Iterative Energy Minimization for Quantum Molecular Dynamics

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From quantum dynamics to eigenvalue problems
Imaginary-Time Quantum Dynamics

- **Quantum dynamics**

  \[
  \text{Repeat} \\
  |\psi\rangle \leftarrow \exp(-i\hat{H}\Delta t)|\psi\rangle \\
  \]

- **Imaginary-time quantum dynamics**: \(i\Delta t \rightarrow \Delta \tau\)

  \[
  \text{Repeat} \\
  |\psi\rangle \leftarrow \exp \left(-\hat{H}\Delta \tau\right)|\psi\rangle \\
  |\psi\rangle \leftarrow |\psi\rangle / \sqrt{\langle \psi | \psi \rangle} \\
  \frac{\partial}{\partial \tau} \psi(x, \tau) = \frac{\hbar}{2m} \frac{\partial^2}{\partial x^2} \psi(x, \tau) - \frac{V(x)}{\hbar} \psi(x, \tau) \\
  \exp (-\hat{H}\Delta \tau) = \exp (-V(x)\Delta \tau/2) \exp \left( \frac{V^2}{2} \Delta \tau \right) \exp (-V(x)\Delta \tau/2) \\
  \]

- **Filtering in the ground state**

  **Eigensystem**: \(\hat{H}|n\rangle = \epsilon_n |n\rangle \quad \epsilon_0 \leq \epsilon_1 < \cdots \quad \langle m|n\rangle = \delta_{mn} \)

  \[
  \exp (-\hat{H}\tau)|\psi_{\text{init}}\rangle = \exp (-\hat{H}\tau) \sum_{n \geq 0} |n\rangle \langle n| \psi_{\text{init}}\rangle \\
  = \sum_{n \geq 0} |n\rangle \langle n| \psi_{\text{init}}\rangle \exp (-\epsilon_n \tau) \quad \tau \rightarrow \infty |0\rangle \langle 0| \psi_{\text{init}}\rangle \exp (-\epsilon_0 \tau) \\
  \]

\[
\]
Obtaining Excited States

- **Filter-project imaginary-time quantum dynamics**

  Repeat
  \[ |\psi\rangle \leftarrow \exp(-\hat{H} \Delta \tau) |\psi\rangle \]
  \[ |\psi\rangle \leftarrow |\psi\rangle - |0\rangle \langle 0| |\psi\rangle \]
  \[ |\psi\rangle \leftarrow |\psi\rangle / \sqrt{\langle \psi | \psi \rangle} \]

  \[ (1 - |0\rangle \langle 0|) \exp(-\hat{H} \tau) |\psi_{\text{init}}\rangle \xrightarrow{\tau \to \infty} |1\rangle \]

- **Problem:** Convergence is too slow

  \[ \rightarrow \]

  **Solution:** Use the conjugate-gradient method (see next viewgraphs)

- **If all the eigenstates (not only a few lowest-lying states) are needed**

  \[ \rightarrow \]

  **Use matrix diagonalization (see the next section)**
**Functional Derivative Basics**

- **Functional derivative**: \( \delta E = \int dr \frac{\delta E}{\delta f(r)} \delta f(r) \)  
  
  - **Example 1**:  
    \[
    E[f(r)] = \int dr (f(r))^2
    \]
    \[
    E[f(r) + \delta f(r)] - E[f(r)] = \int dr \{[f(r) + \delta f(r)]^2 - f^2(r)\} = \int dr [2f(r)\delta f(r) + \delta f^2(r)]
    \]
    \[
    \therefore \frac{\delta E}{\delta f(r)} = 2f(r)
    \]

- **Example 2**:  
  \[
  E[\rho(r)] = \frac{1}{2} \int dr \int dr' \frac{\rho(r)\rho(r')}{|r-r'|}
  \]
  \[
  E[\rho(r) + \delta \rho(r)] - E[\rho(r)] = \frac{1}{2} \int dr \int dr' \frac{[\rho(r) + \delta \rho(r)][\rho(r') + \delta \rho(r')] - \rho(r)\rho(r')}{|r-r'|}
  \]
  \[
  = \frac{1}{2} \int dr \int dr' \frac{\rho(r')\delta \rho(r') + \rho(r)\delta \rho(r') + \delta \rho(r)\delta \rho(r')}{|r-r'|}
  \]
  \[
  = \int dr \int dr' \frac{\rho(r')}{|r-r'|} \delta \rho(r)
  \]
  \[
  \therefore \frac{\delta E}{\delta \rho(r)} = \int dr' \frac{\rho(r')}{|r-r'|}
  \]
Rayleigh-Ritz Variational Principle

- **Complex functional derivative**
  \[ \psi(r) = \psi_1(r) + i\psi_2(r); \quad \psi^*(r) = \psi_1(r) - i\psi_2(r) \]

- **Energy functional**
  \[ E[\psi(r)] = \frac{\langle \psi|\hat{h}|\psi \rangle}{\langle \psi|\psi \rangle} = \frac{\int dr \psi^*(r)\hat{h}(r)\psi(r)}{\int dr \psi^*(r)\psi(r)} = \frac{\int dr \psi^*(r) \left[ -\frac{\nabla^2}{2} + n(r) \right] \psi(r)}{\int dr \psi^*(r)\psi(r)} \]

- **Gradient (for a normalized wave function)**
  \[ \frac{\delta E}{\delta \psi^*(r)} = (\hat{h}(r) - \langle \psi|\hat{h}|\psi \rangle)\psi(r) \]

- **Steepest descent**
  
  Repeat
  \[ \psi(r) \leftarrow \psi(r) - \Delta\tau (\hat{h}(r) - \langle \psi|\hat{h}|\psi \rangle)\psi(r) \]
Conjugate Gradient Method

1. **Conjugate gradient:** Does not spoil the minimizations in the previous iteration steps

2. **Line minimization:** Directly moves to the minimum along the conjugate-gradient direction

\[
\text{for } i \leftarrow 1 \text{ to Max\_iteration} \\
\text{if } i = 1 \\
\quad \tilde{g}_i \leftarrow g_i \\
\text{else} \\
\quad \tilde{g}_i \leftarrow g_i + \frac{g_i \cdot g_i}{g_{i-1} \cdot g_{i-1}} \tilde{g}_{i-1} \\
\text{endif} \\
\quad \psi_i \leftarrow \psi_{i-1} + \frac{g_{i-1} \cdot g_{i-1}}{\tilde{g}_i \cdot h \cdot \tilde{g}_i} \tilde{g}_i \\
\quad g_i \leftarrow g_{i-1} - \frac{g_{i-1} \cdot g_{i-1}}{\tilde{g}_i \cdot h \cdot \tilde{g}_i} h \cdot \tilde{g}_i \\
\text{if convergent, exit} \\
\text{endfor}
\]

M.C. Paynet *et al.*, *Rev. Mod. Phys.* **64**, 1045 ('92)
Quantum Molecular Dynamics

- Born-Oppenheimer (adiabatic) approximation: Electron wave function \( \psi(r_1, \ldots, r_{\text{Nelectron}}) \) is determined with fixed nuclei positions \( R_n \) \( (n = 1, \ldots, N_{\text{nucleus}}) \):

\[
\psi^*(r_1, \ldots, r_{\text{Nelectron}}) \leftarrow \text{argmin}_{E} E[\psi(r_1, \ldots, r_{\text{Nelectron}}), \{R_n\}]
\]

- Newton’s equations for the classical motion of nuclei:

\[
M_n \frac{d^2}{dt^2} R_n = - \frac{\partial}{\partial R_n} E[\psi^*(r_1, \ldots, r_{\text{Nelectron}}), \{R_n\}]
\]

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F. Shimojo et al., Phys. Rev. Lett. 104, 126102 ('10); ibid. 111, 066103 ('13)
16,661-atom QMD simulation of Li$_{441}$Al$_{441}$ in water on 786,432 IBM BlueGene/Q cores

K. Shimamura et al., *Nano Lett.* **14**, 4090 ('14)
Nonadiabatic Quantum Molecular Dynamics

- Excited states: Linear-response time-dependent density functional theory [Casida, ’95]
- Interstate transitions: Surface hopping [Tully, ’90; Jaeger, Fisher & Prezhdo, ’12]
Simulating SF in Amorphous DPT

- Move up from molecules to microstructures
- Challenge: Unprecedented $10^4$-atom NAQMD simulation
- Computational approach: Divide-conquer-recombine (DCR) NAQMD

- Divide-conquer-recombine NAQMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT
NAQMD-informed Kinetic Monte Carlo

- NAQMD-KMC exciton population dynamics reproduces the experimentally observed two time scales (~1 & 100 ps) in amorphous DPT

**Experiment**

W. Mou et al., *Appl. Phys. Lett.* 100, 173301 ('13)

Photoexcited Carriers in MAPbI$_3$

- Organometal halide perovskites (e.g. methylammonium lead iodide, CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$) for solar cells with high power conversion efficiency > 20%
  

- Nonabiabatic QMD simulation
  
  Pb & I sublattices act as disjunct pathways for rapid & balanced transport of free electrons & holes—electron (63% Pb-6p) & hole (90% I-5p);
  
  diffusion coefficients $D_e = (1.16\pm0.31)\times10^{-2}$ cm$^2$/s & $D_h = (1.01\pm0.42)\times10^{-2}$ cm$^2$/s
  
  Expt: $D_e = (1.7\pm1.1)\times10^{-2}$ cm$^2$/s & $D_h = (1.1\pm0.7)\times10^{-2}$ cm$^2$/s [Stranks et al., *Science* 342, 341 (’13)]

• In ultrafast ‘electron & X-ray cameras’, laser light hitting a material is almost completely converted into nuclear vibrations — key to switching material properties on & off at will for future electronics applications

• High-end quantum simulations reproduce the ultrafast energy conversion at exactly the same space & time scales, & explain it as a consequence of photo-induced phonon softening

I. Tung et al., *Nature Photon.* **13**, 425 (’19)
Quantum Molecular Dynamics Simulations

V. Kochat et al., Adv. Mater. 29, 1703754 ('17)

A. Krishnamoorthy et al., Nanoscale 10, 2742 ('18)
Detailed lecture notes on quantum molecular dynamics (QMD) simulations are available at a USC course home page

EXTREME-SCALE QUANTUM SIMULATIONS

Course Description
Computer simulation of quantum-mechanical dynamics has become an essential enabling technology for physical, chemical & biological sciences & engineering. Quantum-dynamics simulations on extreme-scale parallel supercomputers would provide unprecedented predictive power, but pose enormous challenges as well. This course surveys & projects algorithmic & computing technologies that will make quantum-dynamics simulations metascalable, i.e., "design once, continue to scale on future computer architectures".

http://cacs.usc.edu/education/cs699-lecture.html