L2

Born-Oppenheimer Approximation and Beyond

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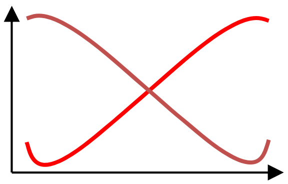
Adiabatic x diabatic x nonadiabatic

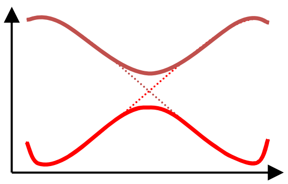
Diabatic x adiabatic

From Greek *diabatos*: to be crossed or passed

diabatic = with crossing

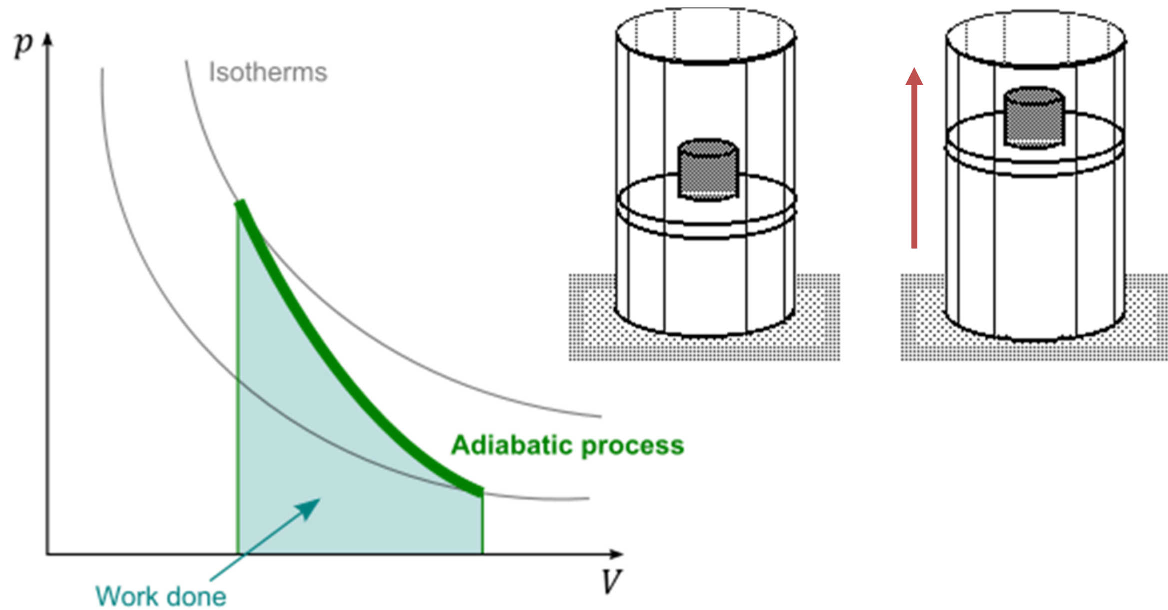


a-diabatic = without crossing



non-a-diabatic = with crossing!?

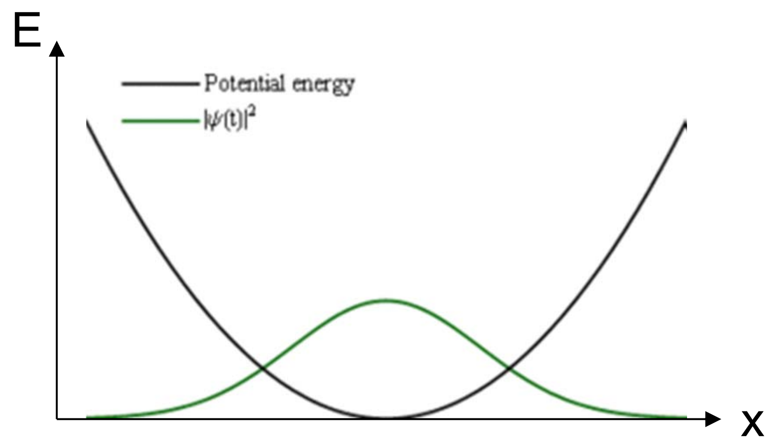
In thermodynamics

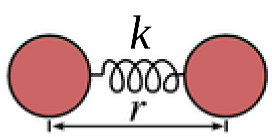


without exchanging (cross) heat or energy with environment

In quantum mechanics

"A physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum." Adiabatic theorem (Born and Fock, 1928).

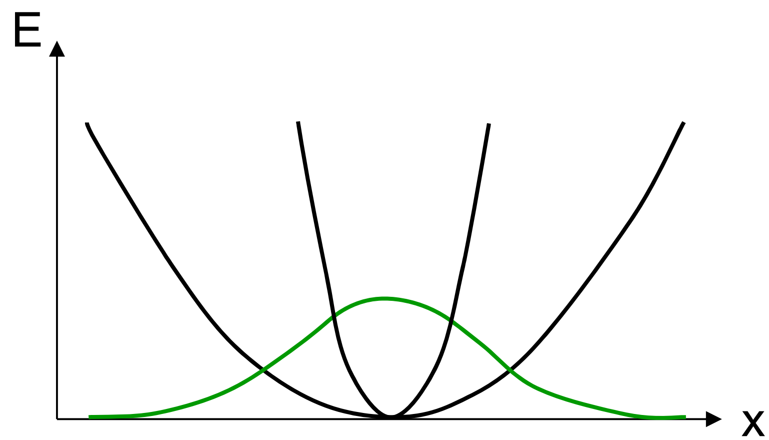


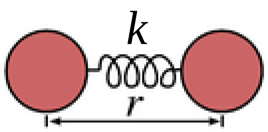


In this example (**adiabatic process**), the spring constant *k* of a harmonic oscillator is slowly (adiabatically) changed. The system remains in the ground state, which is adjusted also smoothly to the new potential shape. Its state is always an eingenstate of the Hamiltonian at each time ("no crossing").

In quantum mechanics

"A physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum." Adiabatic theorem (Born and Fock, 1928).





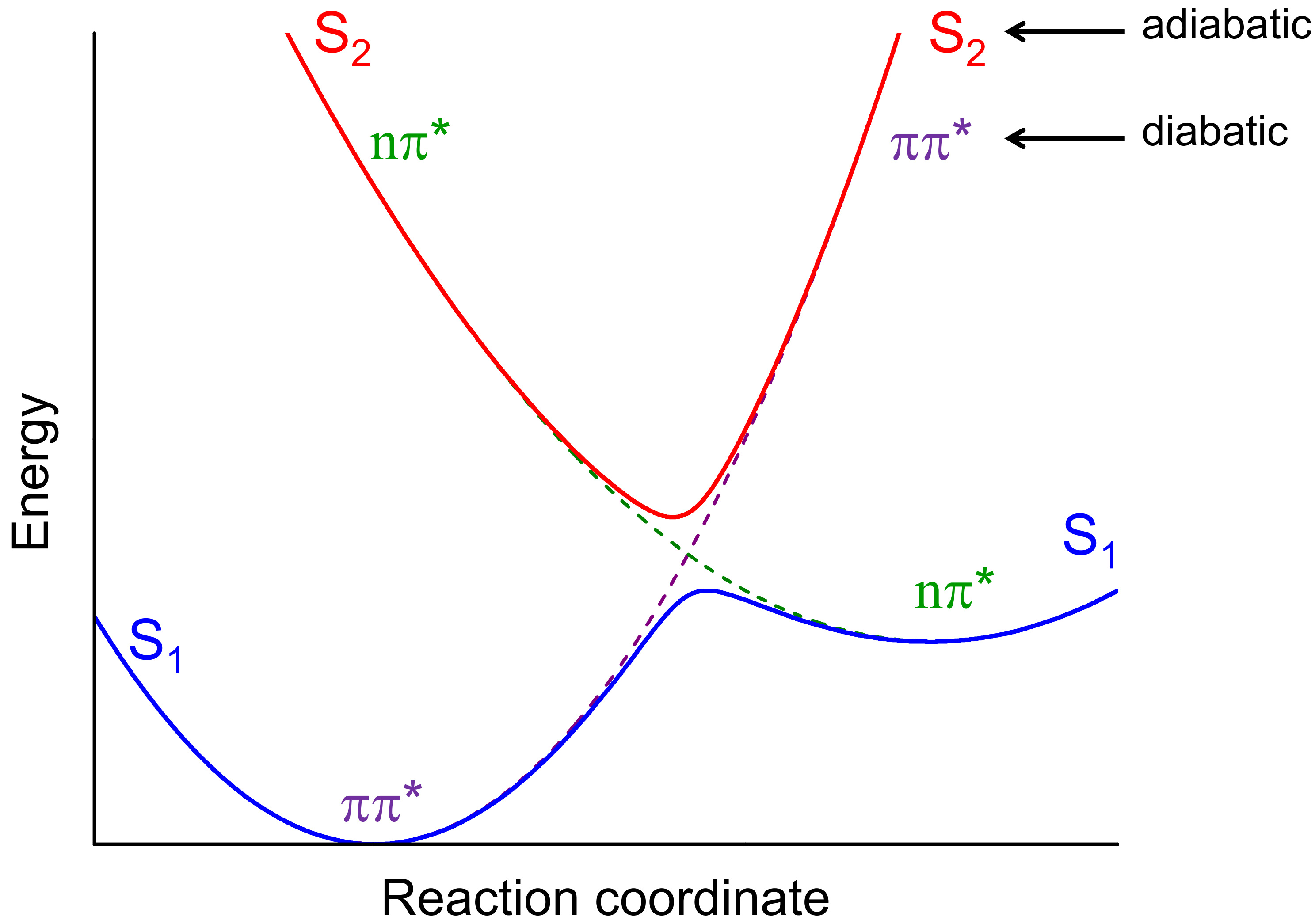
In this example (**diabatic process**), the spring constant *k* of a harmonic oscillator is suddenly (diabatically) changed. The system remains in the original state, which is not a eingenstate of the new Hamiltonian. It is a superposition ("crossing") of several eingenstates of the new Hamiltonian.

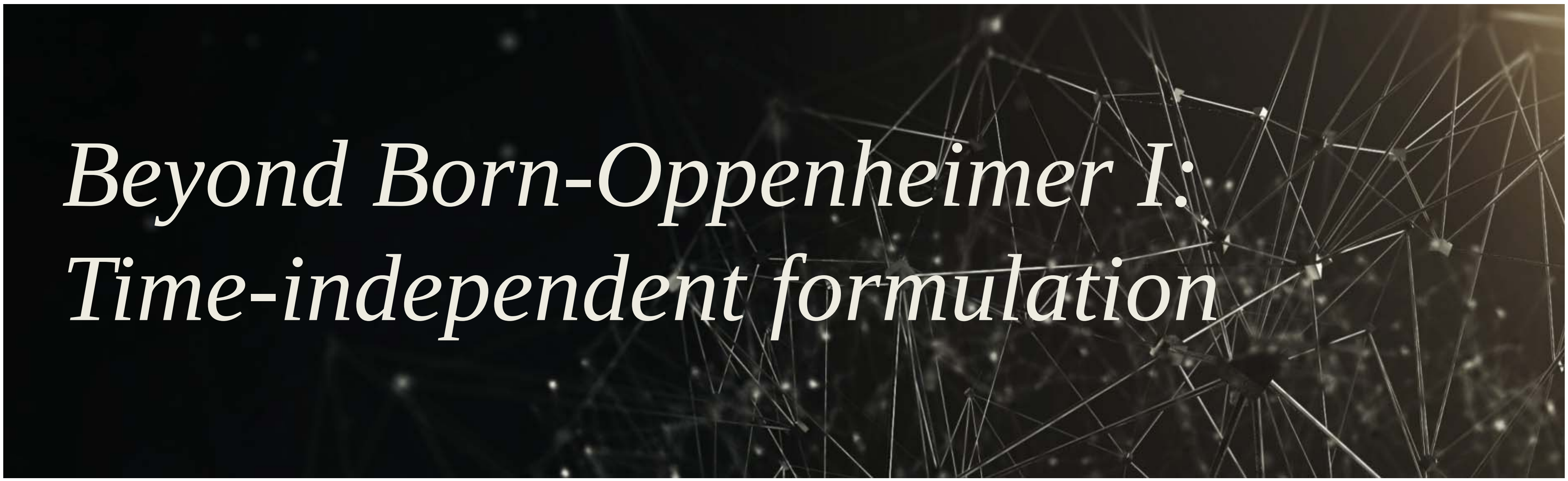
In quantum chemistry

“The nuclear vibration in a molecule is a slowly acting perturbation to the electronic Hamiltonian. Therefore, the electronic system remains in its instantaneous eigenstate if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum.”

This is another way to say that:
The electrons see the nuclei instantaneously frozen

In quantum chemistry





Beyond Born-Oppenheimer I: Time-independent formulation

Time-independent formulation

$$(\mathbf{H}-U)\Phi = 0$$

$$\mathbf{H} = T_N + H_e$$

- T_N – Kinetic energy nuclei
- H_e – potential energy terms

$\{\psi_i\}$ which solves: $(H_e - E_i)\psi_i = 0$ (adiabatic basis)

$\psi_i = \psi_i(\mathbf{r};\mathbf{R})$ depends on the electronic coordinates **r** and parametrically on the nuclear coordinates **R**.

$$\langle \psi_i | \psi_k \rangle = \delta_{ik}$$

Since $\{\psi_i\}$ is a complete basis, any function in the Hilbert space can be exactly written as a linear combination of ψ_i.

$$\Phi(\mathbf{r},\mathbf{R}) = \sum_{k=1}^{N_s} \chi_k(\mathbf{R})\psi_k(\mathbf{r};\mathbf{R})$$

χ_k nuclear wave function

$$\mathbf{H} = T_N + H_e$$

$$(\mathbf{H} - U)\Phi = 0$$

Multiply by ψ_i at left and integrate in the electronic coordinates

$$(E_i - U)\chi_i + \sum_{k=1}^{N_s} \langle \psi_i | T_n \chi_k | \psi_k \rangle = 0$$

$$T_N = -\frac{\hbar^2}{2}\sum_{I=1}^{N_{at}} \frac{\nabla_I^2}{M_I} = -\frac{\hbar^2}{2}\nabla_M^2$$

$$\nabla^2 AB = (\nabla^2 A)B + 2\nabla A \cdot \nabla B + A\nabla^2 B$$

Non-adiabatic coupling terms

Prove it!

$$[U - (T_N + E_i)]\chi_i + \sum_{k=1}^{N_s}\left[\hbar^2 \nabla_M \chi_k \cdot \langle \psi_i | \nabla_M \psi_k \rangle - \chi_k \langle \psi_i | T_N \psi_k \rangle\right] = 0$$

$$\left[U-\left(T_N+E_i\right)\right]\chi_i+\sum_{k=1}^{N_s}\left[\hbar^2\nabla_M\chi_k\cdot\langle\psi_i|\nabla_M\psi_k\rangle-\chi_k\langle\psi_i|T_N\psi_k\rangle\right]=0$$

If non-adiabatic coupling terms = 0

$$\left[U-\left(T_N+E_i\right)\right]\chi_i=0$$

Nuclear vibrational problem.

If E_i is expanded to the second order around the equilibrium position:

$$E_i=E_i\left(\mathbf{R}_{eq}\right)+\frac{1}{2}\sum_{k=1}^{3Nat}\sum_{l=1}^{3Nat}\left(\frac{\partial E_i}{\partial q_k\partial q_l}\right)_{eq}q_kq_l \qquad q_k=M_k^{1/2}\left(x_k-x_{k,eq}\right)$$

it can be treated by normal mode analysis.

Beyond Born-Oppenheimer II: Time-dependent formulation

Time-dependent formulation

$$\left(i\hbar \frac{\partial}{\partial t} - \mathbf{H} \right) \Phi(\mathbf{r}, \mathbf{R}, t) = 0$$

$$\mathbf{H} = T_N + H_e$$

- T_N – Kinetic energy nuclei
- H_e – potential energy terms

$\{\psi_i\}$ which solves: $(H_e - E)\psi_i = 0$ (adiabatic basis)

$\psi_i = \psi_i(\mathbf{r}; \mathbf{R})$ depends on the electronic coordinates **r** and parametrically on the nuclear coordinates **R**.

Since $\{\psi_i\}$ is a complete basis, any function in the Hilbert space can be exactly written as a linear combination of ψ_i.

$$\Phi(\mathbf{r},\mathbf{R}) = \sum_{k=1}^{N_s} \chi_k(\mathbf{R})\psi_k(\mathbf{r};\mathbf{R})$$

$\chi_k = \langle \psi_k | \Phi \rangle$ nuclear wave function

$$\mathbf{H} = T_N + H_e$$

$$\left(i\hbar \frac{\partial}{\partial t} - \mathbf{H}\right)\Phi(\mathbf{r},\mathbf{R},t) = 0$$

Multiply by ψ_i at left and integrate in the electronic coordinates

Prove it!

$$\left[i\hbar \frac{\partial}{\partial t} - (T_N + E_i)\right]\chi_i + \sum_{k=1}^{N_s}\left(i\hbar\left\langle \psi_i \middle| \frac{\partial}{\partial t}\psi_k \right\rangle - \langle \psi_i | T_N \psi_k \rangle\right)\chi_k = 0$$

Time dependent Schrödinger equation for the nuclei

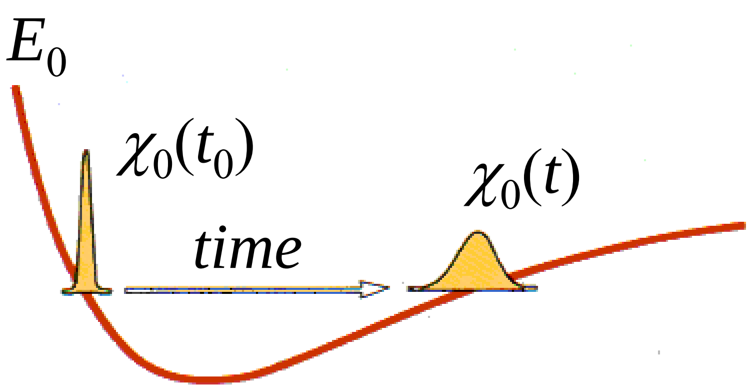
Nonadiabatic coupling terms

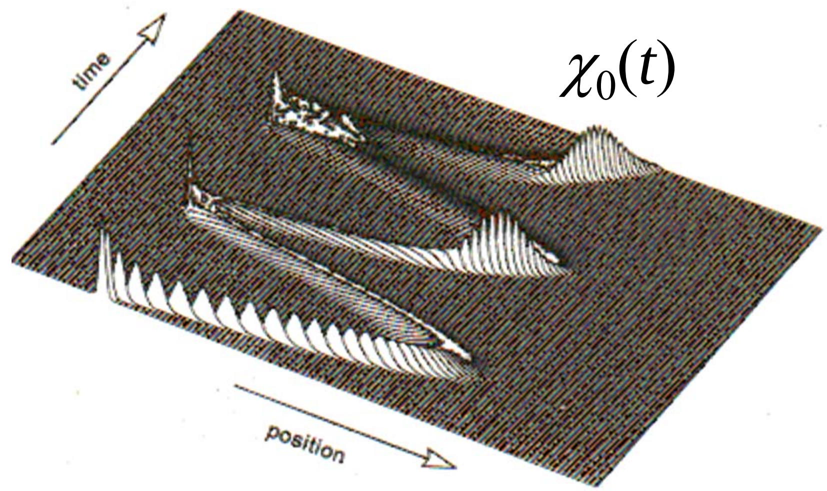
$$\left[i\hbar\frac{\partial}{\partial t}-\left(T_N+E_i\right)\right]\chi_i+\sum_{k=1}^{N_s}\left(i\hbar\left\langle\psi_i\left|\frac{\partial}{\partial t}\psi_k\right.\right\rangle-\left\langle\psi_i\left|T_N\psi_k\right.\right\rangle\right)\chi_k=0$$

First suppose the couplings are null (adiabatic approximation):

$$\left[i\hbar\frac{\partial}{\partial t}-\left(T_N+E_i\right)\right]\chi_i=0$$

Independent equations for each surface.





Classical limit of nuclear motion

$$i\hbar\frac{\partial\chi_i}{\partial t}-\left(T_N+E_i\right)\chi_i=0$$

Adiabatic approximation

$$\chi_i(\mathbf{R},t)=A(\mathbf{R},t)\exp\left[\frac{i}{\hbar}S(\mathbf{R},t)\right]$$

Write nuclear wave function in polar form

$$S(\mathbf{R},t)=\int_0^t L\,dt'$$

The phase (action) is the integral of the Lagrangian

$$\frac{\partial S}{\partial t}+\sum_I\frac{\left(\nabla S\right)^2}{2M_I}+E_i=\sum_I\frac{\hbar}{2M_I}\frac{\nabla^2 A}{A}$$

$$\frac{\partial S}{\partial t}+\sum_I\frac{\left(\nabla S\right)^2}{2M_I}+E_i=0$$

Classical limit $\hbar\rightarrow 0$

Tully, Faraday Discuss. **110**, 407 (1998)

Hamilton-Jacobi Equation

$$\frac{\partial S}{\partial t}+\sum_I \frac{\left(\nabla S\right)^2}{2M_I}+E_i=0$$

To solve the Hamilton-Jacobi equation for the action is totally equivalente to solve the Newton`s equations for the coordinates!

Newton equation

$$-\nabla E_i = M_I \frac{d^2\mathbf{R}_I}{dt}$$

In the classical limit, the solutions of the time dependent Schrödinger equation for the nuclei in the adiabatic approximation are equivalent to the solutions of the Newton`s equations.

In which cases does this classical limit lose validity?

In which cases does this classical limit lose validity?

1

adiabatic quantum terms ≠ 0

$$\frac{\partial S}{\partial t} + \sum_I \frac{(\nabla S)^2}{2M_I} + E_i = \sum_I \frac{\hbar}{2M_I} \frac{\nabla^2 A}{A}$$

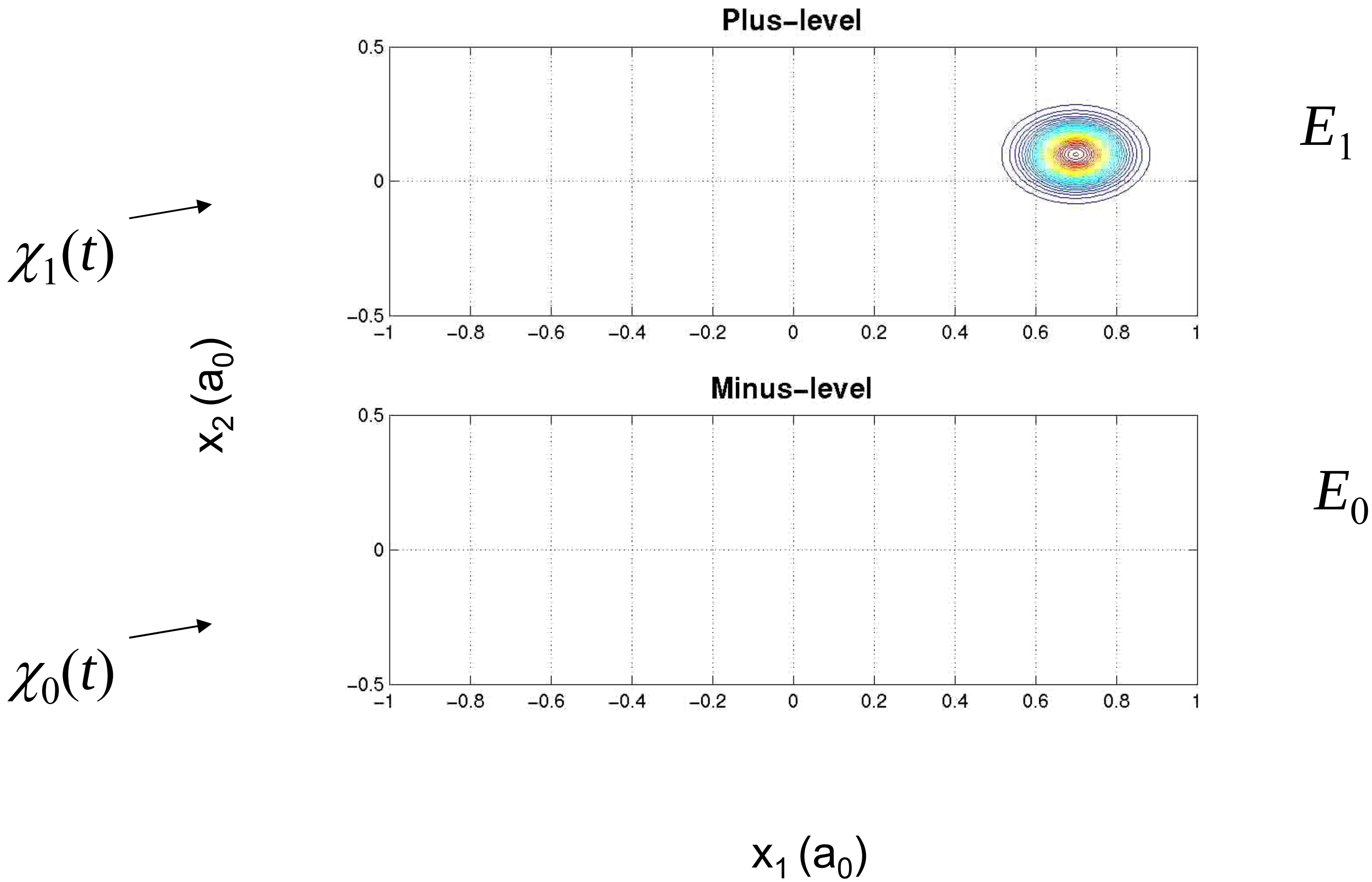
2

nonadiabatic coupling terms ≠ 0

$$\left[i\hbar \frac{\partial}{\partial t} - (T_N + E_i) \right] \chi_i + \sum_{k=1}^{N_s} \left(i\hbar \left\langle \psi_i \middle| \frac{\partial}{\partial t} \psi_k \right\rangle - \left\langle \psi_i \middle| T_N \psi_k \right\rangle \right) \chi_k = 0$$

Non-adiabatic coupling terms

$$\left[i\hbar\frac{\partial}{\partial t}-(T_N+E_i)\right]\chi_i+\sum_{k=1}^{N_s}\left(i\hbar\left\langle\psi_i\left|\frac{\partial}{\partial t}\psi_k\right.\right\rangle-\left\langle\psi_i\left|T_N\psi_k\right.\right\rangle\right)\chi_k=0$$



Key ideas

$$\Phi(\mathbf{r},\mathbf{R}) = \sum_{k=1}^{N_s} \chi_k(\mathbf{R})\psi_k(\mathbf{r};\mathbf{R})$$ Born-Huang Model

$$\Phi(\mathbf{r},\mathbf{R}) \approx \chi_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$ Adiabatic approximation

$$\left\{\begin{array}{l} (H_e - E_i)\psi_i = 0 \\ \left[U - (T_N + E_i)\right]\chi_i = 0 \end{array}\right\}$$ Born-Oppenheimer Approximation

$$\left[U - (T_N + E_i)\right]\chi_i + \sum_{k=1}^{N_s} \underbrace{\left[\hbar^2 \nabla_M \chi_k \cdot \langle \psi_i | \nabla_M \psi_k \rangle - \chi_k \langle \psi_i | T_N \psi_k \rangle\right]}_{\text{Nonadiabatic coupling terms}} = 0$$

Nonadiabatic coupling terms