Approximate methods I
Variational method

Quantum Chemistry

Lesson 5

Contents

1. Ritz variational method and its use in QC
2. Variational Monte Carlo methods
3. Diffusion Monte Carlo methods

Ritz variational method

Ritz variational principle

$$\widehat{H}|\varphi_k\rangle = E_k|\varphi_k\rangle \quad (E_0 < E_1 < \dots) \quad \Rightarrow E_0 = \min_{\|\psi\|=1} \langle\psi|\widehat{H}|\psi\rangle = \min_{\psi\in\mathcal{H}\setminus\{0\}} \frac{\langle\psi|\widehat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

"Proof" (purely discrete, non-degenerate energy spectrum)

- $|\psi\rangle = \sum_{k=0}^{+\infty} c_k|\varphi_k\rangle, \quad \langle\psi|\psi\rangle = \sum_{k=0}^{+\infty} |c_k|^2 = 1$
- $|c_0|^2 = 1 - \sum_{k=1}^{+\infty} |c_k|^2$
- $\langle\psi|\widehat{H}|\psi\rangle = \sum_{k=0}^{+\infty} E_k|c_k|^2 = E_0|c_0|^2 + \sum_{k=1}^{+\infty} E_k|c_k|^2 = E_0 + \sum_{k=1}^{+\infty}(E_k - E_0)|c_k|^2$
  - $\langle\psi|\widehat{H}|\psi\rangle \geq E_0$
  - $\langle\psi|\widehat{H}|\psi\rangle = E_0 \Leftrightarrow c_1 = c_2 = \dots = 0$

[wiki, wiki]

Ritz variational method

Application in QC

- energy functional (normalized wave functions!)
  - $\mathcal{E}(\psi) \equiv \langle\psi|\hat{H}|\psi\rangle = \int \psi^*(1,2,\dots,N)\hat{H}\psi(1,2,\dots,N)\mathrm{d}1\mathrm{d}2\dots\mathrm{d}N$
  - „function“ of functions (= functions of infinitely many variables, countably many on separable Hilbert spaces)

- constrained extreme / minimum
  - constraint: $\langle\psi|\psi\rangle = 1$

- approximations?
  - no approximations up to now, but ...
  - the red-highlighted variational problem is not in general solvable (either analytically or numerically) → approximations are needed

Ritz variational method

Application in QC

- approximations
  - $|\psi\rangle = |\psi(a_1, \dots, a_n)\rangle$, neboli $\psi = \psi(1,2, \dots, N; a_1, \dots, a_n)$
    - a function of a given form with a finite number of adjustable parameters
    - $\mathcal{E}(\psi) \to E(a_1, \dots, a_n)$, a function of finitely many variables
    - a non-linear optimization problem (the numerical mathematics provide a plethora of efficient methods)
  - for example, $|\psi\rangle = \sum_{k=1}^{n} c_k |\phi_k\rangle$
    - $\langle\psi|\hat{H}|\psi\rangle = \sum_{j,k=1}^{n} {c_j}^* c_k H_{jk}$, kde $H_{jk} = \langle\phi_j|\hat{H}|\phi_k\rangle$
    - $\sum_{j,k=1}^{n} {c_j}^* c_k S_{jk} = 1$, kde $S_{jk} = \langle\phi_j|\phi_k\rangle$
    - quadratic programming methods

Ritz variational method

Application in QC – technical issues

- evaluation of $\langle\psi|\hat{H}|\psi\rangle$
  - multidimensional integral: $\int \psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x})\,\mathrm{d}\mathbf{x} = \int |\psi(\mathbf{x})|^2 \frac{\hat{H}\psi(\mathbf{x})}{\psi(\mathbf{x})}\mathrm{d}\mathbf{x} \equiv \int |\psi(\mathbf{x})|^2 E_{\mathrm{lok}}(\mathbf{x})\mathrm{d}\mathbf{x}$ which ...
  - has to be calculated numerically (approximations)
- optimization of functions of many variables, $E(a_1, \ldots, a_n)$
  - various (approximate) methods
    - local (gradient-based)
    - global (stochastic)
      - Monte Carlo methods (simulated annealing)
      - evolutionary (genetic) algorithms
      - swarm algorithms
      - …
- computational costs
  - powerful computers are needed

Variational Monte Carlo methods

Monte Carlo methods

- a class of stochastic methods for calculating multi-dimensional integrals $\int p(\mathbf{x}) f(\mathbf{x}) \mathrm{d}\mathbf{x}$, $p(\mathbf{x}) \geq 0$
  - *Markov chains* corresponding to (probability) distribution function $p(\mathbf{x})$, $\{\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_{\mathcal{M}}\}$, $\mathcal{M} \to +\infty$
  - e.g., *Metropolis algorithm*
    - ansatz $\mathbf{x}_1$ (arbitrary)
    - change proposal from step ℓ to step $\ell + 1$:
      - $\mathbf{x}_\ell \to \mathbf{x}_{\mathrm{new}} = \mathbf{x}_\ell + \Delta\mathbf{x}$
      - accepted with probability $p(\mathbf{x}_{\mathrm{new}})/p(\mathbf{x}_\ell)$, $\mathbf{x}_{\ell+1} = \mathbf{x}_{\mathrm{new}}$
      - otherwise rejected, $\mathbf{x}_{\ell+1} = \mathbf{x}_\ell$
  - $\int p(\mathbf{x}) f(\mathbf{x}) \mathrm{d}\mathbf{x} \approx \frac{1}{\mathcal{M}} \sum_{\ell=1}^{\mathcal{M}} f(\mathbf{x}_\ell)$

Variational Monte Carlo method

- the MC (Metropolis) algorithm applied to the calculation of $\int |\psi(\mathbf{x})|^2 E_{\mathrm{lok}}(\mathbf{x}) \mathrm{d}\mathbf{x} \approx \frac{1}{\mathcal{M}} \sum_{\ell=1}^{\mathcal{M}} E_{\mathrm{lok}}(\mathbf{x}_\ell)$

NIC Series Vol. 10, chapter *Monte Carlo Methods: Overview and Basics* (page 1) and subchapter *Variational Quantum Monte Carlo* (page 28)

Variational Monte Carlo methods

Pros

- a general form of function $\psi(\mathbf{x})$

Technical issues

- stochastic methods $\longrightarrow$ statistical uncertainties
- convergence issues at the end of optimization iterations (and/or gradient-based methods)

Another issue

- particular form of $\psi(\mathbf{x})$ (physics-based arguments, experience, ...)

Diffusion Monte Carlo methods

Idea

- time-dependent Schrödinger equation with imaginary time
  - $\hat{H}|\psi(t)\rangle = i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} \quad \rightarrow \quad \hat{H}|\psi(\tau)\rangle = -\hbar\frac{\partial|\psi(\tau)\rangle}{\partial\tau} \quad (\tau = it)$
  - $|\psi\rangle = \sum_{k=0}^{+\infty} c_k(\tau)|\varphi_k\rangle, \quad \hat{H}|\varphi_k\rangle = E_k|\varphi_k\rangle, \quad E_0 < E_1 < \ldots$
  - $c_k(\tau) = c_{k0}e^{-\frac{E_k}{\hbar}\tau}$
  - $|\psi(\tau)\rangle = \sum_{k=0}^{+\infty} c_{k0}e^{-\frac{E_k}{\hbar}\tau}|\varphi_k\rangle = e^{-\frac{E_0}{\hbar}\tau}\left(c_{00}|\varphi_0\rangle + \sum_{k=1}^{+\infty} c_{k0}e^{-\frac{E_k-E_0}{\hbar}\tau}|\varphi_k\rangle\right) \longrightarrow c_{00}e^{-\frac{E_0}{\hbar}\tau}|\varphi_0\rangle$
- and its similarity to the diffusion equation (with chemical reactions)
  - $-\frac{\hbar^2}{2m}\Delta\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \quad \rightarrow \quad -\frac{\hbar^2}{2m}\Delta\psi + V\psi = -\hbar\frac{\partial\psi}{\partial t} \quad \rightarrow \quad \frac{\hbar}{2m}\Delta\psi - \frac{V}{\hbar}\psi = \frac{\partial\psi}{\partial\tau}$
    - particle density: $c = \psi$
    - diffusion: $D = \frac{\hbar}{2m}$
    - first-order chemical reaction: $k = -\frac{V}{\hbar}$

NIC Series Vol. 10, selected parts of chapter *Diffusion and Green's Function Quantum Monte Carlo Methods, Diffusion Quantum Monte Carlo* (page 29) in particular

Diffusion Monte Carlo methods

Implementation

- points randomly distributed in a domain of the system configuration space ($\mathbb{R}^{3N}$), *walkers*
- repeated iterations (over all the walkers included)
  - diffusion in the configuration space
  - creation / disappearance of walkers
  - periodical adjustment of the number of walkers (a much longer period)
- in the limit of infinitely many iterations, the population of walkers will be distributed in the configuration space with a density proportional to φ_0 (ground-state wave function)
- the ground-state energy is obtained, e.g., from the time dependence of the number of walkers (between the adjustment steps): $N \sim e^{-\frac{E_0}{\hbar}\tau}$

Diffusion Monte Carlo methods

Pros

- no *à priori* assumption concerning the wave function form (→highly accurate calculations)
- easily parallelized (appropriate for supercomputers)

Contras

- stochastic methods ⟶ statistical uncertainties
- systematic errors (biases):
  - finite (imaginary) time ($\tau \to \infty$ is needed)
  - finite (non-zero) time step ($\Delta\tau \to 0$ is needed)
  - approximations used in the simultaneous inclusion of the diffusive motion of walkers and the chemical reaction
- ground-state wave function must be real valued and must not change its sign (walkers density)
  - works well for bosons (as well as for distinguishable particles)
  - but not for fermions, specific "tricks" are to be employed (and other approximations are to be used)
- resulting wave function is given by the (final) population of walkers (no analytic formula is available) ...
- who are distributed in the configuration space with a density $\sim\varphi_0$ ...
- but, for calculations one needs φ_0^2 (or an analytic formula of φ_0)

The end of lesson 5.