



Reply to comment on ‘Multiple quantum coherences in liquid state NMR and nonlinear optics; collective vs. local origin’ [Chem. Phys. Lett. 357 (2002) 327]

S. Mukamel *

Department of Chemistry, University of Rochester, P.O. RC Box 270216, Rochester, NY 14627-0216, USA
Department of Physics and Astronomy, University of Rochester, P.O. RC Box 270216, Rochester, NY 14627-0216, USA

Received 2 October 2002; in final form 4 October 2002

Abstract

The close analogy between the multiple quantum resonances observed in NMR and many-body effects in time and frequency domain nonlinear optical spectroscopy is explained. The nonlinear exciton Equations provide a systematic hierarchical method for incorporating and classifying collective effects beyond the mean-field level. The apparent inconsistencies pointed out by Jeener are caused by terminology differences which are clarified.

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Predicting nonlinear spectroscopic signals in the condensed phase is a complex many-body problem both in the NMR and in the optical regime. The purpose of article [1] was to point out that the analysis of NMR resonances observed by Warren, and the ensuing lively debate in the NMR community could benefit from a systematic methodology developed in the studies of the optical response of molecular aggregates and semiconductors, where closely related effects have been well known. Communication between the two fields is hindered by a terminology barrier, and I am delighted to add these clarifying remarks in response to Jeener’s insightful comments [2].

In many-body theory (be it classical or quantum) it is common to describe the dynamics using a hierarchy of dynamical variables (single body, two body, etc.) [3]. Proper truncation of the hierarchy at the right level is the key for numerous approximations and practical calculations. Truncation at the single body level by factorizing all higher variables is known as the mean-field approximation. The ‘classical’ NMR approach, denoted in optics as the local field approximation, is based on this level of theory. This approach, which works quite well for the NMR experiments, was developed in optics in order to connect the magnitudes of frequency domain polarizabilities with macroscopic susceptibilities [4]. It has been extended to the time domain where it predicts new interaction-induced signals [5,6] resulting from losing the control over time ordering: even if the

* Fax: 1-585-506-0205.

E-mail address: mukamel@chem.rochester.edu

incoming pulses are short and well separated, the local fields can be longer and may act in a different time sequence than the original pulses. The mean-field computation of optical and NMR signals can be readily made by incorporating the local field correction to the Bloch equations [7]. Frequency shifts and distorted lineshapes in NMR have been accounted for at this level of theory [8]. The classical Clausius-Mossotti equation predicts red shifts in the optical response for precisely the same reason [9]. Warren started with the fully many-body density matrix but then made a series of approximations that eventually reduced the result to the mean-field level. His derivation provides a physically motivated rationale for the mean-field approximation but does not go beyond it.

The standard many-body hierarchy as implemented by the nonlinear exciton equations, [10] provides a systematic and practical way to go beyond the local field level. It incorporates intermolecular effects, reduces naturally to the mean-field level when appropriate, and allows a study of many-body correlation effects at an affordable computational cost. Knowledge of the full many-body density matrix taking into account explicitly all dipole couplings, is neither feasible nor desirable since n quantum resonances only require looking at n particles simultaneously and typically n is much smaller than the total number of spins.

The next level of the hierarchy, equations of motion involving single and two body variables, have been applied to molecular aggregates [11]. It predicts new and shifted multiple quantum resonances, two exciton, three exciton, etc., cooperative spontaneous emission (superradiance), and exciton effects in pump probe and photon echo spectroscopies [9].

I fully agree with Jeener on the distinction between coherence and correlation [12]. In the condensed phase many molecules (or spins) are driven simultaneously and the many-body density matrix contains oscillations at all multiple of the fundamental frequency. However, since the dipole is a single body operator, these coherences do not affect its expectation value in the absence of coupling between spins, and are not observable in optics as well as NMR [12]. This coupling can be described either in a single body picture

through the local classical field or in a two body picture.

Some interaction-induced effects such as multi-quantum resonances are predicted by both single and two particle levels of the hierarchy but the underlying microscopic dynamics are very different. A multiple quantum coherence exists in a many-body system provided all spins are all driven by the same field and oscillate in phase even when the spins are not correlated and the total density matrix may be factorized at all times into a product of individual spins. Multi-quantum resonances obtained at the lowest level of the hierarchy only reflect coherence and no correlation. Intermolecular coherence implies in-phase oscillation of various spins; correlation means that the density matrix may not be factorized into a product of single spin matrices. Only the higher level of the hierarchy which includes intermolecular variables takes into account correlation effects as well. Consequently, the lowest, mean-field, level predicts a two exciton resonance at twice the fundamental frequency whereas the two particle level of the hierarchy predicts a multiplicity of shifted resonances [11]. Only the latter, which require the explicit inclusion of higher variables, should be labelled as genuine many-body effects.

The many-body hierarchy offers a natural classification of various types of resonances. We have denoted the classical mean-field level which includes coherence but no correlation as LFMQC. Correlation effects enter only in the next level of the hierarchy and the corresponding additional multi-quantum resonances which are absent at the mean-field level were denoted CIMQC.

From a theoretical standpoint, the distinction between intramolecular (short range) and intermolecular (long range) couplings on a microscopic level is somewhat problematic since short and long range portions of the same interaction are treated differently. Since both effects originate from the same coupling there is a subtle issue of double bookkeeping of interactions. This double counting may be cleanly resolved in optics by dividing the field into its transverse and longitudinal components. This is not possible in NMR where the long wavelength approximations holds. The nonlinear exciton equations allow to make this distinction

unambiguously in both cases. The difference between LFMQC and CIMQC is in the microscopic treatment which avoids double counting of interactions and allows to retain the desired amount of microscopic detail.

Acknowledgements

The support of the National Science Foundation Grant No.(CHE-0132571) and the National Institutes of Health Grant No. 1 RO1 GM59230-01A2 is gratefully acknowledged.

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