An (Electronic) Spin on Nuclear Dynamics near Conical Intersections

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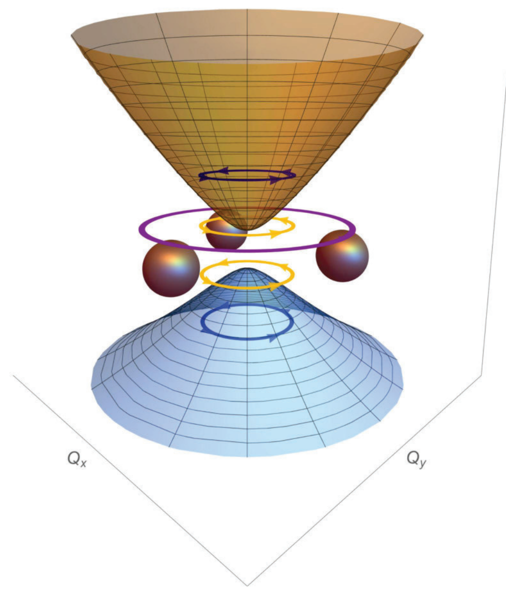
VISTA, 2 October 2024



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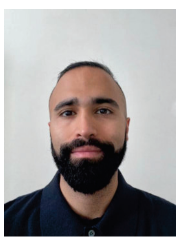
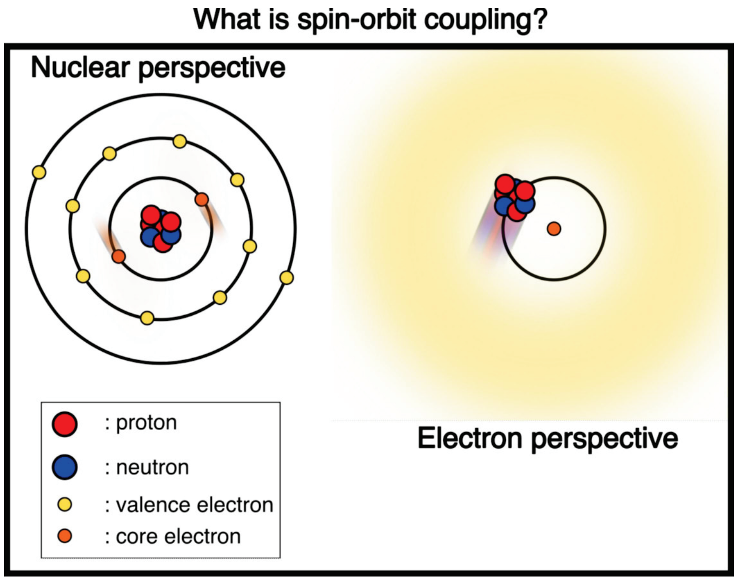


Twana Cheragwandi

Nanna H. List

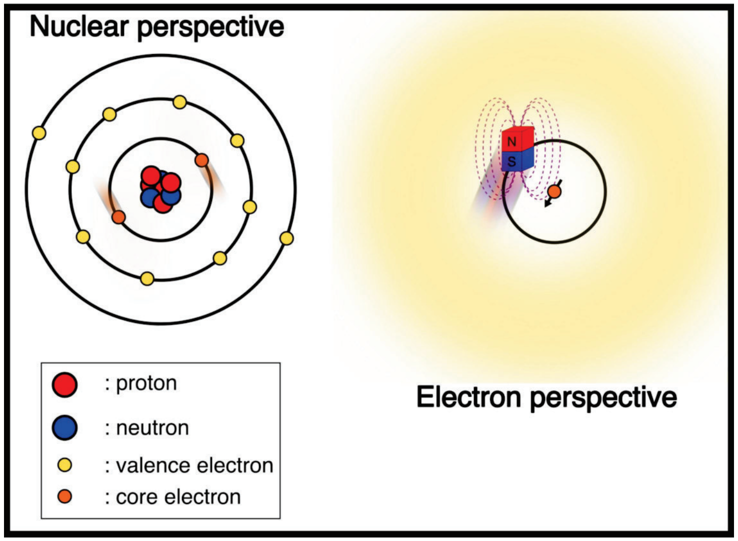
Wenner-Gren Foundations

Research Focus: Synergism between SO Coupling and non-Adiabatic Dynamics



Research Focus: Synergism between SO Coupling and non-Adiabatic Dynamics

What is spin-orbit coupling?



SO coupling

- SO coupling is often treated perturbatively

$$\hat{H}_e = \hat{H}_0 + \hat{H}_{SO}; \quad \hat{H}_{SO} = \sum_{\nu=1}^{N_n} \xi_\nu \hat{\boldsymbol{\ell}}_\nu \cdot \hat{\boldsymbol{S}}$$

$$\xi_\nu = \frac{e}{2m_e^2c^2} \frac{Z_\nu e}{4\pi\epsilon_0 |\boldsymbol{r} - \boldsymbol{R}_\nu|^3}; \quad \hat{\boldsymbol{\ell}}_\nu = (\boldsymbol{r} - \boldsymbol{R}_\nu) \times \hat{\boldsymbol{p}}$$

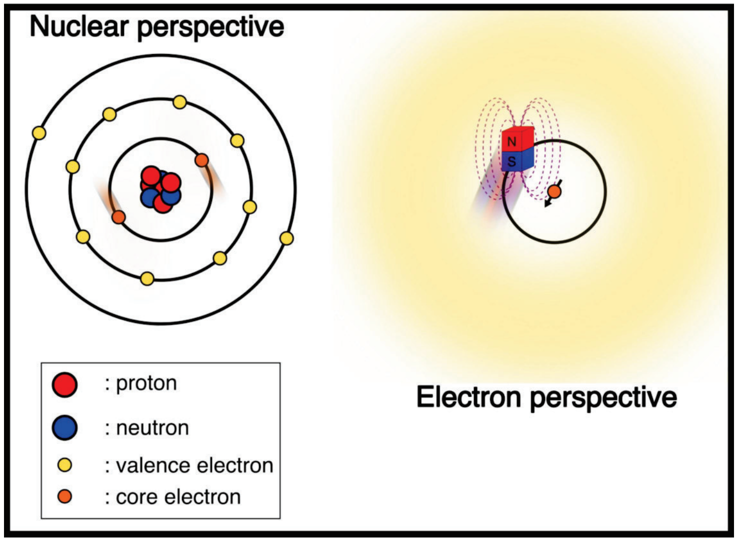
Born-Oppenheimer approximation

- Born-Huang expansion:
  $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_n \chi_n(\boldsymbol{R}, t)\psi_n(\boldsymbol{r}; \boldsymbol{R})$
  with: $\hat{H}_e\psi_n(\boldsymbol{r}; \boldsymbol{R}) = V_n(\boldsymbol{R})\psi_n(\boldsymbol{r}; \boldsymbol{R})$
- BO Ansatz: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) \approx \chi_n(\boldsymbol{R}, t)\psi_n(\boldsymbol{r}; \boldsymbol{R})$
- Nuclear EOM:
  $\Big(\frac{-\hbar^2}{2}(\boldsymbol{\nabla}_R - i\boldsymbol{A}_n)^2 + \tilde{V}_n(\boldsymbol{R})\Big)\chi_n = i\hbar\partial_t\chi_n$
- Non-adiabatic coupling: $\boldsymbol{A}_n = \langle\psi_n|i\boldsymbol{\nabla}_R|\psi_n\rangle$
- relevant if:
  1. a magnetic interaction is present (such as an external magnetic field or SO coupling)
  2. a conical intersection is present on the PES

$$\exists \boldsymbol{R}_0 \text{ s.t. } V_n(\boldsymbol{R}_0) = \boldsymbol{V}_m(\boldsymbol{R}_0)$$

Research Focus: Synergism between SO Coupling and non-Adiabatic Dynamics

What is spin-orbit coupling?



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$$\xi_\nu = \frac{e}{2m_e^2 c^2} \frac{Z_\nu e}{4\pi\epsilon_0 |\boldsymbol{r} - \boldsymbol{R}_\nu|^3}; \quad \hat{\boldsymbol{\ell}}_\nu = (\boldsymbol{r} - \boldsymbol{R}_\nu) \times \hat{\boldsymbol{p}}$$

Ehrenfest Theorem

- Semi-classical force: $\boldsymbol{F}_N = \boldsymbol{F}_V + \boldsymbol{F}_m$

$$\boldsymbol{F}_V = -\boldsymbol{\nabla}_R \tilde{V}_n(\bar{\boldsymbol{R}}); \quad F_{m;\mu} = \sum_{\nu=1}^{3N_n} \Omega_{n;\mu\nu} \dot{\bar{R}}_\nu$$

- field strength tensor:

$$\Omega_{n;\mu\nu} = \partial_\mu A_{n;\nu} - \partial_\mu A_{n;\mu}$$

- three-dimensional case:

$$\boldsymbol{F}_m = \boldsymbol{B}_n \times \dot{\bar{\boldsymbol{R}}}; \quad \boldsymbol{B}_n = \boldsymbol{\nabla}_R \times \boldsymbol{A}_n$$

D. Ceresoli *et al.* *Phys. Rev. B, Condens. Matter*, **2007**, *75*, 161101
T. Culpitt *et al.* *J. Chem. Phys.*, **2021**, *155*, 024104

Overview of the Presentation

Overall research goals:

- understand the underlying physics
- develop theory beyond perturbative treatment of SO
- fundamental approach (four-component relativistic theory)

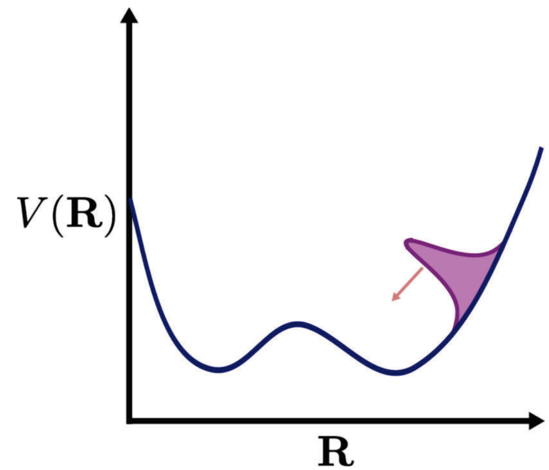
Overview of the Presentation

Presentation goal:

Illustrate the synergism between spin-orbit- and non-adiabatic coupling using a simple triatomic model

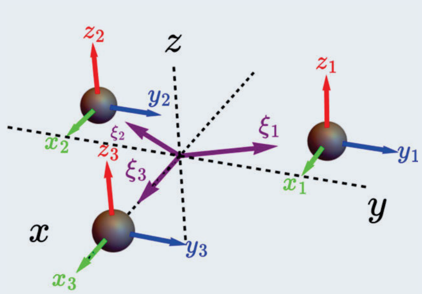
General strategy

- system: triatomic molecule (X_3)
- nuclear wave function propagated on the adiabatic PES
- simulation repeated:
  1. with and without SO coupling
  2. with and without non-adiabatic coupling



The Model: Standard $E \times e$ Jahn-Teller System

Triatomic model (X_3)



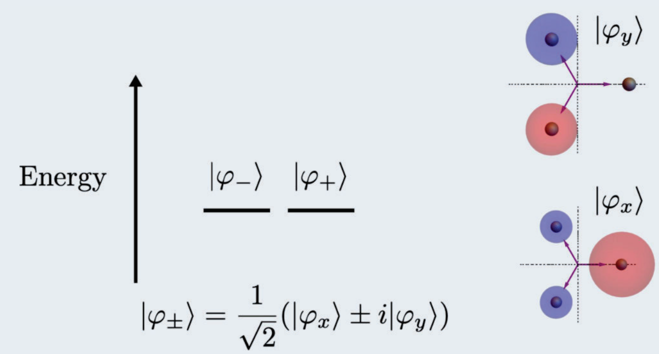
- 3 s-orbitals → 3 MOs (A, E)
- only E orbitals are occupied
- 1 electron

electronic

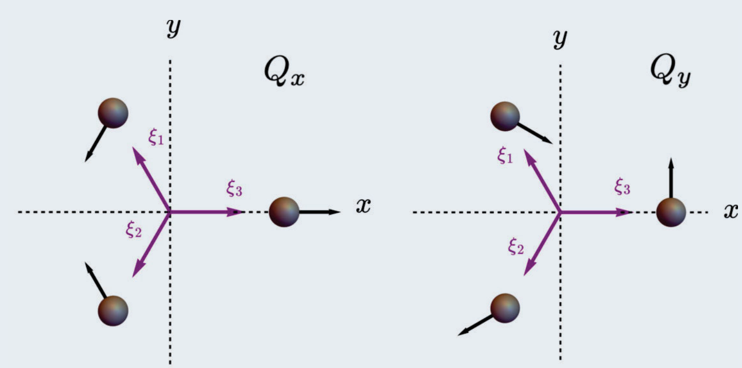
- three normal modes (Q_1, Q_x, Q_y)
- allowed motion: (Q_x, Q_y)

nuclear

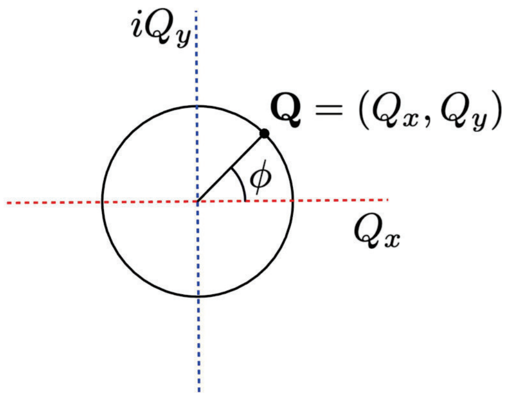
Electronic (E)



Nuclear (e)



Diabatic Representation of the Model Hamiltonian



$$\phi = \arctan(Q_y/Q_x)$$

$$Q = \sqrt{Q_x^2 + Q_y^2}$$

Polar form normal modes

Deriving the LVC model

- Diabatic Hamiltonian

$$\hat{H}_d = \hat{T}_N \mathbb{I}_2 + \hat{W}(\boldsymbol{Q}); \quad W_{mn}(\boldsymbol{Q}) = \langle \varphi_m | \hat{H}_e | \varphi_n \rangle$$

- Second-order expansion:

$$W(\boldsymbol{Q}) = W(0) + \sum_{i=x,y} \frac{\partial W}{\partial Q_i}|_{Q=0} Q_i + \sum_{i=x,y} \frac{\partial^2 W}{\partial Q_i^2}|_{Q=0} Q_i^2 + \cdots$$

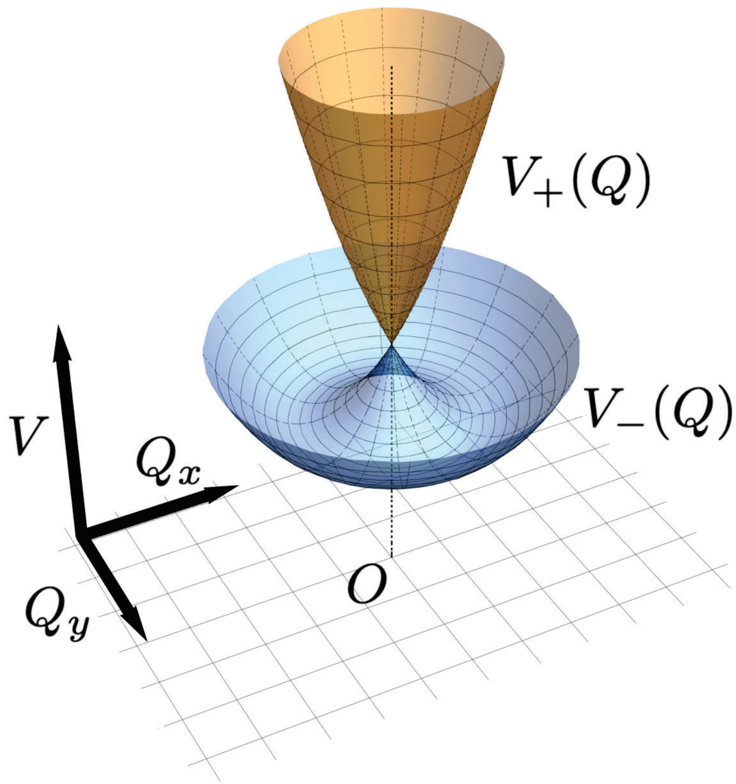
- LVC model:

$$\hat{W}(\boldsymbol{Q}) = \begin{pmatrix} E_0 + kQ^2 & Qe^{-i\phi} \\ Qe^{i\phi} & E_0 + kQ^2 \end{pmatrix}$$

- how can this be related to?

$$\hat{H}^n_{ad} = \frac{-\hbar^2}{2} (\boldsymbol{\nabla}_R - i\boldsymbol{A}_n)^2 + \tilde{V}_n(\boldsymbol{R})$$

Adiabatic Potential Energy surfaces



G. A. Worth and L. S. Cederbaum, *Annu. Rev. Phys.*, **2004**, *55*, 127–128

Diagonalization of the diabatic potential

- Diagonalization yields the adiabatic potential

$$S(\boldsymbol{Q})W(\boldsymbol{Q})S^{\dagger}(\boldsymbol{Q}) = \begin{pmatrix} V_+(\boldsymbol{Q}) & 0 \\ 0 & V_-(\boldsymbol{Q}) \end{pmatrix}$$

where

$$V_{\pm}(\boldsymbol{Q}) = E_0 + kQ^2 \pm gQ$$

- adiabatic states

$$|\psi_n(\boldsymbol{Q})\rangle = \sum_{m=\pm} S_{nm}|\varphi_m\rangle$$

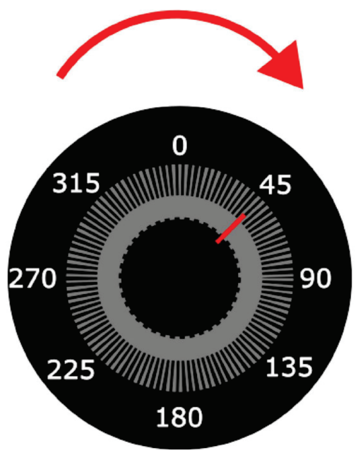
- diagonalization defined up to a local phase

$$\boxed{|\psi_{\pm}(\boldsymbol{Q})\rangle \rightarrow e^{i\Theta(\boldsymbol{Q})}|\psi_n(\boldsymbol{Q})\rangle}$$

$$\Theta(\mathbf{Q})$$

Single-valued

- simpler states
- $\boldsymbol{A}_n \neq 0$
- more complicated $\hat{H}^n_{ad}$



Multi-valued

- more complicated states
- $\boldsymbol{A}_n = 0$
- simpler $\hat{H}^n_{ad}$

$$\boldsymbol{A}_n \rightarrow \boldsymbol{A}_n - \nabla_Q \Theta(\boldsymbol{Q})$$

Pacher, T. Mead, L. S. Cederbaum, Köppel, H. *J. Chem. Phys.* **1989**, *91*, 7057–7062 Mead, C. A.; Truhlar, D.G. *J. Chem. Phys.* **1979**, *70*, 2284–2296

Single-Valued Adiabatic Functions

Single-valued

- adiabatic wave function

$$|\psi_\pm(\phi)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \pm 1 \\ e^{i\phi} \end{pmatrix}$$

- single-valued

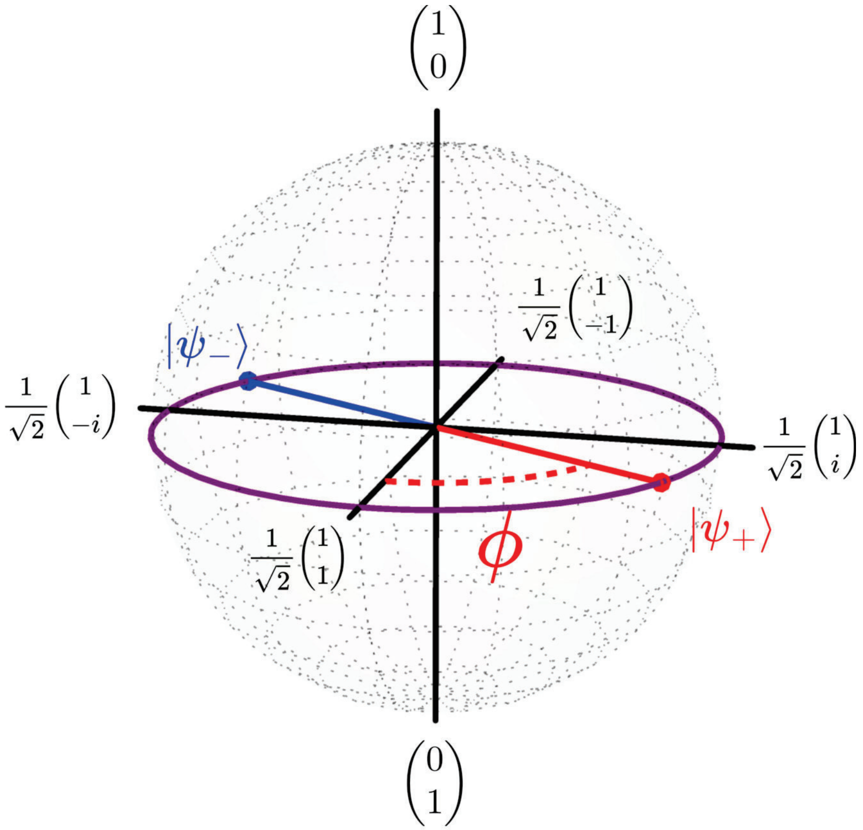
$$|\psi_\pm(\phi + 2\pi)\rangle = |\psi_\pm(\phi)\rangle$$

- non-adiabatic coupling

$$\boldsymbol{A}_\pm = \frac{-1}{2} \boldsymbol{\nabla}_R \phi = \frac{-\boldsymbol{e}_\phi}{2Q}$$

- adiabatic Hamiltonian

$$\hat{H}^{ad}_\pm = \hat{T}_N + V_\pm(Q) + \frac{\hbar}{2MQ^2}(\hat{L}_z + \frac{\hbar}{2})$$

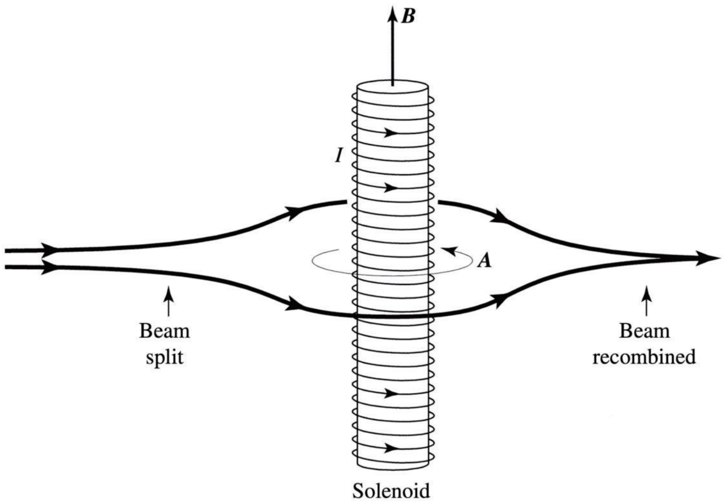


The Molecular Aharonov-Bohm Effect

Field Strength Tensor

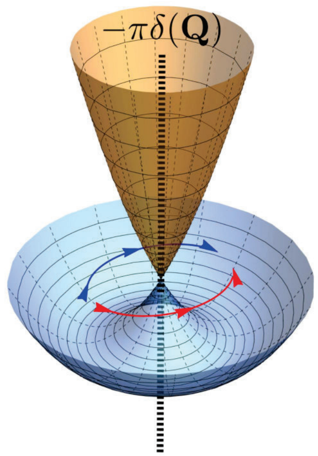
$$\Omega_{-;xy} = -\pi\delta(\boldsymbol{Q})$$

Aharonov-Bohm Effect



Griffiths Introduction to Quantum Mechanics (3rd ed.)

Molecular Aharonov-Bohm Effect



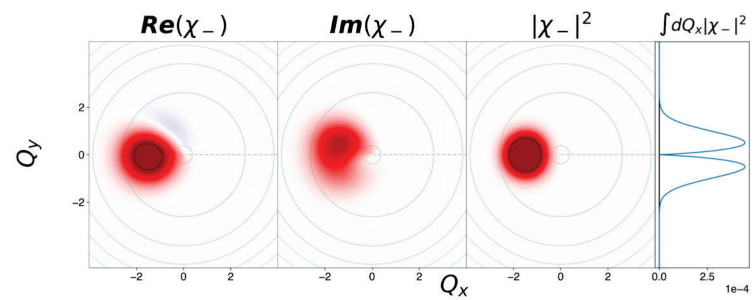
Mead, C. A.; Truhlar, D.G. *J. Chem. Phys.* **1979**, *70*, 2284–2296

Nuclear Dynamics on Lower Adiabatic Surface (Single-Valued Electronic States)

$k = 2$; $g = 6$; $\chi_-(\boldsymbol{Q}, 0) = \exp[-\frac{k}{2}(\boldsymbol{Q} - \boldsymbol{Q}_0)]$; $\boldsymbol{Q}_0 = Q_{min}\boldsymbol{e}_x$

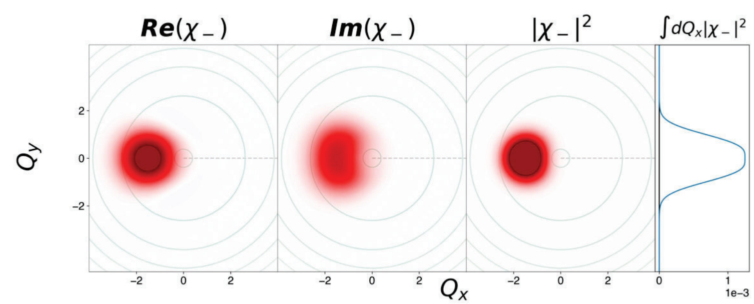
($\boldsymbol{A}_- \neq 0$)

$$\hat{H}^{ad}_{\pm} = \hat{T}_N + V_{\pm}(Q) + \frac{\hbar}{2MQ^2}(\hat{L}_z + \frac{\hbar}{2})$$



($\boldsymbol{A}_- = 0$)

$$\hat{H}^{ad}_{\pm} = \hat{T}_N + V_{\pm}(Q) + \cancel{\frac{\hbar}{2MQ^2}(\hat{L}_z + \frac{\hbar}{2})}$$



$E \times e$ Jahn-Teller System with SO Coupling

What changes?

- Hamiltonian: $\hat{H}_e \rightarrow \hat{H}_0 + \hat{H}_{SO}$
- 3 s-orbitals $\rightarrow$ $(3s_\alpha\text{-}orbitals, 3s_\beta\text{-}orbitals)$
- 6 MOs: $(4A_{3/2},^1 E_{1/2},^2 E_{1/2})$
- nearly degenerate $(2A_{3/2},^1 E_{1/2},^2 E_{1/2})$ shell occupied

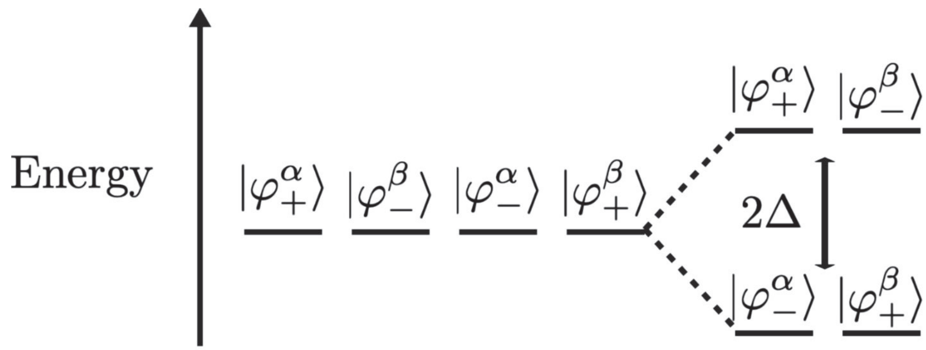
Time-reversal

- time-reversal operator: $\hat{\mathcal{K}} = i\hat{K}\sigma_y$
- Kramers partners

$$\hat{\mathcal{K}}|\varphi^\alpha_\pm\rangle = |\varphi^\beta_\mp\rangle; \quad \hat{\mathcal{K}}|\varphi^\beta_\pm\rangle = -|\varphi^\alpha_\mp\rangle$$

- Kramers degeneracy
$\langle\varphi^\alpha_\pm|\hat{H}_e|\varphi^\alpha_\pm\rangle = \langle\varphi^\alpha_\pm|\hat{\mathcal{K}}^{-1}\hat{\mathcal{K}}\hat{H}_e\hat{\mathcal{K}}^{-1}\hat{\mathcal{K}}|\varphi^\alpha_\pm\rangle = \langle\varphi^\beta_\mp|\hat{H}_e|\varphi^\beta_\mp\rangle$

SO splitting



$$|\varphi^\alpha_\pm\rangle = \varphi_\pm|\alpha\rangle \qquad |\varphi^\beta_\pm\rangle = \varphi_\pm|\beta\rangle$$

Diabatic Representation Including Spin-Orbit Coupling

The LVC model revised

- four-dimensional diabatic Hamiltonian

$$\hat{H}_d = \hat{T}_N \mathbb{I}_4 + \hat{W}(\boldsymbol{Q})$$

- diabatic potential matrix

$$W(\boldsymbol{Q}) = \begin{pmatrix} \langle \varphi_+^\alpha | \hat{H}_e | \varphi_+^\alpha \rangle & \langle \varphi_+^\alpha | \hat{H}_e | \varphi_-^\beta \rangle & \langle \varphi_+^\alpha | \hat{H}_e | \varphi_-^\alpha \rangle & \langle \varphi_+^\alpha | \hat{H}_e | \varphi_+^\beta \rangle \\ \langle \varphi_-^\beta | \hat{H}_e | \varphi_+^\alpha \rangle & \langle \varphi_-^\beta | \hat{H}_e | \varphi_-^\beta \rangle & \langle \varphi_-^\beta | \hat{H}_e | \varphi_-^\alpha \rangle & \langle \varphi_-^\beta | \hat{H}_e | \varphi_+^\beta \rangle \\ \langle \varphi_-^\alpha | \hat{H}_e | \varphi_+^\alpha \rangle & \langle \varphi_-^\alpha | \hat{H}_e | \varphi_-^\beta \rangle & \langle \varphi_-^\alpha | \hat{H}_e | \varphi_-^\alpha \rangle & \langle \varphi_-^\alpha | \hat{H}_e | \varphi_+^\beta \rangle \\ \langle \varphi_+^\beta | \hat{H}_e | \varphi_+^\alpha \rangle & \langle \varphi_+^\beta | \hat{H}_e | \varphi_-^\beta \rangle & \langle \varphi_+^\beta | \hat{H}_e | \varphi_-^\alpha \rangle & \langle \varphi_+^\beta | \hat{H}_e | \varphi_+^\beta \rangle \end{pmatrix}$$

C. Alden Mead. *Chem. Phys.* **1980**, *49*, 33–38.
H. Koizumi and S. Sugano, *JCP*, **1995**, *102*, 4472–4481.

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$$\hat{H}_d = \hat{T}_N \mathbb{I}_4 + \hat{W}(\boldsymbol{Q})$$

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$$= \begin{pmatrix} w & v \\ -v^* & w^* \end{pmatrix}$$

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H. Koizumi and S. Sugano, *JCP*, **1995**, *102*, 4472–4481.

Diabatic Representation Including Spin-Orbit Coupling

The LVC model revised

- four-dimensional diabatic Hamiltonian

$$\hat{H}_d = \hat{T}_N \mathbb{I}_4 + \hat{W}(\boldsymbol{Q})$$

- diabatic potential matrix

$$W(\boldsymbol{Q}) = \begin{pmatrix} \langle \varphi_+^\alpha | \hat{H}_e | \varphi_+^\alpha \rangle & 0 & \langle \varphi_+^\alpha | \hat{H}_e | \varphi_-^\alpha \rangle & 0 \\ 0 & \langle \varphi_-^\beta | \hat{H}_e | \varphi_-^\beta \rangle & 0 & \langle \varphi_-^\beta | \hat{H}_e | \varphi_+^\beta \rangle \\ \langle \varphi_-^\alpha | \hat{H}_e | \varphi_+^\alpha \rangle & 0 & \langle \varphi_-^\alpha | \hat{H}_e | \varphi_-^\alpha \rangle & 0 \\ 0 & \langle \varphi_+^\beta | \hat{H}_e | \varphi_-^\beta \rangle & 0 & \langle \varphi_+^\beta | \hat{H}_e | \varphi_+^\beta \rangle \end{pmatrix}$$

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$$\hat{H}_d = \hat{T}_N \mathbb{I}_4 + \hat{W}(\boldsymbol{Q})$$

- diabatic potential matrix

$$W = \begin{pmatrix} E_0 + \Delta + kQ^2 & gQ_- & 0 & 0 \\ gQ_+ & E_0 - \Delta + kQ^2 & 0 & 0 \\ 0 & 0 & E_0 + \Delta + kQ^2 & gQ_+ \\ 0 & 0 & gQ_- & E_0 - \Delta + kQ^2 \end{pmatrix}$$

reordering of basis: $(|\varphi_+^\alpha\rangle, |\varphi_-^\beta\rangle, |\varphi_-^\alpha\rangle, |\varphi_+^\beta\rangle) \rightarrow (|\varphi_+^\alpha\rangle, |\varphi_-^\alpha\rangle, |\varphi_-^\beta\rangle, |\varphi_+^\beta\rangle)$

C. Alden Mead. *Chem. Phys.* **1980**, *49*, 33–38.
H. Koizumi and S. Sugano, *JCP*, **1995**, *102*, 4472–4481.

Diabatic Representation Including Spin-Orbit Coupling

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$$\hat{H}_d = \hat{T}_N \mathbb{I}_4 + \hat{W}(\boldsymbol{Q})$$

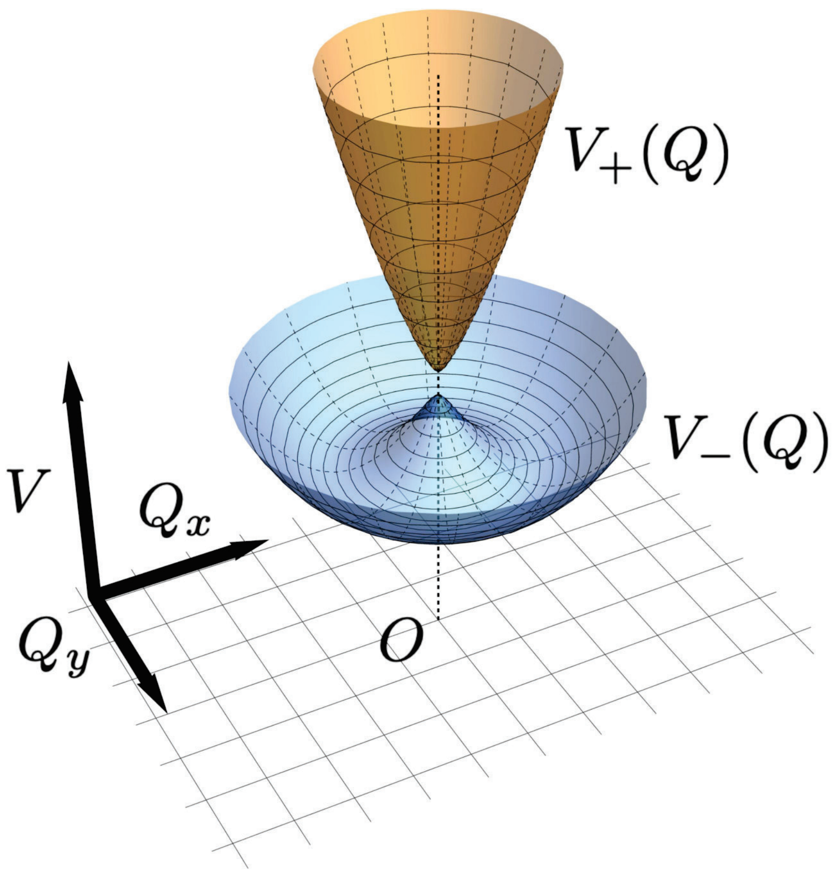
- diabatic potential matrix

$$w(\boldsymbol{Q}) = \begin{pmatrix} E_0 + kQ^2 + \rho\cos\theta & \rho\sin\theta e^{-i\phi} \\ \rho\sin\theta e^{i\phi} & E_0 + kQ^2 - \rho\cos\theta \end{pmatrix}$$

$$\rho = \sqrt{\Delta^2 + g^2 Q^2}; \quad \theta = \arctan\left(\frac{gQ}{\Delta}\right)$$

C. Alden Mead. *Chem. Phys.* **1980**, *49*, 33–38.
H. Koizumi and S. Sugano, *JCP*, **1995**, *102*, 4472–4481.

Adiabatic Potential with SO Coupling



Diagonalization of the diabatic potential matrix

- similar approach to obtain the adiabatic potential

$$S(\boldsymbol{Q})W(\boldsymbol{Q})S^\dagger(\boldsymbol{Q}) = \begin{pmatrix} V_+(\boldsymbol{Q}) & 0 \\ 0 & V_-(\boldsymbol{Q}) \end{pmatrix}$$

- adiabatic potential

$$V_\pm(\boldsymbol{Q}) = E_0 + kQ^2 \pm \sqrt{\Delta^2 + g^2 Q^2}$$

- no conical intersection

$$V_\pm(0) = \pm\Delta$$

- adiabatic states defined up to a local phase

Adiabatic States

Single-valued

- single-valued functions with two angles

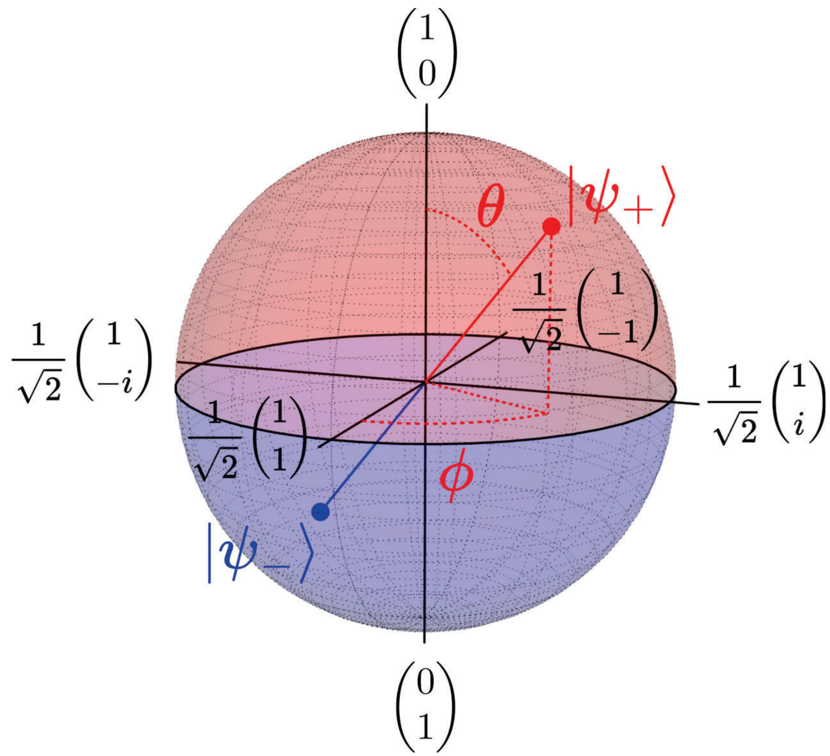
$$|\psi_+\rangle = \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} e^{i\phi} \end{pmatrix}; \quad |\psi_-\rangle = \begin{pmatrix} -\sin\frac{\theta}{2} e^{-i\phi} \\ \cos\frac{\theta}{2} \end{pmatrix}$$

- non-adiabatic coupling

$$\boldsymbol{A}_\pm = \pm\frac{1}{2Q}(1 - \cos\theta)\boldsymbol{e}_\phi$$

- adiabatic Hamiltonian

$$\hat{H}^{ad}_\pm = \hat{T}_N + V_\pm(Q) \mp \frac{\hbar}{2Q^2}(1 - \cos\theta)(\hat{L}_z + \frac{\hbar}{2})$$



Pseudo-Magnetic Field with SO Coupling

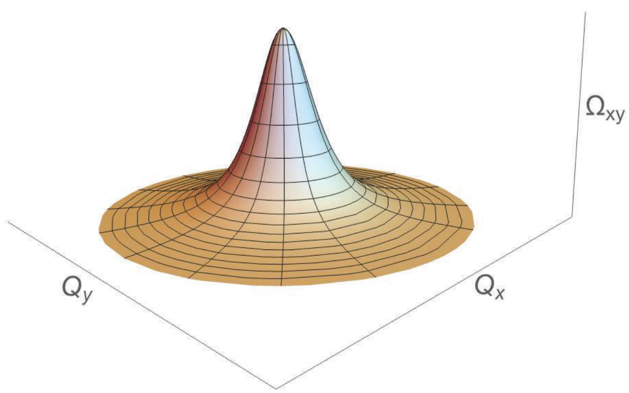
Field Strength Tensor

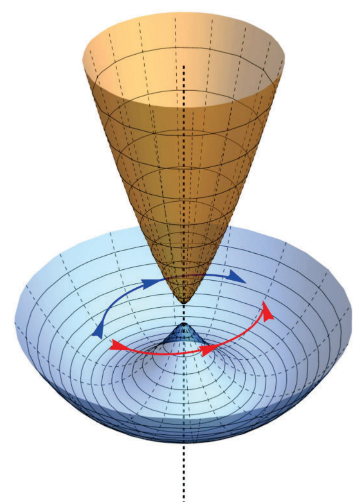
- pseudo-magnetic field

$$\Omega_{\pm;xy} = \pm \frac{g^2 \Delta}{2(\Delta^2 + g^2 Q^2)^{3/2}} = \pm \frac{g^2}{\sqrt{\Delta}} \cos^{3/2}\theta$$

- pseudo-magnetic force:

$$\boldsymbol{F}_{\pm} = \pm \frac{g^2}{\sqrt{\Delta}} \cos^{3/2}\theta \left(v_{Q_x} \boldsymbol{e}_x - v_{Q_y} \boldsymbol{e}_y \right)$$

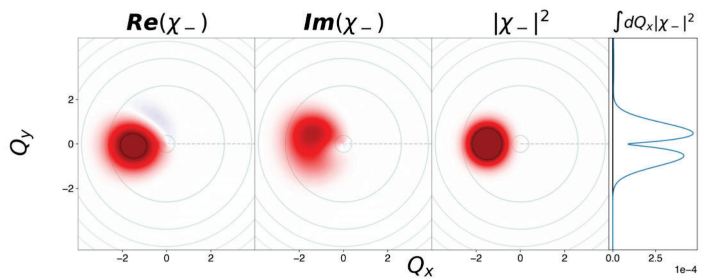




C. Alden Mead, *Chem. Phys.* **1980**, *49*, 33–38.

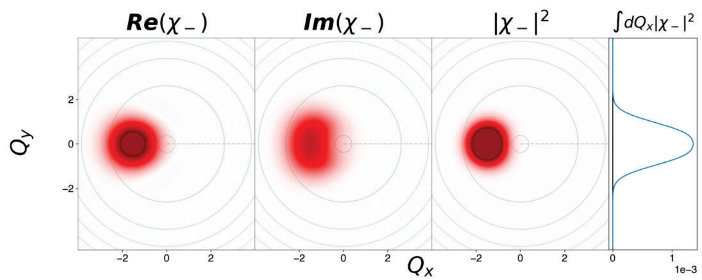
Dynamics of the Nuclear Wave Function Including SO Coupling

$k = 2$; $g = 6$; $\Delta = 0.2$; $\chi_-(\boldsymbol{Q}, 0) = \exp[-\frac{k}{2}(\boldsymbol{Q} - \boldsymbol{Q}_0)]$; $\boldsymbol{Q}_0 = Q_{min}\boldsymbol{e}_x$



$(\boldsymbol{A}_- \neq 0)$

$$\hat{H}^{ad}_- = \hat{T}_N + V_-(Q) + \frac{\hbar}{2Q^2}(1 - \cos\theta)(\hat{L}_z + \frac{\hbar}{2})$$



$(\boldsymbol{A}_- = 0)$

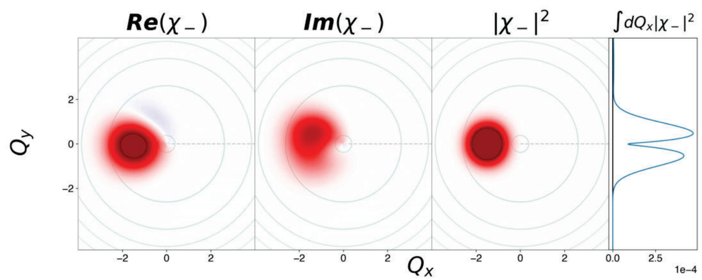
$$\hat{H}^{ad}_- = \hat{T}_N + V_\pm(Q) \cancel{+ \frac{\hbar}{2Q^2}(1 - \cos\theta)(\hat{L}_z + \frac{\hbar}{2})}$$

Dynamics of the Nuclear Wave Function Including SO Coupling

$k = 2$; $g = 6$; $\Delta = 0.2$; $\chi_-(\boldsymbol{Q}, 0) = \exp[-\frac{k}{2}(\boldsymbol{Q} - \boldsymbol{Q}_0)]$; $\boldsymbol{Q}_0 = Q_{min}\boldsymbol{e}_x$

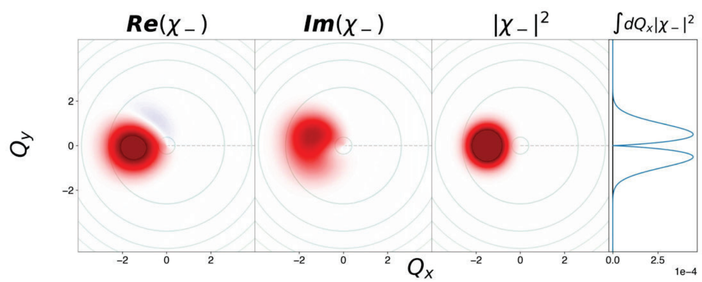
SO-coupled; $\boldsymbol{A}_- \neq 0$:

$$\hat{H}^{ad}_- = \hat{T}_N + V_-(Q) + \frac{\hbar}{2Q^2}(1 - \cos\theta)(\hat{L}_z + \frac{\hbar}{2})$$



No SO; $(\boldsymbol{A}_- \neq 0)$:

$$\hat{H}^{ad}_\pm = \hat{T}_N + V_\pm(Q) + \frac{\hbar}{2MQ^2}(\hat{L}_z + \frac{\hbar}{2})$$



Summary and Outlook

Without SO coupling:

- single- or multi-valued functions
- similarities with the AB effect

With SO coupling:

- cumbersome to define multi-valued functions s.t. $\boldsymbol{A}_n = 0$
- pseudo-magnetic force
- propagated wave function becomes more turbulent

What's on the horizon

- Exact SO coupling (4c relativistic formulation)

$$\hat{H}_D = i\hbar c\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta mc^2 + V$$

- Non-Abelian effects

$$W(\boldsymbol{Q}) = \begin{pmatrix} \langle\varphi_+^\alpha|\hat{H}_e|\varphi_+^\alpha\rangle & \langle\varphi_+^\alpha|\hat{H}_e|\varphi_-^\beta\rangle & \langle\varphi_+^\alpha|\hat{H}_e|\varphi_-^\alpha\rangle & \langle\varphi_+^\alpha|\hat{H}_e|\varphi_+^\beta\rangle \\ \langle\varphi_-^\beta|\hat{H}_e|\varphi_+^\alpha\rangle & \langle\varphi_-^\beta|\hat{H}_e|\varphi_-^\beta\rangle & \langle\varphi_-^\beta|\hat{H}_e|\varphi_-^\alpha\rangle & \langle\varphi_-^\beta|\hat{H}_e|\varphi_+^\beta\rangle \\ \langle\varphi_-^\alpha|\hat{H}_e|\varphi_+^\alpha\rangle & \langle\varphi_-^\alpha|\hat{H}_e|\varphi_-^\beta\rangle & \langle\varphi_-^\alpha|\hat{H}_e|\varphi_-^\alpha\rangle & \langle\varphi_-^\alpha|\hat{H}_e|\varphi_+^\beta\rangle \\ \langle\varphi_+^\beta|\hat{H}_e|\varphi_+^\alpha\rangle & \langle\varphi_+^\beta|\hat{H}_e|\varphi_-^\beta\rangle & \langle\varphi_+^\beta|\hat{H}_e|\varphi_-^\alpha\rangle & \langle\varphi_+^\beta|\hat{H}_e|\varphi_+^\beta\rangle \end{pmatrix}$$