

Lecture 8 - Calculation of Forces in Quantum Chemistry

QC Forces

Analytic
Gradients

Geometry
Optimization

- 1 The potential surface
- 2 Analytic gradients and Hessians
- 3 The Hellman-Feynman theorem
- 4 Geometry optimization
- 5 Transition state calculations

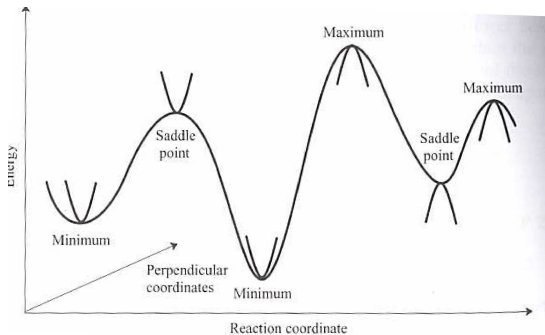
The Potential Surface

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- Separation of nuclear and electronic coordinates with Born-Oppenheimer approximation allows to compute $E(\{\vec{R}_j\})$



The Hellman-Feynman Theorem

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System with a hamiltonian $H(\lambda)$. Associated eigenvectors $|i(\lambda)\rangle$ and eigenvalues $E(\lambda)$

$$H(\lambda)|i(\lambda)\rangle = E(\lambda)|i(\lambda)\rangle \quad (1)$$

$$\langle i(\lambda)|i(\lambda)\rangle = 1 \quad (2)$$

The H-F theorem says:

$$\frac{dE}{d\lambda} = \langle i(\lambda)|\frac{dH}{d\lambda}|i(\lambda)\rangle \quad (3)$$

It allows to simplify expressions a lot for eg $H = H_0 + V(\lambda)$ – entire H_0 term disappears!

Analytic Gradients and Hessians

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- Hessian construction is *expensive*. Guess it (1? Force field?) and update in subsequent steps.
- Several update schemes exist. BFGS most popular

$$H_n = H_{n-1} + \Delta H$$
$$\Delta H_{\text{BFGS}} = \frac{\Delta g \Delta g^T}{\Delta g \cdot \Delta x} - \frac{(H \Delta x)(\Delta x^T H)}{\Delta x^T H \Delta x}$$

Molecular Gradients

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Compute gradient as:

$$\vec{g}_A = \frac{\partial E}{\partial \vec{R}_A}$$

Molecular gradient has $3N_A$ elements!

- Some degrees of freedom do not change total energy – correspond to Hessian eigenvalues equal to 0.
- $3N_A - 6$ non-redundant coordinates.

Analytic Gradients

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- Brute force gradient calculation by finite differences:

$$\frac{\partial E}{\partial \vec{x}_A} = \frac{E(x_A + \Delta) - E(x_A - \Delta)}{2\Delta}$$

- Unstable and time-consuming. Last resort.
- Analytic gradients for HF:

$$E = \text{Tr } H_0 D + \frac{1}{2} \text{Tr } F^{2\text{el}} D$$

- Integral derivatives needed:

$$\frac{\partial T_{pq}}{\partial \vec{x}_A}$$

Geometry Optimization

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- Steepest descent: Follow the gradient!
- Conjugate gradient methods.
- Newton-Raphson.
- Hessian Update.
- Extrapolation.

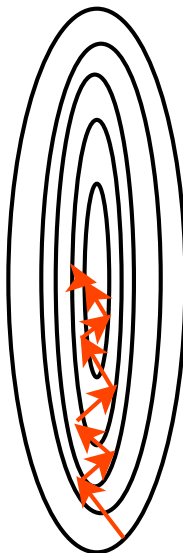
Steepest Descent

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- 1 Follow the gradient:
 $\vec{d} = -\alpha \vec{g}$
- 2 Step length from an adaptive scheme – or linear search.
- 3 Robust.
- 4 Slow convergence at the end



Conjugate Gradient

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- 1 Conjugate gradient: a steepest descent method with history.

$$\vec{d}_i = -\vec{g}_i + \beta_i \vec{d}_{i-1}$$

- 2 Several ways to choose β . Polak-Ribiere proposed:

$$\beta_i^{\text{PR}} = \frac{\vec{g}_i \cdot (\vec{g}_i - \vec{g}_{i-1})}{\vec{g}_{i-1} \cdot \vec{g}_{i-1}}$$

- 3 Conjugate gradient needs to be occasionally restarted.
- 4 Step length issue...

Newton-Raphson Methods

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- The Newton-Raphson method expands the true function to second order around the current point \vec{x}_0 :

$$f(\vec{x}) = f(\vec{x}_0) + \vec{g} \cdot (\vec{x} - \vec{x}_0) + \frac{1}{2}(\vec{x} - \vec{x}_0)^T H(\vec{x} - \vec{x}_0)$$

- For perfectly quadratic surface, we make step to the minimum of the surface directly

$$-H\vec{g} = \vec{x} - \vec{x}_0$$

- In reality, trust radius must be employed. . .

Transition State Calculations

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- 1 Transition state defined as a state with one negative Hessian eigenvalue.
- 2 Steepest descent works always for geometry optimization (may be slow).
- 3 No such algorithm for TS localization.