Quantum effects in chemistry: seven sample situations

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Abstract

Significant quantum effects in chemistry range from static structure (electronic and geometrical) through dynamical behavior, including optical properties, conductance, relaxation, decoherence, and thermalization. We outline seven situations in which molecular systems exhibit ineluctably quantum behavior. These range from situations in which the community can understand the problem quantitatively and conceptually (for example for dilute sets of spins in NMR) to femtosecond/attosecond situations, which the community understands only primitively. In condensed phase, the dynamics will always evolve in a system/bath environment, and we discuss here how to pose, and to start understanding, problems of that sort.

Keywords: coherence; relaxation; electron transfer; excitons; energy transfer; electron transport

1. Quantum Chemistry

Historically, the first applications of quantum mechanics in chemistry occurred within two years of the introduction of quantum mechanics, with the formulation of the Born-Oppenheimer separation between nuclear and electronic motion [1], and the treatment of the hydrogen molecule by Heitler and London [2]. In the eighty-three years since that time, the issue of quantum effects in chemistry has taken on many meanings. This Solvay Conference examines the challenges that occur due to quantum effects in chemistry, in the context of the experimental and conceptual landscape of 2010. In this short article, I discuss six special cases, in each of which quantum effects are important, and then conclude (Section 8) with some technical but significant issues that arise in the general description of quantum dynamical molecular evolution.

This first section deals very briefly with the historically important case of quantum chemistry, which is the major success story in the area of quantum effects in chemistry. Sections 2-5 outline specific conceptual and experimental steps that have been taken by presenters at the Solvay Conference, within the particular focus session for which this paper is the rapporteur. We address (Sections 6-8) some aspects of quantum dynamical evolution, including discussion of a non-equilibrium, open system problem as represented by molecular transport junctions.

Quantum chemistry is the 800-pound gorilla in the conference room. Starting from the work in 1927, it has advanced steadily, and must now be counted as among the greatest successes in the theoretical chemistry of the 20th century. Partly this success is due to the obvious importance of the field, since chemists always have cared about the structure and stability of molecules. Partly it is because of the advent of electronic computers that permitted the appropriate calculations to be made. Partly it is because of the advances in crystallography, electron scattering, and...
spectroscopy that permitted structures of small and medium sized molecules to be analyzed very accurately. Finally, it succeeded because of very dedicated work by a number of brilliant individuals over eight decades.

It is also possible to ascribe the success that quantum chemistry has achieved to the fact that the problem was very clearly defined. In terms of fundamental constants, the problem of quantum chemical electronic structure calculations is to solve the stationary state Schrödinger equation in a limit \( (kT \to 0, c \to \infty, m/e \to 0, \rho \to 0) \). Here, \( k \), \( T \), \( c \), \( m_e \), \( m \), and \( \rho \) are respectively Boltzmann’s constant, the temperature, the speed of light, electron mass, mass of characteristic atom, and the density of the sample. These conditions correspond to zero temperature, nonrelativistic, frozen nucleus, infinitely dilute samples. Under these conditions, one can define computational “model chemistries” for particular categories of molecules. Work in the last three decades of the twentieth century brought about the concept of “model chemistries” [3] and great success in so doing: if one now chooses to calculate the geometry of a newly synthesized molecule containing (say) fourteen carbons, twenty hydrogens, and a couple of oxygens and nitrogens, the “model chemistry” corresponding to MP/2 solution to the static Schrödinger equation using a 6-31G** basis set will give the geometry accurately to 0.02 Å in bond length, and with comparable accuracy in bond angles.

The successes in solving these “model chemistries” are huge, and the influence in the chemical sciences appropriately large. Most organic chemists (and people well beyond chemistry including geologists, biologists, physicists, and engineers) now utilize electronic structure calculations to find geometries and suggest properties [4].

1.1. Outline: Quantum Dynamical Effects in Dense Systems

The rapporteur function of this paper involves discussion of four elegant contributions, that focus on quantum effects beyond the stationary ground state of isolated molecules. These are largely short-time phenomena, because for electronic systems interacting with a dense-states bath, decoherence will always cause the loss of phase dependent behavior on long enough time scales. In most of these situations, the assumptions made above about isolated molecules are no longer true \( (kT \neq 0, m \neq m_0, \rho \neq 0) \). These are the situations that chemistry confronted in its earliest days, when people were interested in liquids and solids. This attention to condensed phase matter has become crucial to contemporary chemistry and to its applications in collaborative ventures with other sciences including physics, materials science, chemical engineering, and biology [5]. Since coherent quantum evolution is largely a short time phenomenon, our understanding of its processes and behaviors has advanced with the availability of accurate short time measurement. From the nanosecond timescales of flash photolysis through the picosecond timescales that were called “ultrafast” in the 1970s (using etalons, and the beginnings of fast laser spectroscopy) to the femtosecond timescale that was made available and relatively straightforward by the advent of titanium sapphire lasers through to the attosecond timescale that will challenge our understanding of the dynamics surrounding the Born-Oppenheimer principle, and is already beginning to be pursued [6].

The protocols applied to make measurements using these short-time techniques involve either multi-pulse excitation/detection, multidimensional correlation spectroscopy, or single molecule spectroscopy.

In most of these situations, we want partial information, since in condensed matter there may be \( 10^{20} \) atoms or so in the studied volume and its intimately coupled neighborhood. Since full theoretical quantum dynamics on this number of particles is both unnecessary and impossible, the theoretical techniques used to interpret the data are those appropriate to situations in which we are interested in the behavior of a subsystem coupled to an environment. The most popular such approach is the density matrix technique [7-11], where the trace over the bath gives the reduced density matrix corresponding to the system and its dynamics. The second approach is the QM/MM scheme, in which one treats the quantum mechanics and dynamics of the system subject to an external bath that is treated classically [12,13]. Finally, the self-energy formalism evolving from nonequilibrium Green’s functions can be used to describe the quantum statistical mechanics of subsystems [14-18]. The second of these is the most popular in the chemical community, the first is the most popular for specifically pursuing dynamical quantum effects in molecular processes, and the third is the least common, but perhaps the most powerful. Remarks on these will be made in Sections 6-8.
The next four sections overview the contributions of the other speakers in this session, and suggest some of the challenges that arise in trying to understand the evolution of molecules in the quantum dynamics regime.

2. The contribution from the Kauffmann Group

The contribution from the Kauffmann Group deals with “the choreography of functionally important modes in optical dynamics of complex molecules”. This contribution utilizes two-dimensional electron correlation spectroscopy to access quantum kinetics, including the intramolecular vibrational relaxation regime. The systems studied are large molecules, including phthalocyanines, carotenoid/purpurine dyads, and pinacyanol chloride. Vibronic coupling pathways dictate both vibrational transfer and the redistribution, accessing the IVR regime.

This work uses multidimensional spectroscopy to investigate nuclear dynamics following an electronic excitation, and the evolution of quantum wave packets and their dynamics over short time scales up to, say, one picosecond. As part of this investigation, the Kauffmann Group works [19,20] in the sub ten-femtosecond regime to examine energy transfer in these dyads, observing strongly damped, off diagonal, oscillatory signals as would be expected for situations with this sort of intersubunit coupling.

3. The contribution from the Wolf Group

The contribution from the Wolf Group extends this molecular emphasis to examine interfacial dynamics. It uses the technique of two-photon photoemission, which has been beautifully developed by the Berlin group [21], combined with surface science techniques to study the dynamics following photoinjection of electrons from a metal into the adsorbate. The subsequent solvation and localization of the electron within the adlayer is the issue to be examined and illuminated.

This research is the successor to the work [22,23] on the time-dependent Stokes shifts carried out in the 1970’s and 1980’s, to determine dynamical relaxation of nuclear modes around a newly-introduced charged species. Here, however, the photoinjection of the bare electron gives a cleaner system, because the counterion (a hole in this case) is screened by the electrons of the metal. The full dynamics involving molecular dipole reorientation and inertial motion can then be examined. The observation is that the behavior depends strongly on the phase ordering in the adlayer. In crystalline structures, Wolf’s group sees relaxation processes over a time scale of $10^{12}$ times longer than in amorphous materials! This huge difference is explained in terms of the relevant energy landscapes that the electron would explore in fully crystalline versus fully amorphous materials.

These lovely experiments characterize nuclear relaxation phenomena around excess charge, that is introduced very rapidly into a specific place in an adlayer. The characterization of the dynamics, and its understanding in terms both of the motions and the static and dynamic disorder of the nuclei in the adlayer, is characteristic of the best work on interfacial dynamics.

4. The contribution from the Scholes Lab

The contribution from the Scholes Lab in Toronto comes from one of the leaders in investigating very short-time quantum coherences in real systems [24-26]. In this contribution, they focus on conjugated polymers, which are of interest both fundamentally and because of their applications in bulk heterojunction molecular photovoltaic cells [27-29]. It has been clearly established now (and follows from some arguments originally given by Flory half a century ago [30]) that conformational subunits in conjugated polymers are linked by regions of disorder, and that the energy moves among these conformational subunits by a Förster-like process [31], migrating on characteristic picosecond time scales, and winding up in the energy sink (the site with the reddest adsorption structure). This can
be understood utilizing simple models, that extend the two-site Förster mechanism to multiple sites along the disordered structure of the conjugated polymer [32].

At shorter time scales, the Scholes group and others [33] have shown that the dynamics among the photoexcited conformational subunits exhibit quantum coherence in the transport of excitation between nearby subunits. Probably most interestingly, vibrational motions along the conjugated chains themselves seem to delocalize the excitation energy. Scholes presents both the observations and a mechanistic argument about how the chemical bonds introduce quantum effects in the dynamics of energy transfer.

Energy transfer has become the area in which some of the most striking and elegant spectroscopic studies have been done, studies that indicate the appearance of quantum coherence in situations in which it would not be expected [34]. While some of these observations can be understood using density matrix theory and some special assumptions about the nature of the relaxation processes [35], their observation in several different systems, in several different laboratories, suggests that the standard arguments from complete and careful simulations of systems like the solvated electron [36,37] or isolated chromophore dynamics in solution [38] are not necessarily relevant to large molecular species. (If they were, the conclusion that follows from the work of many authors that in polar solvents decoherence is essentially complete on the time scale of a few tens of femtoseconds [39] might preclude some of the long-time coherences observed in polymers, and in biological and biomimetic systems).

5. The contribution by the Waldeck Lab

The contribution by the Waldeck Lab deals with some fundamental conceptual issues involving pathways for coherent transfer between molecular sites. Effectively, the authors argue [40-42] that if one chooses to measure and describe electronic tunneling from a given site to another within a molecule, many different quantum mechanical pathways might be accessed. Nuclear reorganization can evolve, and eventually an optimal tunneling geometry (corresponding classically to the activated complex picture of Eyring [43]) can be found. Then, conceptually, the electron is imagined to tunnel through a barrier presented by the nuclear geometry. The tunneling can occur by a single pathway, but might occur by several different pathways, and quantum phase interferences among those pathways can occur in the propagation scheme [44-50]. This quantum interference among coupling pathways can be important in electron transfer kinetics. Decoherence among these pathways can arise from inelastic effects in the molecules, or from motions that describe either pure dephasing ($T_2^*$) or energy relaxation ($T_1$). As examples, the authors discuss biological and biomimetic systems, where nuclear fluctuations, as might be expected, help to determine the nature of the bridges and which ones are utilized.

This work deals not so much with coherence along a single quantum trajectory, but rather with the phenomenon of phase interference, familiar from the two-slit problem. Such phase interferences are responsible for some of the mechanistic regularities of organic chemistry, such as the very weak coupling between meta-substituted sites in benzene, compared to the much stronger interaction between sites that are para or ortho to one another. Indeed, a significant part of physical organic chemistry is based on arguments concerning coherence and phase cancellation [44,51].

The understanding of pathways is highly intuitive to most chemists; this contribution focuses on the concepts involved, and the situations under which coherence effects can be observed clearly, or molecular motion can lead to decoherence. Such concepts have been recently investigated experimentally in specially-designed two-path systems [52], and their explanation in terms of the shaky pathways scheme [53] seems quite powerful.

These four contributions suggest four of the most important areas in which coherences and quantum effects are now seen in condensed phase chemistry (vibrational interactions with electronic states, injection at surfaces and structural relaxations around introduced charges, coherence effects in energy transfers in disordered and model systems, and interference among different pathways in electron tunneling processes).
6. Density Matrices, Partial Information, and Hot Injection

The introductory article by Rice covered many of the issues confronting our current understanding and formulation of quantum effects in dynamical systems. In Sections 6-8, we suggest a few situations, in which such difficulties can occur. In this chapter, we will deal with situations in which we wish only partial information on a subsystem, interacting with a larger heat bath. These correspond to closed systems in the sense that the number of electrons, \( n_e \), within the system, is fixed. Energy can flow in and out of the system, and in this sense it resembles the canonical ensemble of classical statistical mechanics.

Under these conditions, we can represent the density matrix operator by Eq. 1, where \( i \) and \( j \) label arbitrary basis functions. The full density matrix describes the full system, and its dynamics are fixed by the quantum Liouville equation, Eq. 2. We are generally interested only in the dynamics of a subsystem (e.g. a molecule dissolved in fluid). We then [7-11] define the reduced density matrix

\[
\hat{\rho}_{i,j} = \langle \psi | \rho | \psi \rangle = \langle \psi | \hat{\rho} | \psi \rangle
\]

(1)

\[
i \hbar \frac{d}{dt} \hat{\rho} = [\hat{H}, \hat{\rho}]
\]

(2)

\[
\sigma = \text{Tr}_B (\rho)
\]

(3)

\[
\hat{H}_{\text{total}} = \hat{H}_{\text{system}} + \hat{H}_{\text{bath}} + \hat{H}_{\text{interaction}}
\]

(4)

\[
i \hbar \frac{d}{dt} \hat{\sigma} = (\hat{H}_{\text{system}}, \hat{\sigma}) + i \hbar d \hat{\sigma}/dt_d
\]

(5)

It then follows that, if we represent the total Hamiltonian of the physical sample by Eq. 4, the evolution of the reduced density matrix \( \sigma \) can be written as Eq. 5. Here the \( d \) subscript in the last term implies dissipative behavior, behavior corresponding to decoherence and relaxation within the quantum subsystem, caused by the last two terms in Eq. 4.

There are many formulations of the dissipative term, some of which are Markovian and quite general (usually called Lindblad models [54-58]), whereas others are approximated at second order, in the expansion of the density matrix (Redfield theory [59]). More recent treatments have been developed. One can indeed expand to higher orders in the density matrix, resulting in diagrammatic expansions using double sided Green’s functions. This has been elegantly introduced and utilized by Mukamel and his group [10].

Sophisticated analyses using these schemes are common in descriptions of condensed phase chemical dynamics. But as was pointed out in a significant paper [55] by Tannor and collaborators, each of these schemes suffers from one or another fundamental inadequacy (Redfield equations can give negative populations, Lindblad approximations are only accurate up to an unknown intensity parameter, and are not necessarily translationally invariant). Nevertheless, sophisticated analyses using these schemes are indeed common in descriptions of condensed phase chemical dynamics.

To introduce multilevel, not-necessarily Markov relaxation process, Kosloff has introduced the so-called stochastic surrogate model Hamiltonian [60,61]. This is represented by Eq. 6, where \( B \) and \( B' \) represent the primary bath (here taken as two-level systems rather than harmonic oscillators) and the secondary bath (also consisting of two-level systems).

\[
H_{\text{total}} = H_S + H_B + \hat{H}_{sa} + \hat{H}_{sv} + \hat{H}_{sb} + \hat{H}_{sv}
\]

(6)
The secondary bath B’ couples to the primary bath, and effectively gives the elements of the primary bath a lifetime (a similar scheme was utilized by Subotnik and collaborators [62] in constructing a model for molecular transport junctions utilizing a density matrix approach – see Section 7). In this formulation, the $H_{BB'}$ effectively gives the states of the bath represented by B a lifetime. Kosloff has developed a convenient swapping scheme that describes the full time evolution of the system subject to these two baths. This avoids any Markovian assumption, and by appropriate selection of the system’s matrix element in the $H_{SB}$ term, one can propagate computationally the system Hamiltonian, and deduce the effects of bath relaxation and decoherence. This is a promising scheme, because it is computationally relatively straightforward, and yet is non-Markov, and readily interpreted in a physical way.

As an artificial example, we consider [63] the photodynamics in a three-state problem. Fig.1 gives the three lowest potential energy surfaces of an anharmonic diatomic molecule. Upon photoexcitation from the ground state to the acceptor (bright) state labeled b, the wave packet starts to evolve on the excited state, and eventually crosses the curve into the dark state, or acceptor state, a. When the wave packet hits the outer wall of the potential corresponding to the dark state, it is reflected. If, now, it can decohere before it gets back to the crossing between the bright and dark states, then (following the initially nonintuitive but quantum mechanically correct) argument given in the classic review [64], the system simply cannot cross. Therefore, if the bottom of the dark state potential is higher than the bottom of the bright state potential, the excess energy denoted $E_B$ in Fig.1 can be captured by the dark state, and remain there. The energy $\Delta E_B$ is thus prevented from thermalizing, and if injection of the electron from the dark state into the electrode then follows, the thermal excitation within the initial Franck-Condon vertical excitation from the ground state to the bright state can be partially trapped; $\Delta E_B$ represents this trapped energy. It is, however, no longer in the vibrational manifold, but rather in the electronic energy of the dark state. Subsequent injection into the electrode thus captures not only the energy corresponding to the bright state minimum, but also the excess vibrational energy which is accessed by the Franck-Condon, vertical excitation.

This sort of capture of energy before it can transform from electronic to vibrational (heat bath) was first suggested by Nozik, who called it hot injection [65]. Nozik was mostly interested in semiconductor quantum dot systems, but while the example presented here is artificial, nevertheless if the decoherence process is fast enough (a few femtoseconds in this case), then indeed energy can be captured using this hot injection formulation.

Details of the argument here are given in Ref. [63]. Unpublished work from the Kosloff group suggests that in two-dimensional systems, far better capture of the excess vibrational energy into the electronic manifold can occur, and this could cause hot injection to be useful in organic photovoltaic systems. One interesting aspect of this dark state capture of vibrational excitation is that, in this case, it is the decoherence rather than the coherence that permits manipulation of energy capture.

The utilization of decoherence effects to improve evolution behavior has also been seen [66,67] in new work from a very different part of the chemical dynamics interest spectrum. Plenio and coworkers, [67] and also Aspuru-Guzik and co-workers [66], pursued the FMO complex that was observed [34] to exhibit long-lasting quantum coherences. These investigators saw an unanticipated sort of resonance, when the energy gap frequency between states was comparable to the decoherence rate. Under these conditions, the energy transfer efficiency can actually be enhanced by the decoherence [64]; in this sense, it resembles the “hot injection” situation, in that the decoherence actually favors the process that is wished. Such interactions between spacings in the system and frequencies of decoherence are reminiscent, also, of nmr lineshape behavior.
7. Self Energies, Time Scales, and Some Molecular Transport Issues

Density matrix methods were originally developed for canonical, closed systems. They are, generally, the method of choice for the analysis of quantum decoherence problems, because they so beautifully permit an understanding of partial information. In open quantum systems, where the number of electrons is neither an integer nor a known quantity, density matrix schemes are substantially more difficult to formulate [68]. Under these conditions, the most attractive way to deal with understanding transport is to use the nonequilibrium Green’s function formulation. The formalism here is a bit complex [14-18, 69], and in this section we will simply note some of the understandings that have been gained, and mention issues such as time scales and interferences.

Experimentally, the molecular junction transport system has been extensively explored over the last twenty years [70-73]. A large number of experimental test beds, many devolving from more traditional mesoscopic physics, some from electrochemistry, have been used [74-80].
Fig. 2 shows the electrochemical break junction scheme [78] that has the advantage of measuring current through a molecular transport junction, but also of providing enough statistics to estimate significant physical issues including (in particular) geometric variation. The simplest model for a molecular transport junction is shown in Fig. 3.

![Diagram of molecular transport junction](image)

**Fig. 3.** Highly schematic picture of transport junctions for measurement of molecular conductance and quantum dot conductance.

Voltage is applied between two electrodes, with the molecule bound to both electrodes through individual binding sites. This is the theoretical model that is nearly always used, and in many cases it is believed that the experiment measures something very much like this.

The experimental and theoretical analysis of molecular transport junctions has become quite active, and with more than a thousand papers published on the subject, this is not an appropriate place for review. These systems are appropriate here, because they offer examples of open quantum systems interacting with baths, but the baths are not the harmonic oscillator or two-level system baths that are appropriate for the modeling of quantum coherence, decoherence, and dynamics in isolated (or solvated) molecular systems.

The fundamental understanding of what happens [81] in molecular transport was provided by Landauer [82], Buttiker, and Imry [83]. They were concerned not with molecular transport, but with a similar problem in mesoscopic systems. A simple picture of such systems is a quantum dot behavior, as sketched in Fig. 3b: here the two electrodes can cause charge to flow through the system consisting of the macroscopic electrodes and the nanoscopic quantum dot. The Landauer/Imry (L/I) approach is based on the understanding that the decoherence and loss of quantum effects are caused by a bath, but that bath comprises the electronic states of the leads – it is a Fermi bath, not a Bose bath or classical bath. But it effectively relaxes the system, can cause full quantum decoherence, and permits irreversible flow of current from the higher to the lower potential.

The Landauer argument is a lovely one, because it is so simple. The resulting Landauer/Imry (L/I) equation for the zero-voltage current is

$$g = g_0 \sum_{\text{channels}, i} T_{i,i}$$

(7)

Here $g_0 = 2e^2/h$, where $e$ is the electronic charge, $h$ is Planck’s constant, and $g_0$ is the fundamental quantum of conductance (77.48 microsiemens). The transmission coefficients $T_{i,i}$ describe behavior in channel $i$. Fundamentally, Eq. 7 says that “conductance is scattering” - as the electrons pass from the macroscopic lead into the nanoscopic/mesoscopic system (be it a quantum dot, or an ultra-thin heterostructure layer, or a molecular entity), it can scatter elastically, either into the product bath or back to the reactant bath. If in each channel only forward scattering happens (so that its $T_{i,i}$ is unity), summing over all transport channels that are transverse to the electrode pair gives the number of channels times the quantum of conductance.

This is a remarkable construct: note that it has little to do with Ohm’s law, because here conductance is quantized, and the only considered inelastic behavior is from the electrons in the leads. The most striking examples are seen experimentally for metallic wires, as shown in Fig. 4; the typical conductance quantization is seen, exactly at the values suggested by the Landauer formula.
While Eq. 7 is useful for certain metallic wire systems, it is less effective for molecular systems. There are three reasons for this: first, it is difficult to define what one means by a transverse channel in the molecular situation. Second, molecules do have vibronic coupling, and it is difficult to include that simply in the Landauer formulation. Third, the electronic structure of molecules is not normally thought of in channels – to be consistent with the advanced computational methods available for molecular entities, it is more convenient to formulate the problem using a fundamental nonequilibrium approach, that can deal with interelectronic interactions, vibrational and classical baths, photonic excitation, and so forth. This is offered by the nonequilibrium Green’s function (NEGF) method [14-18,69,84].

The NEGF method was originally developed for problems of nonequilibrium statistical mechanics and for quantum transport. It bears a close relationship to the two-sided Green’s function approach of Mukamel [10], but generalizes the density matrix scheme, because there are two different times, with different time orderings, associated with NEGF. Because of the time ordering, four different Green’s functions are generally used: the retarded, advanced, greater, or lesser Green’s functions. Each has its own associated self-energy, and they differ simply because of the time orderings. The equations of motion for these Green’s functions are typical many-body equations, in that no closed-form solution exists except for very special cases. There are many approaches to solving the NEGF equations, utilizing perturbation theory, or decoupling methods, or scattering approximations. It is then possible to develop self-energy terms that describe interactions of the molecular system (as chosen) with the environment.

For the example of transport between two metallic electrodes, ignoring any corrections to the Born-Oppenheimer approximation (no vibronic coupling) and no photonic coupling, the Caroli [85] equations 8 will hold. Here $G$ is the retarded Green’s

$$I(V) = \frac{2e^2}{h} \int T(E,V) |f_i(E) - f_j(E)| dE$$

$$T(E,V) = \text{Tr} \{ \Gamma_r(E,V) G^\dagger(E,V) \Gamma_i(E,V) G(E,V) \}$$

$$G^x(E,V) = (E - H_{\text{er}} - \Sigma_{\text{res}})^{-1}$$

$$\Gamma_\lambda = i [\Sigma_\lambda - \Sigma_\lambda^\dagger]$$

$$\lambda = i, f$$
function, and $\Gamma$ is the so-called spectral density. The understanding of these equations is straightforward: the transmission $T$ given by Eq. 8b is equivalent to the sum over channels in the Landauer expression. The spectral density refers to the coupling between the “extended molecule” (the molecule plus a small number of atoms representing part of the electrode; these are included to describe properly the coordination of the molecular entity to the electrode) and the two electrodes.

The Green’s function $G$ is given by eq.8c, in terms of the full self-energies. These self-energies contain real and imaginary parts – the real part corresponds to the energy shifting of the system levels by the environment. The imaginary part (in the simplest situation that the Caroli equations describe, again neglecting all interactions with any bath except for the electronic one in the leads) describes the coupling between the electronic states of the extended molecule and the electronic states in the leads. At a frequency corresponding to an excitation on the extended molecule, the first two terms in the eq.8c will give zero, and the self-energy terms will cancel the spectral density terms in eq.8b, so that effectively the transmission is $g_0$, and the $L/I$ limit holds.

The integration in eq.8a says that for any given voltage, the Fermi functions $f_i$ and $f_f$ are necessary for the correct statistical counting: the electron must go from a full electrode level to an empty one, for the transition to be allowed. Since these factors contain the Fermi energy $E_F$, we need to be careful in choosing $E_F$ for the real situation. This is usually taken to be $E_F$ of the bare metal, but this is almost certainly incorrect, because the metal in a molecular transport junction will have molecules attached to it, and its geometric structure will certainly not be that of the perfect crystal. These modifications should shift the relevant $E_F$, and this issue, called the “band lineup problem” makes calculations of the actual current or conductance in molecular transport junctions challenging (though it can be overcome by actually calculating $E_F$ for the full system).

This formulation of molecular conductance is purely quantal; the quantum of conductance $g_0$ contains Planck’s constant. The problem of “quantized conductance” was effectively discussed by Landauer in the 1950s, and so this quantum effect is neither new nor unanticipated. But for molecular systems, the area has only been discussed since the 1990s, and very interesting progress has been made. We will limit ourselves here to two significant issues: first, interference effects for multiple quantum channels; second, decoherence effects and the transition from tunneling to hopping motion.

7.1. Interference Effects in Transport Junctions

Pi systems contain delocalized electrons, that can be described, qualitatively, by very simple tight-binding or Huckel models. Since they are delocalized, we might expect interference between pathways. Indeed, this is the mechanism by which we understand that (for example) in benzene rings the interaction between substituents at meta sites is very much smaller than that at ortho or para sites. Other coherence-driven molecular effects include ring currents in NMR [86], cross conjugation [87,88], and transfer through squaraine structures [89].

Recent analyses of current patterns through organic molecules strung between metallic electrodes, using either extended Huckel theory or tight binding density functional calculations, have been completed by Solomon and co-workers [90-94]. These illustrate some aspects of molecular interference. The formalism to develop the tunneling currents [95,96] follows directly from the Landauer transmission, and Eqs.8. It is then necessary to determine the surfaces through which the charge will move, and to recall that currents can run both forward and backward. The result is not only a calculation of the conductance, but an interpretive mechanism for understanding the conductance.

In these calculations, there is no direct treatment of decoherence, because the structures start with the Landauer (elastic) formulation, and no dephasing-type terms are permitted, other than the spectral density itself (this is at the frontier, and should be explored soon; some initial considerations using the Buttiker probe approach have appeared [96]).
Fig. 5. A simple cross coupling situation. Transport through the cross-coupled link (bottom) shows interference patterns absent in the linear link (above).

Fig. 6. A three-ring reversal in the current passing through a molecule. The arrow diameter is proportional to the current between leads (at lower right and left). Blue arrows point against the voltage gradient, and are characteristic of interference behavior.

Figs. 5, 6 illustrate the current flow pictures that one calculates, for different systems. Fig. 5 illustrates the simplest example of cross conjugation: cross conjugation is defined [97] as “three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other”. The simplest example is a T junction (stub resonator) situation. The transmission from one side to the other of cross conjugated versus normally conjugated systems are shown: the deep minimum in the center of the curve arises because the pi system transport is destructively interfered with by the cross conjugation, leading to the transmittance dip, with conduction being dominated (in this energetic region) by the sigma system. Then the cross conjugated system conducts less well than the fully-conjugated system, and indeed comparably to the sigma-only (presence of methylene groups in the backbone) structure. Unpublished work (M. Wasielewski et al.) has investigated these effects using electron transfer, rather than conductance, measurements. The results are in substantial agreement with these predictions, with the cross-conjugated molecules showing anomalously low rates.
Earlier measurements also bear this out. Mayor and collaborators measured [98] conductance in two different molecules, one characterized by para linkages and the other by meta linkages: the doubly meta-linked species conduct essentially an order of magnitude less well than the para-linked ones, again because of interferences in the pi system.

Fig.6 indicates the kinds of current branching situations that occur near interferences (interferences occur at given values of the voltage, since the transmission is voltage dependent, and so are the currents and the conductance). The three-ring structures correspond to currents flowing forwards and backwards (blue and red in the picture). They are often found near interference minima in the pi system. In unpublished work, Solomon has also found that some of the gating structures (in which photoisomerization is used to switch between a highly conductive and a less conductive entity) can be described well in terms of these current flow pictures.

While these current calculations are done using a relatively primitive basis set, and do not deal with correlation or vibronic coupling or decoherence problems in any way, nevertheless they are instructive. One purpose for doing theory is to interpret and predict experiment, and these local current maps are helpful in that regard.

7.2. Decoherence and Turnovers

Quantum mechanics can describe systems that are generated when an electron donor (for electron transfer) or an electrode (for electron transport) injects an electron onto a molecular bridge (consisting of one or a series of local orbitals that can be occupied by the transferring electron) and then onto a different large entity, (an acceptor in donor/bridge/acceptor electron transfer, or an electrode in voltage-dependent current spectroscopy).

![Energy level diagram](image)

Fig. 7. Schematic energy level picture for either a donor/bridge/acceptor molecule or a molecular transport junction (in the latter case, the red sites are the highest occupied electrode band states).

When the gap between the levels on the bridge (Fig.7) and the donor/acceptor states is large, one expects a “superexchange” kind of process, in which the rate of electron transfer (or the conductance) falls off exponentially with distance. This can be rationalized in many ways, the simplest of which is to use one-electron perturbation theory, with the smallness parameter being the ratio of the intersite tunneling integral over the donor-bridge energy level difference.

Extensive modeling has demonstrated [99-103], and observations have shown [104-107], that as the bridge gets longer, coherence can be destroyed by either $T_1$-type or pure dephasing processes. In either situation, one eventually reaches a case where the quantum behavior is no longer coherent over the whole bridge, and a transition (sometimes gradual, sometimes abrupt) to hopping type incoherent transport occurs. This was predicted by a simple density matrix treatment; the prediction, and some early experimental results, for DNA species are given in Fig.8.
These turnovers are fascinating, because they occur in many systems. We can rationalize these behaviors utilizing a time scale argument. The tunneling matrix element can be compared with the polaron stabilization energy (equivalent to the Marcus reorganization energy). When the tunneling matrix element is larger, the tunneling is coherent, and then there isn’t time for the electron to trap itself locally.

Another time of interest is the so-called Landauer/Buttiker contact time, which is supposed to be the time that the electron actually spends in the forbidden region between donor and acceptor (or between electrodes). In a semiclassical approximation [108], this time

\[ t_{\text{contact}} \approx N\hbar / \Delta E_G \]  

is simply given by eq.9, where N is the length of the chain in repeating units, and \( \Delta E_G \) is the gap energy – the energy between donor (or acceptor) levels and bridge levels. As the gap becomes zero, the system becomes fully delocalized. It can then transfer directly (the transmittance goes to one, and one would expect quantum conductance as in Fig.4) or, since the time formally becomes very large, trapping might occur on the bridge.

The issue of bridge trapping by polarons has been examined extensively for conducting polymers, both theoretically and experimentally. One interesting question issue is the time scale of charge transport versus the time scale of polaron formation. The polaron coupling is proportional to the density of electrons on the bridge; if \( \Delta E_G \) is large, the populations are small, and one expects that the golden rule formula, with the perturbation proportional to the square of the population, will indicate that the vibronic coupling is very weak. Whether or not the polaron formation time is the same for electrons moving with kinetic energy and for electrons localized at one site seems unclear.

If one takes an empirical approach to the decoherence, simply using the representation with relaxation terms added to the off-diagonal elements of the density matrix, one can actually show that para-, ortho-, and meta-type effects completely disappear, when the dephasing gets strong enough. An example is shown for the Davidene molecule in Fig.9 – this is not surprising, but it is an interesting prediction if these measurements are ever made. Similar considerations have been suggested [96] for actual molecular devices, based on interference.
8. Theoretical Worries, Technical but Significant

Dealing with the quantum dynamics of molecular systems interacting with a condensed phase environment has made great progress experimentally, theoretically, and computationally. Density matrix, QM/MM and nonequilibrium Green’s function approaches are useful for formulating and understanding the quantum/classical dynamics. Moreover, computational advances (particularly the use of Feynman path integral methods for model problems [110,111], density functional theory and time-dependent density functional theory for electronic structure and response, and extensive simulation methodologies, all coupled with substantial advances in the technology of computation (including most recently GPU cards)) have allowed meaningful calculations to be done. Nevertheless, several challenges need to be overcome before analysis of real chemical systems, with the electronic structure details and the dynamics, can be completed. Here we simply note some of these, and suggest possible solutions.

8.1. Basis Sets, and Pointer Basis

When density matrices are used (as they broadly are) to describe quantum dynamical evolution and relaxation in molecular systems, we need basis sets to represent the systems (interacting with the bath). Quantum chemistry provides an extensive set of basis sets for use in static structures, but a question like how energy transfer occurs between a phthalocyanine and a nearby quinone poses the problem of basis sets in a different way. In perturbation theories, one needs to calculate the matrix elements of a perturbation between initial and final states -should they be stationary states? Usually not, because one is generally experimentally interested in initial states that have been photoexcited, excited by collision or ionization – that is, these are not equilibrium eigenstates. These states can be generated computationally, by computing the time evolution under the exciting field from an initial ground state [112]. This excited wave function should represent the initial state in the chemical dynamics.

If one is interested in the evolution of this initially-excited molecular state, it needs to be represented somehow in terms of the basis. For model systems as simple as a two- or three-level model, this is not a problem. But in applications to real systems, we need to represent this initial state such that its evolution can be computed. Again, as long as we operate within a full basis (we study the complete problem quantum mechanically), the propagation is straightforward although so time consuming that as of 2011 it is impractical. But if the calculation is of density matrix or NEGF type, to describe the effects of the bath interaction with the system, the problem becomes more complex. Several problems with the basis set then follow. For a two-level system, in which the field enters through Bloch-type relaxation of the diagonal and off-diagonal elements of the density matrix, the dynamics can be completely different depending on the representation in which the T1 and T2 relaxations are applied. To pick an extreme situation, for a two-site orthogonal system, one could choose either the local states or the fully delocalized...
states as the basis functions for the density matrix. Limiting ourselves to pure dephasing, it is clear that using the local basis can result in the system being trapped in either the left or the right localized state, when the dephasing rate overwhelms the tunneling. But if the eigenstate basis is used, the system remains in the fully delocalized, nodeless, “binding” structure, if (again) the dephasing is fast enough.

These are trivial examples of the so-called pointer state problem. The pointer basis is supposed to be the most reasonable in which to carry out quantum dynamical relaxation calculations. The difficulty is agreeing on what the pointer basis might be. There has been discussion of this in the literature [113,114], but it seems that this situation is not yet resolved. The usual approach is to revert to a model, in which one assumes an initial state that is fully localized, assumes a coupling Hamiltonian (often of simple Huckel type), and carries out the dynamics assuming some sort of bath. This could be some form of the so-called spin-boson system [64] (a two level molecular system coupled to a set of harmonic oscillators corresponding to the bath). Even that is complicated, though it completely avoids the problem of the choice of basis sets.

8.2. Initial optical preparation

If a full molecular representation in terms of a reasonable electronic structure basis is used, it is possible [112] to generate a photoexcited state by propagating the initial static ground state under the perturbation $V$ as $\exp(-iVt/\hbar)$. But the optical interaction with the molecule is proportional to the molecular dipole operator, and this can distribute density throughout the molecule. That initially prepared state will generally not resemble our intuitive notion of, say, an optically excited donor state in an electron transfer reaction, or an initial exciton state for energy transfer. Intuitively, we expect that over a very short time (a few tens of femtoseconds) a sort of electronic decoherence occurs, causing effective localization of the charge into something that closely resembles a localized excited state. These modifications are not the same sorts of shifts that are measured at much longer times by the time-dependent Stokes shift spectrum, because that is often dominated by relatively slow motions (for example rotations) in the environment. Intuitively, the sorts of decoherence involved in making an initial photoexcited state correspond to “chopping off the tails” of the photoexcited, largely delocalized, state to form a reasonably localized photoexcited state. This has been addressed by the (interesting but still far from complete) idea of einselected (environment - induced superselection) states, that are the appropriate initial states for the quantum dynamics. The einselection process [113,114] arises from the system/bath coupling, and occurs very much faster than other timescales in the system. The states formed by the einselection process may be pointer states, and in the simplest view they are minimally influenced by the bath. Issues of generality and uniqueness still surround this notion, which has been used only for a few selected model systems. Still, these are significant issues, particularly as the bath changes from aqueous solution (where coherences last only very short times, usually less than 100 femtoseconds) to slower-relaxing hosts such as less polar liquids, bio-environments, polymers, solids or glasses.

One way around this problem, investigated in the context of energy and of electron transfer, is to choose a state that is maximally localized, in the Edmiston-Ruedenberg sense. In an initial study, Subotnik and collaborators [115] were able to match very well classic energy transfer studies, utilizing these localized initial electronic states.

8.3 Overlap issues

It is convenient to assume (almost always assumed in formal derivations), that the initial and final states are orthogonal to one another. But conventional orbital basis sets, as used in electronic structure calculations, are hardly ever orthogonal. They can be made orthogonal by Lowdin or Schmidt or other procedures, but this leaves difficulties in understanding what happens at short times after photoexcitation.

Suppose we imagine a very fast photoexcitation of an electron in site A, where the localized orbitals A and B are not orthogonal. The prepared state is then just $c^+_A |\bar{0}\rangle$, with $c^+_A$ the creation operator on A. Then we find for the population on B at this initial time:
\( n_s(0) = \langle 0 | e_{\alpha}^{\dagger} e_{\beta} e_{\beta} e_{\alpha} | 0 \rangle \)

(10)

this follows from the anticommutation relations between the creation and destruction operators, and \( S_{AB} \) is the overlap integral. This suggests that the expectation value of the population on site B, even at time zero, is the square of this overlap integral. This raises the question of whether or not we can actually separate donor and acceptor states using this sort of molecular basis. The interpretations can become quite difficult; it appears that when the electron is created on site A, there is a small part of it that is on site B even at zero time. Perhaps the same sort of rapid relaxation (einselection) referred to in Section 8.1 could occur here too, but formally this is a nettle.

8.4 Other molecular systems

Coherence became an important theme in modern condensed phase science with the development of magnetic resonance. Issues of relaxation phenomena and loss of phase were brilliantly handled by the pioneers of magnetic resonance spectroscopy. Magnetic resonance is the first situation in which coherence and its loss have been significant issues. It is also a fortunate place for doing this kind of work, because the eigenvalue spectrum of the spins is generally very sparse – for a proton, there are only two levels. This means that relatively simple representations like the spin-boson one are appropriate, and it also means that there is enough time to do all sorts of wonderful pulse sequencing and pulse shaping, both to measure and to drive the system.

The systems described in this manuscript (and indeed in this volume) are different. They involve coherences that are electronic in origin, and coherence in energy transfer and charge transfer becomes a dominant issue. Because these systems are not sparse, and because in many cases (in particular polar materials and polar environments) the interactions with the environment are very strong, the existence of long time coherence is unusual, and understanding it requires a new approach to this second situation for the decoherence problem, involving quantum effects in chemistry.

There is a third area that has been explored only slightly. Vibrational coherences can also occur, and indeed one might argue that they are partway between magnetic resonance and electronic behavior. Unlike magnetic resonance, their eigenvalue spectrum is not sparse, and Fermi resonances and near-Fermi resonances are common. But unlike electronic phenomena, their coupling to the bath is often quite weak. This allows coherences of quite high orders to be observed, even in relatively large systems.

A wonderful example is found in the recent work of Wright [116,117], who examined, in particular, a rhodium dicarboxyl chelate organometallic compound and was able to observe very high-level coherences, to understand them both energetically and dynamically, and to suggest (in collaboration with Sibert) that they could be described very well in terms of only two degrees of freedom. This vibrational coherence spectroscopy is another example of coherent quantum effects in chemistry, and here the understanding and mastery of coherences is probably halfway between its elegant state in spin systems and its challenging state in electronic systems. One task for the conceptual mastery of dynamical quantum effects in chemistry is to transfer some of the learnings that occurred with spins and vibrations to the challenging and significant area of electronic coherence behaviour.

8.5 Variational Principles

When the system is both open and nonequilibrium (for example, electron transport in junctions under voltage), a particular problem occurs. Because the number of electrons is not known, and because the momentum of electrons is finite since current is flowing, the standard derivation of the Rayleigh-Ritz variational principle fails. While there are time-dependent variational principles that may well be valid, it is difficult to use these to optimize geometry. The usual approach is to optimize the geometry in the absence of the field, and then to assume that the geometry remains unchanged in the presence of the nonequilibrium potential and electronic momentum. This is generally not correct, and the issue of optimized geometry under current flow conditions is one of the challenges remaining in the field of molecular transport junctions.
These four issues represent some of the next chapter in our understanding of how to understand nonequilibrium quantum dynamical systems. Very recent work by Martinez has focused on another issue: what coordinates should be used to conceptualize the dynamics? Using GPU-enabled very fast computation, he was able to generalize the description of a reaction coordinate, by permitting the overall computed dynamics (in his case QM/MM dynamics) to be expressed in terms of the motions of the molecule itself and the surrounding solvent [118]. This idea of allowing the computation to suggest its own coordinates is attractive, and may well provide a different approach to understanding the molecular pathways, molecular interferences, and molecular decoherence that characterize quantum dynamics of electronic energy and charge in condensed phase.

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