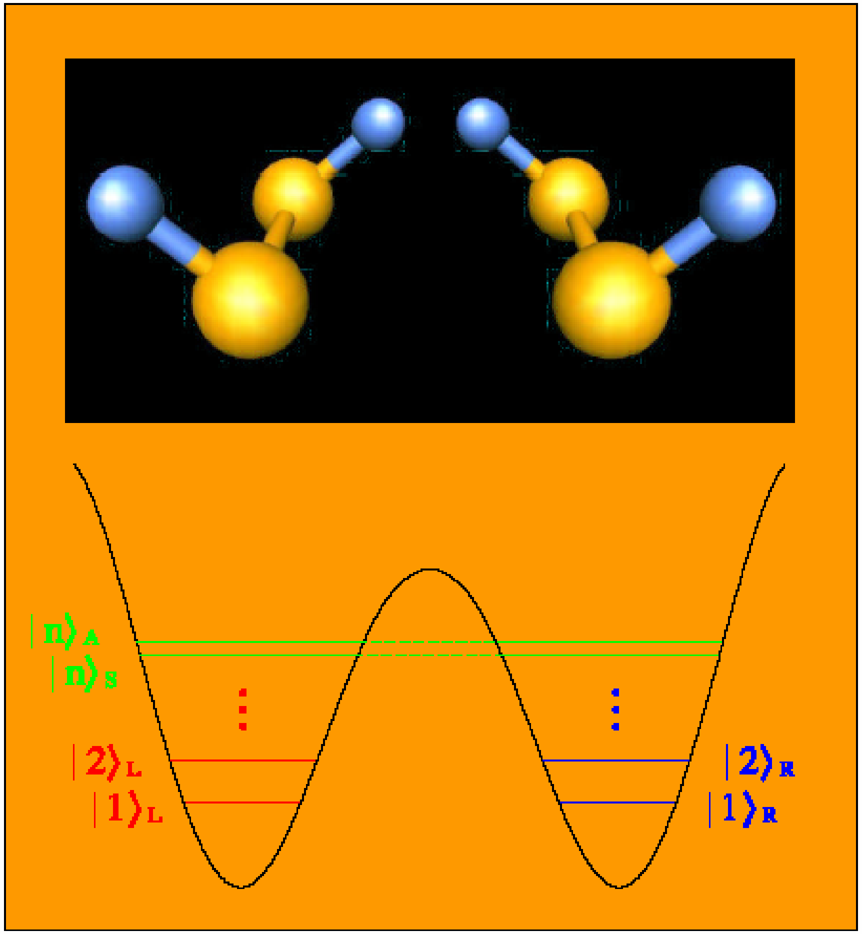
Optical chiral discrimination, the electric Stern-Gerlach effect and the "Hund Paradox"



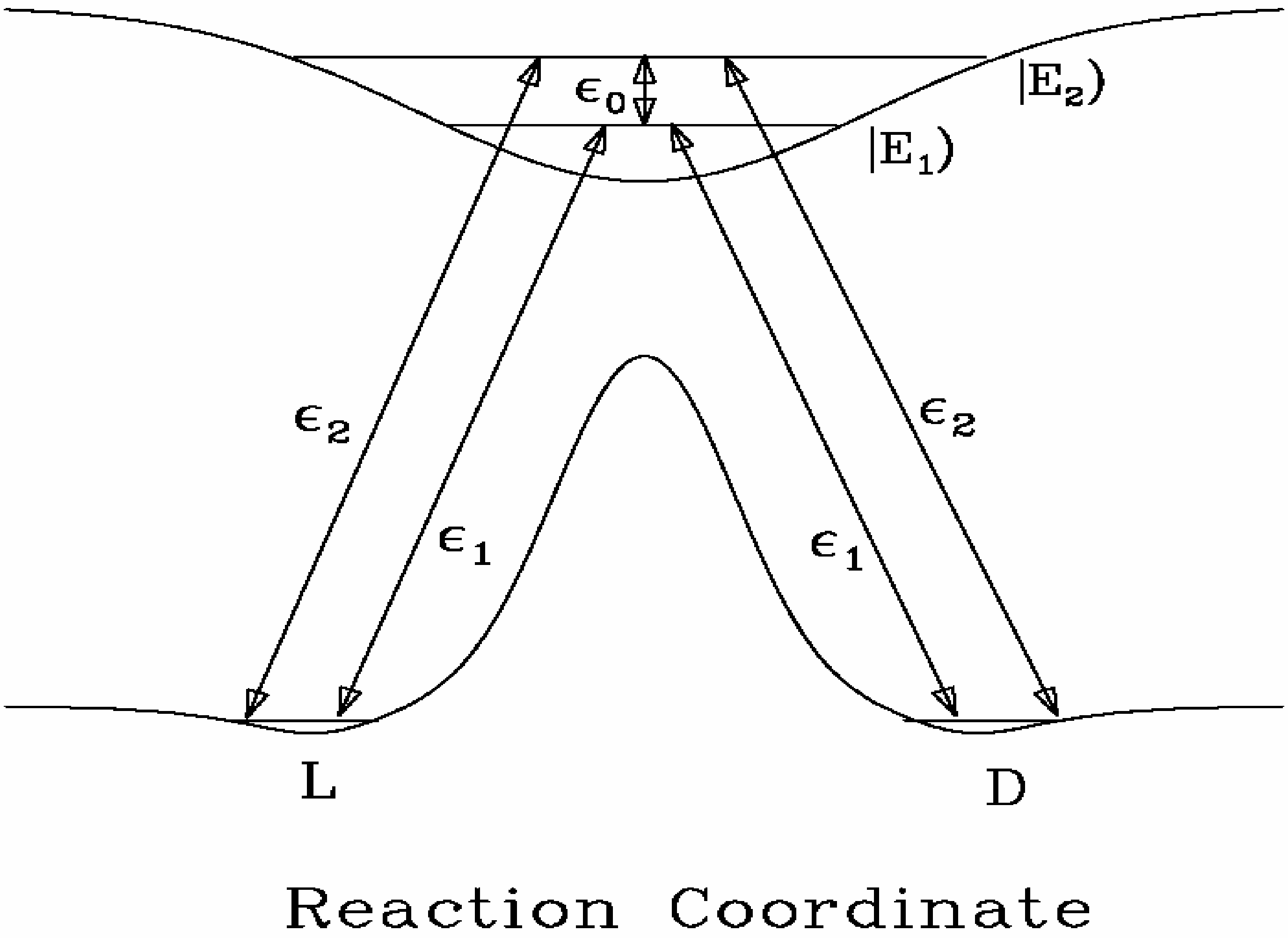
Why are the below barrier A/S states never observed?

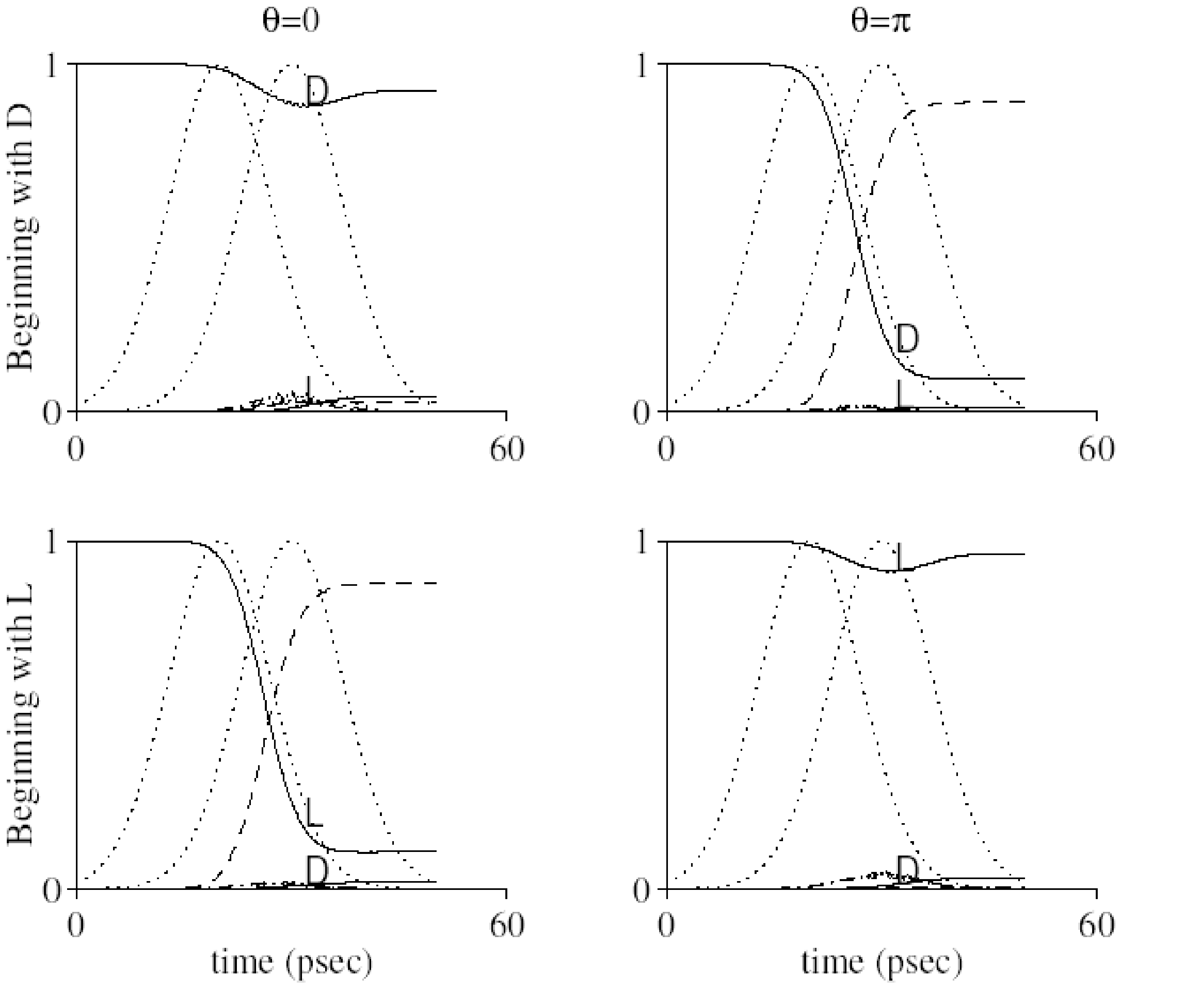
Moshe Shapiro, Univ. British Columbia

KITP Quantum Control Conf, May 22, 2009

The purification of a mixture of molecules with opposite handedness by optical means

E. Frishman, P. Brumer and MS, Phys. Rev. Lett. **84**, 1669 (2000)



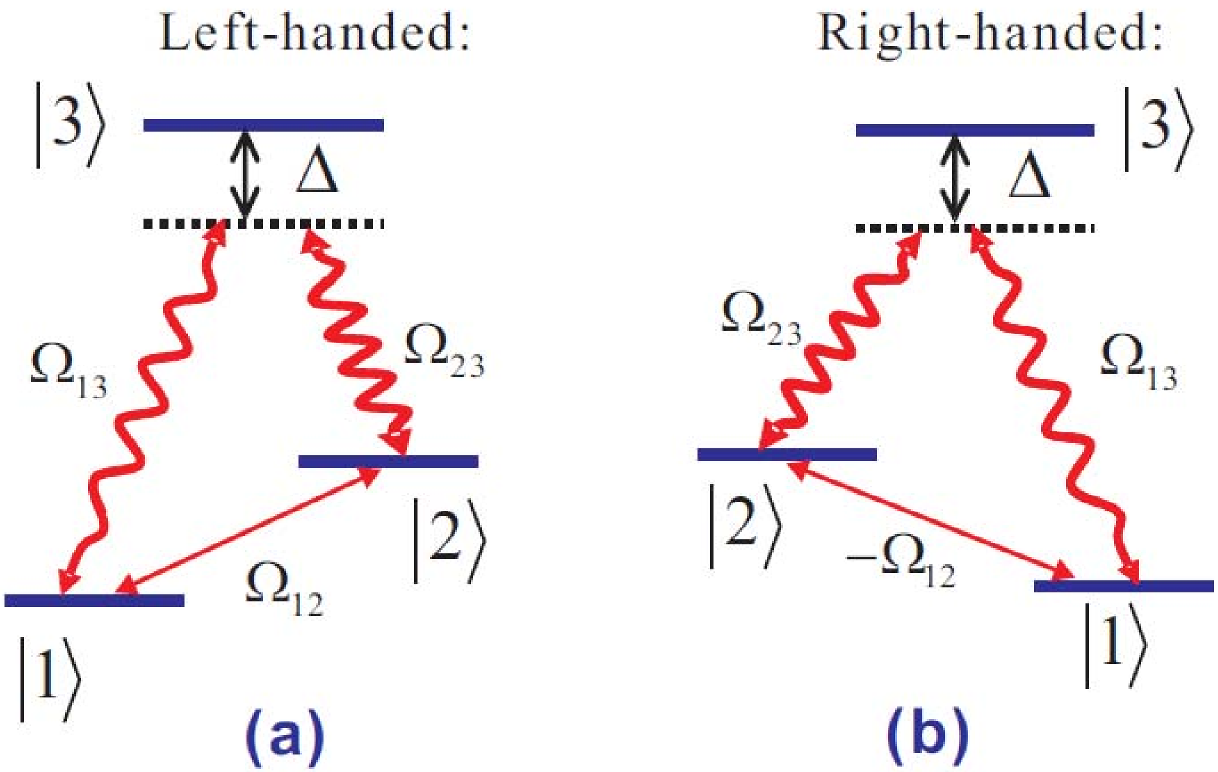

θ=0
θ=π
Beginning with D
Beginning with L
D
L
1
0
60
time (psec)

“Loop” adiabatic passage in chiral molecules

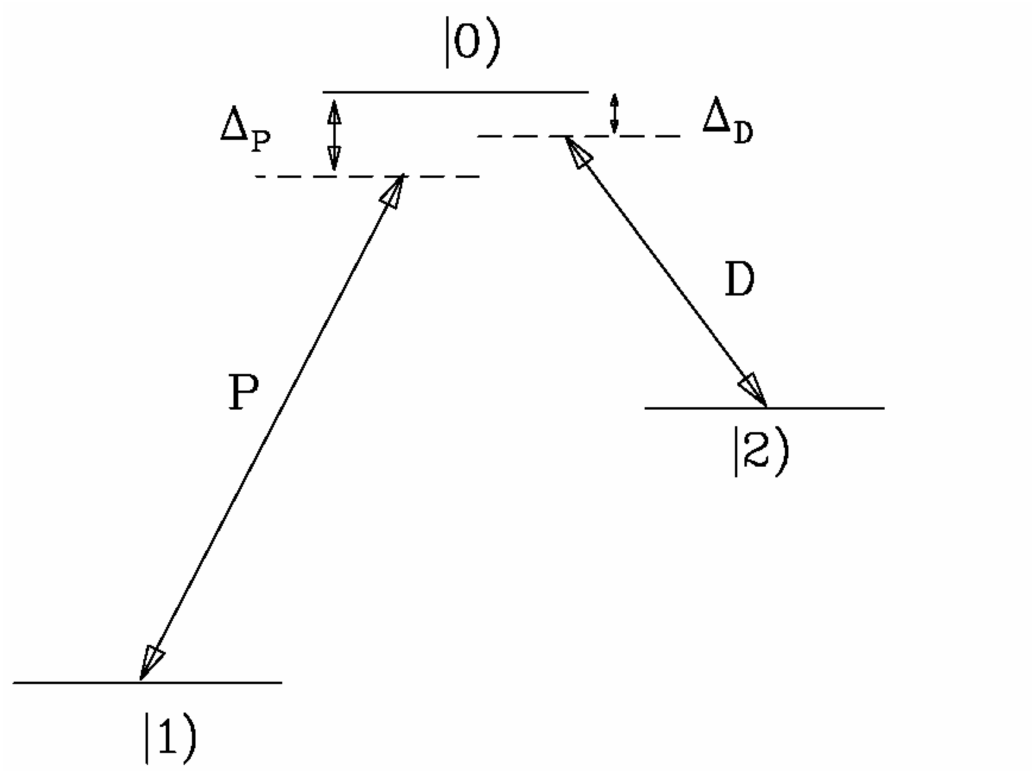
P. Král and M. Shapiro, Phys. Rev. Lett. **87**, 183002 (2001)

P. Král, I. Thanopoulos, M. Shapiro, and D. Cohen, Phys. Rev. Lett. **90**, 033001 (2003).

I. Thanopulos, P. Král, and M. Shapiro, J. Chem. Phys. **119**, 5105 (2003)



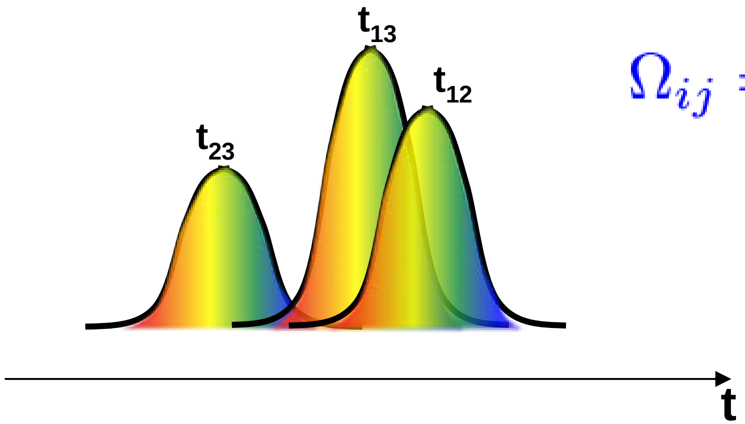
Adiabatic passage in non-chiral molecules



In chiral molecules loop adiabatic passage the Hamiltonian is

$$H = \sum_{j=1}^{3} \hbar\omega_j |\, j\,\rangle\langle\, j\,| + \sum_{i>j=1}^{3} \left(\hbar\Omega_{ij}(t) e^{-i\omega_{ij}t} |\, i\,\rangle\langle\, j\,| + h.c.\right),$$

where $\Omega_{ij}(t) \equiv \mu_{ij}\,\mathcal{E}_{ij}(t)/\hbar = |\Omega_{ij}(t)|\, e^{i\phi_{ij}} = \Omega^*_{ji}(t)$



$$\Omega_{ij} = \Omega^o_{ij} e^{-(t - t_{ij})^2/\sigma^2_{i,j}}$$

The wave function is $|\mathcal{X}(t)\rangle = \sum_{n=1}^{3} c_n(t)\, e^{-i\omega_n t}\, |\, n\rangle\,,$

where $\mathbf{c}(t) = (c_1, c_2, c_3)^T$ foll

the Schrödinger equation $\dot{\mathbf{c}}(t) = -i\,\mathsf{H}(t)\cdot\mathbf{c}(t)\,,$

$$\text{with}\;\; \mathsf{H}(\mathrm{t}) = \begin{bmatrix} 0 & \Omega_{12}^{*} & \Omega_{13}^{*} \\ \Omega_{12} & 0 & \Omega_{23}^{*} \\ \Omega_{13} & \Omega_{23} & 0 \end{bmatrix}.$$

What is the role of the phase?

Symmetry-broken states: $|\, i^{\pm}\, \rangle$

$|i^{\pm}\rangle = \quad |S_i\rangle \pm \quad |A_i\rangle$, where $|\, S_i\, \rangle$ and $|\, A_i\, \rangle$ are the *symmetric* and *antisymmetric* states of the two systems

Therefore, dipole transitions between states $|i^{\pm}\rangle$ and $|j^{\pm}\rangle$ in left and right-handed systems are

$$\Omega_{ij}^{\pm} = \pm [\qquad \langle\, S_i\, |\mu|\, A_j\, \rangle + \qquad \langle\, A_i\, |\mu|\, S_j\, \rangle]\, \mathcal{E}_{ij}/\hbar$$

The two enantiomers are influenced by *different phases* $\varphi^{\pm}$ $(\varphi^{-} - \varphi^{+} = \pi)$ of the products $\Omega_{12}^{\pm}\, \Omega_{23}^{\pm}\, \Omega_{31}^{\pm}$

This π-change can give $|1\rangle \rightarrow |3\rangle$ and $|1\rangle \rightarrow |2\rangle$ transfers in the left and righ-handed enantiomers, respectively, or vice versa, according to the common phase φ_f of *laser fields* $\mathcal{E}_{ij}$

Diagonalize H

$$\lambda_1 = \frac{1}{3}\left(\frac{2^{1/3}a}{c} + \frac{c}{2^{1/3}}\right),$$

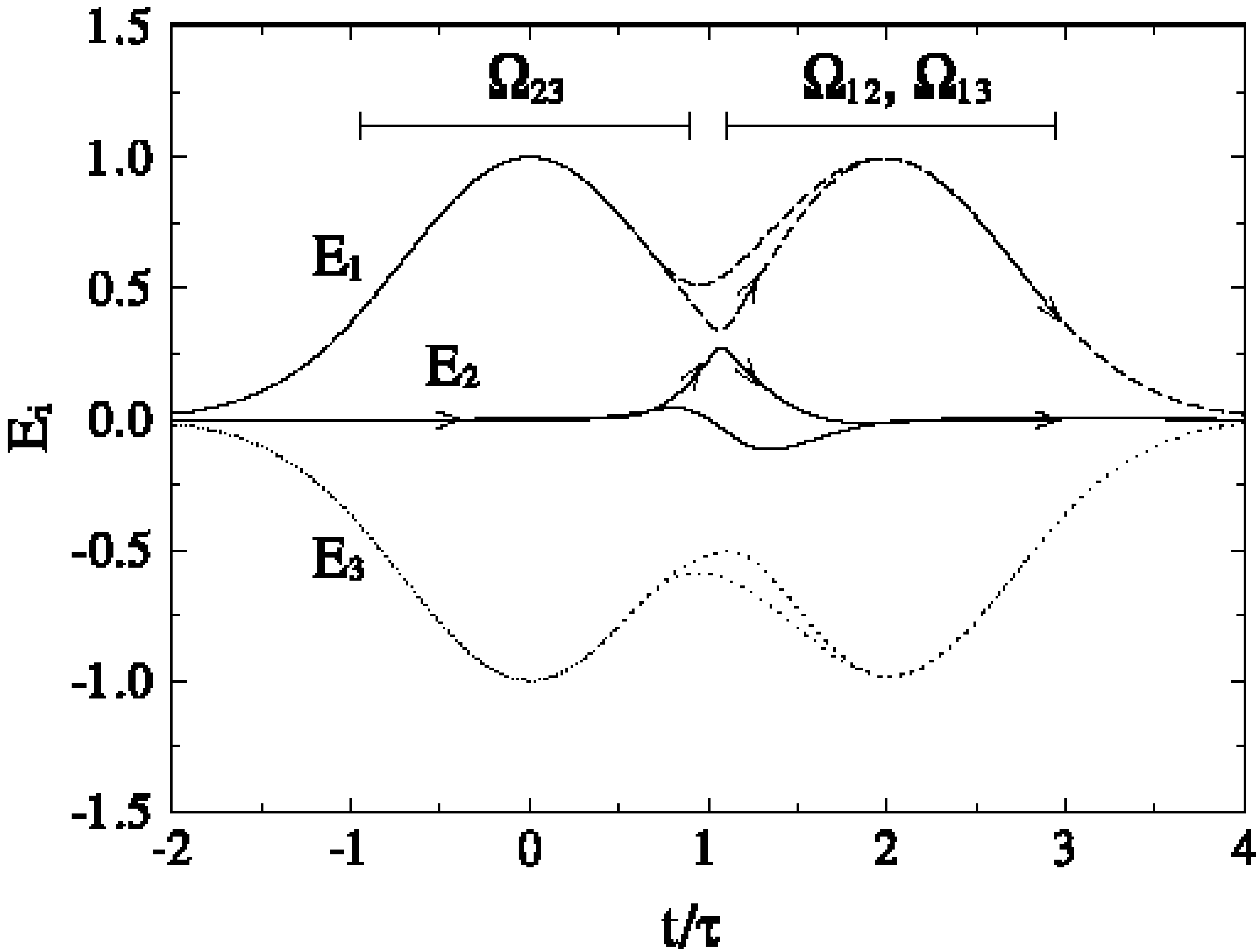
$$\lambda_{2,3} = \frac{1}{3}\left[\frac{-(1 \pm i\sqrt{3})a}{2^{2/3}c} - \frac{(1 \mp i\sqrt{3})c}{2^{4/3}}\right],$$

$$a = 3\left(|\Omega_{1,2}|^2 + |\Omega_{2,3}|^2 + |\Omega_{3,1}|^2\right), \qquad b = 3^3 2 Re\mathcal{O},$$

$$c = \left[b + \sqrt{b^2 - 4a^3}\right]^{1/3},$$

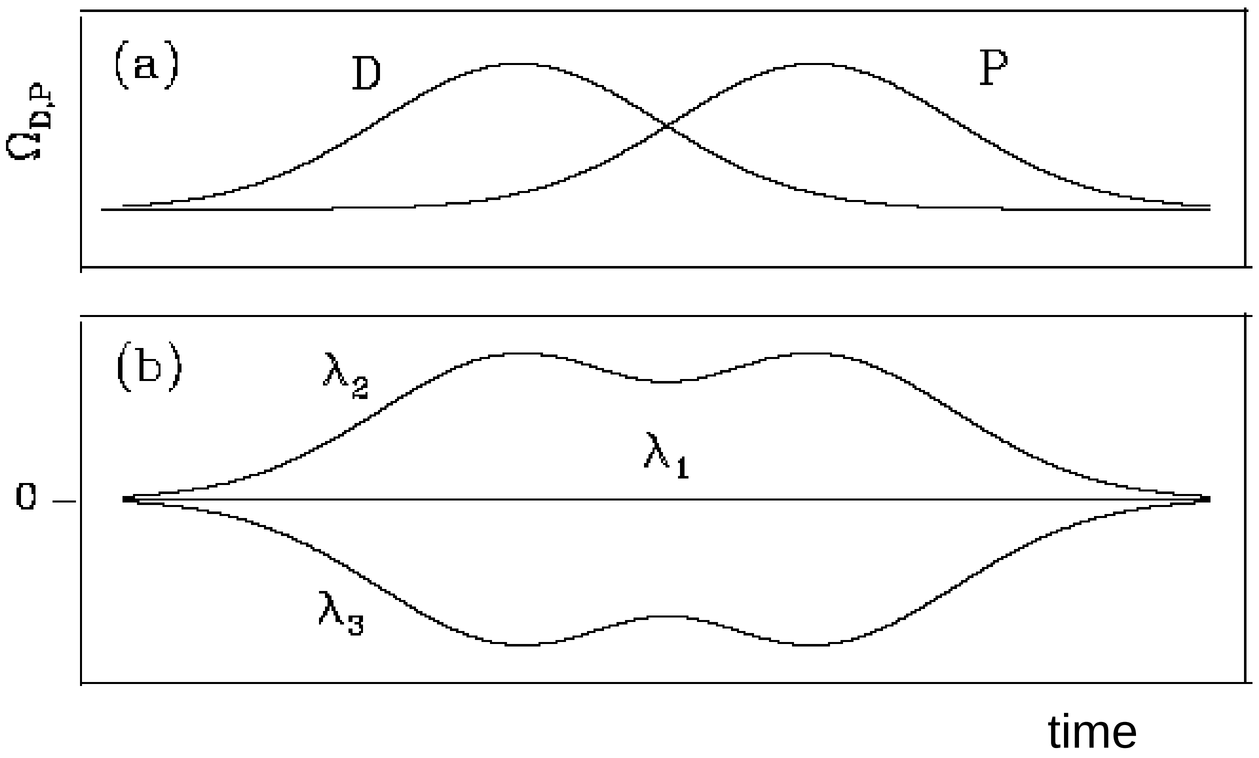
with $\mathcal{O} = \Omega_{1,2}\Omega_{2,3}\Omega_{3,1}e^{-i\Sigma t}$. $\Sigma \equiv \Delta_{12} + \Delta_{23} + \Delta_{31}$,

Loop adiabatic eigenvalues
(possible only for chiral molecules)

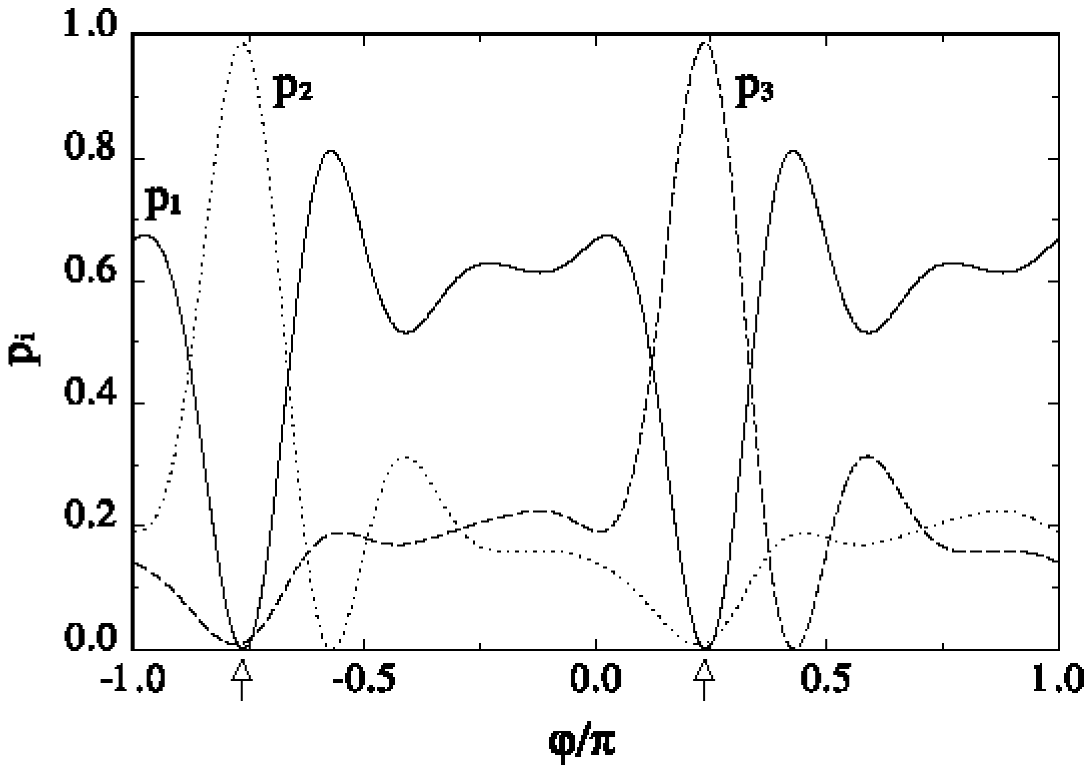


In the loop system the eigenvalues depend on the phases

Adiabatic eigenvalues for non-chiral molecules



$$\lambda_1 = 0\ ,\ \lambda_{2,3}(t) = \pm\left[|\Omega_P(t)|^2 + |\Omega_D(t)|^2\right]^{1/2}$$



Coherent phase control of the population transfer

The Electric Stern-Gerlach Effect for chiral molecules

Yong Li, C. Bruder, and C. P. Sun **PRL 99,** 130403 (2007)

Xuan Li and M. Shapiro

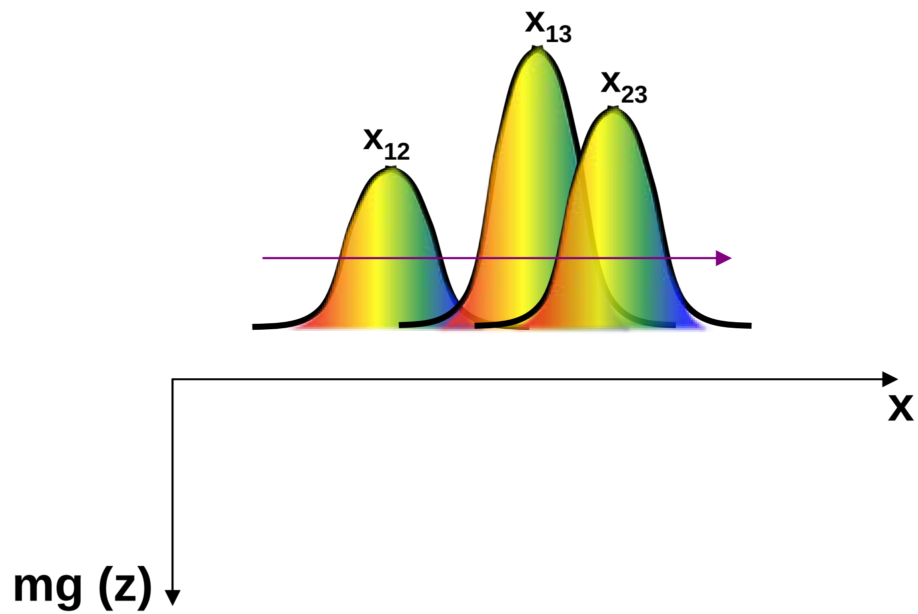
The Electric Stern-Gerlach Effect for chiral molecules

Yong Li, C. Bruder, and C. P. Sun **PRL 99,** 130403 (2007)

Xuan Li and M. Shapiro

$$H_{tot} = H_{CM}(\mathbf{r}) + H$$

$$\Omega_{ij} = \Omega^{o}_{ij} e^{-(x-x_{ij})^2/\sigma^2_{i,j}} e^{-ik_{ij}z/\hbar}$$



Expand the total wavefunction in the dressed states, $|\chi_i(\mathbf{r})\rangle$, as

$$|\Psi(\mathbf{r})\rangle = \sum_i^3 \phi_i(\mathbf{r})\,|\chi_i(\mathbf{r})\rangle .$$

The expansion coefficients vector $\underline{\phi}(\mathbf{r}) \equiv (\phi_1, \phi_2, \phi_3)^T$

$$i\hbar\frac{\partial}{\partial t}\underline{\phi} = \underline{\underline{\hat{\mathbf{H}}}}\,\underline{\phi}$$

Expand the total wavefunction in the dressed states, $|\chi_i(\mathbf{r})\rangle$, as

$$|\Psi(\mathbf{r})\rangle = \sum_i^3 \phi_i(\mathbf{r})\,|\chi_i(\mathbf{r})\rangle.$$

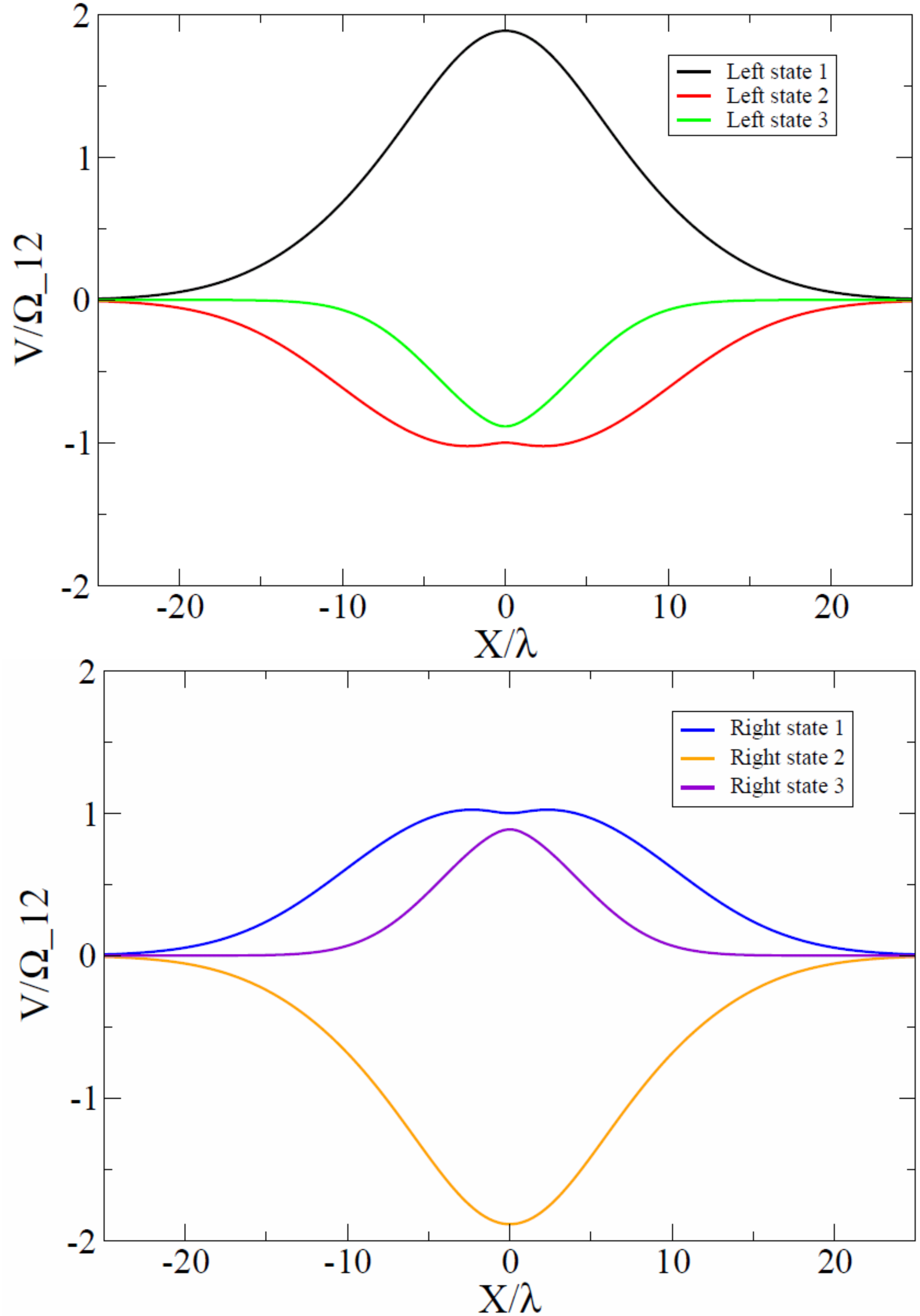
The expansion coefficients vector $\underline{\phi}(\mathbf{r}) \equiv (\phi_1, \phi_2, \phi_3)^T$

$$i\hbar\frac{\partial}{\partial t}\underline{\phi} = \underline{\underline{\mathbf{H}}}\,\underline{\phi}$$

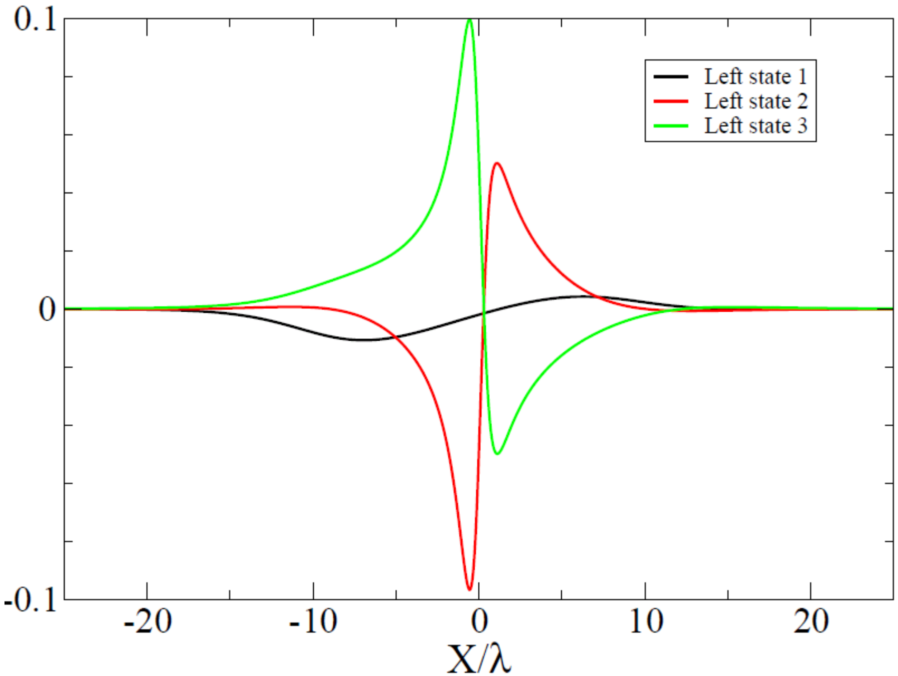
where

$$\underline{\underline{\mathbf{H}}} = \frac{1}{2m}\left(i\hbar\nabla + \underline{\underline{\mathbf{A}}}(\mathbf{r})\right)^2 + \underline{\underline{V}}(\mathbf{r})$$

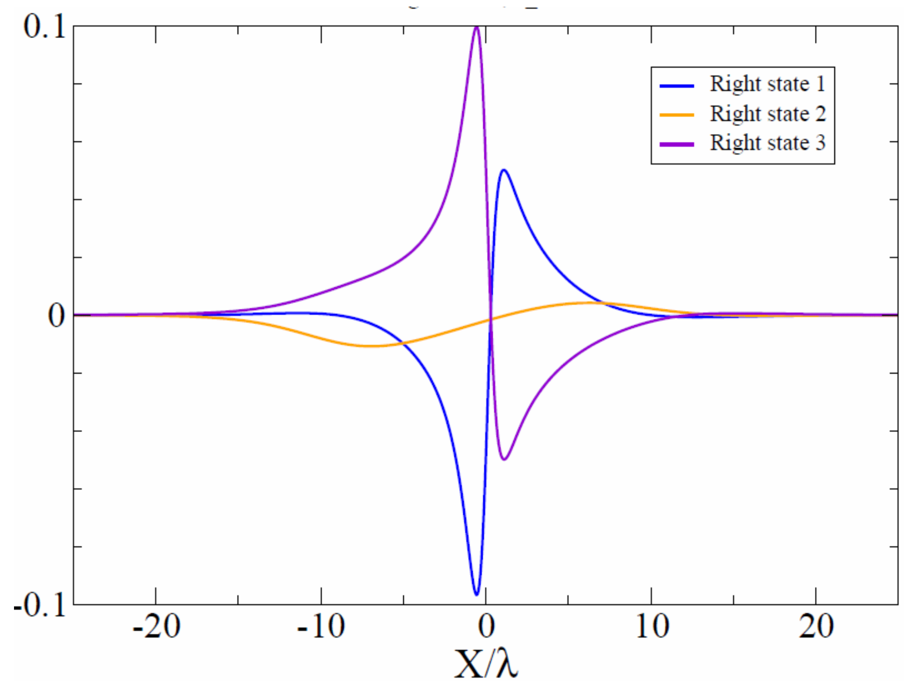
$$\left[\underline{\underline{\mathbf{A}}}\right]_{i,j} = i\hbar\,\langle\chi_i\,|\nabla\,\chi_j\rangle \qquad \left[\underline{\underline{V}}\right]_{i,j} = \lambda_i\delta_{i,j}$$


Left state 1
Left state 2
Left state 3
V/Ω_12
X/λ
Right state 1
Right state 2
Right state 3
V/Ω_12
X/λ

Pseudo-magnetic field, Left-handed states



Pseudo-magnetic field, Right-handed states



The three states are viewed as pseudospin 1 with

$$|m_S = +1\rangle \equiv |\chi_1(\mathbf{r})\rangle$$

$$|m_S = 0\rangle \equiv |\chi_2(\mathbf{r})\rangle$$

$$|m_S = -1\rangle \equiv |\chi_3(\mathbf{r})\rangle\,.$$

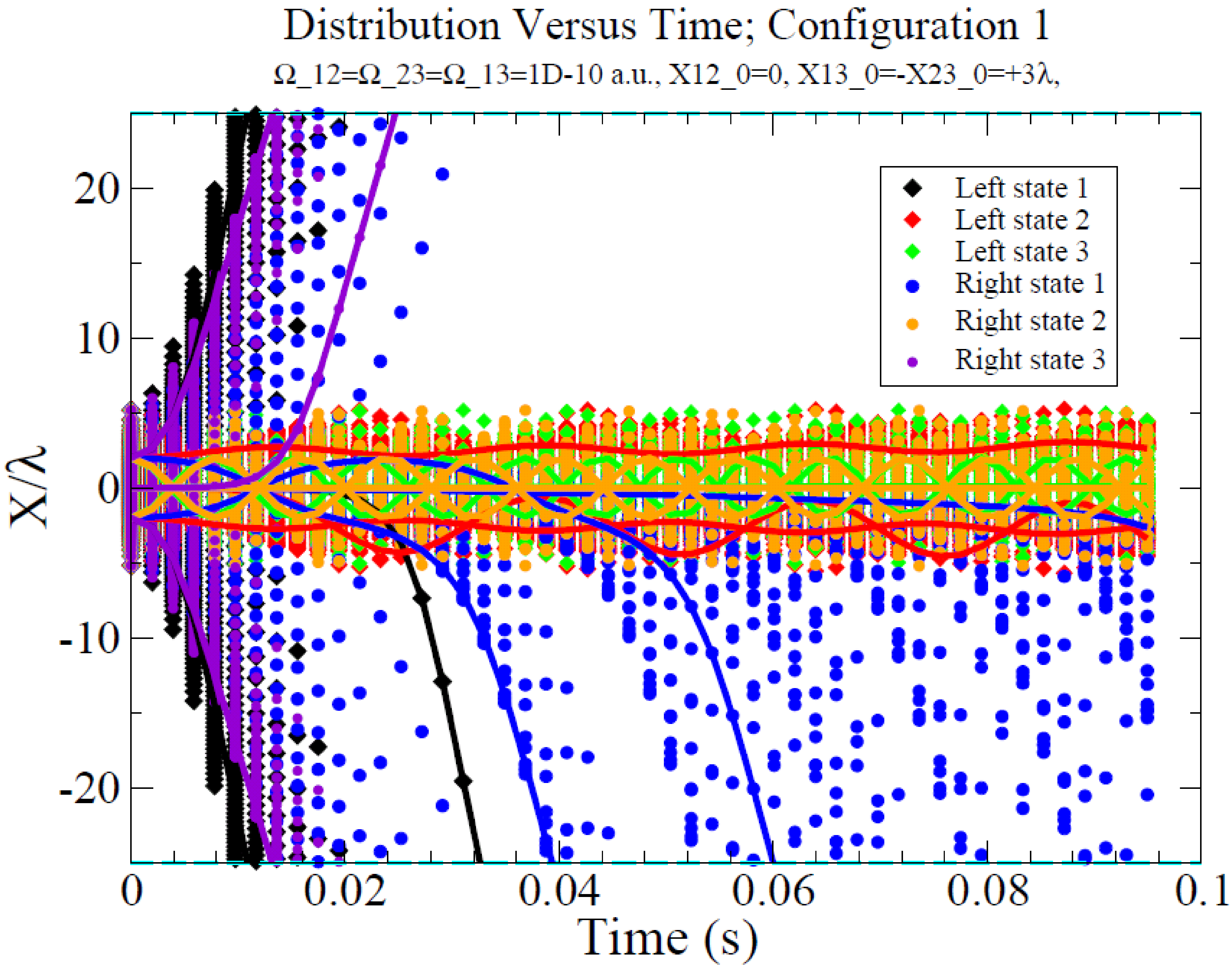
The vector potential satisfies the Coulomb gauge,

$$\nabla \cdot \mathbf{A}_i = 0.$$

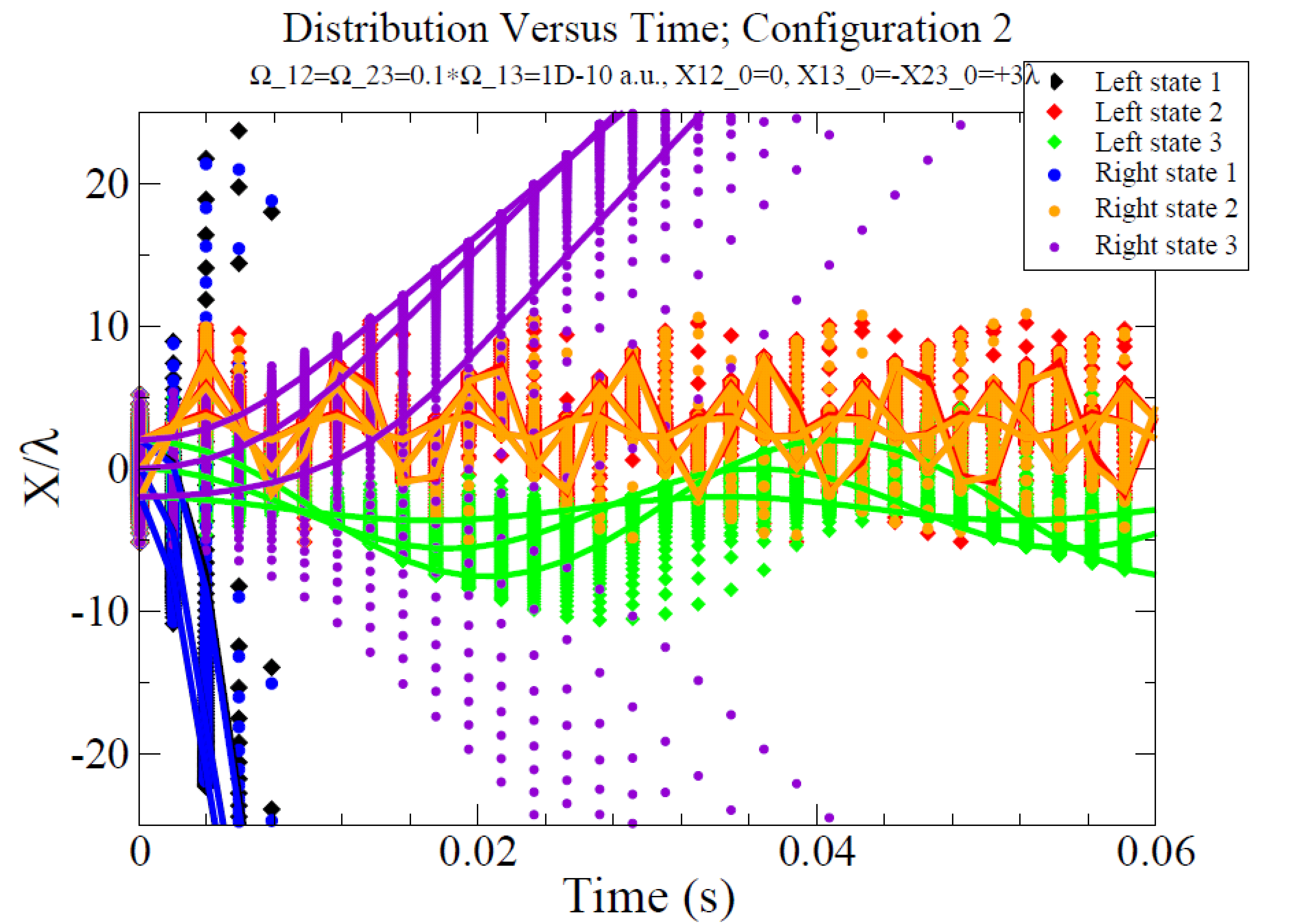
The dynamics for the center of mass motion:

$$\dot{x}_i = \frac{p_{ix}}{m}, \quad ,\dot{z}_i = \frac{p_{iz} - A_{iz}}{m}, \quad ,\dot{p}_{iz} = mg,$$

$$\dot{p}_{ix} = \frac{\hbar}{m}\left[\frac{\partial A_{iz}}{\partial x} p_{iz} - A_{iz}\frac{\partial p_{iz}}{\partial x}\right] - \frac{\partial V_i}{\partial x}$$



Distribution Versus Time; Configuration 1
Ω_12=Ω_23=Ω_13=1D-10 a.u., X12_0=0, X13_0=-X23_0=+3λ,
Left state 1
Left state 2
Left state 3
Right state 1
Right state 2
Right state 3
20
10
0
-10
-20
X/λ
0
0.02
0.04
0.06
0.08
0.1
Time (s)


Distribution Versus Time; Configuration 2
Ω_12=Ω_23=0.1*Ω_13=1D-10 a.u., X12_0=0, X13_0=-X23_0=+3λ
Left state 1
Left state 2
Left state 3
Right state 1
Right state 2
Right state 3
20
10
0
-10
-20
X/λ
0
0.02
0.04
0.06
Time (s)

The Hund Paradox and the Formation of Schroedinger Cat States

P. Král, I. Thanopulos, and M. Shapiro, Phys. Rev. A **72**, 020303 (2005)

Loop adiabatic passage for light Cat States