CHAPTER VI

CONCLUDING REMARKS

In this dissertation, we have presented nonlinear wave packet interferometry (WPI), a form of multidimensional electronic spectroscopy which uses two phase-locked pulse-pairs to excite and probe molecular dynamics. By controlling the relative spectral phase between pulses, nonlinear WPI is used to isolate the wave-packet interference effects in an excited electronic population as a function of the inter-pulse delays. With access to the measured interferogram, which is proportional to the molecular state amplitude, we have devised a means to reconstruct a one-pulse target wave packet from knowledge of the interferogram and a collection of three-pulse reference wave packets.

In Chapter II, we reviewed the ideas salient to the development of WPI. We examined in detail the theory of linear WPI,[1,2] which uses a single pulse-pair to excite and isolate bilinear interference effects, i.e. contributions to the population linear in the two applied fields. We also discussed using the linear WPI interferogram as input into a molecular state reconstruction scheme. Such an approach, called quantum state holography (QSH), was taken originally by Leitchle et al, who showed through computational examples that shaped vibratioanl wave packet could be accurately reconstructed.[3,4] But the types of target wave packets that can be reconstructed using QSH are limited to preparation on a well-known potential energy surface and in the region of

the Franck-Condon point. But with detailed knowledge of the potential energy siurface, an alternative to experimental state reconstruction is direct numerical calculation of the prepared target state. Experimental implementations of QSH demonstrated how wave packet reconstruction could drive adaptive pulse-shaping schemes.[5]

In Chapter III, we introduced the theory of one-color nonlinear WPI,[6] in which each pulse-pair resonates with the same electronic transition. A multitude of wave packets must be accounted for in the theoretical analysis, but we have found that by combining population measurements with specific values of the locking-angles, the two quadrilinear interferences in the population can be independently detected. The latter interference terms are distinguished by their dependence on the phase-locking angles (either the sum or difference), and each is equivalent to a sum of two wave packet overlaps. We found for a model harmonic system the two overlaps are always mixed and cannot be further separated. But for a dissociative system, one of the overlaps can be diminished when dynamical considerations are taken into account. Molecular state reconstruction can then be performed using the nonnegligible overlap. Our numerical examples yielded highly accurate reconstruction of the dissociating target states. And unlike QSH, the target state of a nonlinear WPI reconstruction is not limited to the Franck-Condon region of the electronically-excited potential surface. These results suggest that state reconstruction could be useful for investigating the dynamics underlying photochemical reactions, even though a one-color reconstruction technique requires detailed information about the potential surface on which the target state is prepared.

In Chapter IV, we showed how two-color nonlinear WPI circumvents the need for information about the target-state Hamiltonian. In this chapter, each pulse-pair resonates with a different electronic transition and the isolable quadrilinear interference terms are always equivalent to a single wave-packet overlap. The information necessary for reconstruction is therefore immediately obtainable. In addition, preparation of reference states in a two-color experiment uses an auxiliary electronic level, rather than the electronic level in which the target state is prepared. Though detailed information about the auxiliary level is necessary, we demonstrated by way of numerical simulations that a shaped nuclear wave packet can be reconstructed in the absence of information about the governing Hamiltonian. These results support the use of a two-color reconstruction technique as a complement to current adaptive pulse-shaping experiments. As the latter experiments are often undertaken in the absence of detailed information about the target-state Hamiltonian, the present reconstruction technique could be used to identity the dynamics underlying a successful (or failed) quantum control strategy.

Chapter V consists of work performed in collaboration with Jeff Cina and Dmitri Kilin and provides a demonstration of two-color nonlinear WPI for a model energy-transfer complex.[7] Tailored sequences of electronic excitations in the chromophores are accomplished by controlling the polarization of the pulses, as well as the phase-locking angles. Through control of the latter, quadrilinear interference terms to the population of the one-exciton levels can be isolated. These interference terms are linear in the chromophore-chromophore scalar coupling J and are interpreted as the overlap between a one-pulse target state, which is the result of energy transfer between exciton levels, and a

three-pulse reference state, which is independent of *J*. For the model harmonic surfaces, phase-space diagrams explain the fringe structure present in the interferograms for the case of equal-site and down-hill energy-transfer processes. The two-color experiments proposed in this work should be capable of probing the optically-induced target state dynamics found, for instance, in photosynthetic light-harvesting complexes, and the entanglement between electronic and nuclear degrees of freedom. It also appear possible that the energy-transferred target state could be reconstructed from the two-color interferogram, though future studies will need to test this.

Of course, there are a few open questions concerning experimental implementations of nonlinear WPI. First, no account for electronic or vibrational relaxation has been made in our analysis. For gas-phase molecules, this omission is most likely not significant; radiative and collisional lifetimes are anticipated to be much longer than the femtosecond to picosecond time-scales for the nuclear dynamics. Then, the electronic population, the physical observable of interest, should be accurately represented by the theory presented here. But in the condensed phase, relaxation dynamics are anticipated to be more significant, and new terms must be incorporated into the system Hamiltonian. In addition, the time scales for electronic decoherence in condensed phase systems can be as short as or shorter than the time scales of excited-state nuclear dynamics. For such strongly-coupled many-body systems, Schrödinger's equation is intractable, even with the exact molecular Hamiltonian (which is itself elusive). But it may be possible to advance the concepts presented in this dissertation into the condensed phase. To do so would necessitate approximation, most likely by

partitioning the problem into a coupled system and bath. Tracing out the bath degrees of freedom would leave a description of the system in terms of a reduced density matrix. If possible, reconstruction of the reduced density matrix could then serve as an amplitude level probe of electronic or vibrational relaxation following an electronic excitation.

Given the current state of the experimental capabilities, nonlinear WPI experiments are clearly possible, and the theoretical results we report suggest one-color and two-color experiments should be successful in reconstructing molecular states. Though one-color experiments require target-state Hamiltonian information for state reconstruction, they are the easiest implemented and the most natural starting point for investigations along these lines. But two-color experiments hold the promise of “real” state reconstruction, i.e. without knowledge of the target-state Hamiltonian, and offer a new opportunity for experimenting with the quantum states of molecules.

Notes

1. N. F. Scherer, R. J. Carlson, A. Matro, M. Du, A. J. Ruggiero, V. Romero-Rochín, J. A. Cina, G. R. Fleming, and S. A. Rice, J. Chem. Phys. **95**, 1487 (1991).

2. N. F. Scherer, A. Matro, L. D. Ziegler, M. Du, R. J. Carlson, J. A. Cina, and G. R. Fleming, J. Chem. Phys. **96**, 4180 (1992).

3. C. Leichtle, W. P. Schleich, I. Sh. Averbukh, and M. Shapiro, Phys. Rev. Lett. **80**, 1418 (1998).

4. I. Sh. Averbukh, M. Shapiro, C. Leichtle, and W. P. Schleich, Phys. Rev. A **59**, 2163 (1999).

5. T. C. Weinacht, J. Ahn, and P. H. Bucksbaum, Nature **397**, 233 (1999).

6. J. A. Cina, J. Chem. Phys. **113**, 9488 (2000).

7. J. A. Cina, D. S. Kilin, and T. S. Humble, J. Chem. Phys. **118**, 46 (2003).