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9.1 Dynamical Concepts, Tools, and Terminology

Since “Perturbations in The Spectra of Diatomic Molecules” was published in 1986, new concepts and experimental capabilities have altered profoundly the

way we think about both the structure and the dynamics of molecules (Heller, 1981; Zewail, 1996 and 2000). Because it better engages our experience of the macroscopic world, the *time-evolving* localized state or “wavepacket” concept has begun to displace the more abstract concepts of basis states and *stationary* eigenstates. Since insights generated by the older time-independent and the newer time-dependent pictures are complementary, it would be foolish to permit the enthusiasm for things new to sweep things old into oblivion. This chapter is intended to aid in the process of building bridges between the stationary state and wavepacket communities. It also takes a tentative first step into the area explicitly prohibited by the title of this book, the dynamics of polyatomic molecules. A central justification for a book dedicated to the spectra and dynamics of diatomic molecules is that all of the concepts, models, and analysis tools developed for diatomic molecules are applicable to polyatomic molecules.

9.1.1 The Time-Dependent Picture: Terminology

Just as a satisfactory approximation to the exact solution of the time-independent Schrödinger equation for a many-electron molecule must be expressed in a form that belies the apparent simplicity of the spectrum, so too is the exact solution of the time-dependent Schrödinger equation often opaquely complex. For the time-independent problem, insight comes from defining a suitable *zero-order model* $(\mathbf{H}^{(0)}, \{\psi_i^{(0)}\}, \{E_i^{(0)}\})$, specifying the essential *coupling terms* $(\mathbf{H}^{(1)})$ and *coupled quasidegenerate states*, and then *decoupling* the states of interest in the specific experiment from the infinite number of remote-perturber states by an implicit or explicit *Van Vleck transformation* (see Section 4.2). The result is a *spectroscopic effective Hamiltonian model*, \mathbf{H}^{eff} , which is of a profoundly different nature than the exact Hamiltonian, \mathbf{H} , even though the notation and terminology used to describe both \mathbf{H}^{eff} and \mathbf{H} are misleadingly similar (see Section 4.4.2). \mathbf{H}^{eff} is a vastly simplified model in which microscopic forces and the response of the system to those forces are identified, the essential coupling terms are arranged in a hierarchy of importance, and the dimensionality of the spectroscopically relevant part of state space is reduced from that of the full state space so that intuition can complement and focus computation.

When the state of a molecule evolves under the influence of a time-independent \mathbf{H} , structure and dynamics are two sides of the same coin. Since the same \mathbf{H} appears in the time-independent and time-dependent Schrödinger equations, an \mathbf{H}^{eff} -based intuitive picture of the molecular structure generates an intuitive, causal, *mechanistic* picture of molecular dynamics.

A dynamical mechanism consists of the following elements: (i) creation of a *nonstationary state*; (ii) departure of the nonstationary state from its initial location in coordinate or state space; (iii) long time evolution, including partial rephasings and decay.

(i) A *nonstationary state* is created at $t = 0$. This initial state, which is localized in coordinate or state space, is specified perfectly in terms of a linear

combination of a small number (often only one) of zero-order states,

$$\Psi(t=0) = \sum_i a_i \psi_i^{(0)}. \quad (9.1.1)$$

Typically, $\Psi(0)$ is called the “*bright state*.” This name is chosen precisely because this $\Psi(0)$ is a member of the special class of localized states that can be created at $t = 0$ by exciting from a purposefully selected initial eigenstate with a short pulse ($\sim 100fs$) of electromagnetic radiation. The excitation pulse that creates the bright state is called the “*pluck*.” [Heller and Gelbart, 1980] (ii) The initially prepared localized state, $\Psi(t)$, moves away from its $t = 0$ starting location, either in state-space (dephasing: $a_i(t) = \langle \psi_i^{(0)} | \Psi(t) \rangle \neq a_i(0)$) or coordinate-space ($\langle \mathbf{x}(t) \rangle \equiv \langle \mathbf{x} \rangle_t = \langle \Psi(t) | \mathbf{x} | \Psi(t) \rangle \neq \langle \mathbf{x} \rangle_0$) or both. This moving away from itself is conveniently expressed as an *autocorrelation function*, $\langle \Psi(t) | \Psi(0) \rangle$ or as a *survival probability*, $P(t) \equiv |\langle \Psi(t) | \Psi(0) \rangle|^2$. The reason for the initial decay of the autocorrelation function is either a force (the negative of the gradient of the potential energy surface) acting on the center of a spatially localized $\Psi(0)$ or a coupling term, $\mathbf{H}^{(1)}$, which causes population to “flow” (in state space) from the bright state into a manifold of “*dark states*” (see Fig. 9.1). It is usually possible (and instructive) to identify the specific causes for all of the qualitative features (initial decay rate, times at which of partial recurrences occur, and the amplitudes of these recurrences) in the early-time behavior of $\langle \Psi(t) | \Psi(0) \rangle$. (iii) The evolution of $\Psi(t)$ can embody many classes of dynamical behavior, including recurrent oscillation between the initial bright state and a small number of dark states (quantum beats), localized evolution among a small group of states that exhibit complementary brightness/darkness for different detector set-ups, irreversible dephasing (exponential or multi-exponential decay) into a (quasi)-continuum, and localized evolution into a “doorway state” followed by irreversible decay.

A dynamical “mechanism” is specified by answering the classic questions about the time-evolution of an isolated system: *where does it start, how fast does it leave, what causes it to leave, where does it go next, and why does it go there?* Answers to all of these questions are obtainable by constructing an appropriate \mathbf{H}^{eff} model following the techniques presented in Chapters 1-8. The parameters that define the \mathbf{H}^{eff} may equally well be defined by fitting the information contained in a frequency domain (transition frequencies, intensities, and linewidths) or a time domain (arrival times of the wavepacket at a specified location in coordinate or state space, decay rates, transfer rates, and recurrence times and amplitudes) experiment.

9.1.2 Solution of the Time-Dependent Schrödinger Equation

The time-dependent Schrödinger equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathbf{H} \Psi. \quad (9.1.2)$$