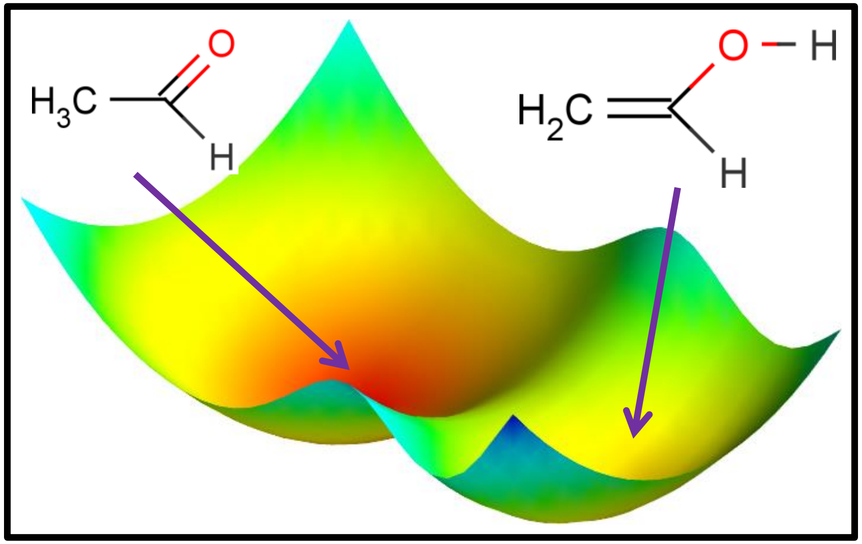
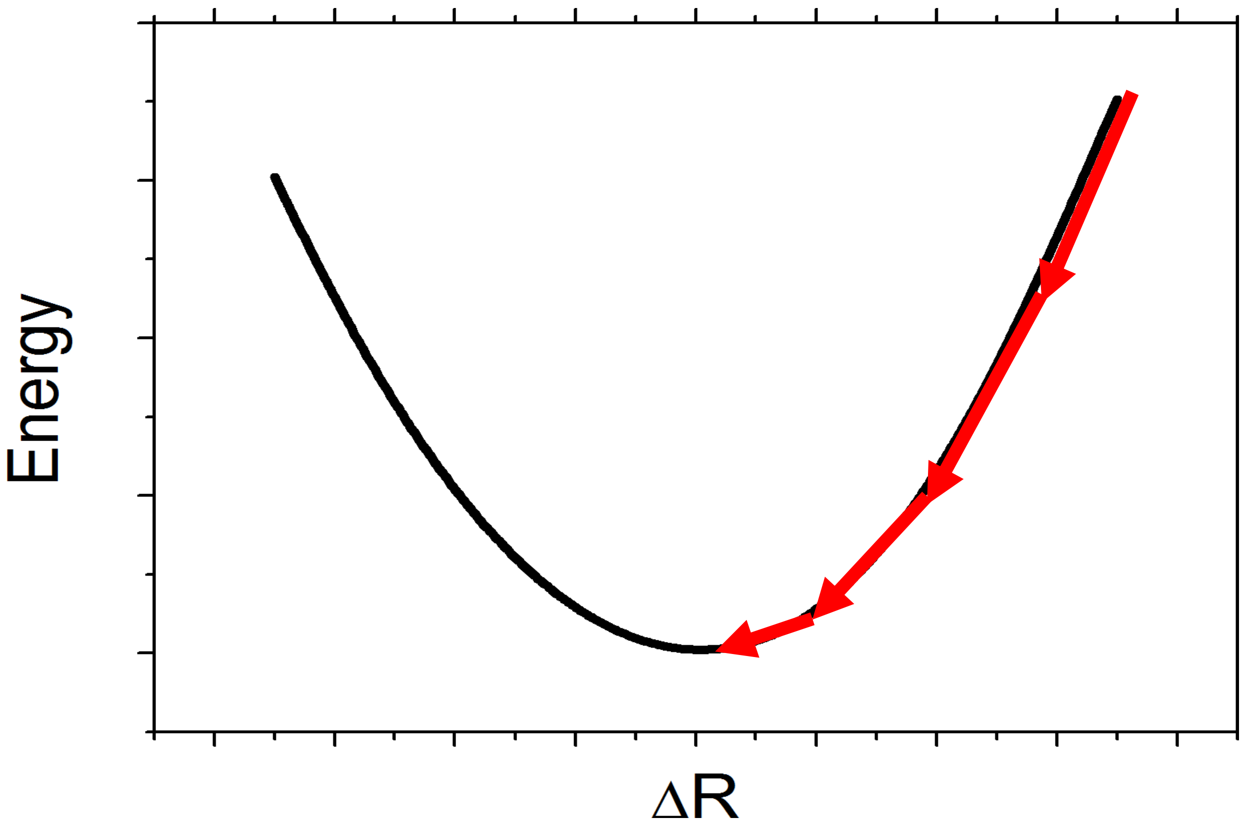
Applications of Electronic Structure Methods

Gradients and steepest descent



Gradient-Based Methods

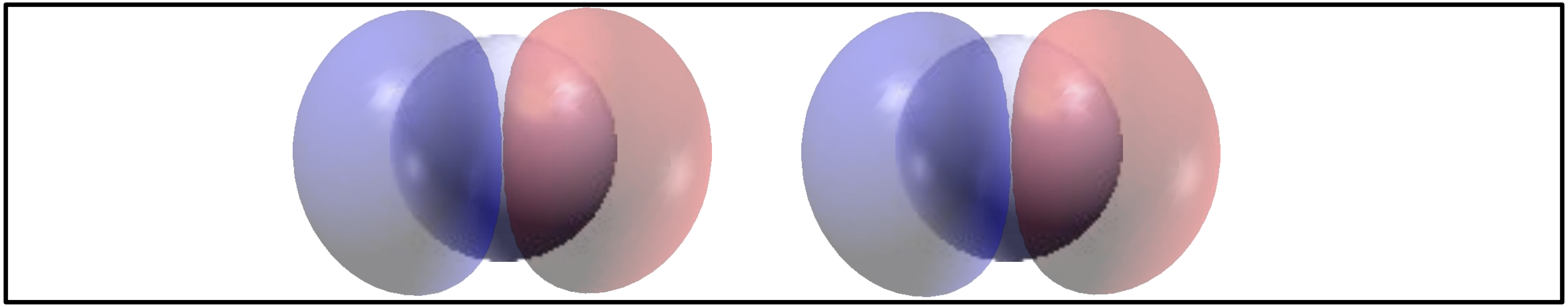
Calculate „force" acting on atoms: $$F = \frac{\delta E}{\delta R}$$



Gradient-Based Methods

Search for minimum by following the gradient

$$\frac{\delta E}{\delta R} = \langle \Psi_0 | \frac{\delta \hat{H}}{\delta R} | \Psi_0 \rangle + \langle \frac{\delta \Psi_0}{\delta R} | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 \rangle | \hat{H} | \frac{\delta \Psi_0}{\delta R} \rangle$$



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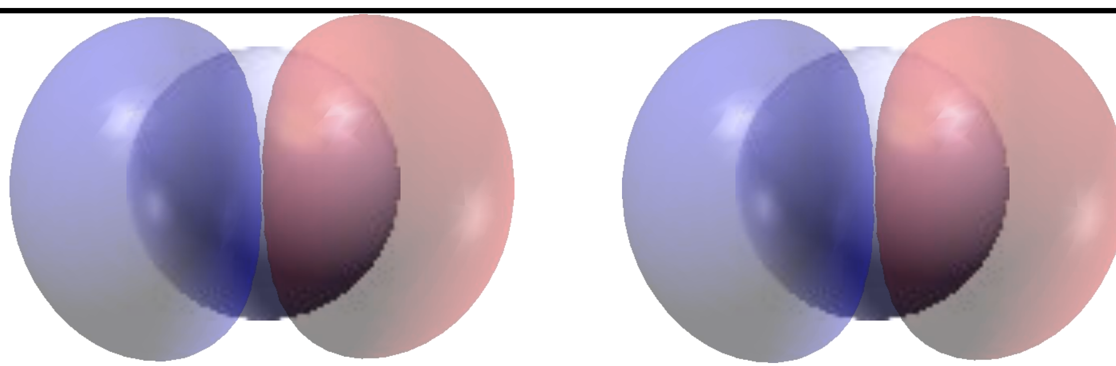
affects only $V^{nuc\text{-}nuc}$ and $V^{e\text{-}nuc}$

$$F_i^{Hellman-Feynman} = Z_i \sum_j \nabla R_i \frac{Z_j}{|R_i - R_j|} + \int d^3r \; n(r) \nabla R_i \frac{Z_i}{|R_i - r|}$$



Gradient-Based Methods

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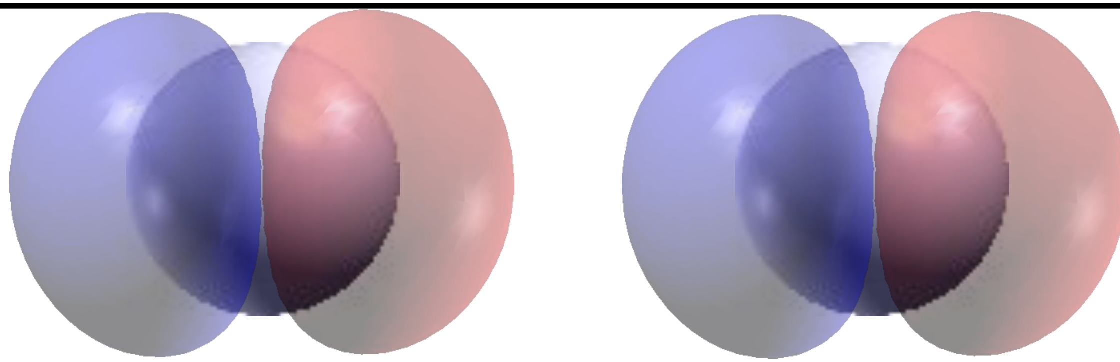
$$\frac{\delta \Psi_0}{\delta R} = \cancel{\frac{\delta \Psi_0}{\delta c} \frac{\delta c}{\delta R}} + \frac{\delta \Psi_0}{\delta \phi} \frac{\delta \phi}{\delta R}$$

First term vanishes



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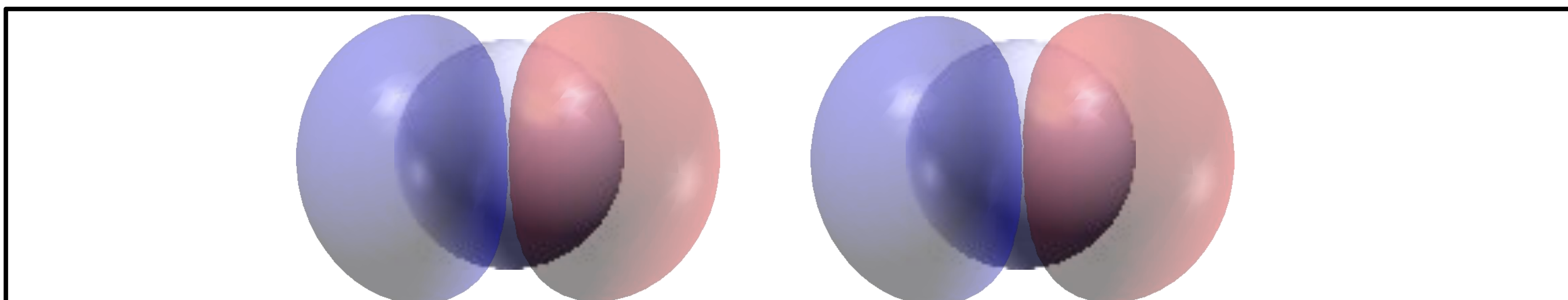
$$\frac{\delta \Psi_0}{\delta R} = \frac{\delta \Psi_0}{\delta c} \frac{\delta c}{\delta R} + \cancel{\frac{\delta \Psi_0}{\delta \phi} \frac{\delta \phi}{\delta R}}$$

Second term vanishes for plane waves, but not for LCAOs



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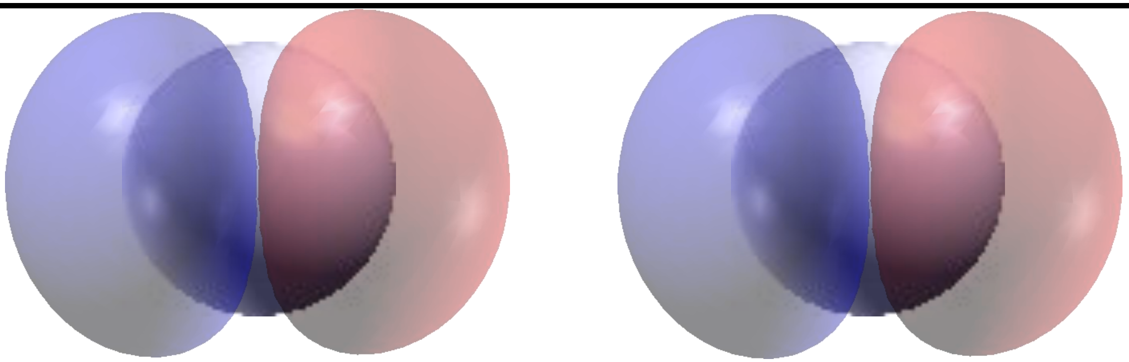
Additional contributions from atom-centered approximations:

- **Multipole expansion**
- **Relativistic corrections**
- **(Integration grids)**



Gradient-Based Methods

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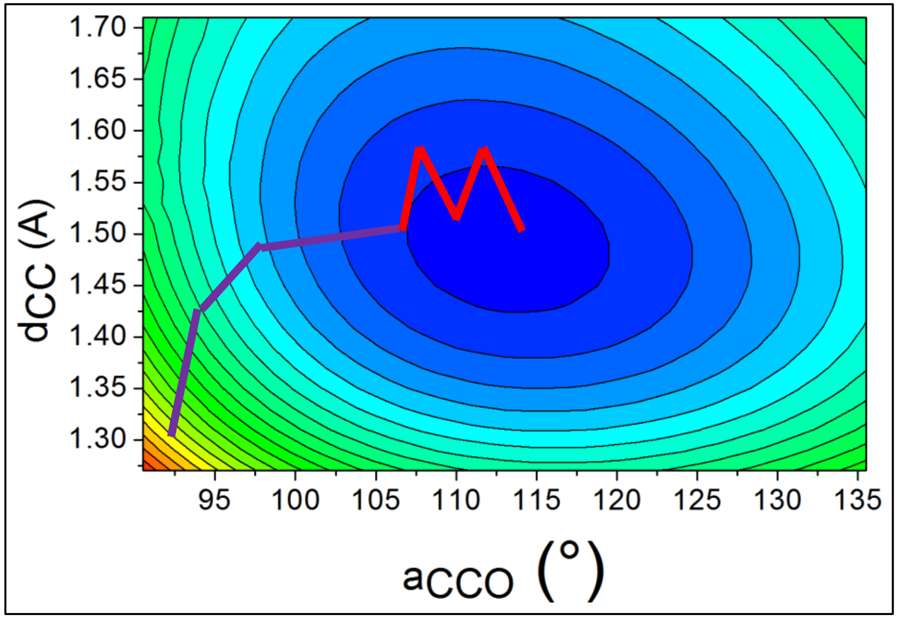
Once we have the forces, how do we find a minimum?

Geometry Update – Steepest Descent

Follow negative gradient to find minimum

$$R^{n+1} = R^n - \alpha F(R^n)$$

Underrelaxation method:
comparable to linear mixing



- ❖ **Step length α variable**
- ❖ **Guaranteed but slow convergence**
- ❖ **Oscillates near minimum**
- ❖ **Not suitable for saddle points**

Improved versions:

- **Line minimization** (optimal step length)
- **Conjugate gradient [1]**

[1] M. Hestenes, E. Stiefel (1952). "Methods of Conjugate Gradients for Solving Linear Systems"