Non–Adiabatic Transitions in a Simple Born–Oppenheimer Model

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We begin with a brief description of the Time–Dependent Born–Oppenheimer Approximation of molecular quantum mechanics. We then discuss non–adiabatic transitions for the special situation described by

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

in the small ϵ (Born–Oppenheimer) limit, where $h(x)$ is a 2×2 matrix. We assume the eigenvalues of $h(x)$ have an avoided crossing with a small ϵ–independent gap and that the total energy is above the maximum of both these eigenvalues. 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 $\exp\left(\,-\,C/\epsilon^2\,\right)$. 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 naïve approximation and classical energy conservation.