Radiationless transitions through avoided crossings

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Understanding the quantum dynamics for transitions through actual or avoided crossings of electronic energy levels is one of the great open problems of quantum chemistry. Here we explain the context of transitions through avoided crossings, and present a novel method based on superadiabatic representations, leading to an explicit formula for a large class of one-dimensional models.

Keywords: Landau-Zener transitions, avoided crossings, superadiabatic representations

1. Radiationless transitions

Radiationless transitions are a peculiar but important reaction mechanism in nature: a photon is absorbed by a molecule, lifting the electronic configuration to an excited state. The nuclei of the molecule are then no longer near their minimal energy configuration, and start to move according to the time-dependent Born-Oppenheimer approximation (see below). At some point along the path of the nuclear configuration, the electronic energies of the ground state and the excited state, both of which are functions of the nuclear configuration, approach each other very closely. It is at this point that the electronic wave function can switch back into the ground state, without emitting a photon. The molecule then falls back into the ground state, or a metastable state, or it dissociates, and the surplus energy is dissipated via vibrations. Radiationless transitions are very fast, they happen on a femtosecond time scale and thus well before any spontaneous decay of the excited state to the ground state would occur. This makes them ideal candidates e.g. for the mechanism of reception of light in the retina, where the re-emission of a photon would be a most unwelcome event. And indeed, it is known that the cis-trans isomerisation of retinal rhodopsin is facilitated by a radiationless transition [1].

While the basic mechanism of radiationless transitions is well-understood, it is one of the great open problems of quantum chemistry to reliably predict the wave function of the molecule after such a transition. The reason is that the Born-Oppenheimer approximation, which is at the basis of almost all methods in quantum molecular dynamics, breaks down at a crossing of electronic energy levels. Thus straightforward molecular dynamics fails. It can be improved by surface hopping

algorithms of various degrees of sophistication [2, 3], but the obtained accuracy is still not quite satisfactory. Or one can use a priori methods that do not rely on the Born-Oppenheimer decoupling of dynamics, like MCTDH [4]. But this is numerically expensive, especially when the transition is much smaller than the original wave function, as is the case for avoided crossings. Here we describe another, analytical method that relies on superadiabatic representations [5, 6]. In the case of a diatomic molecule we obtain an explicit formula for radiationless transitions which agrees well with high precision a priori computations.

2. Adiabatic and superadiabatic representations

The Schrödinger equation of a diatomic molecule is given by

$$\mathrm{i}\varepsilon\partial_t\psi(x,t) = H\psi(x,t), \tag{1}$$

with Hamiltonian $H = -\frac{\varepsilon^2}{2}\partial_x^2 + H_{\mathrm{el}}(x)$. $x \in \mathbb{R}$ is the effective nuclear coordinate, and H_{el} is the electronic Hamiltonian, containing the kinetic energy of the electrons, and all interaction potentials. The time scale is chosen such that in a time interval of order one, the nuclei move by a distance of order one. H_{el} and thus its spectrum depend parametrically on x, and one statement of Born-Oppenheimer theory is that if a wave function is of the form $\psi(x,y) = \psi_0(x)\chi(x,y)$, with $y \mapsto \chi(x,y)$ an eigenfunction of $H_{\mathrm{el}}(x)$ for each x with energy $E(x)$, then under the evolution (1) the wave function stays of the above form, to leading order in ε. Moreover, it is given by $\psi(x,t) = \psi_0(x,t)\chi(x,y)$ with $\psi_0(x,t)$ the solution of $\mathrm{i}\varepsilon\partial_t\psi_0(x,t) = (-\varepsilon^2\partial_x^2/2 + E(x))\psi_0(x,t)$. In other words, the dynamics decouples according to the energy bands $E(x)$, which themselves act as effective potentials. While the theory is true in great generality [6], here we only need a very special case. Namely, we assume that H_{el} only acts on a two-dimensional Hilbert space, meaning that we assume that all energy bands save two are unimportant for the effect we want to study. While this assumption cannot as yet be rigorously justified, it is one that is almost always made in the context or radiationless transitions. H_{el} then becomes a 2×2 matrix V, and we have

$$H = -\frac{\varepsilon^2}{2}\partial_x^2\boldsymbol{I} + V(x) \qquad \text{with} \quad V(x) = \begin{pmatrix} X(x) & Z(x) \\ Z(x) & -X(x) \end{pmatrix} + d(x)\boldsymbol{I} \tag{2}$$

$\boldsymbol{I}$ is the 2×2 unit matrix, and H acts on wave functions $\psi \in L^2(\mathrm{d}x, \mathbb{C}^2)$, i.e. square integrable functions with values in $\mathbb{C}^2$. By the non-crossing rule [7], the energy levels generically will not cross for one degree of freedom. Therefore $\rho(x) = \sqrt{X^2+Z^2} \geq \delta > 0$ for all $x \in \mathbb{R}$, and we assume that X and Z are analytic so that ρ is analytic in a strip containing the real axis.

We now transform (2) to a representation where H becomes approximately diagonal. It is implemented by the unitary transform U acting on $L^2(\mathrm{d}x, \mathbb{C}^2)$ by with $Uf(x) = U_0(x)f(x)$, and such that U_0 diagonalizes V. Putting $\psi_{\mathrm{a}}(x,t) = U_0(x)\psi(x,t)$ we obtain the Schrödinger equation in the adiabatic representation,

$$\mathrm{i}\varepsilon\partial_t\psi_{\mathrm{a}}(x,t) = H_0\psi_{\mathrm{a}}(x,t), \qquad \psi_{\mathrm{a}}(x,0) = \psi_{\mathrm{a},0}(x), \tag{3}$$

where to leading order in ε,

$$H_0 = U_0 H U_0^* = -\frac{\varepsilon^2}{2}\partial_x^2 \boldsymbol{I} + \begin{pmatrix} \rho(x) + d(x) & -\varepsilon\kappa_0(x)(\varepsilon\partial_x) \\ \varepsilon\kappa_0(x)(\varepsilon\partial_x) & -\rho(x) + d(x) \end{pmatrix}. \tag{4}$$

Here, $\kappa_0 = (Z'X - X'Z)/(Z^2 + X^2)$ is the adiabatic coupling element. As a consequence of the choice of time scale solutions of (3) oscillate with frequency $1/\varepsilon$, and thus the operator $\varepsilon\partial_x$ is actually of order one. The dynamics in the two components of ψ_a decouple to leading order in ε, and are Schrödinger evolutions with potentials given by the energy bands $\pm\rho(x)$; this is the Born-Oppenheimer approximation we described above.

A local minimum of ρ is called an avoided crossing. Let us assume that $x = 0$ is a global minimum, and that V is asymptotically constant for large $|x|$. A radiationless transition can then be obtained by starting the Schrödinger evolution with an initial wave packet $\psi_\mathrm{a}(x, 0)$ such that its second component $\psi_\mathrm{a}^-(x, t)$ is zero, and its first component $\psi_\mathrm{a}^+(x, t)$ is localized at some $x_0 \ll 0$, and with sufficient momentum to propagate to positive values of x. $\psi_\mathrm{a}^-(x, t)$ is called the transmitted wave packet. Up to errors of order ε^2, it can be calculated straightforwardly by first order perturbation theory. Let us write $H^\pm = -\frac{\varepsilon^2}{2}\partial_x^2 \pm \rho(x) + d(x)$ for the Hamiltonian generating the uncoupled dynamics in the upper, resp. lower, band. With $\phi(x) = \psi_\mathrm{a}^+(x, 0)$, we have

$$\psi_\mathrm{a}^-(t) = -\mathrm{i}\varepsilon \int_{-\infty}^{t} \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}(t-s)H^-} K_0 \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}sH^+} \, \phi \, \mathrm{d}s. \tag{5}$$

Above, $K_0 = \kappa_0(x)(\varepsilon\partial_x)$ is the adiabatic coupling operator. From (5), we would expect radiationless transitions to be of order ε. But while this is true in the transition region, they are much smaller in the scattering regime. Indeed, if one were to do compute (5) numerically, one would find that the L^2 norm of ψ_a^- rises to order ε around $t = 0$, while decaying to an exponentially small value in ε later. This phenomenon is the reason why it is very difficult and time-consuming to obtain accurate quantitative predictions of the transmitted wave function through (5): one has to compute a highly oscillatory integral up to exponential accuracy in ε.

At this point, superadiabatic representations are helpful. They have been developed in the simpler Landau-Zener-Majorana model of adiabatic quantum transitions [8–10], where essentially the nuclear degree of freedom is replaced by a deterministic trajectory, and only electronic transitions are studied. The idea, first found by Berry in [5] and later proven to work rigorously in [11–13], is to find a change of coordinates in which the off-diagonal elements of the potential energy matrix are of order ε^n instead of just order ε. Such a representation is then called the n-th superadiabatic representation; it is asymptotic in n in that the coupling elements are really of order $\varepsilon^n n!$, and thus the limit $n \to \infty$ cannot be taken. Instead, by optimizing n one obtains what is called the optimal superadiabatic representation, where transitions are uniformly exponentially small and have the universal shape of an error function.

To construct and asymptotically understand superadiabatic representations in the context of (2) is a very difficult and not yet fully solved problem. However, in the case of sufficiently high momentum of the wave function at the crossing point, it has been done in [14] in the case of $d(x) = 0$, and in [15] in the general case. Above, 'sufficiently high' means in theory at least $\sim \varepsilon^{-1/3}$, but in practice the results described below agree extremely well with high precision numerical solutions for a wide range of parameters. In [14] it is shown that for every $n \in \mathbb{N}$, there exists a unitary U_n, given by a pseudo-differential operator, acting in $L^2(\mathbb{R}, \mathbb{C}^2)$. With $H_n = U_n^{-1} H U_n$, to leading order we have

$$H_n = -\frac{\varepsilon^2}{2}\partial_x^2 \boldsymbol{I} + \begin{pmatrix} \rho(x) + d(x) & \varepsilon^{n+1} K_{n+1}^+ \\ \varepsilon^{n+1} K_{n+1}^- & -\rho(x) + d(x) \end{pmatrix}. \tag{6}$$

Therefore, with $\psi_n = U_n \psi$, (5) can be replaced by

$$\psi_n^-(t) = -\mathrm{i}\varepsilon^n \int_{-\infty}^{t} \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}(t-s)H^-} K_{n+1}^- \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H^+} \, \phi \, \mathrm{d}s. \tag{7}$$

Equation (7) describes the wave function in the n-th superadiabtic representation, which agrees with the adiabatic one in the scattering regime. The *superadiabatic coupling operator* K_n can be obtained by a recursive scheme detailed in [14].

3. The transmitted wave function

It is not immediately clear that (7) is useful for calculating the transmitted wave function: K_n is given by a complicated recursive scheme, and the propagators $H^\pm$ are not explicitly known for general potentials. However, a series of 'good fortunes' allows for significant simplifications. Firstly, by the Darboux principle of asymptotic theory, the operator K_n is determined by the complex singularities of the adiabatic coupling function $\kappa_0(x)$ that are closest to the real axis. We refer to [13] for discussion of the Darboux principle and a rigorous application of it. The transition operator K_n then becomes extremely localized, in that its application on a function differs significantly from zero only if that function has support near $x = 0$. As discussed in [15], this enables us to replace the full propagators $\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}(t-s)H^\pm}$ by the linearized ones in (7). The result is a rather explicit, if somewhat lenghty, formula for the transmitted wave function, see equation (10) of [15]. It simplifies further when $d(x)$ is near constant at the transition point $x = 0$. In that case, and for times $t \gg \sqrt{\varepsilon}$, the transmitted wave packet is given by

$$\widehat{\psi^-}^{\varepsilon}(k,t) = \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}tH^-} \, 1_{\{k^2 > 4\delta\}} \frac{v+k}{2|v|} \, \mathrm{e}^{\mathrm{i}\frac{\tau_\delta}{2\delta\varepsilon}|k-v|} \, \widehat{\phi}^{\varepsilon}(v), \tag{8}$$

where $v = v(k,\delta) = \mathrm{sgn}(k)\sqrt{k^2 - 4\delta}$, and the constants τ_δ and δ can be calculated from ρ. For a function f, $\widehat{f}^{\varepsilon}(k) = \frac{1}{\sqrt{2\pi\varepsilon}} \int \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}kq} f(q) \, \mathrm{d}q$ denotes its semiclassical Fourier transform.

Formula (8) not only allows to compute the transmitted wave function to high accuracy with very little numerical effort, but also provides physical intuition about

the transition mechanism. Namely, the portion of $\widehat{\psi^\varepsilon}$ with momentum k is obtained by choosing the portion of the upper band wave function at the crossing point having the correct momentum $v(k)$ according to energy conservation. This is then multiplied with a Landau-Zener factor that in general cannot be guessed, but for large incoming momenta converges to the one suggested by classical Landau-Zener theory [13]. One consequence of this is that the momentum of the outgoing wave packet is larger than could be expected from energy conservation alone: portions of the incoming wave function that are faster behave less adiabatically, and are more likely to make the transition.

Let us finally note a somewhat embarrassing feature of (8): it is most likely not asymptotically correct in ε, for finite incoming momenta. The reason is that our knowledge about the asymptotics of the operators K_n is not very good, and so we are confined to either large incoming momenta, or relatively large ε. While from a practitioner's point of view, (8) does very well for all cases that can be compared to ab initio calculations with reasonable effort, it is unsatisfactory from the point of view of exponential asymptotics. In [16], an alternative, asymptotically correct, formula is given for the transmitted wave function. But it is not nearly as easy to interpret or implement as (8). One would expect that there is an asymptotically exact formula that retains the general shape of (8), with the constants τ_δ replaced by different ones or possibly non-constant expressions. However, so far no such formula has been found, let alone proved.

References

[1] R. Schoenlein, L. Petenau, R. Mathies and C. Shank, *Science* **254**, 412(Jan 1991).
[2] C. Lasser, T. Swart and S. Teufel, *Commun. Math. Sci.* **5**, 789(Jan 2007).
[3] J. Tully, *J Chem Phys* **93**, 1061(Jan 1990).
[4] G. A. Worth, H. D. Meyer, H. Koeppel, L. S. Cederbaum and I. Burghardt, Using the mctdh wavepacket propagation method to describe multimode non-adiabatic dynamics(Jan 2008).
[5] M. Berry, *Proceedings of the Royal Society of London. Series AMathematical and Physical Sciences* **429**, 61(May 1990).
[6] S. Teufel, p. 236.
[7] J. von Neuman and E. Wigner, *Phys. Z.* **30**, 467 (1929).
[8] L. Landau, *Physics of the Soviet Union* **2**, 46 (1932).
[9] C. Zener, *Proceedings of the Royal Society of London. Series A* (Jan 1932).
[10] E. Majorana, *Il Nuovo Cimento (1924-1942)* (Jan 1932).
[11] G. Hagedorn and A. Joye, *Comm. Math. Phys.* **250**, 393(Jan 2004).
[12] V. Betz and S. Teufel, *Ann. Henri Poincaré* **6**, 217 (2005).
[13] V. Betz and S. Teufel, *Comm. Math. Phys.* **260**, 481 (2005).
[14] V. Betz, B. D. Goddard and S. Teufel, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **465**, 3553(Nov 2009).
[15] V. Betz and B. Goddard, *preprint* (2009).
[16] G. A. Hagedorn and A. Joye, *Ann. Henri Poincaré* **6**, 937 (2005).