Geometric phase effects in the excited state dynamics of N-dimensional linear vibronic coupling model

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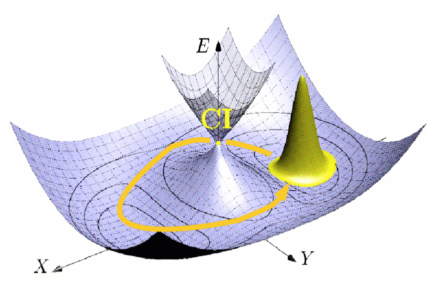
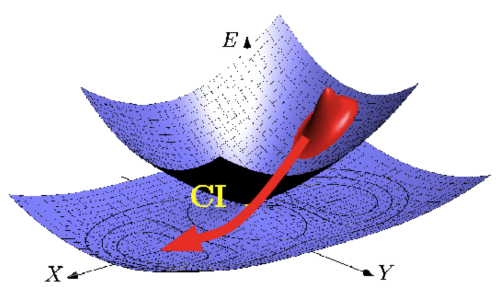
Introduction

- Molecular wave function in the adiabatic representation
  $$\Psi(r,R,t) = \Sigma_j \chi_{n,j}(R,t)\phi_{e,j}(r;R)$$
  $$H_e\phi_{e,j} = E_j(R)\phi_{e,j}(r;R)$$
- If electronic surfaces, $E_j(R)$, intersect conically, geometric phase (GP) makes the electronic functions double-valued.
- To compensate for that:[1]
  $$\phi_{e,j}(r;R)e^{-i\theta(R)}$$
  $$\chi_{n,j}(R,t)e^{i\theta(R)}$$





Questions:

- When is GP important?
- What is the impact of extra nuclear degrees of freedom (DOF)?

Motivation:

To develop a qualitative picture of GP effects in excited state dynamics of large system.

Modeling the system

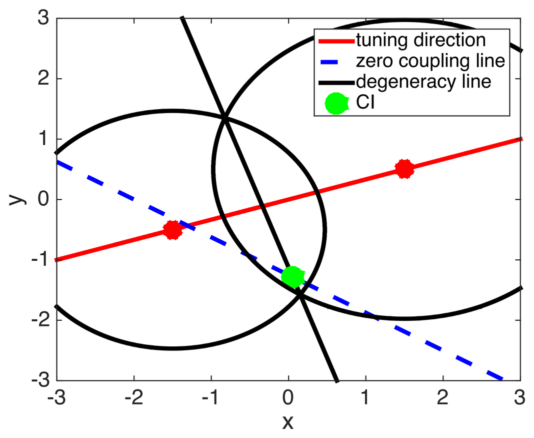
N-dimensional LVC Hamiltonian for nuclear DOF

$$H_{ND} = \sum_j^N (p_j^2 + \omega_j^2 q_j^2)\mathbf{1}_2 + \begin{bmatrix} -\kappa_j q_j & c_j q_j \\ c_j q_j & \kappa_j q_j \end{bmatrix} + \begin{bmatrix} -\delta & 0 \\ 0 & \delta \end{bmatrix}$$

The short-time dynamics can be examined by an effective 2D system[2]. Extra DOF modify the 2D parameters.

Diabatic representation (GP is implicit)

$$H = -\frac{1}{2}\nabla^2\mathbf{1}_2 + \begin{bmatrix} V_{11} & V_{12} \\ V_{12} & V_{22} \end{bmatrix}$$
$$V_{11,22} = \frac{1}{2}[\omega_x^2(x \mp x_0)^2 + \omega_y^2 y^2 \mp \Delta]$$
$$V_{12} = c_x x + c_y y + \Delta_{12}$$



Adiabatic representation (no GP if single-value real wave functions are used):

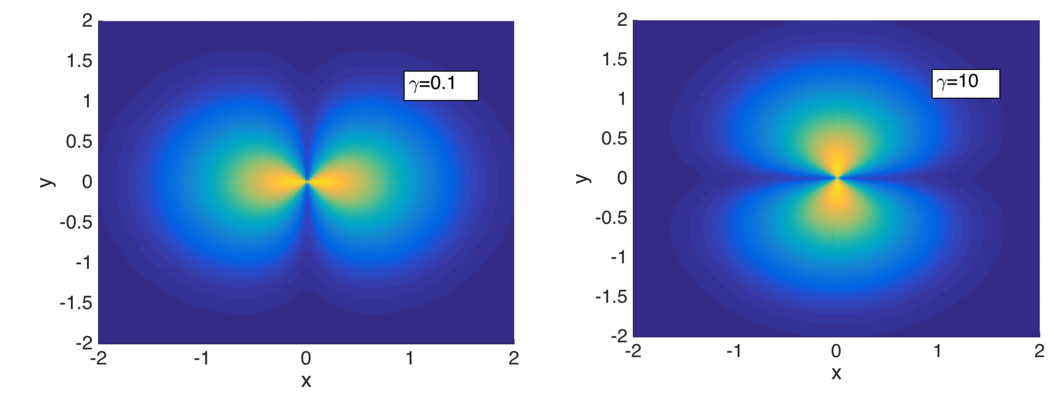
$$H_{adi} = -\tfrac{1}{2}\nabla^2\mathbf{1}_2 + \begin{bmatrix} W_- & 0 \\ 0 & W_+ \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} \\ -\tau_{12} & \tau_{22} \end{bmatrix}$$
$$W_\pm = \frac{1}{2}(V_{11}+V_{22}) \pm \frac{1}{2}\sqrt{(V_{11}-V_{22})^2 + 4V_{12}^2}$$
$$\tau_{ij} = -\langle\phi_i|\nabla\phi_j\rangle\nabla - \tfrac{1}{2}\langle\phi_i|\nabla^2\phi_j\rangle$$

GP effects for transfer

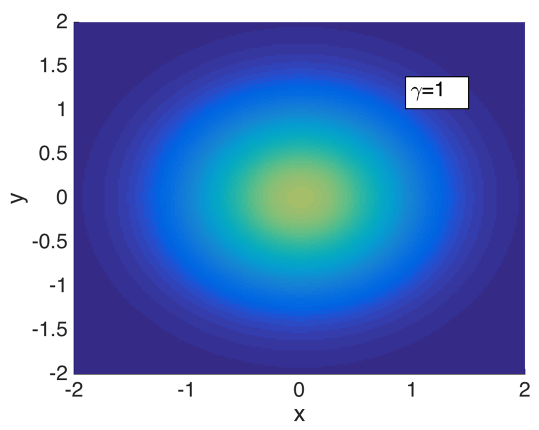
Expand the nuclear wave function:
$$\chi = \chi_{nontran} + \chi_{tran}$$

Nontransferable part:
$$\tau_{12}\chi_{nontran} = 0\times\chi_{nontran}$$

Exact solution:
$$\chi_{nontran}(r,\theta) = R\sqrt{\gamma\sin^2\theta + \gamma^{-1}\cos^2\theta}, \quad \gamma = \frac{c_y}{\omega_x^2 x_0}$$



In Mexican hat model (i.e. $\gamma = 1$): $\chi_{nontran} = R$

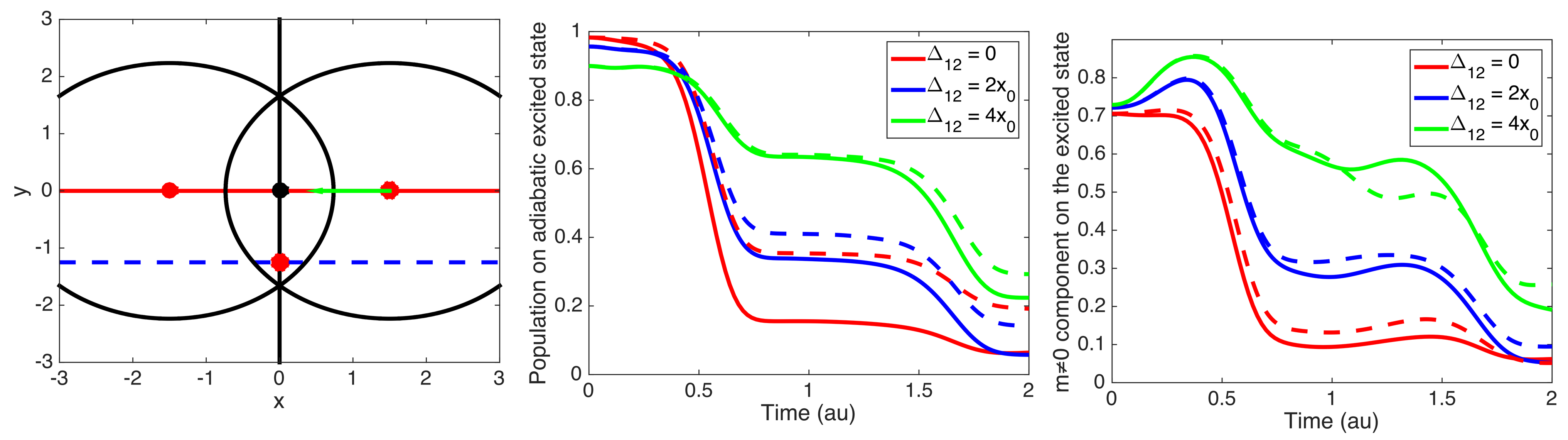


It is the angular-momentum free (m=0) component of a wave packet[3].
Good approximation to $\chi_{nontran}$ when $\gamma \sim 1$.

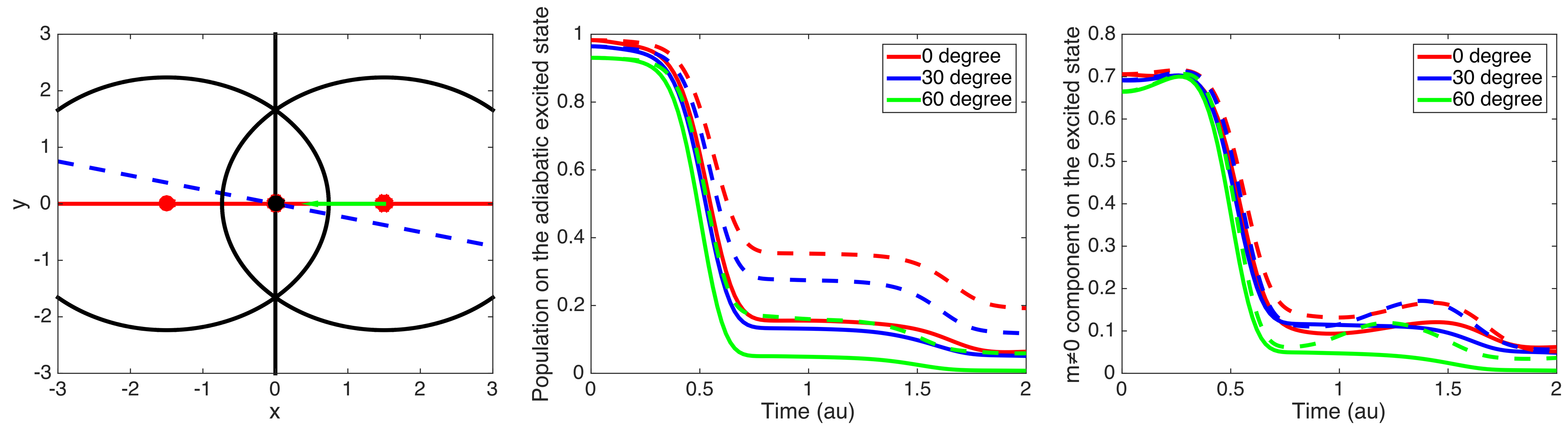
How geometry affects the nontransferable weight (m=0) and the importance of GP

Population plots: solid - with GP, dashed - without GP.

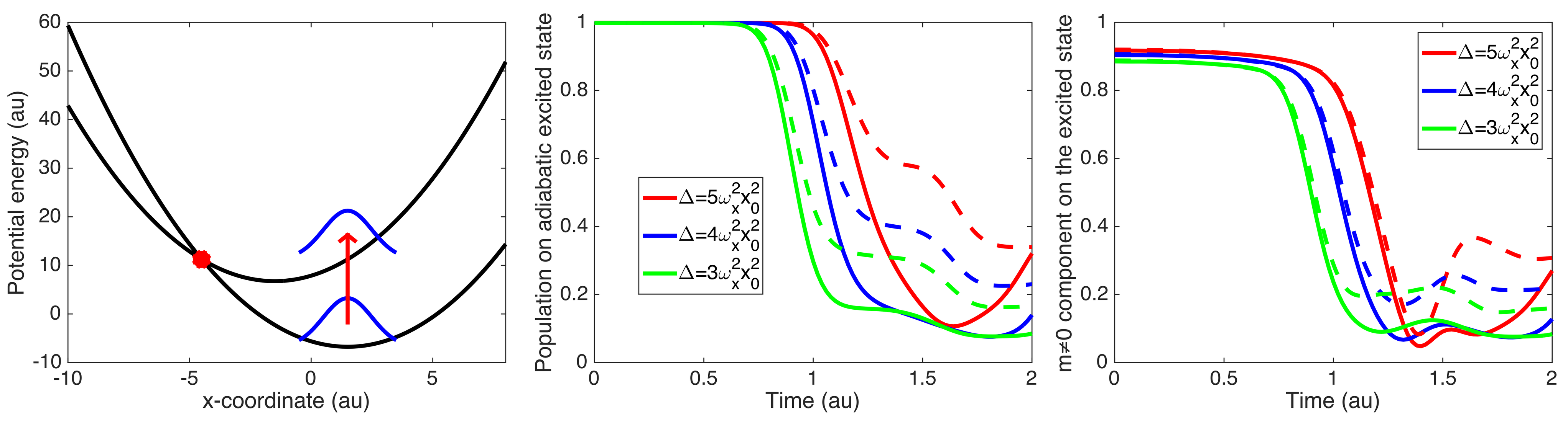
Constant coupling (Δ_{12}): a shift of CI along y-axis



Orthogonality of coupling: breaking down of the wave packet's symmetry



Difference in potential minima (Δ): a change in kinetic energy



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