DOE/ER/60473--T1

DE90 010793

SELECTIVE EXCITATION, RELAXATION, AND ENERGY CHANNELING IN MOLECULAR SYSTEMS

Comprehensive Progress Report

May 1987 - April 1990

William C. Rhodes

Institute of Molecular Biophysics

Department of Chemistry

Florida State University

Tallahassee, Florida 32306

April 1990

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG05-86ER60473

SELECTIVE EXCITATION, RELAXATION, AND ENERGY CHANNELING IN MOLECULAR SYSTEMS

William C. Rhodes
Institute of Molecular Biophysics
Department of Chemistry
Florida State University
Tallahassee, Florida 32306

Grant #: DE-FG05-86ER60473

Department of Energy

TABLE OF CONTENTS

SELECTIVE EXCITATION, RELAXATION, AND ENERGY CHANNELING IN MOLECULAR SYSTEMS

Comprehensive Progress Report

INTRODUCTION

The research here involves theoretical studies of the response, relaxation, and correlated motion in the time-dependent behavior of rather large molecular systems. By large systems, we mean systems having a large number of degrees of freedom. They range in size from a single large polyatomic molecule to a protein molecule in its natural environment. By response we mean the changes in the electronic and vibrational motion of a molecule (or a portion of a molecule we can call a chromophore) due to interactions with an externally applied field (such as light) or to intermolecular interactions in systems not at equilibrium. Such responses are the associated relaxation and the channeling of energy as the system moves toward a new equilibrium.

The present studies are part of an ongoing development of a research program which historically includes the following topics.

(1) Electronic spectral properties of helical biological polymers. Focus has been on the relation between conformation and optical properties, such as absorption spectral structure (e.g., hypochromism) and circular dichroism.

(2) Nonradiative transitions in molecules. Focus has been placed on the role of the exciting light in determining the structure of the prepared excited state. The role of intramolecular interactions and modulation by the molecular medium have been studied in previous phases of this work.

(3) Macroscopic system dynamics. Focus is on the role of the medium in modulating the dynamics of a molecule (a chromophore). Emphasis is placed on the effects of coherent structure, coherence relaxation (memory), and the interplay of coherence and dissipation in determining how kinetics arises from coherent quantum dynamics.

(4) Biomolecular dynamics. Focus is placed on the role of subsystem modulation (e.g., by low-frequency vibrational modes) in the channeling of processes in biological macromolecules and on the role of subsystem cycles in the natural functions of protein molecules. Emphasis is placed on the nature of thermodynamic modes and the microscopic basis of entropy.

Our recent work, as represented by items (3) and (4) above, has led to a meaningful syntheses of the older themes stated in items (1) and (2). Presently, the central theme of our research is subsystem modulation dynamics, in which the dynamics of physical properties associated with certain substructures (or degrees of freedom), referred to as the primary subsystem, are modified by interaction with the remaining degrees of freedom, referred to as the background. We are interested in systems that are both weakly and strongly displaced from equilibrium. Fundamental conceptual themes are: coherence - correlation - memory - dissipation - symmetry breaking (localization and stabilization) - adiabatic motion.

The primary goal of our research program has a two-fold nature:

(i) To understand the role of subsystem modulation by background degrees of freedom in determining the dichotomy between dissipation and coherence in the quantum dynamics of molecular systems and the relation between coherent quantum dynamics and dissipative kinetics in model systems;

(ii) To understand the fundamental quantum and thermodynamic nature of macromolecular cyclic processes in natural biological functions such as enzymes, G-proteins, and membrane channel proteins.

Both aspects of this goal are important, but it is the second which promises the most important new results.

Following is a summary of our most important results.

I. DAVYDOV SOLITON THEORY

The molecular level mechanisms whereby biological systems transform energy and transfer signal (information) has been a major topic of speculation and study for many years. In 1973 Davydov proposed a mechanism of energy transfer in proteins, whereby the amide I vibrational energy (mainly carbonyl vibration) is transferred along the alpha helix. A simple exciton mechanism is not adequate because, as is well known, excitons tend to spread as they travel, due to coherent dispersion. However, another mechanism of energy transfer, by which the energy remains localized as it travels, involves solitons. Solitons have a long history going back to the observations of solitary wave motion by Scott Russell in 1834 and coming into vogue as a pervasive phenomenon in many fields of physics since the 1965 paper of Zabusky and Kruskal in which the name soliton was introduced. Solitons differ from excitons in that the soliton equation of motion is nonlinear.

In the Davydov model nonlinearity is introduced by the coupling of the exciton (formed by the amide I vibration) and a lower-frequency vibration of the helix "lattice", which we refer to as the phonon mode. For the latter, Davydov used the longitudinal motion of this entire amide group, while in the later work of Scott, et al., the out-of-plane motion of the hydrogen bond proton of alpha-helix was used. The structure of the Hamiltonian is the same for both, whereby the coupling between the exciton and the phonon mode is linear in the phonon mode coordinate.

The essential feature of Davydov soliton theory which leads to a nonlinear Schrodinger equation for the exciton amplitudes are the following two assumptions:

(i) The state vector for the exciton-phonon system is taken to be a direct product of an exciton state and a coherent phonon state (or else a superposition of such products).

(ii) The parameters of the state vector (exciton amplitudes and phonon coherent state parameters) obey Hamilton's equations in which the expectation value of the system Hamiltonian serves as Hamilton's function.

There have been several books and literally hundreds of papers written on Davydov soliton theory. Some papers (mainly by Brown and Lindenberg, et al.) have involved critical analyses of the theory and implications that there are problems. But the overwhelming majority support the

existence of Davydov solitons, at least a low temperature. The latter is based on numerical calculations, with use of the two Davydov assumptions. Therefore, such conclusions are not surprising.

In our work we have developed a method of treating the time-dependent Schrodinger equation which avoids both of the Davydov assumptions. The method involves transforming the Schrodinger equation to a new basis in which the phonon mode basis vectors are displaced by an amount dependent on the phonon-exciton coupling in the Hamiltonian. This produces a form which lends itself to numerical calculations by supercomputer vector processing.

The development of algorithms and the numerical calculations on a Cyber 205 supercomputer were carried out by Anthony Nicholls as part of his dissertation research. Following is a summary of key portions of our results. Details may be found in the published paper (Rhodes and Nicholls).

Figures 1 and 2 illustrate key features of our results. λ^2 in the coupling between the exciton and the phonon mode. Roughly, $\lambda^2 > 1$ is strong coupling and $\lambda^2 < 1$ is weak coupling. The value used by other workers, based on the amide spectroscopic parameters, is (approx.) $\lambda^2 = 0.05$. The exciton is localized at one end of the helix at $t = 0$. Recurrence is defined as the appearance of the maximum of the exciton probability at the other end. The variance is defined as the mean square deviation of the exciton probability from the mean. The larger the variance the more localized is the exciton.

Fig. 1 shows how the exciton becomes delocalized as it migrates along the helix. The delocalization actually increases with increasing exciton-phonon coupling. Fig. 2 shows the dependence of the recurrence probability of the exciton on the exciton-phonon coupling. The different curves show the cumulative contribution of states of increasing phonon number to the recurrence probability. The peaks for $\lambda^2 = 1$ and $\lambda^2 = 2$ are due to the fact that the exciton tends to carry along either one or two phonons. Other phonons simply trail along in the wake.

FIGURE CAPTIONS:

Figure 1: Variance of the primary excitation as a function of time for selected values of the coupling parameter λ^2: ($\square$) = 0, (0) = 1/8, (X) = 1, (Δ) = 1/4, (+) = 1/2, ($\Diamond$) = $2^{1/2}$, ($\clubsuit$) = $2^{3/2}$.

Figure 2: Background level contributions to the recurrence probability for the $N = 10$, $n = 5$ model. (Increasing levels are cumulative).

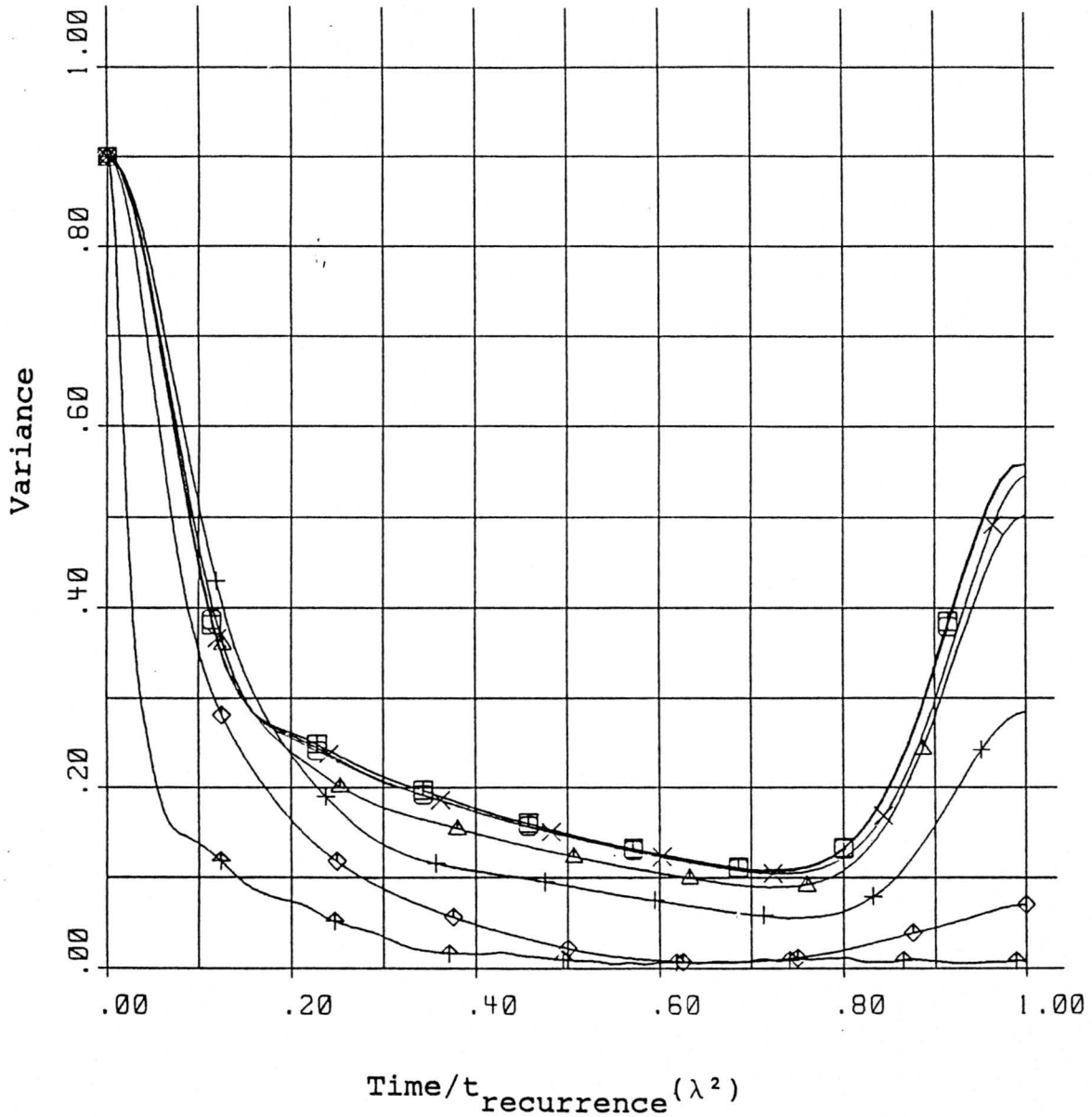
Variance
1.00
.80
.60
.40
.20
.00
.00
.20
.40
.60
.80
1.00
Time/t recurrence (λ²)

FIGURE 1

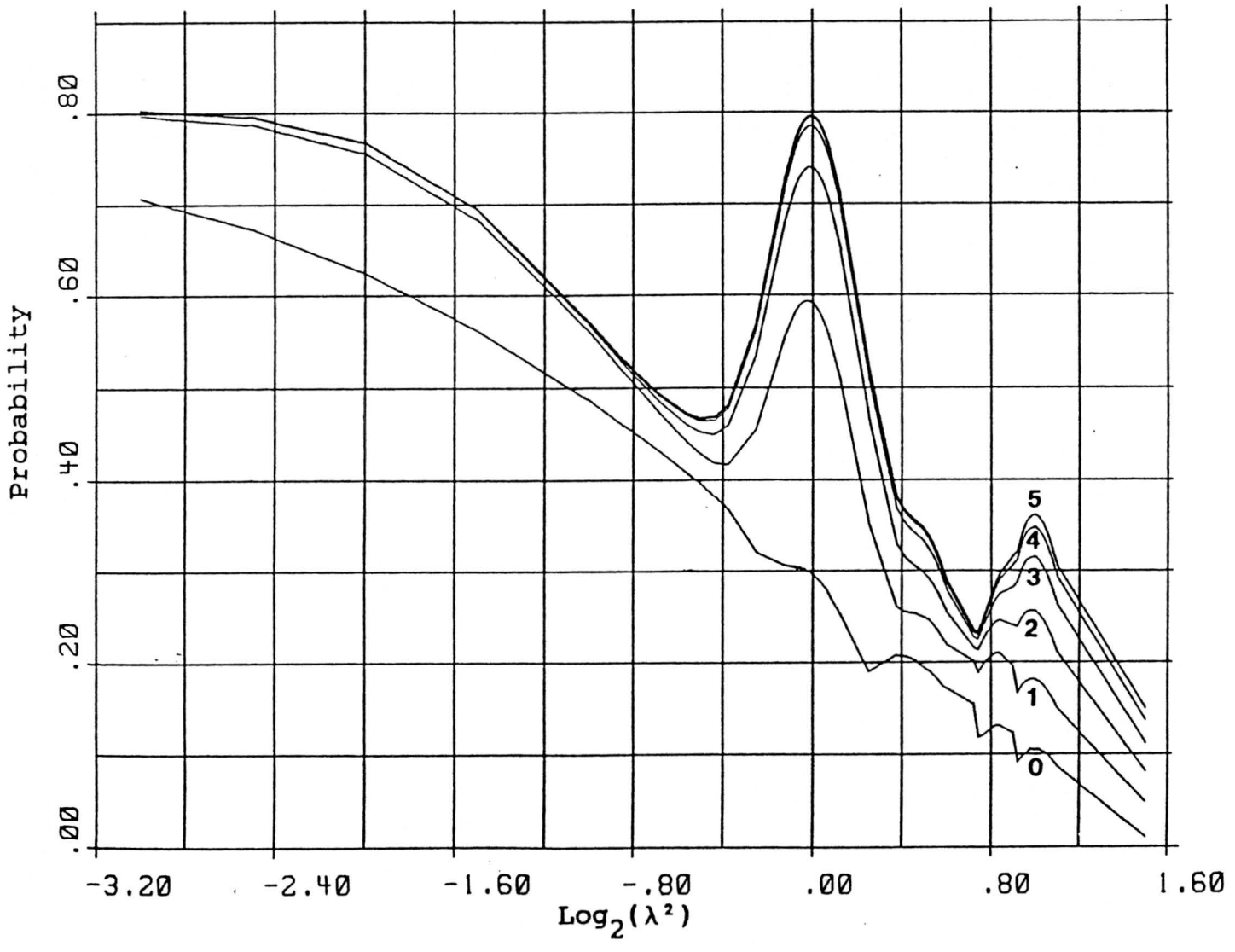
Probability
.80
.60
.40
.20
.00
-3.20
-2.40
-1.60
-.80
.00
.80
1.60
Log2(λ²)
5
4
3
2
1
0

FIGURE 2

Our results show unequivocally that the Davydov soliton, as a localized entity, simply does not exist! Analyses of the equation of motion shows why this is so. As the exciton moves from one amide group to another the phonon mode at each site moves under different potentials. Accordingly, the phonon mode states cannot remain coherent.

II. SQUEEZED STATES

In the past few years, the subject of squeezed states has become a "hot topic" in the literature, the reasons being both its fundamental quantum theoretical nature and its potential practical importance in electronics and optics (e.g., fiber optics) communications. This subject deals with the properties of the basic commutator relation between the position coordinate and its conjugate momentum operator. The nonzero constant value of the commutator leads directly to a minimum product (uncertainty) relation between the variances (or rms deviations) of the position and momentum of a particle. This results in a minimum "noise level" which is intrinsically quantum mechanical in nature.

The basic position-momentum commutator relation may be generalized to dimensionless coordinates and momenta, and is applicable to such variables as the components of the electromagnetic field (e.g., electric and magnetic field components). For the latter, one kind of field component plays the role of coordinate and the other kind plays the role of momentum.

Squeezing consists of scaling one variable ("coordinate") with a scale factor and scaling the other variable (momentum) with the reciprocal scale factor. The basic commutator and the resulting product of variances are invariant to squeezing, but the variance of one variable is reduced at the expense of the other.

Our research on this topic has led to the following new results:

A. Time Evolution of Stable Squeezed States

It was shown that, for a single mode of an electromagnetic field, only quadratic Hamiltonians can preserve squeezed states for all time. Also, we find that no single Hamiltonian can preserve minimum uncertainty for all squeezed minimum uncertainty states.

B. Time-dependent Invariants and Stable Unitarily Transformed Coherent States

Time-dependent Hermitian invariants, having stable coherent states as eigenvectors, are obtained for the Hamiltonian of a single-mode electromagnetic field. This result is generalized to any Hamiltonian that preserves any particular class of unitarily transformed coherent states, such as squeezed states.

C. The Nonexistence of Proper Eigenstates of Squeezed Operators

Operators which produce squeezed states are exponential functions of the squares of the creation and annihilation operators of the field modes (harmonic oscillators). We have shown that proper eigenstates of squeeze operators do not exist. Proper eigenvectors are those having finite norm. The consequence of this is that the eigenstates of squeeze operators may have only generalized eigenstates which may be normalized to a Dirac delta function associated with continuous spectra. (An analogous situation for displacement operators has been shown by Robert Fulton.)

D. Squeezing in Harmonic Oscillators with Time-dependent Frequencies

We have shown that squeezing is always generated in a harmonic oscillator with time-dependent frequency for any nonvanishing rate of frequency change, sudden or smooth. We have also developed an exact operator approach producing the resulting time-dependent transition probabilities among the eigenstates of the initial Hamiltonian. These results are important for applications to time-dependent processes in molecules associated with light absorption or scattering (radiative and radiationless transitions).

E. Eigenstates of Unitary k-Boson Operators

We have generalized the results for squeeze operators to the case in which the exponential form depends on the k-th power of the boson creation and annihilation operators (rather than simply being quadratic in each). The eigenvalues turn out to be k-fold degenerate. We also find the eigenstate wavefunctions in the harmonic oscillator basis in terms of orthogonal polynominals and associated distribution functions. Explicit results have been obtained for the eigenfunctions and eigenvalue spectra for the cases $k = 1$ and $k = 2$.

III. MULTIMODE MOLECULAR QUANTUM MECHANICS

The dynamics of vibrational motion of molecules on electronic energy surfaces have been studied by several researchers in recent years. Most (if not all) of these studies make use of Gaussian wavepackets moving on surfaces that are either harmonic or not, depending on the system. Such studies are applicable to molecular dynamics of large-molecule systems and to molecular spectroscopic processes (e.g., Raman scattering).

We have extended our studies on squeeze operators to include multimode systems, as is represented by the vibrations of a polyatomic molecule. We find that we are able to handle, in an exact analytic manner, situations that are more general than those to which Gaussian wavepackets have been applied. Following is a summary of our recent results.

A. Multimode Squeeze Operators and Squeezed States

We have shown that the time-evolution operator for a general N-mode quadratic Hamiltonian can be expressed as a product of an N-mode squeeze operator, an N-mode rotation operator, and an N-mode displacement operator multiplied by an overall phase factor. The multimode squeeze and rotation operators are formulated such that they have analogous algebraic properties to their single-mode counterparts. There exists a set of parameters to describe squeezing in multimode Gaussian squeezed states. Disentangling, normal ordering and other properties have been determined.

B. Dynamics of Time-dependent Multimode Harmonic Oscillators

We have developed a general expression for the time-dependent transition amplitude between any two eigenstates of a multimode harmonic potential which undergoes a sudden change in frequencies, masses, and normal coordinates. Earlier studies by other researchers usually involves the ground state. Our method does not have this restriction, which makes it potentially valuable for studies of dynamics of spectroscopic processes in molecules.

IV. THE PHASE OPERATOR OF QUANTUM MECHANICS

The fact that the commutator of the position coordinate $\hat{x}$, and its conjugate momentum operator, $\hat{p}$, is $i\hbar$ is fundamental to almost all aspects of quantum mechanics. One may regard $\hat{x}$ and $\hat{p}$ to be the Cartesian coordinates of a two dimensional space (phase space). By transforming to polar coordinates one produces the complex combinations of $\hat{x}$ and $\hat{p}$ which constitute the harmonic oscillator (or number) creation and annihilation operators, $\hat{a}^+$ and $\hat{a}$, respectively.

Dirac was among the first to attempt to find Hermitian operators for the phase angle and radial coordinate of the polar form. The corresponding exponential form of the phase operator should be unitary.

Dirac was unable to find consistent properties of the phase and radial operators arising from a polar decomposition of $\hat{a}$ and $\hat{a}^+$. Numerous workers have attempted to do so in the intervening 60 years. The problem has been recognized to involve the fact that the exponential phase operator so obtained is not unitary. The difficulty concerns the fact that the number operator, which is $\hat{a}^+\hat{a}$, has a lower bound (zero); i.e., it is not unbounded at both ends of the integer spectrum.

In our approach we have avoided the apparent pitfall of forcing a polar decomposition. By using functions of the quadratures (cos and sin) of the phase we have obtained a Hermitian phase operator in Hilbert space. We have also obtained the eigenvalue and eigenvector spectrum of the phase operator, along with other important properties.

V. QUANTUM THERMODYNAMICS

Consideration of the quantum mechanical nature of thermodynamic components of a molecular system has led us to a formulation of entropy in terms of quanta associated with thermal modes. The thermal modes are treated as harmonic oscillators, a feature which may be generalized later. This approach leads naturally a "picture" of (canonical) thermal equilibrium curves in the energy vs. entropy (E-S) plane.

We have analyzed the properties of the canonical curves for the energy per mode vs. the entropy per mode. The E - S plane is divided naturally into a quantum aberration region (low T and S) and a classical region. Also, we have considered isothermal processes as projections onto the E - S plane.

These studies have led to the following topics which should have importance for molecular-level biological processes.

A. Thermally Generated Work Potential

This concept arises from considering different kinds of thermal modes to have different rates of thermal relaxation. Quenching the system causes the cooling curve in the E - S plane to deviate from the canonical curve in a manner that increases the Helmholtz work potential. We refer to this gain as thermally generated work potential or Q-work.

B. Macromolecule Activation Cycles

Enzymes and many other proteins such as G-proteins and membrane channel proteins undergo cycles as part of their biological function. There is an analogy between such cycles and the cycles of molecular spectroscopy in a medium at constant temperature, in which a molecule is excited and undergoes transitions between excited states, finally returning to its ground state. We have referred to such cycles in biological macromolecules as Macromolecule Activation Cycles (or MAC cycles). The thermodynamic and possible quantum mechanical nature of MAC cycles have been discussed in a recent paper [W. Rhodes, J. Mol. Liquids 41, 165 (1989)].

C. Linear Thermodynamic Relations

In the course of analyzing the properties of canonical thermal curves in the energy-entropy plane, it was observed that the entropy per thermal mode is naturally composed of two parts. One is given by the thermal energy divided by T and the other is simply the remainder. In the classical limit (high T) this thermal energy contribution to S is exactly k (Boltzmann) per mode. At the same time, we discovered in the literature a discussion of the fact that a portion of the entropy change for a given process (e.g., reaction) exactly compensates

for the change in thermal energy for this process. The importance of this balance between thermal energy change and a portion of the entropy change for processes involving (biological) macromolecules was pointed out by Benzinger some years ago [T.H. Benzinger, Nature 229, 100 (1971)].

The portion of the entropy which cancels the thermal energy has come to be called compensation entropy. It has been considered extensively by Lumry, et al., as accounting for the linear relation between ΔH and ΔS for sets of reactions involving similar protein molecules [R. Lumry and R. Gregory, in The Fluctuating Enzyme, ed. by G.R. Welch, John Wiley, New York, 1986].

Our analyses in terms of the quantum mechanical nature of thermal modes shows that the compensation entropy cannot account for the observed linear relation between ΔH and ΔS for any class of reactions. Rather, we find the origin of such linear relations to lie in the changes in the number of thermal modes due to the reaction.

This observation has important implications for linear thermodynamic relations, in general, for the kinds of reactions considered earlier by Leffler and Grunwald [J.E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, John Wiley, New York, 1963].

PUBLICATIONS FOR THE PERIOD: 1987-90

Laboratory of William Rhodes
Chemistry Department
Florida State University

1. On the Circular Dichroism Helix Band for Long Helical Polymers, D.A. Rabenold and W. Rhodes, Biopolymers, 26, 109, (1987).

2. Dynamic Properties of Large Molecular Systems, W. Rhodes, in Math-Chem-Comp, R.C. Lacher, ed., Elsevier, 1988; pp 359-378.

3. Time-dependent Invariants and Stable Unitarily Transformed Coherent States, Xin Ma, Phys. Rev. A 38, 348-350 (1988).

4. Time-evolution of Stable Squeezed States, Xin Ma, J. of Modern Optics 36, 1059-64 (1989).

5. Squeezing in Harmonic Oscillators with Time-dependent Frequencies, Xin Ma and W. Rhodes, Phys, Rev. A 39, 1941-47 (1989).

6. Nonexistence of Proper Eigenstates of Squeeze Operators, Xin Ma and W. Rhodes, Nuovo Cimento 104 B, 159-62 (1989).

7. Coherent Dynamics in Biomolecular Systems, W. Rhodes, J. Molecular Liquids 41, 165-80 (1989).

8. Localization vs. Delocalization of the Davydov Soliton: Dispersive Collapse Under the Schrodinger Equation, W. Rhodes and A. Nicholls, Phys. Rev. Letters 64, 1174-77 (1990).

9. Multimode Squeeze Operators and Squeezed States, Xin Ma and W. Rhodes, Phys. Rev. A (May, 1990).

10. Phase Properties of the Quantized Single-mode Electromagnetic Field, Xin Ma and W. Rhodes, Phys. Rev. A (accepted).

11. Phase of Quantum Harmonic Oscillators, Xin Ma and W. Rhodes, Phys. Rev. A (submitted).

12. Dynamics of Time-dependent Multimode Harmonic Oscillators, Xin Ma and W. Rhodes, Phys. Rev. A (submitted).

13. Eigenstates of Unitary k-Boson Operators, Xin Ma and W. Rhodes, Phys. Rev. A (submitted).

Reprints removed

RELATION TO STATED OBJECTIVES - PLANS FOR CONTINUATION

It was pointed out in the original proposal that the number of specific objectives exceeded what we would probably achieve, but that objectives in each of the areas of research would be attempted. This has turned out to be the case. Most of the objectives not attained are being included in the renewal proposal.

The work on squeezed states and phase operators was not anticipated in the original proposal. However, it fits naturally into the theme of our research.

GRADUATE STUDENTS TRAINED

1. Anthony Nicholls - Doctoral Degree - August, 1988
   Research Topic: Davydov Soliton Theory

2. Xin Ma - Doctoral Degree - December, 1989
   Research Topic: Squeezed States; Phase Operator in Quantum Mechanics

OTHER FEDERAL SUPPORT

The Department of Energy provides sole federal support for this research program.

PRESENT STATE OF KNOWLEDGE

The ways in which biological systems organize, coordinate, and control the various levels of molecular structure, energy channeling, and information processing is one of the most fundamental unsolved problems in science. Until a few years ago the available methods put emphasis on determination of structures and biochemical pathways. Recently, however, the development of computational technology and methods of studying fast processes in complex molecular systems has shifted the emphasis to dynamical and global aspects of molecular level biology. The stage is being set for major breakthroughs in the near future. Quite probably the 21st century will be to biology what the 20th century has been to physics.

One of the central problems of molecular level biology is to understand the relations between energy transformation and control mechanisms. The purpose of our research is to develop concepts and knowledge of principles and mechanisms whereby biological macromolecules operate to control living processes.

Knowledge of how natural systems work is necessary to understand how environmental perturbations, chemical and radiative, affect living organisms at the molecular level.

It is essential that DOE strongly support basic research which is fundamental to its mission; namely, the development of knowledge and understanding of all aspects of energy and its relation to living systems. This includes bioenergetics as well as the effects of environment on life processes. Thus, along with research on energy utilization by society and other practical aspects of energy, this area of basic scientific research is vital to the mission of DOE.