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THEORETICAL OVERVIEW OF CHEMICAL DYNAMICS

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1. Introduction

Chemical dynamics is the link between the potential energy surface (or surfaces) and physically observable chemical phenomena. The potential surface comes in principle from an *ab initio* quantum chemistry calculation (within the Born-Oppenheimer approximation) though in practice it is often constructed by some more approximate model, e.g., semiempirical quantum chemistry or totally empirical "force field" models. The purpose of this Overview is to give a brief snapshot of the present state of the methodology and scope of applications in this area. I will concentrate on chemical dynamics in the gas phase, though much of the methodology (and mentality!) of this field has carried over to the study of dynamical processes in condensed phases, gas-surface collision processes, and also dynamics in biomolecular systems. In these latter fields of application there is obviously strong input from and overlap with statistical mechanics.

Even the field of gas phase theoretical chemical dynamics is too large, however, to give anything but a cursory treatment in a brief overview. I will thus attempt to point out what I think are presently some of the major currents in theoretical chemical dynamics, with references to useful reviews, and I apologize beforehand that the overview will necessarily be biased to areas with which I am most familiar. Sections 2, 3 and 4 discuss molecular collision processes (i.e., scattering), perhaps the most well-defined and rigorous approach to studying chemical dynamics, and Sections 5 and 6 discuss intramolecular dynamics and laser-induced processes.

The four volume set edited by Baer[1] is a recent collection of more detailed reviews of the field, and the two volume set edited by Miller[2] an earlier one. Other more recent collections of reviews are the volume by

Bernstein[3] and that by Bowman.[4]

2. Elastic Scattering

The study of elastic scattering is today quite *passe*, but in the early days of chemical dynamics (the 1960's) it served in important "test bed" role, both experimentally and theoretically, for developing the tools to be used to study more interesting processes. E.g., elastic scattering of the rare gas atoms[5] with each other in the early 1970's was the first test of Y. T. Lee's new "universal" detector in a crossed molecular beam apparatus, applications of which to this and many other processes led to his sharing the 1986 Nobel Prize in Chemistry. Lee's measurements of the differential scattering cross sections allowed the definitive determination of the intermolecular potential energy function V(r) of essentially all the rare gas atoms with each other.

The fully rigorous quantum mechanical elastic differential cross section is given by[6]

$$\sigma_E(\theta) = \left| \frac{1}{2ik} \sum_{\ell=0}^{\infty} (2\ell+1) P_\ell(\cos\theta)(e^{2i\eta_\ell(E)}-1) \right|^2 , \tag{2.1}$$

where the phase shift $\eta_\ell(E)$ for orbital angular momentum ℓ and energy E is determined from the asymptotic form of the regular solution of the radial Schrödinger equation,

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - E \right) f_{\ell E}(r) = 0 , \tag{2.2}$$

with asymptotic boundary condition

$$\lim_{r\to\infty} f_{\ell E}(r) \propto \sin\left(kr - \frac{\pi\ell}{2} + \eta_\ell(E)\right) . \tag{2.3}$$

The procedure is, given the potential function V(r) and a value of the energy E, to solve the Schrödinger equation, Eq. (2.2), for all values of ℓ to obtain the phase shifts, and then to compute the cross section from Eq. (2.1). Even though hundreds (or thousands) of values of ℓ's may be needed for the sum in Eq. (2.1) to converge, this is nevertheless a trivial calculation nowadays. The potential function V(r) is typically determined by assuming

a functional form involving a set of parameters, carrying out the calculation of $\sigma_E(\theta)$ as described, and adjusting the parameters in the potential in a least squares procedure to fit the experimental cross section. Though this least squares fitting procedure is not as elegant as formal "inversion" approaches, it is in practice the most general and straight-forward approach.

Elastic scattering was also the theoretical workhorse in earlier years for developing many *approximate* theoretical methods, and though these approximations are no longer needed for elastic scattering calculations they still serve as useful guides for dealing with more complex processes.

One of the most important examples of this is the *semiclassical* approximation to quantum mechanics: in 1959 Ford and Wheeler[7] described the explicit sequence of approximations by which the rigorous quantum cross section of Eqs. (2.1)-(2.3) degenerates to the completely classical cross section,

$$\sigma_{CL}(\theta) = \sum_k \frac{b_k}{\sin\theta |\Theta'(b_k)|} , \tag{2.4}$$

where $b_k \equiv b_k(\theta)$ are the values of impact parameters b which classically scatter at angle θ, i.e., the roots of the equation

$$|\Theta(b)| = \theta , \tag{2.5}$$

where $\Theta(b)$ is the classical deflection angle as a function of b,

$$\Theta(b) = \pi - \int_{r_0}^{\infty} dr \frac{2b}{r^2} \left(1 - \frac{V(r)}{E} - \frac{b^2}{r^2}\right)^{-1/2} , \tag{2.6}$$

and r_0 is the classical turning point (the largest value r for which the integrand of Eq. (2.6) is zero.) The essential approximations are to use the WKB approximation for the phase shift and the Legendre polynomial, to replace the sum over ℓ by an integral, and then evaluate the integral by the stationary phase approximation. The result is

$$\sigma_{SC}(\theta) = \left| \sum_k \left(\frac{b_k}{\sin\theta |\Theta'(b_k)|} \right)^{1/2} e^{i\phi_k/\hbar} \right|^2 , \tag{2.7}$$

where $\{b_k\}$ are the same as in the classical cross section; they emerge semiclassically as the values of ℓ ($\ell \equiv kb$, $k = \sqrt{2mE/\hbar^2}$) for which the phase in the integral over ℓ is stationary and thus make the dominate contribution to the sum/integral. The phases $\{\phi_k\}$ are the classical action for the kth trajectory that classically scatters at angle θ.

Eqs. (2.1), (2.4), and (2.7) show the generic structure relating quantum, classical, and the semiclassical correction in scattering cross sections. Eq. (2.7) shows clearly that

$$\sigma_{SC}(\theta) = \sigma_{CL}(\theta) + \text{interference terms} , \tag{2.8}$$

so that it is interference between the different classical contributions to the cross section that is the most fundamental effect of quantum mechanics. Bernstein's 1966 review[6] of the semiclassical description of quantum effects in elastic scattering is still one of the best and most comprehensive, and that by Berry and Mount[8] is also insightful. Recently Child[9] has reviewed semiclassical theory more generally.

3. Inelastic Scattering

Inelastic scattering of atoms and molecules is clearly of more physical interest than elastic scattering. This includes excitation or relaxation of rotational and vibrational degrees of freedom and also of electronic states. Rotational/vibrational inelasticity is important in understanding classical transport phenomena in gases, and the vibrational relaxation of highly excited molecules is of crucial importance for describing "unimolecular" reaction in the Lindeman mechanism,[10]

$$A + B \rightarrow A^* + B \tag{3.1a}$$

$$A^* + B \rightarrow A + B \tag{3.1b}$$

$$A^* \rightarrow \text{products} \quad . \tag{3.1c}$$

I.e., after collisional excitation of A to A* by the bath gas B — or A* may

be produced "hot" as the product of some preceding chemical reaction — the important consideration is the competition between collisional stabilization of A* by the bath gas, Eq. (3.1b), and the unimolecular decomposition of A*, Eq. (3.1c). Currently, therefore, there is much effort devoted to learning more quantitatively about vibrational de-activation of highly excited vibrational states.[11] Electronically inelastic collisions are important in many gas laser systems, in the upper atmosphere, and in plasmas. Many of these applications involve one of the collision partners being an ion.

The quantum mechanical description of an inelastic scattering process is straightforward. Leaving aside details involving angular momentum, the wavefunction for the generic situation is expanded as

$$\psi_i(r,\xi) = \sum_j \phi_j(\xi) f_{j\leftarrow i}(r) \ , \tag{3.2}$$

where $\{\phi_j(\xi)\}$ denotes the bound-state eigenfunctions for the internal (rotational, vibrational, and electronic) degrees of freedom (with ξ collectively denoting the appropriate coordinates) of the colliding molecules, and r is the radial (translational) coordinate, i.e., the distance between the centers of mass of the two molecules. The radial function (matrix) $\{f_{j\leftarrow i}(r)\}$ is determined by the coupled-channel (channel being the historical term for the various internal states) Schrödinger equation,

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} - E_j\right) f_{j\leftarrow i}(r) + \sum_{j'} V_{j,j'}(r) f_{j'\leftarrow i}(r) = 0 \ , \tag{3.3}$$

where $V_{j,j'}(r)$ is the matrix of the interaction potential $V(\xi,r)$ with respect to the basis of internal states,

$$V_{j,j'}(r) = \int d\xi \ \phi_j(\xi)^* V(\xi,r) \phi_{j'}(\xi) \ , \tag{3.4}$$

and $E_j = E-\varepsilon_j$, where E is the total energy and ε_j the energy eigenvalue corresponding to ϕ_j (i.e., E_j is the available translational energy for channel j). The boundary conditions for the radial functions are that they be regular for $r \rightarrow 0$, and for large r have an incoming radial wave in initial channel i and outgoing waves in all open channels,

$$\lim_{r\to\infty} f_{j\leftarrow i}(r) \sim -\frac{e^{-ik_j r}}{v_j^{1/2}}\delta_{j,i} + \frac{e^{ik_j r}}{v_j^{1/2}} S_{j,i}(E) , \tag{3.5}$$

where $v_j = \sqrt{2E_j/\mu}$ is the translational velocity for channels j, and $S_{j,i}$ is the S-matrix, in terms of which all scattering cross sections can be expressed. Using Eq. (3.5) in Eq. (3.2) shows that the full wavefunction has the following form are large r,

$$\psi_i(r,\xi) \sim -\phi_i(\xi)\frac{e^{-ik_i r}}{v_i^{1/2}} \quad \sum_j \phi_j(\xi)\frac{e^{ik_j r}}{v_j^{1/2}} S_{j,i} , \tag{3.6}$$

from which one more clearly sees that the initial channel i has an incoming radial wave, and all channels have outgoing (scattered) waves. The S-matrix is a unitary matrix and has the interpretation as the probability amplitude for the $i\to j$ transition; the transition probability is thus

$$P_{j\leftarrow i} = |S_{j,i}|^2 , \tag{3.7}$$

When angular momentum — the orbital angular momentum of relative motion (i.e., the angular degrees of freedom of the translational coordinate *vector* $\vec{r}$) plus any angular momentum from the internal degrees of freedom — is taken account of, one finds that the total angular momentum J is conserved (because of the isotropy of space) and is thus a diagonal label of the S-matrix, $S^J_{j,i}(E)$. The state-to-state differential cross section — the most detailed possible scattering observable — is then given by

$$\sigma_{j\leftarrow i}(\theta) = \left|\frac{1}{2ik_i}\sum_J (2J+1)\, d^J_{m_j,m_i}(\theta)\left(S^J_{j,i}(E)-\delta_{ji}\right)\right|^2 \tag{3.8}$$

where $d^J_{mm'}(\theta)$ is the Wigner rotation function, and m_i,m_j are the projections of the total angular momentum onto the initial and final relative velocity vectors. One can easily recognize the sense in which Eq. (3.8) is the generalization of Eq. (2.1) for the elastic scattering of two structureless particles; in the latter case $J\to\ell$ (i.e., the orbital angular momentum ℓ is the total angular momentum), m_j and $m_i \to 0$, $d^J_{00}00(\theta) = P_\ell(\cos\theta)$, and

$$S^J_{j,i}(E) \to e^{2i\eta_\ell(E)} . \tag{3.9}$$

The theoretical task, therefore, is to solve Eq. (3.3) with the boundary conditions of Eq. (3.5) to obtain the S-matrix, in terms of which the inelastic cross sections are given by Eq. (3.8). Such calculations are relatively straight-forward nowadays,[12] although they can be time consuming if the number of channels is large; the largest calculations which are reasonable at present involve up to ~1000 coupled channels. This may seem like a large number, but consider the number of rotational/vibrational states of a diatomic molecule that have an energy below an energy E,

$$N(E) = \sum_{v=0} \sum_{j=0} (2j+1)\, h(E-\varepsilon_{vj}) \; . \tag{3.10}$$

Using a simple rigid rotor-harmonic oscillator approximation for the energy levels,

$$\varepsilon_{vj} \cong \hbar\omega\,(v+\tfrac{1}{2}) + Bj(j+1) \; ,$$

where ω is the vibrational frequency and B the rotation constant, gives

$$N(E) \cong \frac{E^2}{2\hbar\omega B} \; . \tag{3.11a}$$

For E = 0.1 eV, $\hbar\omega = 2000\ \mathrm{cm}^{-1}$, and $B = 1\ \mathrm{cm}^{-1}$, which are typical of a relatively small diatomic molecule (O_2, N_2, CO), Eq. (3.11a) gives N ~ 160, not too large a number of channels. But for I_2 ($\hbar\omega = 215\ \mathrm{cm}^{-1}$, $B = 0.037\ \mathrm{cm}^{-1}$) at this energy one has $N \cong 40{,}000$! And this is the number of channels for only *one* diatomic molecule; for the collision of two diatomics at energy E one has

$$N(E) \cong \frac{E^4}{4!\hbar\omega_1\hbar\omega_2 B_1 B_2} \; , \tag{3.11b}$$

$$\cong \frac{1}{6} N_1 N_2 \; , \tag{3.11c}$$

where N_1 and N_2 are the number of channels for molecules 1 and 2, respectively. Thus the number of channels involved can become unmanageably large very quickly!

Typically, however, the more channels there are that are strongly

coupled in an inelastic collision the better it is to approximate the dynamics by classical mechanics; i.e., there are more channels the heavier the particles, but this is also the limit in which classical mechanics is a better approximation. Thus there have been many *classical trajectory simulations* of inelastic collision processes.[13] These have the advantage that no approximations other than the use of classical mechanics need be made, and the number of classical equations of motion to be solved (Hamiltonian's equations) grows *linearly* with the number of particles, while the numbers of coupled channels in the coupled-channel Schrödinger equation grows *exponentially* with this number.

There also exist a wide variety of approximate quantum mechanical and semiclassical theories.[14] In various limits some of the degrees of freedom can be treated as slow or fast compared to others, leading to sudden or adiabatic approximations, and in some cases the coupling between translational and internal motion can make perturbation theory a useful approximation.

Classical S-matrix theory[15,9] is a "rigorous" semiclassical theory, rigorous in that it incorporates the full classical mechanics for all degrees of freedom without approximation; it may be viewed as the generalization of the Ford and Wheeler semiclassical description of elastic scattering discussed in Section 2. Thus the inelastic transition probability in this theory is of the form

$$P^{SC}_{j\leftarrow i} = \left| \sum_k P^{(k)1/2}_{j,i} \, e^{i\phi^{(k)}_{j,i}/\hbar} \right|^2 , \tag{3.12}$$

where $P^{(k)}_{j,i}$ is the purely classical contribution to the $i\rightarrow j$ transition from the kth trajectory which leads to it — i.e., the *completely* classical transition probability is

$$P^{CL}_{j\leftarrow i} = \sum_k P^{(k)}_{j,i} \tag{3.13}$$

— and $\phi^{(k)}_{i,j}$ is a classical action integral along the corresponding trajectory. The semiclassical transition probability thus has the same structure as in Eq. (2.8),

$$P^{SC}_{j\leftarrow i} = P^{CL}_{j\leftarrow i} + \text{interference.} \tag{3.14}$$

Interference between the different classical trajectories which contribute to the $i \rightarrow j$ transition will thus cause interference effects (e.g., "rainbows") in the product distribution of internal states analogous to such effects in the angular distribution (i.e., differential cross section) for elastic scattering.

4. Reactive Scattering

Quantum mechanical reactive scattering[16,17,3,4] provides the fundamental and rigorous description of chemical reactions and is thus the type of collision process of most interest to us. Unfortunately it is also the most complicated to deal with because of the lack of one physically appropriate set of coordinates for "translation" and "internal" degrees of freedom. I.e., the natural coordinates for describing translational and internal degrees of freedom for the reactant molecules are not the natural ones for describing those of the products. See reference 16 for a fairly detailed discussion of this "coordinate problem" for reactive scattering.

Because of this problem with coordinates, most of the modern ways of carrying out quantum reactive scattering calculations do not use the straight-forward coupled-channel expansion of Section 3 (though the use of hyperspherical coordinates[18] does allow this approach). Rather a *variational* method[19-21] is used to calculate the S-matrix, and this allows one to use basis functions expressed in terms of different coordinates in a straight-forward manner.

The variational approach received a major boost also when it was realized[19a] that the simplest variational method — the Kohn variational principle, which is essentially the Rayleigh-Ritz variational principle for eigenvalues modified to incorporate scattering boundary conditions — is free of anomalous (i.e., spurious, unphysical) singularities if it is formulated with S-matrix type boundary conditions rather than standing wave boundary conditions as had been typically used previously. It is useful first to state the Kohn variational approach for the general inelastic scattering case of Section 3. Thus the variational expression for the S-matrix is

$$S[\psi_f,\psi_i] = S^{(0)}_{fi} + \frac{i}{\hbar}\langle\psi_f|H-E|\psi_i\rangle\,, \tag{4.1}$$

where ψ_f and ψ_i are variational ("trial") wavefunctions of the form that satisfy the correct boundary conditions [cf. Eq. (3.6)]

$$\psi_\ell(\xi,r) \sim -\frac{e^{-ik_\ell r}}{v_\ell^{1/2}}\phi_\ell(\xi) + \sum_j \frac{e^{ik_j r}}{v_j^{1/2}}\phi_j(\xi)\, S^{(0)}_{j,\ell}\,, \tag{4.2}$$

for ℓ = i and f. In practice we have taken the trial function to be of the form

$$\psi_\ell(\xi,r) = \Phi_\ell(\xi,r) + \sum_j \Phi_j(\xi,r)^*\, C_{j,\ell} + \sum_k \chi_k(\xi,r)\, C_{k,\ell}\,, \tag{4.3}$$

where $\Phi_\ell(\xi,r)$ is an asymptotically incoming radial wave in channel ℓ,

$$\Phi_\ell(\xi,r) \sim \frac{e^{-ik_\ell r}}{v_\ell^{1/2}}\phi_\ell(\xi)\,, \tag{4.4}$$

and $\Phi_\ell{}^*$ is a corresponding outgoing wave. The functions $\{\chi_k\}$ in Eq. (4.3) are an L^2 basis that describes the interaction (small r) region of the composite molecular system. The coefficients $\{C_{j,\ell}\}$ and $\{C_{k,\ell}\}$ in Eq. (4.3) are the variational parameters with respect to which Eq. (4.1) for the S-matrix is extremized; i.e., substituting the functions ψ_f and ψ_i of the form of Eq. (4.3) into Eq. (4.1) gives the S-matrix as a quadratic function of these coefficients, and the variational condition

$$0 = \frac{\partial}{\partial C_\lambda} S(\{C_{j,f}\},\{C_{\ell,f}\},\{C_{j,i}\},\{C_{\ell,i}\})\,, \tag{4.5}$$

for each of the coefficients $C_\lambda = C_{j,f}$, $C_{\ell,f}$, etc., leads to linear equations for the coefficients which are solved by matrix inversion. Using these variationally optimum coefficients in the expression for the S-matrix then gives the following variationally optimum result (within the given basis set) for the S-matrix,

$$S_{f,i} = \frac{i}{\hbar}(M_{f,i} - \mathbf{M}_f^T \bullet \mathbf{M}^{-1} \bullet \mathbf{M}_i)\,, \tag{4.6}$$

where

$$M_{f,i} = \langle\Phi_f|H-E|\Phi_i\rangle \,, \tag{4.7a}$$

$$\mathbf{M}_\ell = \begin{Bmatrix} \langle\Phi_j{}^*|H-E|\Phi_\ell\rangle \\ \langle\chi_k|H-E|\Phi_\ell\rangle \end{Bmatrix}, \tag{4.7b}$$

for ℓ = i and f, and

$$\mathbf{M} = \begin{Bmatrix} \langle\Phi_{j'}^*|H-E|\Phi_j\rangle, \langle\Phi_{j'}^*|H-E|\chi_k\rangle \\ \langle\chi_{k'}|H-E|\Phi_j\rangle, \langle\chi_{k'}|H-E|\chi_k\rangle \end{Bmatrix}. \tag{4.7c}$$

Thus the scattering problem has been cast in the form of a standard quantum mechanical calculation, i.e., computing matrix elements of the Hamiltonian with respect to a set of basic functions and then performing a linear algebra calculation (i.e., the matrix inverse in Eq. (4.6)).

The power of this variational result is that it applies as written also for reactive scattering provided one expands the definition of the channel label also to include an arrangement label. E.g., for an atom-diatom reaction, A+BC(vjm) $\rightarrow$ AB(v′j′m′)+C, the initial channel index i denotes the collection $\equiv$ (a,v,j,m), labeling the arrangement a and quantum state (v,j,m) of that arrangement; the final channel label in this case is f = (c,v′,j′,m′). The only modification of the above formulae in Eqs. (4.1)-(4.7) is in Eq. (4.4), noting that the coordinates appropriate for asymptotic channel ℓ may be different for different channels, i.e.,

$$\Phi_\ell \sim -\frac{e^{-ik_\ell r_\ell}}{v_\ell{}^{1/2}}\,\phi_\ell(\xi_\ell)\,. \tag{4.4′}$$

Reference 16 discusses how this strategy of using different coordinates for different basis functions is the same as that in the LCAO approach for constructing molecular orbitals in electronic structure theory by using atomic orbitals which are expressed in terms of spherical coordinates referenced to (i.e., "centered on") various nuclei.

Many of the recent accurate quantum reactive scattering calculations have utilized the above approach;[19-22] methods using hyperspherical coordinates have been the primary alternative.[23,24,18] Complete state-to-state differential cross section calculations have been carried out for the H+H_2 reaction and its isotopic variants,[19c,22] i.e.,

$$H+H_2(\text{ortho}) \rightarrow H_2(\text{para})+H$$

$$D+H_2 \rightarrow HD+H$$

$$H+D_2 \rightarrow HD+D\ ,$$

and also for the $F+H_2 \rightarrow HF+H$ reaction.[23] Calculations for many other reaction have been carried out for J=0 only.

It is also useful to note that methods have been developed which allow one to calculate the *cumulative* reaction probability (CRP) for a reaction directly, without having to solve for the individual state-to-state S-matrix elements.[25] This is important because the thermally averaged rate constant for a reaction can be expressed as the Boltzmann average of the CRP, N(E),

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE\ e^{-E/kT} N(E)\ . \tag{4.8}$$

The CRP is a sum of reactive probabilities, i.e., squares of S-matrix elements, over all open reactant and product channels,

$$N(E) = \sum_{n_r,n_p} |S_{n_p,n_r}(E)|^2\ , \tag{4.9}$$

where $n_r(n_p)$ labels the asymptotic channel states of the reactant (product). Miller *et al.*[26] showed that the CRP can also be expressed as

$$N(E) = \frac{1}{2}\,(2\pi\hbar)^2\ \mathrm{tr}[\hat{F}\delta(E-\hat{H})\hat{F}\delta(E-\hat{H})]\ , \tag{4.10}$$

where $\hat{H}$ is the Hamiltonian operator and $\hat{F}$ a flux operator. Eq. (4.10) forms the basis for a "direct" calculation since it is explicitly independent of individual reactant and product states. The heart of such calculations is finding a useful way to represent the microcanonical density operator, $\delta(E-\hat{H})$, and several efficient ways have been developed.[26-29]

Finally, any of the inelastic and reactive collision processes may also involve changes in the electronic state.[30] Formally, this requires only the addition of the electronic state index to the channel label in the coupled-channel equations in Eq. (3.3) or basis functions in Eqs. (4.7). In practice,

however, it requires that one know the non-adiabatic coupling (the Hamiltonian matrix elements non-diagonal in the electronic state index) as well as the different potential energy surfaces (the diagonal matrix elements).

5. Intramolecular Dynamics and Unimolecular Reactions

The resurgence of modern research in high resolution spectroscopy has stimulated theoretical studies of intramolecular dynamics. New experimental techniques make it possible to excite molecules to much higher energy states than ordinary one-photon absorption spectroscopy. The underlying vibrational motion is therefore much more complex and not usefully described by the standard normal mode picture.

The theoretical approach for characterizing intramolecular dynamics is in principle quite straight-forward:[31] since the molecular system is bounded, its quantum description is that of stationary states, i.e., eigenfunctions and eigenvalues of the Hamiltonian. One thus just (!) needs to choose an appropriate set of basis functions, form the Hamiltonian matrix, and diagonalize it, and this has indeed been carried out for a variety of small molecules, H_2O, HCN, ... Such calculations allow one to analyze the intramolecular motion in complete detail.

Because the ability to carry out these rigorous quantum calculations is limited to small molecular systems — very much the same kind of limitations as noted above for reactive scattering — there are a variety of approximate methods which are used. Some of these are still within a quantum framework — e.g., various perturbative approximations, sudden/adiabatic separations — and others use classical mechanics,[13] either completely classically or within a semiclassical framework.

The important questions in intramolecular dynamics have to do with how the energy moves between different degrees of freedom. E.g., if a laser excites motion that is predominantly CH stretch motion in benzene, how quickly does this energy move into other degrees of freedom in the molecule, and which of the other degrees of freedom are most effective in accepting this energy?[32] This question becomes even more interesting if some degrees of freedom lead to bond-breaking, in which case one is talking about *unimolecular* reactions.[10]

The rigorous quantum mechanical description of unimolecular reactions is that of Siegert eigenstates.[33] These are eigenfunctions of the Schrödinger equation with *outgoing wave boundary conditions*, and because of the complex boundary condition the eigenvalues are complex,

$\{En-i\Gamma_n/2\}$. The real part of the eigenvalue is the energy of the metastable state of the molecule, and its unimolecular decay rate is given in terms of the imaginary part, $\Gamma_n/\hbar$. (This latter relation is only true if these resonance states are non-overlapping, i.e., $\Gamma_n<\Delta E$ on the average, which means that the molecule on the average lives for at least a few bound state motions before it decays.) The unimolecular decay of the formaldehyde molecule,

$$H_2CO^{\ddagger} \rightarrow H_2 + CO\ ,$$

is one of the best characterized unimolecular reactions, a large number of its complex eigenvalues $\{En-i\Gamma_n/2\}$ having been determined experimentally.[34]

Another major question regarding intramolecular dynamics and unimolecular reactions is the extent to which the underlying dynamics can be described as *chaotic* or not.[35] Chaotic dynamics is a concept from classical mechanics, and the quantum analog is that the set of eigenstates (bound or Siegert) in some energy interval are "strongly mixed", i.e., representable only as a long expansion in any separable basis. The opposite limit of chaotic dynamics is completely integrable (or separable) motion, which in quantum mechanics means that in some set of coordinates the wavefunction would be a product of factors, one for each degree of freedom. Reality, of course, typically lies somewhere between these extremes, with the molecular dynamics appearing to behave chaotically or not depending on the level of excitation and the particular degrees of freedom which are excited. Most of the discussions of chaotic dynamics have been theoretical, for it is very difficult to find a well-defined experimental signature of chaos. It is often stated that such a signature is that a spectrum is "intrinsically unassignable", but this is of course very hard to distinguish from a spectrum that is simply very difficult to assign.

For molecules undergoing unimolecular decomposition, one measure of chaotic dynamics is the *distribution* of the unimolecular decay rates for individual molecular eigenstates that all have (approximately) the same energy (and total angular momentum). The more chaotic the underlying dynamics the narrower will be this distribution about the average, but there will nevertheless be some fluctuations about the average even if the dynamics is completely chaotic.[34,36] This type of analysis has recently been carried out for the unimolecular decay of formaldehyde noted above, and the experimental distributions are consistent with the interpretation that the dynamics is indeed chaotic.

Finally, it should be noted that the enormous amount of experimental

work on van der Waals clusters has stimulated much theoretical effort in describing these systems.[37] Especially interesting has been the vibrational predissociation[38] caused when a laser is used to excite one of the "tight" molecular vibrations, e.g.,

$$\mathrm{Ar} \bullet\bullet \mathrm{HC}\ell(v{=}0) + h\nu \rightarrow \mathrm{Ar} \bullet\bullet \mathrm{HC}\ell(v{=}1) \tag{5.2a}$$

$$\mathrm{Ar} \bullet\bullet \mathrm{HC}\ell(v{=}1) \rightarrow \mathrm{Ar} + \mathrm{HC}\ell(v{=}0)\,. \tag{5.2b}$$

6. Photon-Induced Processes

A variety of photon-induced processes other than simple spectroscopy are also under study nowadays. *Photodissociation*[39] with infrared lasers, which cause vibrational excitation, and also with visible and UV lasers, which cause electronic excitation, are important processes in their own right as well as being useful ways of probing reaction dynamics.

Although photodissociation is often referred to as a "half collision", its quantum mechanical description requires the full scattering wavefunction for the dissociative products. Thus, if $|\psi_{i,1}\rangle$ is the wavefunction for the initial state, in electronic state 1, then the state-to-state photodissociation cross section is given by

$$\sigma_{f\leftarrow i}(\omega) = \frac{4\pi^2\omega}{c}\,|\langle\psi_{E,f,2}|\vec{\mu}\bullet\hat{\varepsilon}|\psi_{i,1}\rangle|^2\,, \tag{6.1}$$

where $\psi_{E,f,2}$ is the scattering wavefunction for total energy $E = E_i + \hbar\omega$ in electronic state 2, and where i and f denote the quantum numbers of the nuclear degrees of freedom in the initial and final states. ($\vec{\mu}$ is the dipole operator and $\hat{\varepsilon}$ the polarization direction of the electronic field vector.) The primary task in computing such cross sections is carrying out the scattering calculation on the final potential energy surface (i.e., electronic state 2) to obtain the scattering wavefunction that appears in Eq. (6.1).

Photodissociation, as described above, corresponds to a continuous wave (CW) laser with frequency ω and polarization $\hat{\varepsilon}$. Eq. (6.1) is also a perturbative result, valid for one-photon dipole allowed transitions. (It is derived via the long time limit of first order time-dependent perturbative theory, leading to the usual Golden Rule expression.) Existence of high power lasers, and more importantly pulsed lasers with controlled wave forms, however, has created interest recently in exploring more general ways that electromagnetic radiation can be used to study and to influence

molecular behavior. Within the standard semiclassical approximation for treating the interaction of the molecular system and the laser, one considers the following time-dependent Hamiltonian,

$$\hat{H}(t) = \hat{H}_{mol} - \hat{\mu}\bullet\vec{E}(t) . \tag{6.2}$$

This is an operator within the space of the molecular degrees of freedom, $\hat{H}_{mol}$ being the field-free Hamiltonian of the molecular system and $\hat{\mu}$ its dipole operator. (Eq. (6.2) obviously also involves the dipole approximation for the coupling between the laser and the molecular degrees of freedom.) For a laser *pulse*, one has $\vec{E}(t)\rightarrow 0$ for $t\rightarrow -\infty$ and $+\infty$, so that one can consider transition probabilities $P_{f\leftarrow i}$ induced between initial and final states $|i\rangle$ and $|f\rangle$ that are eigenstates of $\hat{H}_{mol}$. $P_{f\leftarrow i}$ is a functional of the electric field vector,

$$P_{f\leftarrow i}[\vec{E}(t)] , \tag{6.3}$$

and one can consider the possibility of optimizing the field to enhance specific transitions. Several different strategies have been pursued for choosing the electric field $\vec{E}(t)$, i.e., the laser pulse (or pulses), to affect transitions of interest. Some methods are based on ultrashort (femtosecond, 10^{-15} sec) pulses,[40] and others rely on the coherence of two (or more) CW lasers.[41] A sequence of pulses[42] (stimulated Raman) has also been discussed as a means of enhancing specific dynamical processes. The optimization problem has been considered quite generally as a variational problem,[43,44] i.e., maximizing the functional in Eq. (6.3) subject to some constraints (e.g., a given total pulse power). These approaches all suggest interesting future directions for theoretical studies as the experimental technologies progress to make "laser control" a practical reality.

7. The Future

Predictions of future scientific developments are often quite worthless, but I believe that one can at least envision further progress in theoretical chemical dynamics along two fronts: (1) extension of rigorous methodology to provide benchmark results for larger, though still small, molecular systems, and (2) application of approximate dynamical treatments to evermore complex chemical systems. Prediction (1) will happen without question if for no other reason than the fact that computer power will continue to grow. I was amazed to see a recent advertisement for a new

portable 'notebook' type computer that performs at 8 to 10 megaflops (floating point operations per second) with 16 megabytes of internal memory. I saw in some old notes of mine that the CDC 7600, the top supercomputer all through the 1970's, performed at 3 megaflops! The latest IBM RS 6000 workstation performs at more than 100 megaflops. In addition to increased computer power, though, one should also see advances in methodology that will make the application of rigorous treatments possible for more interesting chemical systems.

There will nevertheless be interest in modeling chemical dynamics of molecular systems much beyond the capacity of rigorous quantum treatments. For some years already, many groups model biomolecular systems using classical trajectory simulation methods. The ideal situation would be to *combine* the accurate quantum treatment of a small sub-system, which involves the primary chemical process of interest, with a more approximate treatment of the much larger remainder of the system. Because classical mechanics is feasible for treating many degrees of freedom, this suggests using it as the "more approximate" method.

One thus seeks ways to combine the accurate quantum treatment of a few degrees of freedom with a classical or semiclassical treatment of the many remaining degrees of freedom. There are many such approaches that already exist, but no single one has emerged as the most generally accurate and useful model. Maybe there is no one universal such approach, but this is an area of intense interest and effort, and one expects to see progress.

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