Quantum Monte Carlo

Variational Monte Carlo

expectation value of energy

$$\frac{\int \Psi_T^*(\mathbf{r},\{\alpha\})\hat{H}\Psi_T(\mathbf{r},\{\alpha\})d\mathbf{r}}{\int \Psi_T^*(\mathbf{r},\{\alpha\})\Psi_T(\mathbf{r},\{\alpha\})d\mathbf{r}} = E(\{\alpha\}) \geq E_0$$

importance sampling (Monte Carlo)

$$p(\mathbf{r}) = \frac{|\Psi(\mathbf{r})|}{\int |\Psi(\mathbf{r}')|d\mathbf{r}'}$$

local energy

$$E_L(\mathbf{r}) = \frac{\hat{H}\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

Sampling of energy, optimise coefficients in wave function

$$\langle \hat{H} \rangle = \int p(\mathbf{r})E_L(\mathbf{r})d\mathbf{r}$$

$$\langle \hat{H} \rangle = \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{r}_i) = \frac{1}{M}\sum_{i=1}^{M} \frac{\hat{H}\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

Quantum Monte Carlo

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wave function

$$\Psi_T(\mathbf{x}) = \exp[J(\mathbf{x})] \sum_i c_i D_i(\mathbf{x})$$

determinant (antisymmetric) of molecular orbitals (again!)

$$D_i(\mathbf{x}) = \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \dots & \varphi_1(\mathbf{x}_n) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \dots & \varphi_2(\mathbf{x}_n) \\ \dots & \dots & & \dots \\ \varphi_n(\mathbf{x}_1) & \varphi_n(\mathbf{x}_2) & \dots & \varphi_n(\mathbf{x}_n) \end{vmatrix}$$

Jastrow factor (electron-electron, eln-nuc, eln-eln-nuc, …)

$$J(\mathbf{r}) = \sum_{i>j}^{N} u(r_{ij}) + \sum_{i=1}^{N} \sum_{I=1}^{N_I} \chi_I(r_{iI}) + \sum_{i>j}^{N} \sum_{I=1}^{N_I} f_I(r_{ij}, r_{iI}, r_{jI})$$

Quantum Monte Carlo

Diffusion Monte Carlo

propagate Schrödinger equation in *imaginary* time

$$i\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t)$$

$$\tau = it$$

diffusion equation of electronic positions and rate equation)

$$-\frac{\partial\Psi^{\mathrm{DMC}}(\mathbf{R},t)}{\partial\tau} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},\tau) + (V(\mathbf{r}) - E_T)\Psi(\mathbf{r},t)$$

project out ground state

Quantum Monte Carlo

Diffusion Monte Carlo

propagate Schrödinger equation in imaginary time

$$-\frac{\partial \Psi^{\mathrm{DMC}}(\mathbf{R},t)}{\partial \tau} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},\tau) + (V(\mathbf{r}) - E_T)\Psi(\mathbf{r},t)$$

expansion in (unknown) eigenstates

$$\Psi(\mathbf{r},t) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{r}) e^{-i(E_n - E_t)t}$$

$$\Psi(\mathbf{r},\tau) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{r}) e^{-(E_n - E_t)\tau}$$

with $E_T = E_0$ we can single out ground state in diffusion process

$$\Psi(\mathbf{r},\tau) = c_0\psi_0(\mathbf{r}) + \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r}) e^{-(E_n - E_0)\tau}$$

Some practical guidelines

Basissets

- STO-3G too small
- 6-31G* & 6-31G** reasonable results
  - DFT often less sensitive to basisset
  - often better than cc-pVDZ
- higher accuracy with cc-pVTZ, better than 6-311G**, etc.
- diffuse functions (aug- or +)
  - anions
  - excited states
  - dispersion bound complexes

Some practical guidelines

Methods

- prefer DFT over HF
- HF < DFT ~ MP2 < CCSD < CCSD(T)
- MPn may not converge with n
  - beyond MP2, use CC
- CASSCF/CASPT2
  - bond breaking, diradicals, excited states, transition metals
  - DFT can be dangerous
- HF, semi-empirical and DFT fail for VDW complexes
  - MP2, CC, dispersion corrected DFT

Some practical guidelines

Always do!

- check if SCF converged!
  - check for multiconfigurational character (MPn/CC:T2)
- check if geometry converged
  - NMA analysis
  - minimum: all postive frequencies
  - transition state: one negative frequency.
  - non-covalent complexes: flat surface, difficult, go by hand
- think of symmetry
  - optimization cannot break symmetry
- know what to expect: think first
  - never thrust the computer
- CASSCF/CASPT2
  - check final natural orbital density matrix
  - check for large orbital rotations

Gradients

Analytical derivatives

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu a}} \frac{\partial C_{\mu a}}{\partial X_A}$$

Hartree Fock solution

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

Hartree-Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

$$P_{\mu\nu} = 2 \sum_{a}^{n/2} C_{\mu a}^{*} C_{\nu a}$$

Gradients

Analytical derivatives

Hartree Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H^{\text{core}}_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

gradient

$$\begin{aligned}
\frac{\partial E}{\partial X_A} \quad = \quad & \textstyle\sum_{\mu\nu} P_{\mu\nu} \frac{\partial H^{\text{core}}_{\mu\nu}}{\partial X_A} \\
& + \tfrac{1}{2} \textstyle\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{V_{NN}}{\partial X_A} \\
& + \textstyle\sum_{\mu\nu} \frac{\partial P_{\mu\nu}}{\partial X_A} H^{\text{core}}_{\mu\nu} + \textstyle\sum_{\mu\nu\lambda\sigma} \frac{\partial P_{\mu\nu}}{\partial X_A} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle
\end{aligned}$$

Gradients

Analytical derivatives

orthogonality of RHF molecular orbitals

$$\sum_{\mu\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} = \delta_{ab}$$

$$2\sum_{\mu\nu} \frac{\partial C_{\mu a}}{\partial X_A} S_{\mu\nu} \quad = -\sum_{\mu\nu} C_{\mu a} C_{\nu a} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

gradient

$$\frac{\partial E}{\partial X_A} \quad = \quad \sum_{\mu\nu} P_{\mu\nu} \frac{\partial H^{\mathrm{core}}_{\mu\nu}}{\partial X_A}$$

$$+\frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1-\frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{V_{NN}}{\partial X_A}$$

$$-\sum_{\mu\nu} Q_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

with

$$Q_{\mu\nu} = 2\sum_{a}^{n/2} \epsilon_a C_{\mu a} C_{\nu a}$$

Gradients

Analytical derivatives

Configuration interaction

$$|\Psi\rangle = \sum_I c_I |\psi_I\rangle$$

general gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A} + \sum \frac{\partial E}{\partial c_I} \frac{\partial c_I}{\partial X_A}$$

MCSCF gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

CI gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A}$$