rangle$ denote the dynamical average and braces $\{\cdots\}$ the geometric average. The transposed transition dipole (row) vector of QM n is denoted by $\tilde{\boldsymbol{\mu}}_n$, and E_0 is the energy of the aggregate initial state. The propagator matrix $G_{nm}(E)$ is that of the Green operator $G(E) = (E - H + i\epsilon)^{-1}$ of the aggregate with total Hamiltonian H. This propagator is expressed in a basis of electronic eigenstates $|\pi_n\rangle$ in which QM n is excited with all others in their electronic ground state. Hence, if vibrational degrees of freedom are included in H, then G_{nm} is still an operator with respect to these coordinates.

The total Hamiltonian is subdivided as $H = H_0 + V$, where H_0 is the sum of the Hamiltonians of individual, noninteracting monomers and V is the interaction operator between monomers. Then we can write formally

$$G = g + gVG, \tag{3}$$

where $g = (E - H_0 + i\epsilon)^{-1}$. The averages in Eq. (2) then include the following situations, where in any specific case one or more of the averages may be involved:

(i) QMs and QA possess additional internal vibrational degrees of freedom. Then $\langle \cdots \rangle$ implies an average over an initial vibrational aggregate state. This also includes an average over states occupied at finite temperature. If the approximation is made that the $\boldsymbol{\mu}_n$ are independent of vibration and the aggregate has a known structure, then the average is performed over G only, i.e.,

$$\boldsymbol{\alpha}^A = \sum_{nm} \{\boldsymbol{\mu}_n \langle G_{nm} \rangle \tilde{\boldsymbol{\mu}}_m\}. \tag{4}$$

(ii) If the QM spectrum is subjected to external influences, leading to effective disorder (inhomogeneous broadening), then an average must be performed over these variations. Usually, this is simulated by assuming varying eigenvalues of H_0 and/or by assuming them to be imaginary.

(iii) For aggregates in which the positions and orientations of the QMs fluctuate, the geometrical average must also be taken.

In Eq. (1), the dipole approximation has been made in the interaction of light with the aggregate. This restricts the size of the aggregate (or at least the size of the delocalization of excitation). However, it implies that only the orientation, and not the absolute location, of the dipole $\boldsymbol{\mu}_n$ is important for light absorption. Then, from Eqs. (2) and (3), we must consider the equation

$$\sum_{nm} \{\boldsymbol{\mu}_n \langle G_{nm} \rangle \tilde{\boldsymbol{\mu}}_m\} = \sum_n \{\boldsymbol{\mu}_n \langle g_n \rangle \tilde{\boldsymbol{\mu}}_n\} + \sum_{nmn'} \{\boldsymbol{\mu}_n \langle g_n V_{nn'} G_{n'm} \rangle \tilde{\boldsymbol{\mu}}_m\}, \tag{5}$$

where we have used the fact that g is diagonal in the basis $|\pi_n\rangle$.

The main approximation is to replace the operator g_n in the second term on the right-hand side of Eq. (5) by its dynamical average $\langle g_n \rangle = \langle g \rangle$, independent of n. This is a generalization and extension of the coherent exciton scattering (CES) approximation used for the special case of ordered aggregates of dye molecules at zero temperature [15,16]. Although not entirely appropriate in the general case considered here, the designation CES will be retained for the sake of continuity. With the CES approximation, the right-hand side of Eq. (5) simplifies to read

$$\langle g \rangle \mathbf{M} + \langle g \rangle \sum_{nmn'} \{\boldsymbol{\mu}_n V_{nn'} \langle G_{n'm} \rangle \tilde{\boldsymbol{\mu}}_m\}, \tag{6}$$

where the tensor $\mathbf{M} = \sum_n \{\boldsymbol{\mu}_n \tilde{\boldsymbol{\mu}}_n\}$ has been introduced. If $\mathbf{R}_{n,n'}$ denotes the tensor that transforms the transition dipole of the n'th QM to that of the nth QM, i.e., $\boldsymbol{\mu}_n = \mathbf{R}_{n,n'} \boldsymbol{\mu}_{n'}$ then the part $\sum_n \boldsymbol{\mu}_n V_{nn'}$ of expression (6) becomes

$$\sum_n \boldsymbol{\mu}_n V_{nn'} = \sum_n V_{nn'} \mathbf{R}_{n,n'} \boldsymbol{\mu}_{n'} \equiv \mathbf{C}_{n'} \boldsymbol{\mu}_{n'}. \tag{7}$$

Within the CES approximation, the tensor $\mathbf{C}_{n'}$ coupling QM n' to all others will be replaced by its geometrical average $\{\mathbf{C}_{n'}\} \equiv \mathbf{C}$. Then the right-hand side of Eq. (5) becomes

$$\langle g \rangle \mathbf{M} + \langle g \rangle \mathbf{C} \sum_{n'm} \{\boldsymbol{\mu}_{n'} \langle G_{n'm} \rangle \tilde{\boldsymbol{\mu}}_m\}, \tag{8}$$

or, using the definition Eq. (2) and solving for $\boldsymbol{\alpha}^A$, gives

$$\boldsymbol{\alpha}^A = \langle g \rangle (1 - \mathbf{C} \langle g \rangle)^{-1} \mathbf{M}. \tag{9}$$

Let $\tilde{x}_i$, $i = 1, 2, 3$ denote the eigenvectors of the tensor $\mathbf{C}$ with eigenvalue C_i, i.e., $\mathbf{C}\tilde{x}_i = C_i \hat{x}_i$. Then for light polarized in the direction $\hat{x}_i$ one obtains, according to Eq. (1), the aggregate spectrum

$$-\mathrm{Im}\hat{x} \cdot \boldsymbol{\alpha}^A \cdot \hat{x} = -\mathrm{Im}\langle G(E) \rangle \sum_n \{|\hat{x}_i \cdot \boldsymbol{\mu}_n|^2\}. \tag{10}$$

From Eqs. (9) and (10), putting $g_I(E) \equiv \mathrm{Im}\langle g(E) \rangle$ and $g_R(E) \equiv \mathrm{Re}\langle g(E) \rangle$, the QA spectral shape function is given by

$$\mathrm{Im}\langle G(E) \rangle = \frac{g_I}{(1 - C_i g_R)^2 + C_i^2 g_I^2}. \tag{11}$$

The function $g_I(E)$, given by the monomer spectral shape, is obtained from experiment or calculation. Then the aggregate spectrum can be calculated in two simple steps:

(i) The function $g_R(E)$ is calculated from the dispersion relation

$$g_R(E) = -\frac{1}{\pi} \mathrm{P} \int_{-\infty}^{\infty} \frac{g_I(E')}{E - E'} dE', \tag{12}$$

where P denotes the principal value.

(ii) The aggregate absorption spectrum is calculated according to Eq. (11), where C_i is estimated or used as a fit parameter.

Clearly, the aggregate spectrum has peaks where $g_R(E) = C^{-1}$ in Eq. (11). (We drop the index on the coupling parameters C_i.) As we will show below, the shape of the aggregate spectrum in this region depends decisively upon the nature of the QM spectrum at this energy. It depends also upon the sign of the interaction C, which shifts the aggregate spectrum with respect to that of the QM. If the QM excited-state spectrum is bounded, usually from below, then a shift in that direction beyond the bound in all cases will lead to $g_R(E) \sim \pm E^{-1}$ [see Eq. (12)], and a single exciton peak is obtained at $E = \pm C$ [see Eq. (11)]. Of course, this extreme case of absolutely vanishing QM absorption, i.e., a lower bound on the spectrum, is not realized in practice, precisely due to the broadening effects described above.

Let us consider typical QM broadened profiles. Taking the QM spectrum to be centered on $E = 0$ and to have a finite width Γ, it is clear from (12) that for $E \gg \Gamma$

$$\langle g(E) \rangle = \frac{1}{E} + i g_I^a(E), \tag{13}$$

where $g_I^a(E)$ is the asymptotic form of g_I for $E \gg \Gamma$. Then from Eq. (11) the QA spectrum is approximately

$$-\mathrm{Im}\langle G(E) \rangle \approx -\frac{E^2 g_I^a(E)}{(E - C)^2 + (C E g_I^a)^2}. \tag{14}$$

Hence:

(A) For an inverse power law in the QM spectral wings, i.e., $g_I^a = \Gamma^{n-1}/E^n$, the peak at $E \approx C$ has width diminishing as $C(\Gamma/C)^{n-1}$. For the Lorentzian case $n = 2$, the aggregate spectrum has the same width Γ as the QM spectrum and indeed the *same shape*; a Lorentzian does not narrow as C increases.

(B) For a Gaussian QM absorption with $g_I^a \propto \sigma^{-1} \exp(-E^2/\sigma^2)$, the width of the QA exciton peak is $\sigma^{-1} C^2 \exp(-C^2/\sigma^2)$ i.e., becomes extremely narrow as C increases.

(C) For a QM obeying the important Urbach-Martienssen (UM) rule [9] in the wings, i.e., $g_I^a \propto k \exp(-k|E|)$, the width of the exciton peak at $E = C$ is of the order $kC^2 \exp(-k|C|)$ i.e., becomes narrower with increasing C but much more slowly than the Gaussian peak.

It is useful to consider further the wings of the QA spectrum (14) itself. Taking $E \gg C$, one has

$$\mathrm{Im}\langle G(E) \rangle = \frac{g_I^a(E)}{1 + (C g_I^a(E))^2} \approx g_I^a(E). \tag{15}$$

This shows that, ultimately, the wings of the QA spectrum have the same shape as the wings of the QM spectrum. In particular, a QM obeying the UM rule will give a QA spectrum obeying the same rule, with the same slope of the linear spectral wings on a logarithmic plot.

To illustrate the application of the CES, we will compare it against spectra calculated using a completely different model similar to methods popular in the theory of exciton line shapes [6,17]. In this approach, vibrations are ignored initially, and a purely electronic aggregate Hamiltonian is diagonalized numerically. However, the transition energies of the various QMs are not identical but fluctuate along the aggregate according to some chosen distribution. The diagonalization is then repeated many times for random choices of the "diagonal disorder," in order to obtain a smooth QA spectrum. In this way, the implicit effects of coupling to vibrations are included. We call this the diagonal-disorder approximation (DDA).

The Hamiltonian of 20 QMs, forming a circular aggregate, whose transition energies vary about some mean position and are uncorrelated, has been diagonalized for a particular random choice of the energies. The calculation has been repeated 50 000 times such that the averaged QM spectrum has a Voigt profile. By varying the parameters of

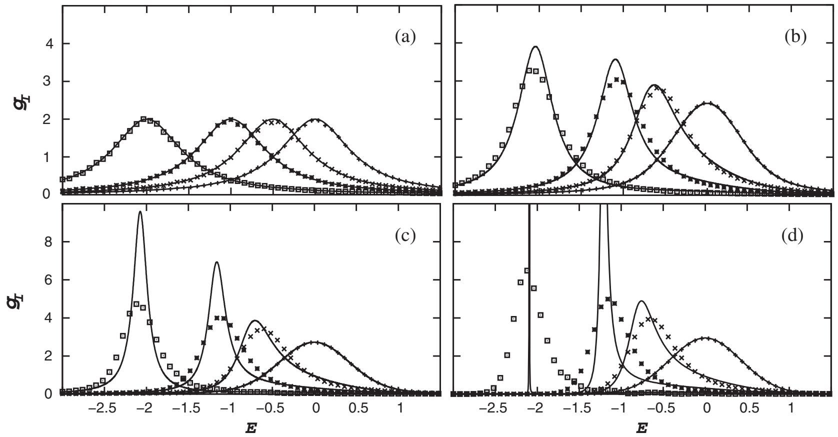

FIG. 1. QA line shapes for coupling strengths (from right to left) $C = 0.0$ (QM), 0.5, 1.0, and 2.0. Points are DDA results and continuous lines the CES results. The Voigt parameters are (a) $\sigma = 0$ (Lorentzian), (b) $\sigma/\Gamma = 1.25$, (c) $\sigma/\Gamma = 38$, and (d) $\Gamma = 0$ (Gaussian).

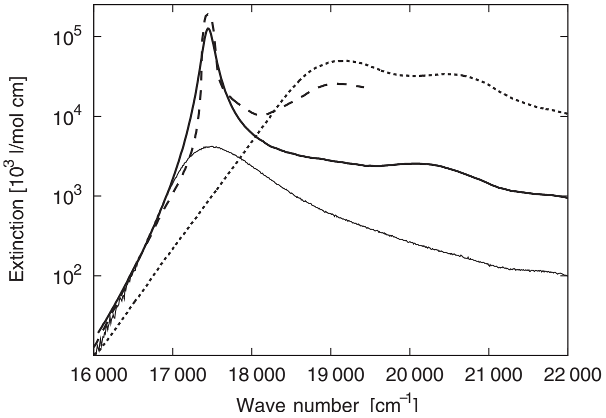

FIG. 2. PIC absorption spectra: dotted line, QM spectrum; dashed line, QA experiment; thick solid line, CES calculation; thin solid fluctuating line, DDA calculation.

the profile, one can extrapolate smoothly between the extreme cases of pure Lorentzian and pure Gaussian QM spectra. In Fig. 1, the DDA spectra are compared with CES results obtained by using the analytic Voigt profile as input to Eq. (12) and then calculating the QA spectrum from the CES formula of Eq. (11). For pure Lorentz broadening, the CES and DDA results are indistinguishable for all coupling strengths C [measured in Fig. 1 in units of the (constant) Voigt profile width]. In this case, the QA CES spectrum is simply the shifted QM Lorentzian spectrum, as can be proved easily from Eq. (11), with $\langle g \rangle = (E + i\Gamma)^{-1}$. In all other cases, the positions of the QA peaks agree and there is good overall agreement in shape. Only in the extreme case of a Gaussian QM spectrum [Fig. 1(d)] is the narrowing of the QA spectrum in the strong coupling case not reproduced by the DDA model. The drastic narrowing of the CES Gaussian peak has been explained above, and it is clear that diagonal disorder will always give a broader peak. What is not clear is which of the two approximations is correct. The question may be academic, since a Gaussian decay of absorption is rarely met in practice. Very common is a spectrum obeying the UM rule [9]. Indeed, for the dye molecule pseudo-isocyanine (PIC) detailed QM and QA spectra have been measured [18] and the presence of UM tails established in both cases (see Fig. 2; of particular note is the UM tail in the region below ca. 18 000 cm^{-1}). This distribution is used as the sampling distribution in the DDA and as $g_I(E)$ in the CES. As seen from the log-linear plot of Fig. 2, the CES gives a good agreement with experiment for the shape, position, and width of the QA exciton peak and particularly reproduces the exponential dependence and slope of the UM tail. The DDA, after averaging 100 000 diagonalizations of an aggregate consisting of 100 monomers, shows overall less-satisfactory agreement with experiment but also reproduces clearly the UM tail of the experiment (both theory curves are normalized to experiment at 16 500 cm^{-1}).

To summarize, we have presented an extremely simple formula to estimate the shape of the absorption spectra of quantum aggregates interacting via long-range forces. When the QM spectrum is known, either from calculation or experiment, the shape of the aggregate spectrum can be calculated from Eq. (11). The coupling strength C may be calculated or used as a fit parameter. In either case, it is dependent upon the detailed geometry of the aggregate. In addition, different light polarizations $\hat{x}$ give rise to different bands with different C values. Hence, the aggregate spectrum provides information on the often unknown aggregate structure. Although the factored form Eq. (9) relies on the CES approximation for its validity, which may be satisfied to a greater or lesser degree in individual cases, its extreme simplicity and the evidence provided by Fig. 2 suggest that the formula may be recommended as a preliminary calculation to be made before embarking on a more exact calculation involving large basis-set diagonalizations in which the degrees of freedom giving rise to broadening must first be included explicitly and then averaged over in a lengthy numerical procedure.

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