

Nonadiabatic Couplings and Conical Intersections: Algorithmic Details

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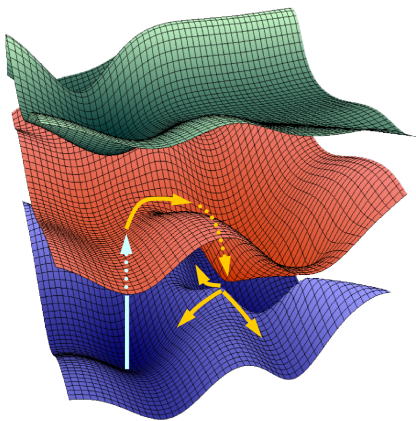
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Potential Energy Surfaces

- ▶ How to find minima?
- ▶ How to find conical intersections?
- Geometry optimization



Minima

- ▶ **Task:** find a local minimum of the PES $E_I(\mathbf{R})$ with respect to the nuclear coordinates $\mathbf{R} = R_1, \dots, R_n$
- ☹ We do not know the functional form of $E_I(\mathbf{R})$
- 😊 We can compute $E_I(\mathbf{R})$ at individual geometries
- 😊 We can compute the energy gradient $\nabla E_I(\mathbf{R})$

Minima

Newton-Raphson Method

- ▶ Find a root of a one-dimensional function $f(x)$

Taylor expansion

$$f(x) = f(x_0) + (x - x_0)f'(x_0)$$

- ▶ Try to find point x_1 where $f(x_1) = 0$

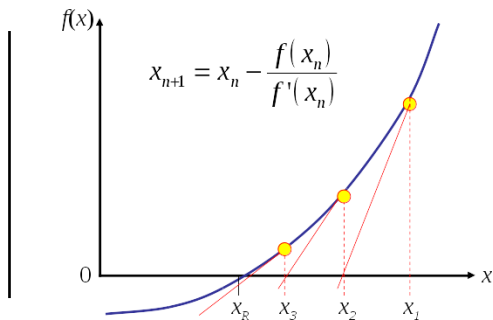
$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}$$

- ▶ Iterate

Minima

Newton-Raphson Method

- ▶ Iterative procedure



Minima

Newton-Raphson Method

- ▶ Find a **stationary point** of a one-dimensional function $f(x)$

Stationary point

$$f'(x) = 0$$

- ▶ Apply Newton-Raphson to the derivative

$$x_1 = x_0 - \frac{f'(x_0)}{f''(x_0)}$$

- ▶ Iterate

Minima

Newton-Raphson Method

- ▶ Find a stationary point of a **multi-dimensional** function $E_I(\mathbf{R})$

Gradient vector

$$\mathbf{g}(\mathbf{R}) = \nabla E_I(\mathbf{R})$$

$$g_i(\mathbf{R}) = \frac{\partial}{\partial R_i} E_I(\mathbf{R})$$

Talyer expansion of the gradient

$$\mathbf{g}(\mathbf{R}) = \mathbf{g}(\mathbf{R}_0) + \mathbf{H} \cdot (\mathbf{R} - \mathbf{R}_0)$$

$$H_{ij} = \frac{\partial^2}{\partial R_i \partial R_j} E_I(\mathbf{R})$$

Minima

Talyer expansion of the gradient

$$\mathbf{g}(\mathbf{R}) = \mathbf{g}(\mathbf{R}_0) + \mathbf{H} \cdot (\mathbf{R} - \mathbf{R}_0)$$

$$H_{ij} = \frac{\partial^2}{\partial R_i \partial R_j} E_I(\mathbf{R})$$

- ▶ Set the gradient to zero

$$\mathbf{R}_1 = \mathbf{R}_0 - \mathbf{H}^{-1} \mathbf{g}(\mathbf{R})$$

- ▶ Iterate

Minima

Quasi-Newton-Raphson Method

$$\mathbf{R}_1 = \mathbf{R}_0 - \mathbf{H}^{-1}\mathbf{g}(\mathbf{R})$$

- ▶ Estimate \mathbf{H}^{-1}
- ▶ *Initial guess*: diagonal Hessian with respect to internal coordinates
intcfl file
- ▶ *Hessian update*

Minima

Direct inversion in the iterative subspace (DIIS)

- ▶ Consider all previous geometries in the optimization
- ▶ `gdiis` program

MXS optimization

MXS optimization

Task $\frac{E_I(\mathbf{R})+E_J(\mathbf{R})}{2} \rightarrow \min$

Condition $E_I(\mathbf{R}) = E_J(\mathbf{R})$

- ☹ The surfaces are **not differentiable** at the conical intersection
- 😊 We can compute the **coupling vectors**
 - ▶ Idea: separate the intersection and branching spaces
 - ▶ **Optimize the energy** in the intersection space
 - ▶ **Minimize the gap** in the branching space

MXS Optimization

Several methods available

- ▶ Gradient projection
- ▶ Lagrange Newton
- ▶ Penalty function

MXS Optimization

Gradient projection

- ▶ Projected gradient in the **intersection space**

Projected gradient

$$\mathbf{g}_p = (\mathbf{1} - \mathbf{g}_{IJ}\mathbf{g}_{IJ}^T - \mathbf{h}_{IJ}\mathbf{h}_{IJ}^T) \nabla E_J$$

\mathbf{g}_{IJ} Gradient difference vector

\mathbf{h}_{IJ} Nonadiabatic coupling vector

- ▶ Minimization of the gap in the **branching space**
 - Follow \mathbf{g}_{IJ}

¹ Bearpark, Robb, and Schlegel 1994, .

MXS Optimization

Lagrange Newton

- ▶ Introduce Lagrange multipliers for the degeneracy

Lagrangian

$$L(\mathbf{R}, \lambda_1, \lambda_2) = E_I(\mathbf{R}) + \lambda_1 \Delta E_{IJ}(\mathbf{R}) + \lambda_2 H_{IJ}$$

- ▶ Optimize the Lagrangian using Newton-Raphson/GDIIS
- ▶ In COLUMBUS

¹ M. Dallos et al. *J. Chem. Phys.* **2004**, 120, 7330.

MXS Optimization

Penalty function

$$f(\mathbf{R}) = \frac{E_I + E_J}{2} c_1 c_2^2 \ln \left(1 + \frac{E_I - E_J}{c_2} \right)^2$$

- ▶ Minimize a **penalty function**
 - Optimize the energy
 - Minimize the gap
- ▶ Optimization **without nonadiabatic coupling vectors**

¹ Ciminelli, Granucci, and Persico 2004, .

Gradients

Energy expectation value

$$E = \langle \Psi | \hat{H} | \Psi \rangle$$

$$E(\mathbf{R}) = \langle \Psi(\mathbf{k}(\mathbf{R})) | \hat{H}(\mathbf{R}) | \Psi(\mathbf{k}(\mathbf{R})) \rangle$$

\mathbf{R} Nuclear geometry

$\mathbf{k}(\mathbf{R})$ Wavefunction parameters (e.g. orbital and CI coefficients)

Gradients

Energy expectation value

$$E(\mathbf{R}) = \langle \Psi(\mathbf{k}(\mathbf{R})) | \hat{H}(\mathbf{R}) | \Psi(\mathbf{k}(\mathbf{R})) \rangle$$

Energy gradient

$$\frac{\partial}{\partial R_x} E(\mathbf{R}) \equiv E^x = \langle \Psi | \hat{H}^x | \Psi \rangle + 2 \sum_i \langle \Psi | \hat{H} \left| \frac{\partial}{\partial k_i} \Psi \right\rangle k_i^x$$

R_x One nuclear coordinate

E^x Derivative of the energy with respect to R_x

k_i^x Derivative of wavefunction parameter k_i with respect to R_x

Chain rule!

Gradients

Variational methods

Energy gradient

$$E^x = \langle \Psi | \hat{H}^x | \Psi \rangle + 2 \sum_i \langle \Psi | \hat{H} \left| \frac{\partial}{\partial k_i} \Psi \right\rangle k_i^x$$

Variationally optimized wavefunction

$$0 = \frac{\partial}{\partial k_i} \langle \Psi | \hat{H} | \Psi \rangle = 2 \langle \Psi | \hat{H} \left| \frac{\partial}{\partial k_i} \Psi \right\rangle$$

- Generalized **Hellman-Feynman theorem**

Energy gradient

$$E^x = \langle \Psi | \hat{H}^x | \Psi \rangle$$

Gradients

Variational methods

- ▶ State-specific MCSCF
- 😊 Variational
- ▶ State-averaged MCSCF
- ☹️ Orbitals not variational
 - Orbitals are optimized for the average energy and not for the individual states*
- ▶ MR-CI
- ☹️ Orbitals not variational

Gradient

State-specific MCSCF

Energy gradient

$$E^x = \langle \Psi | \hat{H}^x | \Psi \rangle$$

Practical steps

- ▶ Compute the 1- and 2-particle density matrices (DM)
`mcscf.x`
- ▶ Transform the DMs to the AO basis
`tran.x`
- ▶ Compute the **AO integral derivatives** and contract them with the DMs
`dalton.x` “abacus”

Gradients

Non-variational methods

Energy gradient

$$\begin{aligned}
 E^x &= \langle \Psi | \hat{H}^x | \Psi \rangle + 2 \sum_i \langle \Psi | \hat{H} \left| \frac{\partial}{\partial k_i} \Psi \right\rangle k_i^x \\
 &= \langle \Psi | \hat{H}^x | \Psi \rangle + \sum_i f_i k_i^x \\
 &= \langle \Psi | \hat{H}^x | \Psi \rangle + \mathbf{f} \cdot \mathbf{k}^x
 \end{aligned}$$

\mathbf{f} Wavefunction gradient

How does the energy change if I change the parameters? – easy

\mathbf{k}^x Geometric parameter derivatives

How do the parameters change if I change the geometry? – difficult

Gradients

We know how the reference wavefunction was constructed!

Reference wavefunction

$$\mathbf{f}_{\text{ref}}(\mathbf{R}, \mathbf{k}(\mathbf{R})) = \mathbf{0}$$

\mathbf{f}_{ref} Wavefunction gradient of the reference wavefunction, e.g. MCSCF
Vanishes since the reference wavefunction was optimized

Geometric derivative

$$\mathbf{f}_{\text{ref}}^x + \sum_j \frac{\partial}{\partial k_j} \mathbf{f}_{\text{ref}} \cdot \mathbf{k}^x = \mathbf{0}$$

$$\mathbf{f}_{\text{ref}}^x + \mathbf{G} \mathbf{k}^x = \mathbf{0}$$

\mathbf{G} Wavefunction Hessian of the reference wavefunction

Gradients

Geometric derivative

$$\mathbf{f}_{\text{ref}}^x + \mathbf{G}\mathbf{k}^x = \mathbf{0}$$

$$\mathbf{k}^x = -\mathbf{G}^{-1}\mathbf{f}_{\text{ref}}^x$$

Energy gradient

$$E^x = \langle \Psi | \hat{H}^x | \Psi \rangle + \mathbf{f} \cdot \mathbf{k}^x$$

$$E^x = \langle \Psi | \hat{H}^x | \Psi \rangle - \mathbf{f}^T \mathbf{G}^{-1} \mathbf{f}_{\text{ref}}^x$$

Gradients

Energy gradient

$$E^x = \langle \Psi | \hat{H}^x | \Psi \rangle - \mathbf{f}^T \mathbf{G}^{-1} \mathbf{f}_{\text{ref}}^x$$

- ▶ Coupled perturbed MCSCF equations
- ▶ *Trick*: Precompute $\mathbf{f}^T \mathbf{G}^{-1}$ as an equation system¹
- ▶ **Z-vector equation**

Z-vector equation

$$\lambda^T = \mathbf{f}^T \mathbf{G}^{-1}$$

$$\lambda^T \mathbf{G} = \mathbf{f}^T$$

- ▶ Independent of the geometric derivative
- ▶ `cigrd.x` program

¹ N. C. Handy, H. F. Schaefer III *J. Chem. Phys.* **1984**, 81, 5031.

Gradients

- ▶ Convert the result into **effective density matrices**
- ▶ Contract with the AO derivative integrals, *as before*

Gradient

State-averaged MCSCF, MR-CI

Practical steps

- ▶ Compute the 1- and 2-particle density matrices (DM)
mcsf.x, (p)ciudg.x
- ▶ Solve the **coupled perturbed equations**
cigrd.x
- ▶ Transform the **effective DMs** to the AO basis
tran.x
- ▶ Compute the AO integral derivatives and contract them with the DMs
dalton.x “abacus”

Gradients

In reality, it is more complicated ...

- ▶ Two types of wavefunction parameters
 - CI-coefficients – variationally optimized for the individual states
 - MO-coefficients
- ▶ Redundant parameters
 - *Orbital resolution can affect MR-CI energies and gradients*

¹ H. Lischka, M. Dallos, R. Shepard *Mol. Phys.* **2002**, 100, 1647.

Nonadiabatic Couplings

Nonadiabatic coupling

$$\mathbf{h}_{12} = \langle \Psi_1 | \nabla \Psi_2 \rangle$$

$$h_{12}^x = \langle \Psi_1 | \Psi_2^x \rangle$$

- ▶ Measures changes in the wavefunction
- ▶ *Is it related to the gradient?*

Nonadiabatic Couplings

Schrödinger Equation

$$\hat{H} |\Psi_2\rangle = E_2 |\Psi_2\rangle$$

$$\hat{H}^x |\Psi_2\rangle + \hat{H} |\Psi_2^x\rangle = E_2^x |\Psi_2\rangle + E_2 |\Psi_2^x\rangle$$

$$\langle \Psi_1 | \hat{H}^x |\Psi_2\rangle + \langle \Psi_1 | \hat{H} |\Psi_2^x\rangle = \langle \Psi_1 | E_2^x |\Psi_2\rangle + \langle \Psi_1 | E_2 |\Psi_2^x\rangle$$

$$\langle \Psi_1 | \hat{H}^x |\Psi_2\rangle + E_1 \langle \Psi_1 | \Psi_2^x\rangle = E_2 \langle \Psi_1 | \Psi_2^x\rangle$$

Nonadiabatic coupling

$$h_{12}^x = \langle \Psi_1 | \Psi_2^x\rangle = \frac{\langle \Psi_1 | \hat{H}^x |\Psi_2\rangle}{E_2 - E_1}$$

Nonadiabatic Couplings

Nonadiabatic coupling

$$h_{12}^x = \langle \Psi_1 | \Psi_2^x \rangle = \frac{\langle \Psi_1 | \hat{H}^x | \Psi_2 \rangle}{E_2 - E_1}$$

- ▶ **Wavefunction derivative** converted into **Hamiltonian derivative**
- ▶ Equation similar to gradient
- Use similar methodology

Nonadiabatic Couplings

Nonadiabatic couplings *vs.* gradients

- ▶ Use transition density matrices instead of density matrices
- ▶ Formalism somewhat more involved, two terms
 - CI coefficient derivative “DCI”
 - CSF coefficient derivative “DCSF”