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Quantum-coherence and correlations in π -conjugated molecules and multichromophoric systems

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Abstract

Chemistry is intrinsically founded on quantum mechanical principles and examples of quantum-mechanical phenomena abound on a range of energy and length scales. In this article some examples of quantum-mechanical phenomena that can be probed by optical spectroscopy are discussed. Recent experimental studies of quantum-coherence in electronic energy transfer in π -conjugated polymers are reported as examples of weak correlations. The nature of the electron-hole binding energy for excitons in organic systems is investigated as a case of intermediate correlations. Possible experimental probes of strong correlations involved in chemical reactions are critically examined in the final section of the paper.

Keywords: energy transfer; exciton; binding energy; double quantum coherence; electron correlation; conjugated polymer

1. Introduction

Chemistry is intrinsically founded on quantum mechanical principles and examples of quantum-mechanical phenomena abound on a range of energy and length scales. However, there has been little attempt in recent times to think explicitly about chemical change in terms of quantum correlations that can, in principle, be measured using spectroscopy. For example, collective electronic states play significant roles in nonlinear optical properties, optical gain in laser media, the dynamics of highly excited states, and production of ‘entangled’ photons. The special properties of those states, their collective nature, can be described in terms of correlations among electrons and holes. Measurement and analysis of electron-hole correlations therefore can help in the design of new materials. During a chemical reaction bonds are broken and formed. Can we follow the evolution of electron correlations in frontier orbitals during such a process? If so, perhaps electronic changes in sequential versus concerted chemical reactions or complicated π - to σ -bond transformations in cycloaddition reactions can be analyzed. In this

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contribution I discuss examples of weak, intermediate and strong electron-hole correlations in photoexcited chemical systems and these correlations are manifest in spectroscopy. I will summarize by suggesting opportunities for chemistry that might be enabled by a deeper understanding of quantum-mechanical correlations.

Weak correlations are usually found in photophysics, where absorption of light initiates a process such as electronic energy transfer, which is the example described in Sec 2. Weak correlations, such as those that form collective states (excitons) in some multichromophoric systems, are those susceptible to decoherence from the environment. Although these correlations diminish with time, they can still play a significant role in light-induced dynamics.

Interactions between molecules, particularly those that involve exchange or transfer of electrons involve intermediate quantum-mechanical correlations. The example to be discussed in Sec 3 is electron-hole binding energy, which is the electrostatic correlation of electrons and holes that help excitons in organic materials resist photodissociation into mobile charge carriers.

The electrons in molecules are strongly correlated. Molecules are formed by combining the electrons in atoms in a non-additive fashion, so that vastly new properties are attained. The theory of quantum mechanics explains the formation of chemical bonds as a superposition of electron waves. For example, a simple π -electron bond is a symmetric linear combination of p -orbitals on two atomic centers, $|\pi\rangle = (|p_1\rangle + |p_2\rangle)/\sqrt{2}$. This π -bond is complemented by an antisymmetric linear combination, the π -anti-bond: $|\pi^*\rangle = (|p_1\rangle - |p_2\rangle)/\sqrt{2}$. A chemical bond is therefore a coherent superposition state of electron wavefunctions at each atomic site. Underpinning this familiar picture of chemical bonding is a powerful quantum-mechanical principle; a probability law that states a probability is not a simple sum of constituent probabilities, but rather involves summation at the amplitude level. Feynman related these amplitude level path summations to vector addition of arrows that makes it clear there is an important phase factor associated with each path (the sign, or direction the arrow points). Hence, properties of a molecule derive from interferences among the different ways that atomic orbitals are combined, at the amplitude level, in coherent superpositions to produce molecular orbitals of various symmetries and energies. A challenge for understanding electrons in molecules and their correlations is to design experiments that provide insights. A possible approach, together with its advantages and difficulties, will be discussed in Sec 4.

2. Weak correlations: Quantum-coherent energy transfer in conjugated polymers

A perfect conjugated polymer would have π -orbitals delocalized in one dimensional along the chain. The electronic structure of such a system is predicted by a semiconductor band model with Peierls distortion [1-3]. Indeed, Schott and coworkers have reported close to ideal polydiacetylene chains with extraordinary coherence lengths [4,5]. In general, however, conjugated polymer chains are highly disordered because the barriers for rotations about bonds in the backbone are not too dissimilar from thermal energies at ambient temperature [6,7]. The resulting twists of the chain break the π -conjugation into a string of smaller conjugation lengths, called conformational subunits, Fig 1. These conformational subunits are considered to be the basic chromophores (light absorbing units) of conjugated polymers. These chromophore units are not isolated from each other, and it has turned out to be a complicated problem to resolve the nature of electronic excited states and how they evolve in time.

From the conformational subunit viewpoint it is clear from Förster's theory of energy transfer that excitation on the blue edge of the absorption spectrum mainly excites short subunits, and energy transfer causes migration of that excitation energy [8] "downhill" to longer subunits, that have lower excitation energies. The model contributes to a useful quantitative understanding of the steady-state fluorescence spectrum, and is consistent with fluorescence line-narrowing studies, and picosecond (and longer time scale) dynamics of energy transfer along and between conjugated polymer chains [9].

This static picture of *very* weakly interacting chromophore subunits, however, is not suited for understanding a number of other experimental results. Three-pulse photon echo peak shift (3PEPS) measurements can quantify static disorder compared to spectral diffusion caused by line broadening or energy transfer [12]. If the Förster model for

intrachain energy transfer in conjugated polymers were accurate, then 3PEPS measurements would measure the inhomogeneous distribution of conformational subunit transition energies. In contrast, 3PEPS studies of MEH-PPV in solution suggested that excitation is initially delocalized over conformational subunits [13]. The initial decay of the 3PEPS data is then assigned to relaxation among these exciton states together with dynamic localization caused by decoherence [14,15]. After approximately 100–200 fs excitation is eventually localized to a conformational subunit and energy transfer proceeds on longer time scales by hopping (Förster) mechanisms, in accord with the model described in the preceding paragraph. In Fig 1b the results of two simulations of pump-probe anisotropy are plotted. The Förster-type hopping model cannot reproduce the ultrafast decay component of the anisotropy measured experimentally [10]. However, a model that accounts for the slightly delocalized nature of conjugated polymer excitonic states (the exciton relaxation model) reveals that the ultrafast component of the anisotropy decay is likely to be relaxation within a manifold of delocalized exciton states, consistent with the 3PEPS results.

Electronic couplings between conformational subunits are generally larger for interchain interactions than intrachain [16,17]. Therefore there have been studies addressing the issue of exciton coherence in films of conjugated polymers to ascertain the exciton size and implications of quantum-coherence on excitation diffusion [18,19]. We recently found that quantum-coherence is involved in the ultrafast dynamics of *intrachain* energy transfer in MEH-PPV (dilute solution at 294 K) [11,20]. The experiment, called two-time anisotropy (TTAD) measures the normal pump-probe anisotropy along the pump-probe time delay T using a heterodyne-detected transient grating. The coherence time τ between the pump pulses that generate the population grating is also scanned. Decay of anisotropy during the coherence time reveals that the optical coherence undergoes energy transfer along the polymer chain—quantum-coherent energy transfer. These results build on the picture gleaned from the earlier 3PEPS studies. The quantum-coherence can be interpreted as the way the eigenstates change with time and that their amplitude evolves coherently among sites on the chain (the basic chromophores) as a result of the strong disorder in chromophore excitation energies (owing to the size dispersion of conformational subunits).

One area where it is thought that coherent energy transfer might be important is organic solar cells [21]. At present the bulk heterojunction is the favored design because it means that excitons only need to diffuse a few nanometers or so to reach an interface, where the exciton dissociates. It is widely thought that a bilayer would be the preferred design if exciton diffusion were not a limiting factor [22]. Surprisingly little is known about exciton diffusion mechanisms in conjugated polymer films and it is tantalizing to imagine, given the enormous advances in our understanding of energy transfer phenomena elucidated over the past two decades, that fundamental advances in design will greatly enhance exciton diffusion lengths and make bilayer organic solar cells feasible. Coherence on its own will likely not be sufficient, but perhaps coupled with complementary advances in self-assembly, then it will be possible to increase exciton diffusion lengths in organic films substantially. The question remains open at the present time.

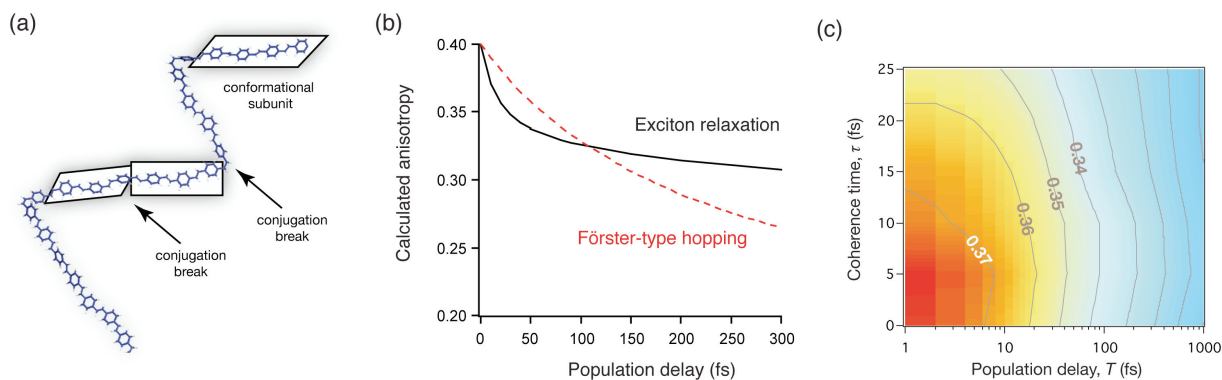


Fig.1. (a) Structure of part of a conjugated polymer (poly(phenylenevinylene), PPV) chain showing examples of conjugation breaks and conformational subunits; (b) Ultrafast anisotropy decays calculated for a PPV chain assuming two different models for energy transfer dynamics [10]; (c) Two-time anisotropy decays measured for MEH-PPV in chloroform solution at 294 K [11].

3. Intermediate correlations: Exciton binding energy

Traditional inorganic solar cells work because photoexcitation (absorption of sunlight) almost directly generates charge carriers—electrons and holes—that move to opposite electrodes under the influence of an electrical potential energy gradient and thereby produce current. This does not happen in organic solar cells because there the most stable species formed by photoexcitation are nanoscale excitons [23], not carriers. Dissociating the carriers efficiently to produce electricity is therefore a much harder task in organic solar cells than in conventional silicon ones. The substantial energetic cost to carrier formation is overcome by combining two materials with appropriate energy levels to make a heterojunction [21,24]. The strong stabilization of electron-hole pairs in organic materials is caused by correlation effects [27] and provides a central challenge to the field of organic solar cells at present [25,26]. To work out how to reduce the exciton binding energy, it makes sense to examine the relative importance of contributions from the different kinds of constituent correlation effects. The aim of this section is to describe those effects.

The highest energy orbital containing electrons in the valence band is lower in energy than the onset of vacant orbitals (conduction band) of a crystalline solid by an energy called the bandgap [28]. After photoexcitation across the bandgap the electron moves freely in the chemical structure relative to the hole left in the valence band, meaning these quasiparticles are uncorrelated charge carriers. Note that this picture just described is based on orbitals. While these orbitals constitute a convenient basis for describing optical excitation, excitons, correlations, or bound electron-hole pairs are not found until excited state wavefunctions are constructed from electron-hole configurations. These configurations are mixed by appropriate two-electron integrals, and the wavefunctions are antisymmetrized to yield eigenfunctions of spin or total angular momentum. When excited state wavefunctions are calculated, it is found that electron-electron interactions lead to a net binding the electron and hole. Thus the optical resonance (optical gap measured in absorption spectroscopy) is often considerably lower in energy than the bandgap. That is certainly the case for organic materials, where the exciton binding energy E_b is large, 0.5 eV up to a few eV, and the barrier to carrier formation after light absorption cannot be surmounted by thermal activation. In contrast, the binding energy is just a few meV for bulk inorganic semiconductors like CdTe.

In the limit that the wavefunctions for electron and hole are very large compared to the size of the molecules and the dielectric constant is large, then sometimes the problem can be reduced to the intuitive hydrogenic model of an electron and hole embedded in a dielectric continuum [30]. In that model, electron-hole correlations are easily understood as the way the electron orbits the hole like in the Bohr model for the hydrogen atom. The motions of the quasiparticles are thus correlated unless they are so far apart that the Coulombic attraction between them is negligible. That picture is identical to the ionization limit of a Rydberg series for a molecule. Electron-hole interaction is screened by the dielectric constant of the phenomenological continuum, which explains why correlations are much stronger in organic materials compared to those in semiconductors such as GaAs or silicon largely because of the low dielectric constant of organic materials

In our model, however, we start by thinking how to partition the kinds of important electron-hole pair configurations involving our collection of chromophores. Films or crystals of organic materials are often described most intuitively in terms of interacting molecules, chromophores, or conformational subunits, and the theory will therefore be based on a Hamiltonian defined in this picture, Eq 1.

$$H = \begin{bmatrix} H_{LE}(1,1) & V_{12}^{ex} & & t_{12} & t_{13} \\ V_{21}^{ex} & H_{LE}(2,2) & & t_{21} & 0 \\ & & \ddots & & \\ & & & H_{CT}(1,2) & t_{23} \\ & & & t_{32} & H_{CT}(1,3) \\ & & & & & \ddots \end{bmatrix} \quad (1)$$

Often organic materials are quite disordered, which affects both the diagonal and off-diagonal elements of Eq 1. This will be ignored explicitly in the following description, though it can be accounted for without changing the basic qualitative picture [29]. Ignoring multiparticle correlations and correlations concerning how the electrons collectively move [31] (see the following section), two distinct kinds of electron-hole configuration can be identified: Locally-excited (LE) configurations where the electron and hole are located on the same chromophore, and charge-transfer (CT) configurations where the electron and hole occupy different sites [29]. The former are the basis for the Frenkel exciton picture, while the latter found the Wannier exciton model. The resulting Hamiltonian, Eq 1, is described in detail in ref [29]. Here I will emphasize key elements.

The diagonal elements as well as the off-diagonal elements introduce various kinds of correlations among the electron and hole. $H_{LE}(i,i)$ comprises the excitation energy of chromophore i corrected for polarization effects due to the surrounding medium. The excitation energy of chromophore i includes the exchange interaction that produces singlet-triplet splitting and accounts for spin-spin correlations. The parallel spins of electrons of a triplet state are more highly correlated, that is, they minimize Coulomb repulsions more effectively than spin paired electrons by virtue of the Pauli exclusion principle. As a result, triplet excitons are stabilized more than singlet excitons. $H_{CT}(i,j)$ includes a polarization-corrected difference between the ionization potential of chromophore i and electron affinity of chromophore j . Additionally it includes a change in electron repulsion energies $-C_{ij}$ (differences in two electron integrals) that is interpreted as electron-hole attraction. This term accounts for the majority of electron hole correlation and has the same interpretation as that in the hydrogenic exciton model discussed above. These ‘diagonal’ contributions to electron-hole correlation are typically insensitive to decoherence because they are characterized by energies quite a bit greater than kT .

The off-diagonal elements of Eq 1 compete in their influence on electron-hole correlations. The excitonic coupling V_{ij}^{ex} correlates the LE configurations by introducing a phase relationship between excitation amplitudes among the chromophores. This interaction provides a correction to the exciton-binding energy. The other important off-diagonal contribution comes from the transfer integrals t_{ij} that serve to mix the CT configurations with each other and with the LE configurations. These terms reduce electron-hole correlations because they mix the ways that electrons and holes can be arranged in the system. As a consequence, a high density of states is found that have the properties of free carriers in the bulk—the electron and hole act independently. This occurs when the electron-hole attraction C_{ij} is much smaller than magnitude of the transfer integrals that promote hopping of electrons and holes from one subunit to another. Hence hopping, or randomization of electron and hole positions with an associated increase in entropy, is favored over collecting configurations with similar electron-hole attractions, i.e. mean separations.

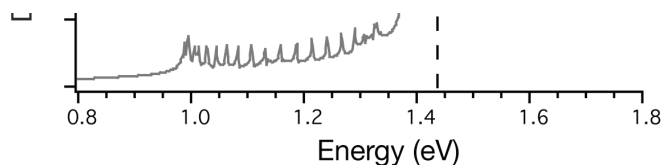


Fig. 2. Calculation of the bound exciton states and carrier-like states (the charge transfer excitons) for a model linear assembly of 20 chromophores. See text for a description and Ref [29] for technical details.

Fig 2 shows a calculation of the density of states of a nanoscale system that results after mixing of the configurations introduced above. Each exciton band appears to be divided into two parts. The lower energy ladder of states are the bound excitons, those wavefunctions dominated by configurations wherein the electron and hole are close enough that their mutual attraction lowers the energy of the state relative to the bandgap. The dense band of charge-transfer exciton states are formed by strong mixing between configurations composed of widely separated electrons and holes and lie primarily above the bandgap energy.

In the case of singlet excitons, the dominant contribution to V_{ij}^{ex} is a long-range Coulombic interaction (incidentally, it is known as the exchange interaction in the molecular orbital representation). This interaction further binds the exciton. However, perhaps the most important role of this term is to distribute oscillator strength among the lowest energy states according to structural parameters. Its significance is seen in the size-dependence of the singlet-triplet splitting, which can be traced back to this interaction. A further important facet of the exchange/Coulomb interaction is that it is responsible for determining the spin eigenstates, thus establishing the rules for spectroscopy. The excitonic interaction V_{ij}^{ex} is also influenced by orbital overlap and these contributions are captured by the transfer integrals that mix LE and CT states [32].

It is a complicated interplay of electrostatic and quantum effects that bind charge carriers, thereby suppressing their separation. Therefore, to work out how to reduce exciton binding energies we must learn how to control the interactions among electrons using chemical structure. This is already the principle behind heterojunctions in some sense, that is, separated electron-hole pair states can be rendered lower in energy than the exciton by a staggered band offset for two components. How heterostructures can be described using the theory just developed is reported elsewhere [33]. The disadvantage of heterojunctions, however, is that the exciton binding energy is reduced in such a manner that it cannot be recovered—that energy is used to separate the electron and hole. That leads to a concomitant reduction in the open circuit voltage of photovoltaic devices based on this architecture. The solution to the problem lies in an intrinsic reduction of the exciton binding energy; that is, reduce electron-hole correlation. While that can be achieved by increasing the dielectric screening in the material, that is not really an option if the system is based on organic molecules. Electron-hole attraction is a mean field effect, so it cannot be easily manipulated owing to the long-range and weak distance dependence of Coulomb interactions. However, is there a way of decreasing the effect of electron-hole attraction by counterbalancing strong electron correlations? That is, perhaps electron-hole attraction can be reduced by the way the electron and hole cause other electrons in the system to respond to photoexcitation. This question is part of the motivation for the next section of the paper.

4. Strong correlations: Making and breaking bonds

Predicting chemical reactivity is a central challenge in chemistry. Mean-field models in chemistry — that is, theories based on orbital energies, symmetries, and shape — have proven to be enormously successful for predicting electronic structure, explaining reactivity, and qualitatively describing spectroscopy. To a significant extent, for example, our understanding of chemical reactivity is guided by Pauling's electronegativity scale; electrons move from electron-rich to electron-poor regions of reactants [34–36]. However, the correlated motions of electrons in molecules are significant. Can we use the correlated response of electrons to promote, or to understand more deeply, concerted chemical change? To answer questions like this it is essential to develop experiments that can test quantum chemical predictions or suggest answers independently. The challenge is that spectroscopy is well suited to measure energy differences, but we really need to adduce the mechanisms that cause these differences. At the

present time this can only be achieved using carefully designed experiments in combination with advanced theoretical calculations.

Recently we reported a demonstration of the two-dimensional optical coherent spectroscopy suggested by Mukamel and co-workers to correlate the double excited electronic states to constituent single excited states [37,38]. The technique, termed two-dimensional double-coherence spectroscopy (2D-DQCS), makes use of multiple, time-ordered ultrashort coherent optical pulses to create double- and single-quantum coherences over time intervals between the pulses. The resulting two-dimensional electronic spectrum maps the energy correlation between the first excited state and two-photon allowed double-quantum states, Fig 3. The principle of the experiment is that when the energy of the double-quantum state, viewed in simple models as a double HOMO to LUMO excitation, equals twice that of a single excitation, then no signal is radiated. However, electron-electron interactions in real systems generate a signal that reveals precisely how the energy of the double-quantum resonance differs from twice the single-quantum resonance. The energy shift measured in this experiment reveals how the second excitation is perturbed by both the presence of the first excitation and the way that the other electrons in the system have responded to the presence of that first excitation.

Single and double quantum transitions are well known in vibrational spectroscopy as the fundamental and overtone frequencies, respectively. Owing to anharmonicity, the overtone is found at a frequency less than twice the fundamental frequency. That is, $\Delta = \omega_{fg} - 2\omega_{eg}$ is negative. That is in contrast to the results reported in our recent work, and for unpublished results on single-wall carbon nanotubes, where we have studied ‘electronic oscillators’. The electronic oscillator problem is considerably more complicated than vibrational oscillators because electronic transition frequencies are determined by the many-body response of electrons in a molecule and quantum-mechanical correlations are important. It is not obvious that electronic single quantum transitions should necessarily have an ‘overtone’ (*vide infra*), but this seems to be what we observe in experiments.

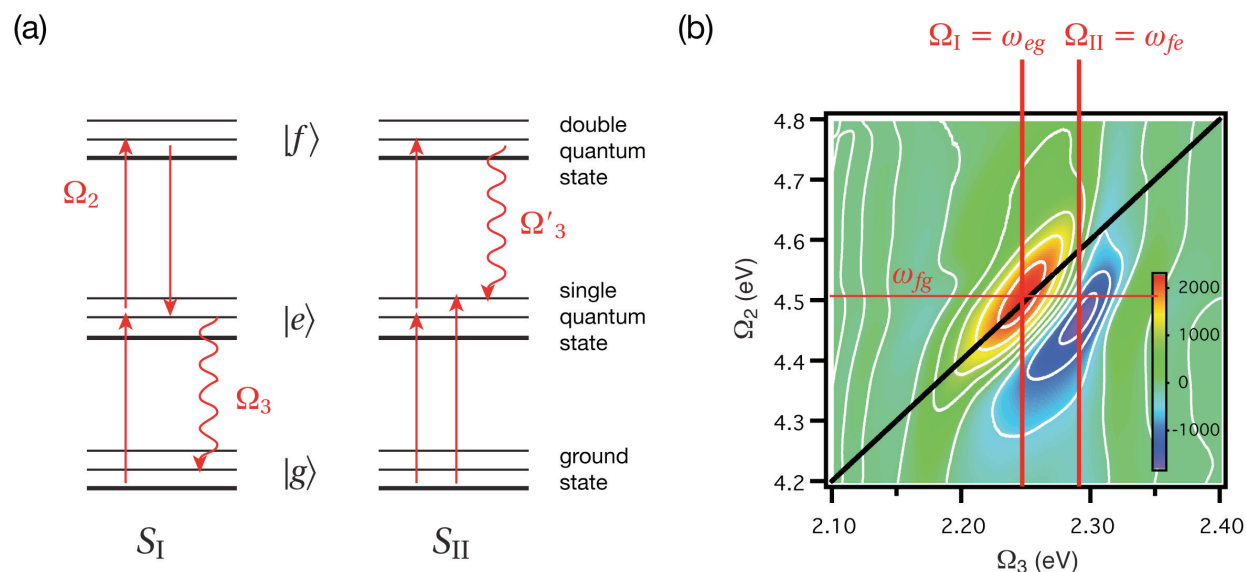


Fig. 3. (a) Illustration of the relevant vibronic manifolds of a molecule and the laser pulse energies (solid red lines) and radiated signals (wavy lines) for the two pathways that interfere to give the DQCS signal; (b) Re 2D-DQC spectrum of the model chromophore Nile red in dichloromethane solution measured with a laser pulse spectrum centered at 2.23 eV [39].

With respect to the aim of elucidating correlations, experiments such as DQCS can indicate the presence of correlations by comparing ω_{fg} with ω_{eg} and ω_{fe} [39-41], but do they reveal enough details for applications and testing of quantum chemical theory [42]? The energy shifts recorded in the experiments (sometimes called the binding

energies of biexcitons) arise from a combination of two important effects. The first, which likely dominates, is captured by theories such as the Hartree–Fock method that evaluate the average electron–hole attractions, electron–electron (hole–hole) repulsions and the quantum-mechanical exchange corrections to these Coulomb interactions by assuming the charges are spread out in space according to the probability that the particle could be found there.

The model picture of explaining single- versus double-quantum transitions is a two-level system. In the ground state the lower orbital (a , the HOMO) is doubly occupied by spin paired electrons, the single-quantum state is formed by promoting of one of these electrons to the upper orbital (b , the LUMO), while the double-quantum state has both electrons occupying b . Representing alpha spin orbital as unbarred and beta spin orbitals with a bar, the corresponding singlet state wavefunctions are:

$$\Psi_0 = |a\bar{a}| \quad (2a)$$

$$\Psi_1 = \frac{1}{\sqrt{2}}(|a\bar{b}| + |b\bar{a}|) \quad (2b)$$

$$\Psi_2 = |b\bar{b}| \quad (2c)$$

It is now easily seen that there are differences in the excitation energies E_{10} and E_{21} owing to changes in electron–electron repulsion in the a versus b orbitals. For example, that would be the case when b is more delocalized than a , as is often the case. However, the big difference is that Ψ_1 experiences a large exchange shift ($J_0 =$ half the singlet–triplet splitting), raising its energy, but Ψ_2 does not, because the spin-paired electrons occupy the same orbital. Hence Ψ_2 appears very strongly bound because $E_{21} \approx E_{10} - 2J_0$. Given that J_0 is usually about 0.5 eV for organic molecules, we cannot see this double-quantum transition relative to the lowest singlet singlet-quantum transition in our experiments because the laser pulses are not broad enough spectrally.

The double-quantum state that is reliably found in DQCS experiments therefore must have a similar exchange correction to that of the single-quantum state, Eq 2b, so it can be found at about twice the transition energy of the lowest singlet excited state. Quantum chemical calculations reported in Ref [39] suggest that hypothesis is correct, and that the minimal model needed to understand DQCS is based four orbitals: two occupied orbitals a and a' and two unoccupied orbitals b and b' in the ground state. The double-quantum state is therefore caused by the double excitation $aa' \rightarrow bb'$. Now E_{21} is not too different from E_{10} , and the small energy shift (apparent binding energy) $\Delta = E_{20} - 2E_{10} = \hbar(\omega_{fg} - 2\omega_{eg})$ is caused by small differences in electron–electron repulsions and the change of the exchange correction J_0 in the single- versus double-quantum state.

The second effect contributing to Δ is explicitly called electron correlation in the quantum-chemical literature and describes the fascinating way that electrons and holes tend to coordinate their motions to minimize repulsions [43]. For example, two electrons might move in a fashion so they avoid crossing paths. The complexity of this problem scales steeply with the number of particles involved. Although present investigations into many-body effects using DQCS provide an important first step to understanding the way groups of carriers interact collectively, it is not yet clear how to quantify mean-field Coulomb repulsions and attractions and their exchange corrections compared to how the transition energies are modified by more complicated correlations in multiparticle motions.

5. Conclusions and Outlook

Intrinsically quantum-mechanical phenomena abound on a range of energy and length scales in chemistry, fundamentally because chemical bonds and interactions are quantum mechanical in nature. In this article some examples of quantum-mechanical phenomena that can be probed by optical spectroscopy were discussed. Recent experimental studies of quantum-coherence in electronic energy transfer in π -conjugated polymers were reported as examples of weak correlations. In cases of more strongly correlated systems, electron-hole binding energy in excitons was dissected into the various kinds of correlations. The point of this was to show how it is the combined effect of different kinds of quantum-mechanical correlations that contribute the exciton binding energy. Simply measuring the energy itself is not enough to understand these interactions. A similar philosophy applied to the goal

of understanding correlations of electrons in chemical bonds, particularly the frontier orbitals of molecules undergoing a chemical reaction. It would be exquisite to follow the way correlations change during a chemical reaction, like a cycloaddition. This would take our understanding beyond mapping energetic barriers, and may provide insight into how to control chemical change through concerted reorganization of electrons. Possible experimental probes of strong correlations involved in chemical reactions were critically examined in the final section of the paper. In particular, the question of what precisely is measured by DQCS spectroscopy was examined. The challenge is how to translate energy differences recorded in spectroscopy into insight about underlying mechanisms. Nonetheless, the ground state, single- and double-quantum excited states are closely related to the states used to construct symmetry correlation diagrams in photocycloaddition reactions (the Woodward-Hoffmann rules), so DQCS can provide direct insights in this case.

Acknowledgements

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References

- [1] G. Hadziioannou, G.G. Malliaras (Ed.), *Semiconducting polymers: Chemistry, physics and engineering*. Wiley-VCH, Weinheim, 2007.
- [2] W.P. Su, J.R. Schrieffer, A.J. Heeger, *Phys. Rev. B* 22 (1980) 2099.
- [3] N.S. Sariciftci (Ed.), *Primary Excitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model*. World Scientific, Singapore, 1997.
- [4] F. Dubin, R. Melet, T. Barisien, R. Grousson, L. Legrand, M. Schott, V. Voliotis, *Nat. Phys.* 2 (2006) 32.
- [5] R. Lécuiller, J. Berréhar, J.D. Ganière, C. Lapersonne-Meyer, P. Lavallard, M. Schott, *Phys. Rev. B* 66 (2002) 125205.
- [6] G. Rossi, R.R. Chance, R. Silbey, *J. Chem. Phys.* 90 (1989) 7594.
- [7] S.N. Yaliraki, R.J. Silbey, *J. Chem. Phys.* 104 (1996) 1245.
- [8] G.D. Scholes, *Annu. Rev. Phys. Chem.* 54 (2003) 57.
- [9] H. Bässler, B. Schweitzer, *Acc. Chem. Res.* 32 (1999) 173.
- [10] T.E. Dykstra, E. Hennebicq, D. Beljonne, J. Gierschner, G. Claudio, E.R. Bittner, J. Knoester, G.D. Scholes, *J. Phys. Chem. B* 113 (2009) 656.
- [11] E. Collini, G.D. Scholes, *Science* 323 (2009) 369.
- [12] G.R. Fleming, S.A. Passino, Y. Nagasawa, *Philos. Trans. R. Soc. Lond. Ser. A* 356 (1988) 389.
- [13] G.D. Scholes, D.S. Larsen, G.R. Fleming, G. Rumbles, P.L. Burn, *Phys. Rev. B* 61 (2000) 13670.
- [14] T.E. Dykstra, V. Kovalevskij, X. Yang, G.D. Scholes, *Chem. Phys.* 318 (2005) 21.
- [15] X. Yang, T.E. Dykstra, G.D. Scholes, *Phys. Rev. B* 71 (2005) 045203.
- [16] D. Beljonne, G. Pourtois, C. Silva, E. Hennebicq, L.M. Herz, R.H. Friend, G.D. Scholes, S. Setayesh, K. Müllen, J.L. Brédas, *Proc. Nat. Acad. Sci.* 99 (2002) 10982.
- [17] J.L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, *Chem. Rev.* 104 (2004) 4971.
- [18] F.C. Spano, J. Clark, C. Silva, R.H. Friend, *J. Chem. Phys.* 130 (2009) 074904.
- [19] W. Barford, C.D.P. Duffy, *Phys. Rev. B* 74 (2006) 075207.
- [20] E. Collini, G.D. Scholes, *J. Phys. Chem. A* 113 (2009) 4223.
- [21] S. Gunes, H. Neugebauer, N.S. Sariciftci, *Chem. Rev.* 107 (2007) 1324.
- [22] F. Yang, S.R. Forrest, *ACS Nano* 2 (2008) 1022.
- [23] G.D. Scholes, G. Rumbles, *Nat. Mater.* 5 (2006) 683.
- [24] J. Peet, A.J. Heeger, G.C. Bazan, *Acc. Chem. Res.* 42 (2009) 1700.
- [25] J.L. Brédas, J.E. Norton, J. Cornil, V. Coropceanu, *Acc. Chem. Res.* 42 (2009) 1691.
- [26] J.C. Bijleveld, R.A.M. Verstrijden, M.M. Wienk, R.A.J. Janssen, *Appl. Phys. Lett.* 97 (2010) 073304.
- [27] D.S. Chemla, J. Shah, *Nature* 411 (2001) 549.
- [28] M. Pope, C.E. Swenberg, *Annu. Rev. Phys. Chem.* 35 (1984) 613.
- [29] G.D. Scholes, *ACS Nano* 2 (2008) 523.
- [30] P.K. Basu, *Theory of the optical processes in semiconductors: Bulk and microstructures*, Oxford University Press, New York, 1997.
- [31] G.D. Scholes, R.D. Harcourt, *J. Chem. Phys.* 104 (1996) 5054.
- [32] R.D. Harcourt, G.D. Scholes, K.P. Ghiggino, *J. Chem. Phys.* 101 (1994) 10521.
- [33] S.S. Lo, Y. Khan, M. Jones, G.D. Scholes, *J. Chem. Phys.* 131 (2009) 084714.
- [34] L. Pauling, *J. Am. Chem. Soc.* 54 (1932) 3570.
- [35] R.S. Mulliken, *J. Chem. Phys.* 3 (1935) 573.
- [36] R.S. Mulliken, *J. Chem. Phys.* 2 (1934) 782.

- [37] Z. Li, D. Abramavicius, S. Mukamel, *J. Am. Chem. Soc.* 130 (2008) 3509.
- [38] J. Kim, S. Mukamel, G.D. Scholes, *Acc. Chem. Res.* 42 (2009) 1375.
- [39] J. Kim, V. Huxter, C. Curutchet, G.D. Scholes, *J. Phys. Chem. A* 113 (2009) 12133.
- [40] K.W. Stone, D.B. Turner, K. Gundogdu, S.T. Cundiff, K.A. Nelson, *Acc. Chem. Res.* 42 (2009) 1452.
- [41] D.B. Turner, K.A. Nelson, *Nature* 466 (2010) 1089.
- [42] G.D. Scholes, *Nature* 466 (2010) 1047.
- [43] S. Wilson, *Electron Correlation in Molecules*, Oxford University Press, Oxford, 1984.