

Non–Adiabatic Scattering Wave Functions in a Simple Born–Oppenheimer Model

We describe mathematical results, obtained in collaboration with Professor Alain Joye, that concern non–adiabatic transitions in a simple molecular dynamics model. We study scattering theory for the time–dependent molecular Schrödinger equation

$$i \epsilon^2 \frac{\partial \psi}{\partial t} = - \frac{\epsilon^4}{2} \frac{\partial^2 \psi}{\partial x^2} + h(x) \psi$$

in the small ϵ (Born–Oppenheimer) limit. We assume the electron Hamiltonian $h(x)$ has finitely many levels and consider the propagation of coherent nuclear states with sufficiently high total energy. We further assume two of the electronic levels are isolated from the rest of the electron Hamiltonian’s spectrum and have an avoided crossing with a small ϵ –independent gap. We compute the leading order behavior for the nuclear wave function associated with the non–adiabatic transition that is generated as the nuclei move through the avoided crossing.

This component is of order $\exp(-C/\epsilon^2)$. It propagates asymptotically as a free Gaussian in the nuclear variables, and its momentum is shifted. The total transition probability for this transition and the momentum shift are both larger than what one would expect from a naive approximation and energy conservation.