

behavior of a “real life” macroscopic system is observed to deviate slightly from the behavior of a well understood but idealized model, the rate at which the deviation grows may be used to identify the specific cause of the deviation. Weak couplings between parts of a macroscopic system often are understood by building a “toy” model that ignores the couplings and then comparing the evolution of the simplified model to that of the real system. The rate at which energy flows from one part of a system to another reveals the intra-system coupling mechanism and the coupling strength. Systematic experiments in which all of the initial excitation is localized sequentially in each of the different subsystems can be used to characterize the coupling mechanisms that are most important dynamically. A perturbative picture, in which the dynamics is controlled by a well-understood  $\mathbf{H}^{(0)}$  and an incompletely-understood perturbation term  $\mathbf{H}^{(1)}$ , is equally valuable for characterizing macroscopic and microscopic worlds. There is no fundamental difference between wavepacket dynamics in state space and in  $\mathbf{q}, \mathbf{p}$  space. The only difference is in the nature of the mental picture one uses to describe and attempt to understand the dynamics. Typically, mechanistic or causal models are built and refined by using well-understood, early-time, localized dynamics in an idealized model to focus one’s attention on the most important but initially uncharacterized aspects of the real behavior.

There are many useful tools to help focus attention on specifiable parts of the behavior of a many-body system, and many of these were listed in Section 9.1.4. The concepts of “bright state,” “doorway state,” and “dark state,” the experimental tools of state-selective excitation and detection, and the analysis tools of wavepackets and survival and transfer probabilities, can provide insights into the causes, preferred pathways, and possibilities for control of intramolecular dynamics.

### 9.1.8 Equations of Motion for Resonance Operators

An enormous amount of dynamical information is encoded in the  $\Psi(r, R, t)$  that arises from any non-eigenstate preparation of a molecular system at  $t = 0$ . One way of displaying intelligible portions of this information is to plot, versus time, the expectation values of various coordinates and momenta, as discussed in Section 9.1.7. There are, however, other kinds of *equations of motion*.

There are several standard results from time-dependent quantum mechanics that will prove useful. The equation of motion of the expectation value of any operator,  $\mathbf{O}$ ,

$$\langle \mathbf{O} \rangle_t = \langle \Psi(r, R, t) | \mathbf{O} | \Psi(r, R, t) \rangle \quad (9.1.80)$$

is obtainable from the commutator of that operator with the exact Hamiltonian,

$$[\mathbf{O}, \mathbf{H}] = \mathbf{O}\mathbf{H} - \mathbf{H}\mathbf{O} \quad (9.1.81)$$

$$i\hbar \frac{d}{dt} \langle \mathbf{O} \rangle_t = \langle [\mathbf{O}, \mathbf{H}] \rangle_t. \quad (9.1.82)$$

This equation is especially useful when  $\mathbf{H}$  can be written as a sum of simpler operators

$$\mathbf{H} = \sum_i \mathbf{h}_i + \sum_{i>j} \mathbf{h}_{ij} \quad (9.1.83)$$

where, for example, the  $\mathbf{h}_{ij}$  coupling term is expressed as a product of operators  $\mathbf{a}_i$  and  $\mathbf{b}_j$

$$\mathbf{h}_{ij} = c_{ij} \mathbf{a}_i \mathbf{b}_j \quad (9.1.84)$$

that are associated with the  $i$  and  $j$  subsystems of the molecule. Often, when  $\mathbf{H}$  can be expressed in this way, the  $[\mathbf{O}, \mathbf{H}]$  commutator yields a very simple operator, which can be thought of as the “*cause of the dynamics*” of  $\mathbf{O}$ , and for which the expectation value is evaluated easily. In this way the cause of the dynamics may be extracted, purely by operator algebra, without reference to the nature of the specific state prepared at  $t = 0$ ,  $\Psi(r, R, 0)$ .

The expectation value of any operator,  $\mathbf{O}$ , can be evaluated by

$$\langle \mathbf{O} \rangle_t = \text{Tr}[\boldsymbol{\rho}(t)\mathbf{O}] \quad (9.1.85)$$

$$\boldsymbol{\rho}(t) = |\Psi(t)\rangle \langle \Psi(t)| = \sum_{i,j} a_i a_j^* |\psi_i\rangle \langle \psi_j| \quad (9.1.86)$$

where  $\Psi$ ,  $\boldsymbol{\rho}$ , and  $\mathbf{O}$  are expressed in the  $\{\psi_i\}$  basis set (which can be either eigenstates or basis states) and the expansion coefficients  $\{a_i\}$  are time-dependent. The trace of the matrix product  $\boldsymbol{\rho}\mathbf{O}$  picks out *only those nonzero products of two expansion coefficients*,  $\rho_{ij} = a_i a_j^*$ , *to which the operator,  $\mathbf{O}$ , is sensitive*.  $\mathbf{O}$  is sensitive to  $\rho_{ij}$  only if  $\mathbf{O}_{ji} \neq 0$ . Once again, operator algebra yields an *a priori* known, simplified sample of the dynamics, independent of the quantitative nature of the specific state prepared at  $t = 0$ .

The density matrix,  $\boldsymbol{\rho}(t)$ , is an  $N \times N$  array of matrix elements, each of which is time-dependent (but  $\rho_{ij} = \rho_{ji}^*$ ). The  $N(N+1)/2$  independent equations of motion, one for each of the  $i \leq j \leq N$  elements of  $\boldsymbol{\rho}$ , are

$$i\hbar \frac{d}{dt} \boldsymbol{\rho} = [\mathbf{H}, \boldsymbol{\rho}] \quad (9.1.87)$$

$$i\hbar \dot{\rho}_{ij} = \sum_k (H_{ik} \rho_{kj} - \rho_{ik} H_{kj}), \quad (9.1.88)$$

which typically leads to a system of coupled differential equations. (Note that the sign of the commutator in Eq. (9.1.87) is opposite that in Eq. (9.1.82).) Once again, the presence of specific non-zero off-diagonal elements in  $\mathbf{H}$  and  $\boldsymbol{\rho}$  focuses our attention on the dynamics of specific *populations* ( $\rho_{ii}$ ) or *coherences* ( $\rho_{ij}$ ).

The system of coupled differential equations embodied in Eq. (9.1.87) describes the dynamics of the system in a numerically explicit but mechanistically opaque manner. A mechanism is a short list of the dynamically most important

coupling terms, a description of how, where, and why these terms act, and the temporal signature (dominant Fourier components) of each term. Jacobson and Field (2000a) propose a “resonance operator” and “rate operator” formalism to tease out the most important cause-and-effect mechanisms from the exact numerical dynamics.

Any effective Hamiltonian can be partitioned into two parts,

$$\mathbf{H}^{\text{eff}} = \mathbf{H}_{\text{diag}} + \mathbf{H}_{\text{res}}, \quad (9.1.89)$$

a diagonal part and a nondiagonal or “resonance” part. The form (and mechanistic transparency) of this partitioning is dependent on the choice of basis set. The expectation value of the energy of any  $\Psi(t)$ , subject to a time-independent  $\mathbf{H}^{\text{eff}}$ , is constant

$$E = \langle \mathbf{H}_{\text{diag}} \rangle_t + \langle \mathbf{H}_{\text{res}} \rangle_t = E_{\text{diag}}(t) + E_{\text{res}}(t). \quad (9.1.90)$$

Energy may be viewed as “flowing” between  $E_{\text{diag}}$  and  $E_{\text{res}}$ . The cause of this energy flow may be traced to specific additive terms in  $\mathbf{H}_{\text{res}}$ ,

$$\mathbf{H}_{\text{res}} = \sum_k \mathbf{O}_k, \quad (9.1.91)$$

where each  $\mathbf{O}_k$  is constructed to be Hermitian. It is useful to partition each  $\mathbf{O}_k$  into two non-Hermitian operators

$$\mathbf{O}_k = \mathbf{\Omega}_k + \mathbf{\Omega}_k^\dagger \quad (9.1.92)$$

where  $\mathbf{\Omega}_k$  and  $\mathbf{\Omega}_k^\dagger$  are matrices composed of all matrix elements  $(\mathbf{O}_k)_{ij}$  where  $i < j$  and  $i > j$ , respectively. All other elements of  $\mathbf{\Omega}_k$  and  $\mathbf{\Omega}_k^\dagger$  are zero. Since  $\mathbf{\Omega}_k$  and  $\mathbf{\Omega}_k^\dagger$  are not Hermitian, their expectation values can be complex numbers, but because  $\mathbf{O}_k$  is Hermitian,  $\langle i | \mathbf{O}_k | j \rangle = \langle j | \mathbf{O}_k | i \rangle^*$ ,

$$\langle \mathbf{O}_k \rangle_t = \langle \mathbf{\Omega}_k^\dagger \rangle_t^*. \quad (9.1.93)$$

Thus

$$\langle \mathbf{O}_k \rangle_t = \langle \mathbf{\Omega}_k + \mathbf{\Omega}_k^\dagger \rangle = \text{real} \quad (9.1.94)$$

and

$$\langle \mathbf{\Omega}_k - \mathbf{\Omega}_k^\dagger \rangle = \text{imaginary}. \quad (9.1.95)$$

The expectation values of a specific resonance operator,  $\mathbf{O}_k$ , and the associated rate operator,  $\mathbf{\Omega}_k - \mathbf{\Omega}_k^\dagger$ , can provide insights into the causes of features in the survival and transfer probabilities,  $P_I(t)$  and  $P_{I \rightarrow F}(t)$ . The importance of a

specific resonance operator,  $\mathbf{O}_k$ , to the dynamics is given by the time average of the expectation value

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \langle \mathbf{O}_k \rangle \equiv \overline{E}_{res,k}. \quad (9.1.96)$$

The *fractional dynamical importance* of the  $k$ -th resonance operator relative to all of the coupling terms in  $\mathbf{H}_{res}$  is

$$f_k = \left| \frac{\overline{E}_{res,k}}{\overline{E}_{res}} \right|. \quad (9.1.97)$$

The mechanistic origin for each Fourier component of the total resonance energy,  $E_{res}(t)$ , may be inferred from the existence of Fourier components in the contribution of the  $k$ -th coupling term to the resonance energy,  $E_{res,k}(t)$ , of the same frequency, phase, and similar amplitude. The expectation value of  $\mathbf{\Omega}_k - \mathbf{\Omega}_k^\dagger$  provides information about the *rates* of specific dynamical processes. The same Fourier components will appear in  $E_{res,k}(t)$  and  $\langle \mathbf{\Omega}_k - \mathbf{\Omega}_k^\dagger \rangle_t$ , but the phases of the Fourier components of  $E_{res,k}(t)$  will lag those of  $\langle \mathbf{\Omega}_k - \mathbf{\Omega}_k^\dagger \rangle_t$ , often by  $\pi/2$ .

Both  $\mathbf{O}_k$  and  $\mathbf{\Omega}_k - \mathbf{\Omega}_k^\dagger$  provide useful insights into the causes and rates of specific dynamical processes. Sections 9.4.9 and 9.4.10 provide analyses of the dynamics of the  $\mathbf{S}$ -uncoupling operator in a  $2S+1\Lambda$  state and the 1 : 2 anharmonic coupling operator that contributes to Intramolecular Vibrational Redistribution (IVR) in a polyatomic molecule and illustrate the diagnostic power of the  $\mathbf{\Omega}_k + \mathbf{\Omega}_k^\dagger$  and  $\mathbf{\Omega}_k - \mathbf{\Omega}_k^\dagger$  resonance and rate operators.

### 9.1.9 The One-Color Pump-Probe Experiment

One of the most important yet simple ideas that ignited excitement about femtochemistry is wavepacket interferometry (Salour and Cohen-Tannoudji, 1977; Scherer, *et al.*, 1990, 1991, 1992; Jonas and Fleming, 1995; Weinacht, *et al.*, 1999), an optical form of Ramsey-fringe spectroscopy (Ramsey, 1990). A molecular system is subjected to two identical optical pulses created by splitting one pulse at a beam splitter. The two pulses are called the “pump” and the “probe”. The time delay between pump and probe pulses is scanned systematically using an optical delay line. The optical arrangement is very similar to that of a Fourier Transform Spectrometer (Heller, 1990). The difference in the paths traveled by the pump and probe pulses,  $\Delta d$ , before the two pulses are recombined at a second beam splitter corresponds to a time delay,  $\Delta t = \Delta d/c$ , where  $c$  is the speed of light.

The fundamental idea is that the pump and probe pulses create wavepackets, which evolve on the excited state potential surface. Interference between the excited state wavefunction amplitudes created by the two pulses affects the population transferred to the excited state. The population that is measurable in a typical incoherent experiment (spontaneous fluorescence, field ionization, excitation to a different excited state by a nanosecond pulsed laser) is proportional