Quantum Alchemy

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Few highly accurate calculations
instead of many intermediate ones

$$\hat{H} = \hat{H}(\underline{Z_i}, \underline{\mathbf{R}_i}, \underline{N_e}, \underline{\sigma})$$

1D

4N   1D, close to $\sum_i Z_i$

Idea
Treat system changes perturbatively[1,2]
Build a Taylor/Padé approximant[3] : **often 100.000 times faster**

Steps
Choose system

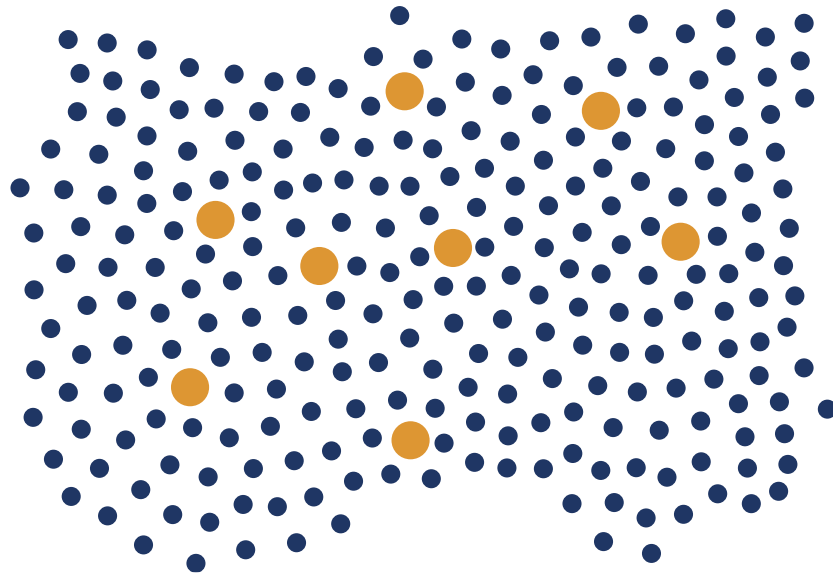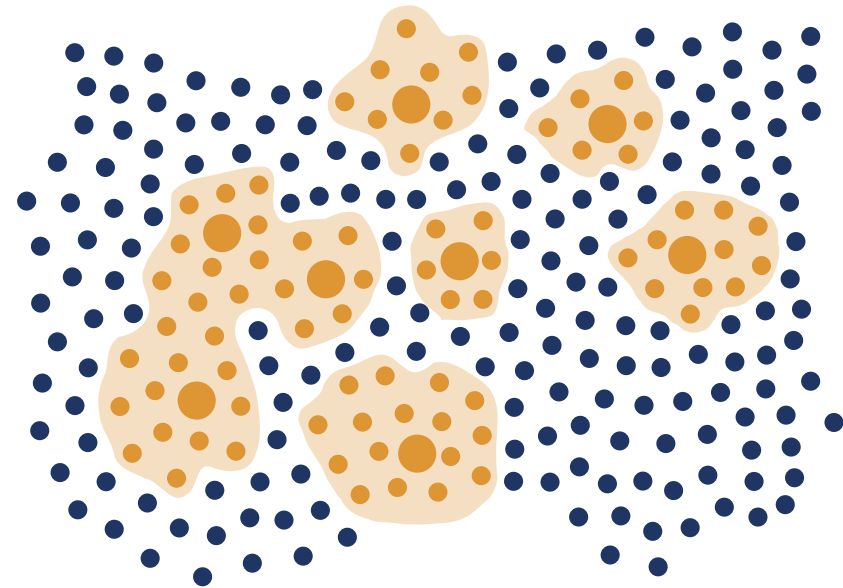Alter system, calculate property response functions

Predict many modified systems

Forwards

Backwards

1 | E. B. Wilson, *J. Chem. Phys.* 1962. **2 | GFvR**, O. A. von Lilienfeld, *Phys. Rev. Res.*, 2020. **3 | GFvR**, *J. Chem. Phys.*, **2021**.

Without Perturbation

With Perturbation

Systems
- Any
- Known
- Approximated

Differentiable / Analytic + Converge quickly

- ✔ Total Energy [1,2]
- ✔ Dipole moments [2]
- ✔ Deprotonation energies [3]
- ✔ Photoelectron circular dichroism [5]

- ✔ Electron density [1,2]
- ✔ Non-covalent interactions [1]
- ✔ Ionisation Energy [4]

- ✔ Orbital eigenvalues [2]
- ✔ Binding energies [1,2]
- ✔ Electron Affinity [4]

In progress

NMR spectra

Tested in: Gaussian, Psi4, PySCF, ORCA, MRCC, cp2k, CPMD
Tested with: HF, DFT, CCSD

1 | GFvR, O. A. von Lilienfeld, *Phys. Rev. Res.*, 2020. 2 | GFvR, *J. Chem. Phys.*, 2021. 3 | GFvR, O. A. von Lilienfeld, *Phys. Chem. Chem. Phys.*, 2020. 4 | E Eikey, A Maldonado, C Griego, GFvR, J Keith, *J. Chem. Phys.*, 2022. 5 | GFvR, A Artemyev, B Lagutin, P Demekhin, *J. Chem. Phys.*, 2024.
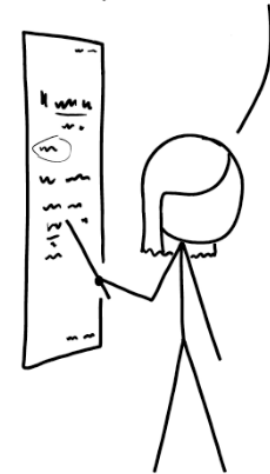
Interpolate between molecular isoelectronic Hamiltonians

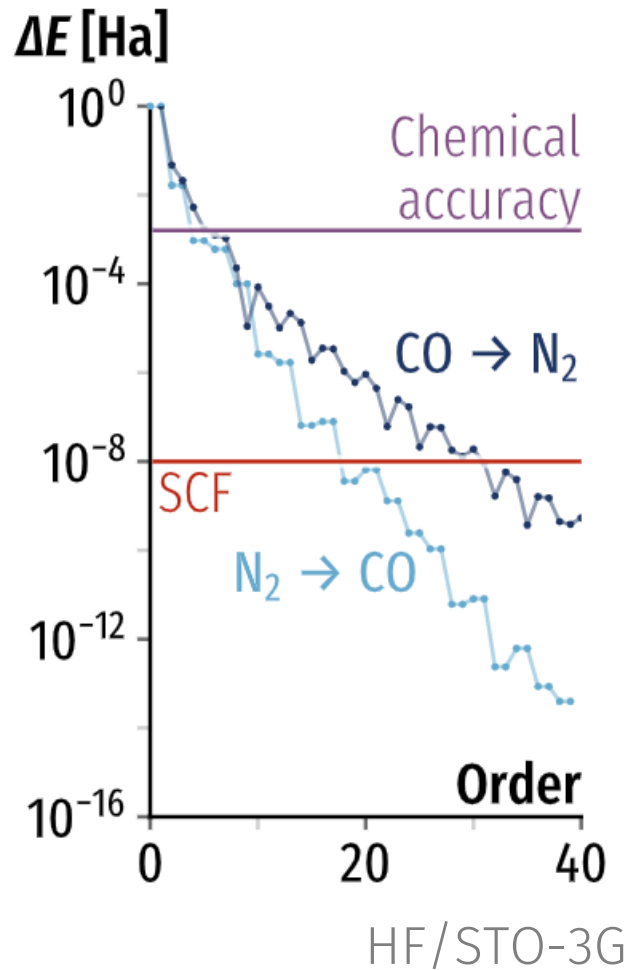$$\hat{H}(\lambda) \equiv \lambda \hat{H}_{\mathrm{t}} + (1 - \lambda)\hat{H}_{\mathrm{r}}$$

Taylor expansion around reference molecule

$$E_{\mathrm{t}} = E_{\mathrm{r}} + \Delta E^{\mathrm{NN}} + \int_{\Omega} d\mathbf{r} \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \Delta v \frac{\partial^n \rho_\lambda(\mathbf{r})}{\partial \lambda^n} \bigg|_{\lambda=0}$$

- Gives consistent energies, densities, forces, …
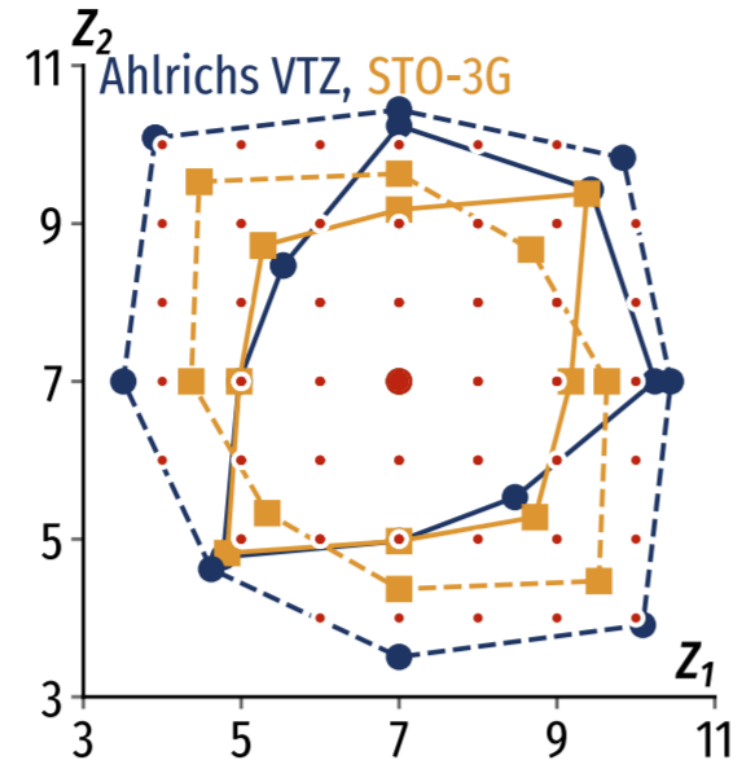- Uses the same derivatives for all predictions

AT THIS POINT, YOU'RE PROBABLY THINKING, "I LOVE THIS EQUATION AND WISH IT WOULD NEVER END!"

WELL, GOOD NEWS!

HF/STO-3G

Taylor expansion
- First terms accurate enough
  - Truncate early
- Converges to the right value
- Large convergence radius
- Scales with chemical space

properties that can be formulated (and calculated) as derivatives of the energy

nth derivative with regard to — change in geometry (R), external electric field (F), external magnetic field (M, nuclear magnetic field (I)

n_R	n_F	n_B	n_I	Property
1	0	0	0	Energy gradient g
2	0	0	0	Harmonic vibrational frequencies ω_i
3	0	0	0	(cubic) anharmonic corrections to vibrational frequecies $\omega_i x_i$
0	1	0	0	Electric dipole moment μ
0	2	0	0	Electric polarizability α
0	3	0	0	(first electric) hyperpolarizability β
0	0	1	0	Magetic (dipole) moment μ
0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant a_i
0	0	0	2	Spin-spin coupling J_{ij} of different nuclei
1	1	0	0	Intensities of fundamental IR transitions
2	1	0	0	Intensities of overtones and combination bands in IR spectra
1	2	0	0	Intensities of fundamental Raman transitions
2	2	0	0	Intensities of overtones and combination bands in Raman spectra
0	1	1	0	Circular dichroism (CD)
0	2	1	0	Magnetic circular dichroism (MCD)
0	0	1	1	Nuclear magnetic shielding ($\rightarrow$ chemical shift in NMR)

mixed
derivatives
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.
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Equivalents
- f(x): total energy $E(\mathbf{R}_i, Z_i)$

Gradients
- Molecular forces
    - Commonly implemented
    - Special derivations
- Alchemical derivatives: electronic electrostatic potential

Hessians
- Normal modes
    - Commonly only for spatial derivatives
    - Special derivations (less often)

What if we have no derivatives?

Approximative derivatives
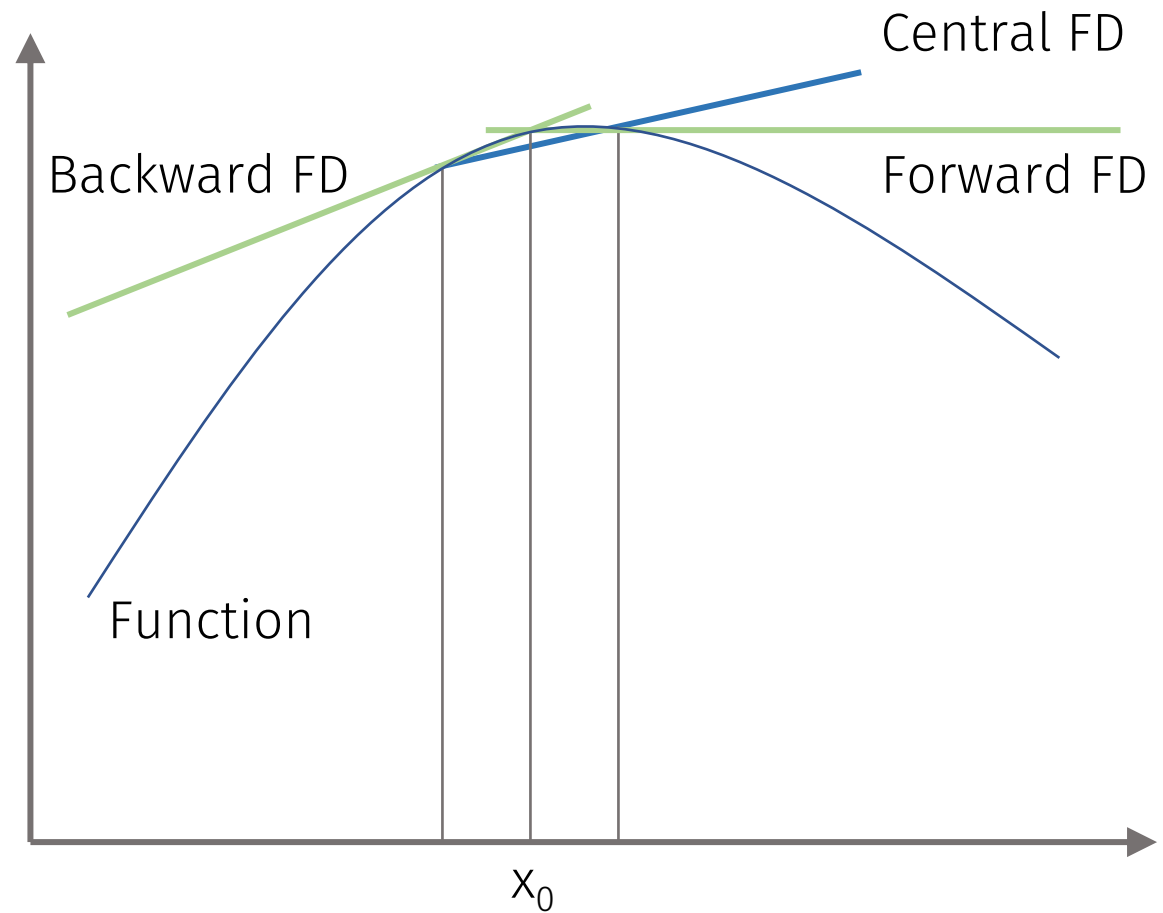- Similar to the limit expression

Variants
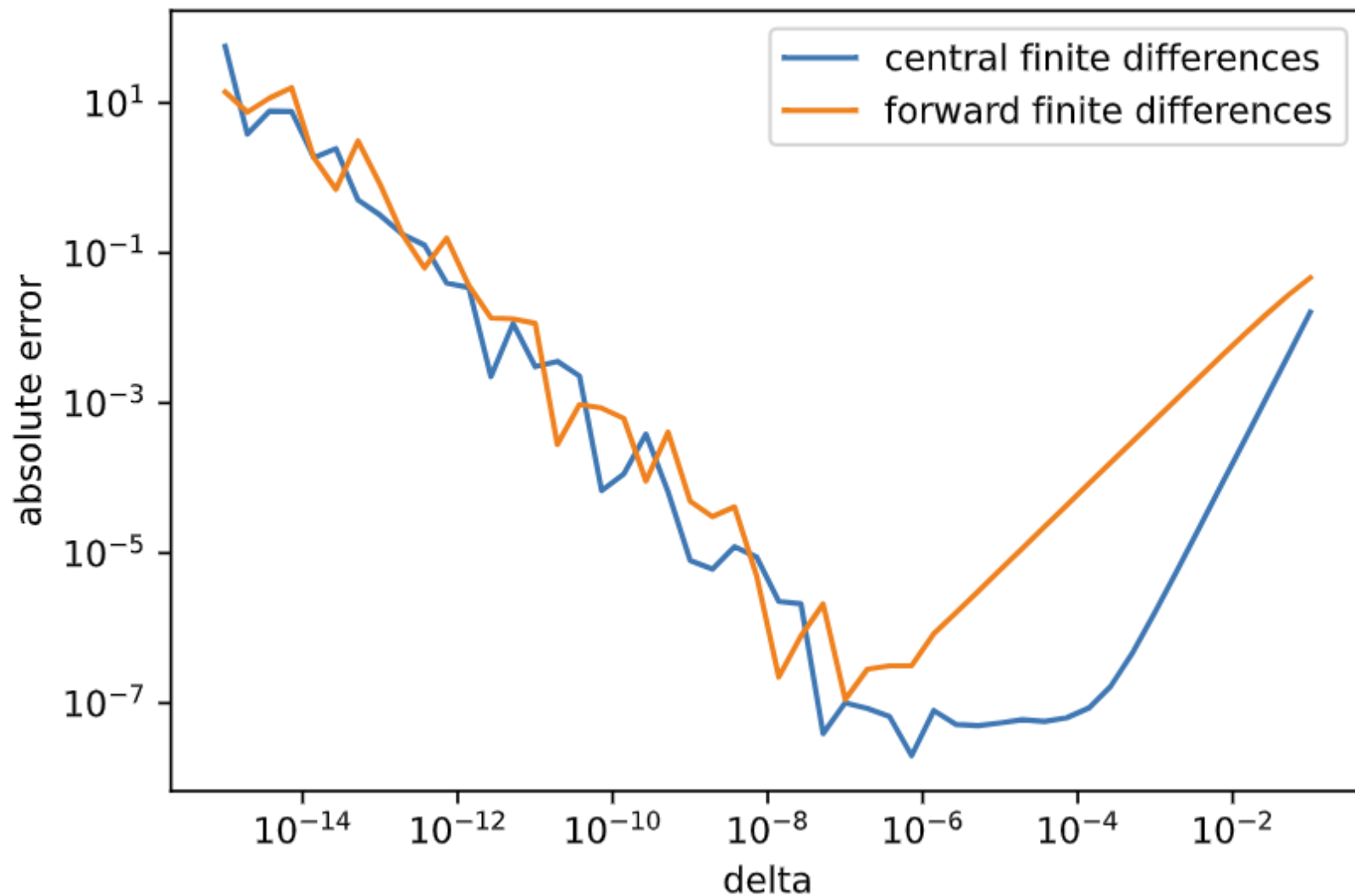- Forward/backward
- Central
- Higher-order

Issues
- Finite displacement
- Numerical stability / finite precision
- Many calculations

Main advantage
- General applicability
- Just points and weights

Central FD

Backward FD

Forward FD

Function

x_0

H-F finite differences vs reference gradient @ 1.0 Angstrom, RHF/cc-pVDZ

$$\frac{\mathrm{d}E}{\mathrm{d}\mathbf{R}} = \frac{\mathrm{d}}{\mathrm{d}\mathbf{R}}\langle\psi|\hat{H}|\psi\rangle$$

$$= \left\langle\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\middle|\hat{H}\middle|\psi\right\rangle + \left\langle\psi\middle|\hat{H}\middle|\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\right\rangle + \left\langle\psi\middle|\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle$$

$$= E\left\langle\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle + E\left\langle\psi\middle|\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\right\rangle + \left\langle\psi\middle|\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle.$$

Cancels if
- Complete basis set
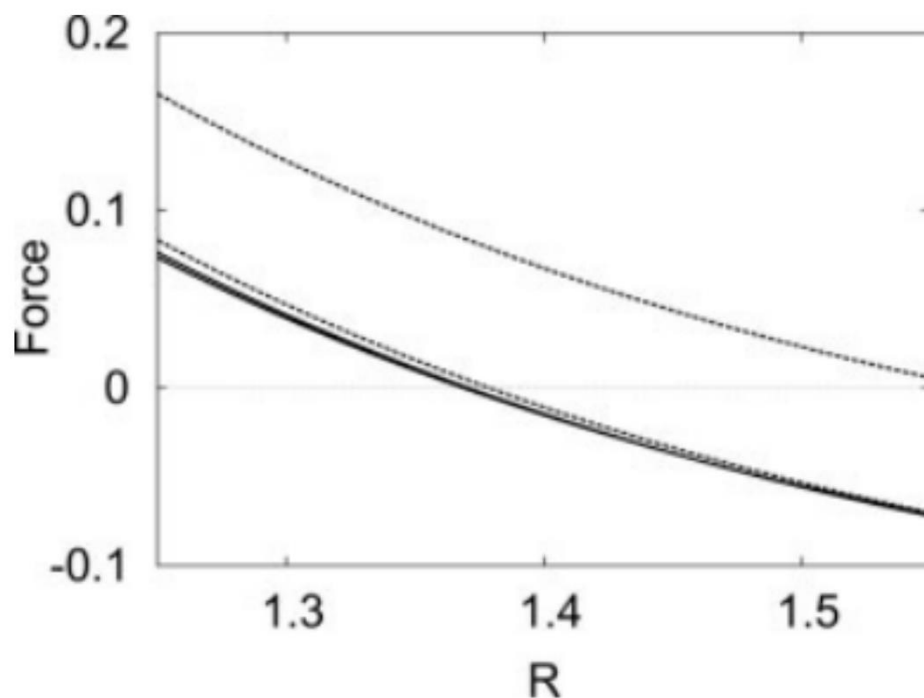- At least: basis set does not change along derivative

Figure 1. Dashed lines: Hellmann-Feynman force (upper) and energy gradient (lower) in H_2 for a minimal basis set (a single 1s($\zeta = 1.2$) function per center). Solid lines: same for the basis set augmented with a 2p($\zeta' = 2.0$) function on each center.

- Complete basis
- Basis does not change along perturbation
  - Includes spatial changes
- Pulay forces / stress

JF Rico, R López, I. Ema, G. Ramírez, *J Comput Chem,* 2007.