Rate Constant Turnovers: Energy Spacings and Mixings[†]

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The golden rule predicts that rate constants are proportional to the squares of mixing matrix elements divided by squared energy differences. As physical problems scale between different coupling limits, the calculated rate constant could first increase with mixing strength, reach a maximum, and then decrease as the mixing strength becomes larger. We demonstrate this general rate behavior as a function of Hamiltonian parameters, both for simple Huckel-type models and for a two-site Hubbard system. We demonstrate that the optical susceptibility in a two-site tunneling problem also shows such behavior. Such turnover phenomena appear to be quite general, as is suggested by scaling arguments.

I. Introduction

Measurement and calculation of first order chemical rate processes such as isomerization, energy transfer, electron transfer, or unimolecular decay, are generally written in terms of the Fermi Golden Rule expression. The Golden Rule approach is also the simplest scheme for calculating susceptibilities and other response phenomena.[1] One nearly always deals, in situations of chemical kinetics, with transitions among the eigenstates of some unperturbed Hamiltonian. This Hamiltonian can be favored either for experimental reasons having to do with relatively easier measurement or particular initial state preparation or for formal reasons involving Hamiltonian structures. Generally, however, it is required that the unperturbed Hamiltonian that defines the states among which the transitions are to be measured has a spectrum that is sparse; that is, the characteristic energy spacings of the unperturbed Hamiltonian must be smaller than the average matrix elements mixing these states.

Under these conditions, the Golden Rule shows that the rate constants between state i and j will increase quadratically as the mixing matrix elements go up and will decrease as the spacings in the spectrum of eigenstates increase.

There are two well-known situations in which the rate constant is observed first to increase then to maximize and finally to decrease as a function of the parameters in the overall system evolution. In the Kramers[2−4] limit corresponding to the situation of barrier escape, the rate constants scale like friction for small friction, and turnover to scale like inverse friction for large friction. In the Marcus inverted regime[5−8] for electron transfer, the functional dependence is $\exp[-(\Delta + \lambda)^2]/4\lambda kT$ (where Δ, λ, k, and T are respectively the exoergicity of the reaction, the reorganization energy, Boltzmann's constant, and the temperature). For fixed λ, this will show a turnover: the rate will increase with $|\Delta|$ for small negative Δ maximize when $\Delta = -\lambda$, and decrease for large absolute values of Δ.

Recent simulations have shown that even more general behaviors are expected simply from the structure of the level Hamiltonian. This is to some extent anticipated, on the basis of the generalized Landau/Zener/Stueckelberg result,[6,9] that the crossing probability P is given by

$$P = 4p(1 - p) \sin \Phi \tag{1}$$

$$p = \exp\left\{-\frac{\pi(\Delta U)^2}{2\hbar\Delta F\left[\frac{2E_k}{\mu}\right]^{1/2}}\right\} \tag{2}$$

$$\frac{\partial P}{\partial p} = (4 - 8p) \sin \Phi \tag{3}$$

Here Φ, ΔF, ΔU, E_k, and μ are respectively the Stueckelberg phase, the difference in slopes of the potentials, the potential energy difference, the kinetic energy, and the reduced mass. This model, which applies to nonadiabatic curve crossing reactions in the semiclassical limit, suggests that the crossing rate will vanish either for zero Hamiltonian mixings or for infinitely large Hamiltonian mixings.

We present here some extremely simple scaling arguments, and examples from two selected two-level models, that show generalized turnover behavior as the Hamiltonian parameters vary. These model Hamiltonians are described solely within electronic space, so that they differ from the Landau−Zener, Marcus, or Kramers behaviors in that the only variations are variations in the electronic structure Hamiltonian itself. Nevertheless, the turnover behavior that we observe is quite reminiscent of the three turnovers suggested by the literature from the 1940s and 1950s.

We will analyze three rate situations: first, the general Huckel scaling problem, involving mixes of tunneling and site energetic contributions. Second, a specific example of the Huckel case for two sites. Third, a slightly less trivial situation using a Hubbard model to characterize the same two-site problem.

Fourth, we calculate the dipole susceptibility (optical strength) for a two level system, and again find the turnover structure.

II. Golden Rule Rates in Mixed Two Level Systems

The turnover phenomena are most easily seen in the simple limit in which the Golden Rule rates are correct. We present here three situations, in each of which a simple Golden Rule rate can be defined. In the next section, we will then examine the turnovers that occur in these three models.

A. General Huckel Scaling. An artificial, but nevertheless instructive, example of turnover phenomena can be derived beginning with a Huckel type model. We consider the set of orthogonal localized basis functions u_k, with their associated creation and destruction operators. Ignoring spin for simplicity, we can write the Hamiltonian

$$H = \sum e_k a_k^+ a_k + \sum t_{kl}(a_k^+ a_l + a_l^+ a_k) \qquad (4)$$

here e_k is the site energy of the kth spatial orbital, and t_{kl} is the tunneling matrix element (Huckel beta) that mixes sites k and l. Two situations can now be examined in a facile fashion. We focus on the rate constant $k_{k \rightarrow l}$. When $|e/t| \gg 1$, the Golden Rule treatment gives directly

$$k_{k \rightarrow l} = \frac{2\pi}{\hbar} \frac{t_{kl}^2 \Gamma}{D_{kl}^2 + \Gamma^2} \qquad (5)$$

Here the energy difference D_{kl} is simply $e_k - e_l$, while Γ is the usual broadening.

In the opposite limit $|e/t| \ll 1$, it is appropriate to define the unperturbed states between which motion occurs as the states that diagonalize the hopping matrix. Under these conditions, then, we can write the Hamiltonian in the space of the delocalized orbitals that diagonalize the t as

$$\tilde{H} = \sum \theta_\sigma a_\sigma^+ a_\sigma + \sum \epsilon_{\sigma\tau}(a_\sigma^+ a_\tau + a_\tau^+ a_\sigma) \qquad (6)$$

Here the unitary transformation that diagonalizes the matrix of t_{kl} makes the site orbitals e_k off diagonal, and therefore the Golden Rule for the rate constant can be written in the form

$$k_{\sigma \rightarrow \tau} = \frac{2\pi}{\hbar} \frac{\epsilon_{\sigma\tau}^2 \Gamma}{\Delta_{\sigma\tau}^2 + \Gamma^2} \qquad (7)$$

Here $\Delta_{\sigma\tau}$ is defined as the energy difference $\theta_\sigma - \theta_\tau$. Now consider general scaling relationships

$$t \rightarrow \xi t \qquad (7a)$$

$$e \rightarrow \chi e \qquad (7b)$$

$$D \rightarrow \chi D \qquad (7c)$$

where ξ and χ are scaling parameters. Since the unitary transformation applied to the **t** and **e** matrices yields, respectively, the θ and ϵ matrices, then the scaling relation for the parameters of the Hamiltonian in the delocalized representation of eq 5 are

$$\theta \rightarrow \xi\theta \qquad (8a)$$

$$\epsilon \rightarrow \chi\epsilon \qquad (8b)$$

$$\Delta \rightarrow \xi\Delta \qquad (8c)$$

For the Golden Rule rates, we obtain in a straightforward fashion

$$\frac{\partial k_{k \rightarrow l}}{\partial \chi} = \left(\frac{2\pi\Gamma}{\hbar} t_{kl}^2\right)\left(\frac{-2D_{kl}^2 \chi}{(D_{kl}^2 + \Gamma^2)^2}\right) \qquad (9a)$$

$$\frac{\partial k_{k \rightarrow l}}{\partial \xi} = \left(\frac{2\pi\Gamma}{\hbar}\right) \frac{2t_{kl}^2 \xi}{D_{kl}^2 + \Gamma^2} \qquad (9b)$$

The scaling argument is straightforward: as the site energy gaps are scaled by the parameter χ, the rate constant decreases (the right-hand side of eq 9a is negative). As the mixing matrix elements are scaled by ξ, $k_{k \rightarrow l}$ increases (the right side of eq 9b is positive).

We now consider the same derivatives in the (Greek index) states that diagonalize the hopping matrix. We then find

$$\frac{\partial k_{\sigma \rightarrow \tau}}{\partial \chi} = \left(\frac{2\pi\Gamma}{\hbar}\right) \frac{2\epsilon_{\sigma\tau}^2 \chi}{\Delta_{\sigma\tau}^2 + \Gamma^2} \qquad (10a)$$

$$\frac{\partial k_{\sigma \rightarrow \tau}}{\partial \xi} = \left(\frac{2\pi\Gamma\epsilon_{\sigma\tau}^2}{\hbar}\right) \frac{-2\Delta_{\sigma\tau}^2 \xi}{(\Delta_{\sigma\tau}^2 + \Gamma^2)^2} \qquad (10b)$$

Now notice that the rate constant increases with χ and decreases with ξ. We thus find straightforward turnovers: as χ increases, the rate constant decreases in the (Arabic suffix) situation of weak intersite mixing and increases in the (Greek suffix) situation of strong intersite mixing. Precisely the opposite behavior occurs with the scaling parameter ξ. Thus we see twin turnovers in this simple limit.

B. Two-Site Huckel Structure. A specific example is found for the two-site, nondegenerate Huckel problem. We then define the parameters as

$$-e_1 = E \qquad e_2 = E \qquad t_{12} = t \qquad (11)$$

and the unitary transformation then results in

$$\theta_1 = t \qquad \theta_2 = -t \qquad \epsilon_{12} = \epsilon_{21} = -E \qquad (12)$$

The interlevel rate constant in the atomic orbital limit (site mixing) is

$$k = \frac{2\pi}{\hbar} \frac{\Gamma t^2}{4E^2 + \Gamma^2} \qquad (13)$$

In the delocalized (molecular orbital type) limit we find

$$k = \frac{2\pi}{\hbar} \frac{\Gamma E^2}{4t^2 + \Gamma^2} \qquad (14)$$

Effectively, on going from the weak mixing to the strong mixing of site orbitals, one simply interchanges the parameters t and E. It is then trivial that the rate constant in the atomic limit will increase with the mixing t, whereas in the delocalized (molecular orbital type) limit the rate constant decreases with an increase in t. Precisely the opposite turnover occurs with the parameter E.

C. Two-Site Hubbard Model. The Hubbard model is a limit of the Pariser–Parr–Pople model, in which off-diagonal repulsions are neglected.[10] It is commonly used for the analysis of narrow band conductivity and magnetism.[11] Some applications to molecular electronic structure have also been given.[10,12] The analysis of the Hubbard model is slightly less trivial than the Huckel situation, because there is no convenient direct diagonalization of the total Hamiltonian.[13]

Specifying to the limit of two sites with orthogonal local basis functions, one can write the Hubbard Hamiltonian as

$$H = t \sum_\sigma (a_{1\sigma}^+ a_{2\sigma} + a_{2\sigma}^+ a_{1\sigma}) + U(a_{1\uparrow}^+ a_{1\uparrow} a_{1\downarrow}^+ a_{1\downarrow} + a_{2\uparrow}^+ a_{2\uparrow} a_{2\downarrow}^+ a_{2\downarrow}) \tag{15}$$

Here the parameters t and U denote, respectively, the electron hopping integral and the on-site Coulomb repulsion between opposite spin electrons. The creation operator $a_{1\sigma}$ creates an electron in the site orbital u_1 with spin component σ, either $\uparrow$ or $\downarrow$. The Hubbard model can be conveniently rewritten in a form suggested by the Hartree−Fock approximation as

$$H = t \sum_\sigma (a_{1\sigma}^+ a_{2\sigma} + a_{2\sigma}^+ a_{1\sigma}) + U\bar{n}_{1\downarrow} a_{1\uparrow}^+ a_{1\uparrow} + U\bar{n}_{1\uparrow} a_{1\downarrow}^+ a_{1\downarrow} +$$
$$U\bar{n}_{2\uparrow} a_{2\downarrow}^+ a_{2\downarrow} + U\bar{n}_{2\downarrow} a_{2\uparrow}^+ a_{2\uparrow} + U a_{1\uparrow}^+ a_{1\uparrow} a_{1\downarrow}^+ a_{1\downarrow} + U a_{2\uparrow}^+ a_{2\uparrow} a_{2\downarrow}^+ a_{2\downarrow} -$$
$$2U\bar{n}_{1\uparrow}\bar{n}_{1\downarrow} - 2U\bar{n}_{2\uparrow}\bar{n}_{2\downarrow} \tag{16}$$

Here we have defined

$$\bar{n}_{j\sigma} \equiv \langle a_{j\sigma}^+ a_{j\sigma} \rangle \equiv \frac{1}{2} \tag{17}$$

The value of $1/2$ occurs if the local sites are (as demanded by the form of (15)) degenerate.

We examine first the molecular orbital limit, in which the local hopping integrals are larger than the repulsions, $|t/U| > 1$. Under these conditions the molecular orbitals defined by

$$a_{\pm\sigma}^+ = \frac{1}{\sqrt{2}}(a_{1\sigma}^+ \pm a_{2\sigma}^+) \tag{18}$$

define the unperturbed states among the transitions will occur. The four states, and their energies, are then given by (with $|V\rangle$ = vacuum state)

$$|1\rangle = a_{+\uparrow}^+ a_{+\downarrow}^+ |V\rangle \qquad E_1 = 2t$$
$$|2\rangle = a_{-\uparrow}^+ a_{+\downarrow}^+ |V\rangle \qquad E_2 = 0$$
$$|3\rangle = a_{+\uparrow}^+ a_{-\downarrow}^+ |V\rangle \qquad E_3 = 0$$
$$|4\rangle = a_{-\uparrow}^+ a_{-\downarrow}^+ |V\rangle \qquad E_4 = -2t \tag{19}$$

The matrix elements of perturbation acting between state 1 and states 2 or 3 vanish; that between states 1 and 4 is the same as between states $|2\rangle$ and $|3\rangle$, with value $U/2$. In this molecular orbital limit, then, the rate of transition between molecular orbital states $|1\rangle$ and $|4\rangle$ is simply

$$k_{1\to4} = \frac{2\pi\Gamma}{\hbar} \frac{(U/2)^2}{\Gamma^2 + 16t^2} \tag{20}$$

In the opposite limit of the atomic orbitals, the unperturbed local states are highly degenerate and are given by

$$|L1\rangle = a_{1\uparrow}^+ a_{2\downarrow}^+ |V\rangle \qquad E = 0$$
$$|L2\rangle = a_{1\downarrow}^+ a_{2\uparrow}^+ |V\rangle \qquad E = 0$$
$$|L3\rangle = a_{1\uparrow}^+ a_{1\downarrow}^+ |V\rangle \qquad E = U$$
$$|L4\rangle = a_{2\uparrow}^+ a_{2\downarrow}^+ |V\rangle \qquad E = U \tag{21}$$

The Golden Rule then yields

$$k_{L1\to L3} = \frac{2\pi}{\hbar} \Gamma \frac{t^2}{\Gamma^2 + U^2} \tag{22}$$

Comparison of eqs 20 and 22 yields behavior that is precisely reminiscent of that seen in sections A and B for the Huckel model: in the strong mixing (molecular orbital) limit, the rate will increase with U and decrease with t^2. Exactly the opposite behavior happens in the atomic orbital limit.

We have thus seen that in all three of these simple model situations, turnover occurs as a function of the continuous variables describing the site energies and hopping integrals for the Huckel model, or the onsite repulsion integrals and tunneling matrix elements for the Hubbard problem.

III. Turnover in Dipole Susceptibility

The principal focus of our discussion involves turnover behavior in the intramolecular electron transfer rate constant as the Hamiltonian parameters change in value. More directly measurable would be an electric susceptibility, arising from interaction of the system dipole with an applied electromagnetic field. Within the Golden Rule formulation, essentially all response phenomena can be treated the same way, and therefore one expects competition between two terms of the Hamiltonian that can again lead to turnover behavior.

It is important to notice that for turnover to occur two Hamiltonian terms must be noncommuting, as they are in (for example), eq 4 or eq 6 or eq 15. Clearly, if the two forms of the Hamiltonian commute, they will have simultaneous eigenfunctions and therefore no turnover can occur.

As a final example, then, we will calculate the susceptibility for the two site model of eq 4. We will specify to the simple parameter set

$$t_{12} = t_{21} = t \qquad t_{11} = t_{22} = 0 \qquad e_2 = 0 \qquad e_1 = e \tag{23}$$

One can then define the imaginary part of the susceptibility as

$$-\mathrm{Im}(\chi) = \sum_{ij} \frac{\Gamma|\langle i|\mu|j\rangle|^2}{(E_i - E_j)^2 + \Gamma^2} \tag{24a}$$

where i and j are states of the system that are mixed by the dipole operator μ. Diagonalizing the Hamiltonian in eq 4, the imaginary susceptibility becomes

$$= \Gamma|\langle +|\mu|-\rangle|^2/(E_+ - E_-)^2 \tag{24b}$$

Here the eigenfunctions are defined by

$$|+\rangle = w|-u_1 + cu_2\rangle$$
$$|-\rangle = w|cu_1 + u_2\rangle \tag{25a}$$

and the energies by

$$E_\pm = \frac{e}{2} \pm \sqrt{e^2/4 + t^2} \tag{25b}$$

We have assumed that the local wave functions u_1 and u_2 are orthogonal, and the normalization factor is defined by

$$w = (1 + c^2)^{-1/2} \tag{26}$$
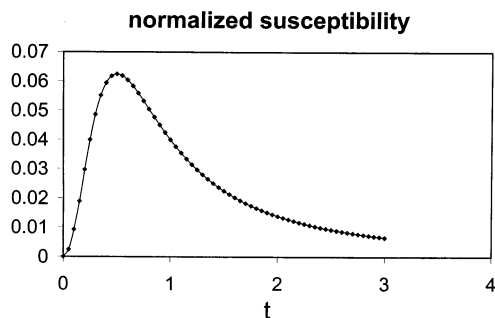
normalized susceptibility

Figure 1. Normalized susceptibility of eq 30, as a function of $|t|$ for $e = 1$. Note the turnover near $|t| = 0.6$.

The mixing coefficient c is given as

$$c = \frac{|t|}{e/2 + [t^2 + e^2/4]^{1/2}} \qquad (27)$$

where the absolute value is used in the numerator because the tunneling matrix elements are generally negative.

To simplify, we will use the Pariser approximation

$$\langle u_i | \mu | u_j \rangle = q_e \delta_{ij} R_i \qquad (28)$$

here q_e is the charge of the electron and R_i is the geometric coordinate of the atom i at which orbital u_i is centered. Defining the overall dipole moment quantity by

$$q_o(R_2 - R_1) \equiv \mu_o \qquad (29)$$

the imaginary part of this susceptibility becomes

$$-(\text{Im } \chi)/\mu_o^2 \Gamma = \frac{c^2}{(1 + c^2)^2 (4t^2 + e^2)} \qquad (30)$$

This susceptibility will, again, exhibit turnover behavior (note that we have ignored the broadening term Γ^2 in eq 24a; this is because that width is small compared to the eigenvalue difference in the denominator of 24b). Limiting values for this susceptibility, then, are

$$-(\text{Im } \chi)/\mu_o^2 \Gamma \rightarrow \begin{cases} 0 & t \rightarrow 0 \\ 0.04 & |t| = 1 \\ 0 & |t| \rightarrow \infty \end{cases} \qquad (31)$$

The susceptibility vanishes when the two states are unmixed, and when the mixing matrix element increases without bound (in taking the limit in eq 31, using units in which $e = 1$).

Figure 1 shows the calculated value of eq 30, where $e = 1$ as t goes from 0 to 4. The turnover behaviors indeed are apparent. Conceptually, the turnover behavior occurs because, when the states are unmixed, it is impossible to transfer the electron from one side to the other (because the susceptibility is proportional to the square of the mixing coefficient c). When the mixing matrix element t becomes very large, the energy denominators simply make it impossible to mix one state with the other. Therefore we expect, and see, turnover behavior here as we do in the rate constants. Once again, the generalized scaling argument of section II.A would have suggested the observed turnover behavior.

IV. Remarks

These extremely simple arguments show that in three particular instances, one will observe turnovers in the rate constant between the eigenstates of unperturbed Hamiltonian

as the relative sizes of parameters describing local site energy differences, onsite Coulomb repulsions and tunneling matrix elements between sites are continuously varied. These turnovers are also preserved in the specific analysis of a model electron transfer system that consists of a bath spectral density, one tightly coupled quantum vibration, and two nondegenerate sites.[14] Turnover is also observed in passing from the atomic limit to the molecular orbital limit in the two-site susceptibility.

For convenience and clarity, we have based our analysis on the Golden Rule, which assumes that one can write

$$H = H_o + V$$

where the eigenstates of H are mixed only weakly by V. The bath in which H is studied is assumed to force localization into eigenstates of H_o. As V increases, the eigenstates of V couple to the bath and are the appropriate objects for which dynamics is defined. This observation suggests that, although formally one can solve the full dynamics problem using the eigenstates of H_o or of V, physical problems will generally[15] have an interaction between system and environment that strongly favors a particular H_o.

The turnovers seen here differ from the Marcus turnover, the Kramers turnover, and the Landau/Zener/Stueckelberg turnover in that they depend explicitly only on the parameters of the electronic structure Hamiltonian; in the Marcus and Landau/Zener models, the turnovers occur as a function of terms that describe the mixing of electronic motion and nuclear behavior. Nevertheless, the general phenomenon remains the same: with continuous change in the given scaling parameter, the rate constant between appropriately defined basis states of the unperturbed Hamiltonian will first increase, then maximize, and then decrease as a function of the particular scaling parameter. Turnover behavior is thus, once again,[14,16] seen in an extensive region of molecular parameter space.

In the analysis of section II, we have used perturbation theory and the Golden Rule. This assumes both that there is a smallness parameter and that there is sufficient dephasing or relaxation that rate processes in fact occur. The assumption concerning dephasing that is made here is that the line width or dephasing lifetime will be the same throughout the regime of Hamiltonian parameters. This is not guaranteed, but for reasonable spectral densities it is a reasonable assumption.

The use of perturbation theory in section II is valid only in the regimes where t/e of eq 4 and t/U of eq 15 are either very small or very large. In this sense, we observe in these sections only the limiting behaviors corresponding to weak mixing and strong mixing, respectively. In these sections, then, we do not observe the full turnover as a function of the parameter, although the scaling arguments clearly support such a turnover. This is very similar to what Kramers did in his first paper, in which he analyzed only the appropriate limits of strong friction and weak friction. In section III, on the dipole susceptibility turnover, the calculation is a numerical one and therefore the entire turnover structure is indeed seen.

A specific situation for which these considerations are directly relevant occurs in mixed-valence compounds,[6,7,8,15−23] including binuclear metal complexes such as $(NH_3)_5$ $RuLRu(NH_3)_5^{5+}$, with L a bridging ligand such as pryazine, 4,4′-bipyidyl, or NCCN. As the nature of L changes from weak mixing (4,4′-bipy) to stronger mixing (pyrazine), the states become symmetric, and the molecular orbitals of eq 6 are a better approximate representation than the localized (on Ru) functions of eq 4. When the two metals have differing ligation environments, the differences are reflected in the D parameter of eq 5: the

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transition from Robin/Day[23] Class II (localized, mixed valence) to Robin/Day Class III (delocalized, average-valent) occurs as $|t/D|$ increases. When $|t/D| \ll 1$, the optical transition is truly an intervalence band, in which density moves from one metal center to the other. When $|t/D| \gg 1$, the appropriate eigenstates are delocalized and the optical peak is a molecular-orbital transition.[24,25] In this sense, there is indeed a turnover in the mixed-valence spectra.

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