Introduction to

Computational Physics

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Franz J. Vesely
University of Vienna

www.ap.univie.ac.at/users/Franz.Vesely/

7. Numerical Quantum Mechanics

Erwin Schrödinger: he gave us the homework

We will skip "big" quantum chemistry (Hartree-Fock and heirs) and confine ourselves to the "slim" physical methods of

— **QM Diffusion Monte Carlo (QMC, DMC)**

— **Path Integral MC (PIMC)**

— **Density Functional MD (DFMD)**

Diffusion Monte Carlo (DMC)

Write E.S.'s equation as

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = H\,\Psi(\mathbf{r},t) \quad \text{with} \qquad H \equiv -\frac{\hbar^2}{2m}\nabla^2 + [U(\mathbf{r}) - E_T]$$

E_T ... *trial energy* (arbitrary, affects only the phase of the wave function)
Introducing an "imaginary time" $s \equiv it/\hbar$ we get

$$\frac{\partial\Psi(\mathbf{r},s)}{\partial s} = D\nabla^2\Psi(\mathbf{r},s) - [U(\mathbf{r}) - E_T]\,\Psi(\mathbf{r},s)$$

with $D \equiv \hbar^2/2m$.

$\Longrightarrow$ Describes dffusion with autocatalysis!

Visualization: population of bacteria diffusing about in a fluid with locally varying nutrient concentration.

Try out various E_T:

- If $E_T = E_0$ (ground state energy), then

$$\lim_{s \to \infty} \Psi(\mathbf{r}, s) \;=\; \Psi_0(\mathbf{r})$$

- If $E_T > E_0$, the weight $I(s) \equiv \int \Psi(\mathbf{r}, s) \, d\mathbf{r}$ will grow exponentially in time s.

- If $E_T < E_0$, $I(s)$ decreases exponentially in time.

$\Longrightarrow$Solve the equation for various E_T, monitor the temporal behavior of $I(s)$ remains stationary, $E_T = E_0$ and $\Psi = \Psi_0$.

How to solve **???** $\Longrightarrow$

Solve the **Diffusion** and **Autocatalysis** parts separately.

Diffusion:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} \;=\; D \, \nabla^2 n(\mathbf{r}, t)$$

$\Longrightarrow$ Solve via Brownian random walk:

$$\mathbf{r}_i(t_{n+1}) \;=\; \mathbf{r}_i(t_n) + \boldsymbol{\xi}_i \,, \quad i = 1, \ldots N$$

with $\xi_{x,y,z}$ Gaussian with $\sigma^2 = 2D \, \Delta t$. Watching an ensemble made up of M systems of N particles each, the mean density

$$p(\mathbf{r}, t) \equiv \langle \delta\left[\mathbf{r}_i(t) - \mathbf{r}\right] \rangle \;=\; \frac{1}{M} \frac{1}{N} \sum_{l=1}^{M} \sum_{i=1}^{N} \delta\left[\mathbf{r}_{i,l}(t) - \mathbf{r}\right]$$

is an estimate for the solution $n(\mathbf{r}, t)$ of the diffusion equation.

Autocatalysis:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = f(\mathbf{r})\, n(\mathbf{r}, t)$$

This is just the *Relaxation equation* with $f(\mathbf{r})$ in place of $-\lambda$!

$\Longrightarrow$Stochastic solution: let systems in the ensemble die or multiply according to their "fitness":
− Systems with many particles at high $f(\mathbf{r})$ are replicated
− Systems with unfavorable configurations are weeded out

Diffusion Monte Carlo:

Consider N particles of mass m, randomly distributed in a region with $U(\mathbf{r})$. Determine the "diffusion constant" $D = \hbar^2/2m$; choose a trial energy E_T, a time step Δs and an initial ensemble size $M(s_0)$.

1. For each system l $(= 1, \dots M(s_0))$ in the ensemble and for each particle i $(= 1, \dots N)$ perform a random displacement step

$$\mathbf{r}_{i,l}(s_{n+1}) = \mathbf{r}_{i,l}(s_n) + \boldsymbol{\xi}_{i,l}, \text{ with } \boldsymbol{\xi}_{i,l} \text{ Gaussian}(\sigma^2 = 2D\,\Delta s)$$

2. For each system l determine the multiplicity

$$K_l = exp\left\{\left[\sum_{i=1}^{N} U(\mathbf{r}_{i,l}) - E_T\right]\Delta s\right\}$$

3. Produce $K_l - 1$ copies of each system. If $K_l < 1$, delete that system with probability $1 - K_l$.
4. If the number M of systems increases systematically, choose a smaller E_T; if M decreases, take a larger E_T.
5. Repeat until M remains constant; then the ground state energy is $E_0 = E_T$ and

$$\Psi_0(\mathbf{r}) = \langle\delta(\mathbf{r}_{i,l} - \mathbf{r})\rangle$$

Applications:

- Compute ground state energy and wave function.
- In this form only applicable to *Bosons* such as ^{4}He.
- Variants: also applicable to fermionic systems.

Path Integral Monte Carlo (PIMC)

Up to now: ground state, i.e. $kT = 0$.

Now: Finite temperature $\implies$

$$\Psi = \sum_n c_n \Psi_n, \qquad \text{where} \quad H\Psi_n = E_n \Psi_n$$

Quantum analog of the Boltzmann factor: *Density matrix*,

$$\rho(\mathbf{r}, \mathbf{r}'; kT) \equiv \sum_n \Psi_n^*(\mathbf{r})\, e^{-H/kT}\, \Psi_n(\mathbf{r}') \;=\; \sum_n \Psi_n^*(\mathbf{r})\, e^{-E_n/kT}\, \Psi_n(\mathbf{r}')$$

$\implies$Average of some observable $a(\mathbf{r})$,

$$\langle a \rangle \;=\; \int a(\mathbf{r})\, \rho(\mathbf{r}, \mathbf{r}; \beta)\, d\mathbf{r} \left/ \int \rho(\mathbf{r}, \mathbf{r}; \beta)\, d\mathbf{r} \equiv Sp[a\rho] \right/ Sp[\rho]$$

with $\beta \equiv 1/kT$.

Example − Free particle:

$$\rho_0(x, x'; \beta) = \left[\frac{m}{2\pi\beta\hbar^2}\right]^{1/2} e^{-m(x-x')^2/2\beta\hbar^2}$$

Thus, $\rho_0(x, x; \beta) = const$, as it should.

But: $\rho(\mathbf{r}, \mathbf{r}; \beta)$ usually too complex!
$\Longrightarrow$ Is there a way to use only simple density matrices? − Yes!!

It can be shown that

$$\rho(x, x'; \beta) = \int dx'' \rho(x, x''; \frac{\beta}{2}) \, \rho(x'', x'; \frac{\beta}{2})$$

R.h.s: *Path integral*, involving two density matrices at $\beta/2$, i.e. double kT.

By iteration,

$$\rho(x_0, x_P; \beta) =$$

$$\int \ldots \int dx_1\, dx_2 \ldots dx_{P-1}\ \rho(x_0, x_1; \frac{\beta}{P}) \ldots \rho(x_{P-1}, x_P; \frac{\beta}{P})$$

(P... "Trotter number")

But:
Higher temperature $P \cdot kT \Longrightarrow$ Lower effect of potential $U(x) \Longrightarrow$ Approach to free particle with density matrix ρ_0

With $P = 5 - 100$ the diagonal element reads

$$\rho(x_0, x_0; \beta) \;=\; A^{P/2} \int \ldots \int dx_1 \ldots dx_{P-1}\, e^{-\beta(U_{int} + U_{ext})}$$

with

$$A \equiv \frac{mP}{2\pi\beta\hbar^2}\,, \qquad U_{ext} \equiv \sum_{p=0}^{P-1} U(x_p)/P\,, \quad U_{int} \equiv \frac{A\pi}{\beta} \sum_{p=0}^{P-1} \left(x_p - x_{p+1}\right)^2$$

And in 3 dimensions:

$$\rho(\mathbf{r}_0, \mathbf{r}_0; \beta) \;=\; A^{3P/2} \int \ldots \int d\mathbf{r}_1 \ldots d\mathbf{r}_{P-1}\, e^{-\beta(U_{int} + U_{ext})}$$

with $A \equiv mP/2\pi\beta\hbar^2$, and

$$U_{ext} \equiv \sum_{p=0}^{P-1} U(\mathbf{r}_p)/P\,, \qquad U_{int} \equiv \frac{A\pi}{\beta} \sum_{p=0}^{P-1} \left|\mathbf{r}_p - \mathbf{r}_{p+1}\right|^2$$
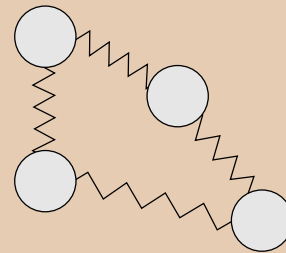
But this looks like a classical Boltzmann factor of a *ring polymer*. The P elements of this polymer feel an external potential

$$u_{ext}(x_p) \;=\; U(x_p)/P$$

and successive links of the ring chain are coupled together by a harmonic bond potential

$$u_{int}(x_p, x_{p+1}) \;=\; \frac{A\pi}{\beta}\left(x_p - x_{p+1}\right)^2$$

where $x_P = x_0$.

classical   quantum mechanical

Therefore:
Monte Carlo of classical ring polymer $\Longleftrightarrow$ MC of single quantum particle

Path integral Monte Carlo for one particle:

A quantum particle in an external potential $U(\mathbf{r})$ is represented by a ring polymer consisting of P links. Let $\mathbf{r} \equiv \{\mathbf{r}_0, \ldots \mathbf{r}_{P-1}\}$ and the total potential energy

$$U_{pot}(\mathbf{r}) \equiv U_{int}(\mathbf{r}) + U_{ext}(\mathbf{r})$$

be given, with

$$U_{int} \equiv \frac{mP}{2\beta^2\hbar^2} \sum_{p=0}^{P-1} |\mathbf{r}_p - \mathbf{r}_{p+1}|^2 \qquad \text{and} \qquad U_{ext} \equiv \frac{1}{P} \sum_{p=0}^{P-1} U(\mathbf{r}_p)$$

1. Displace $\mathbf{r}$ as a whole by $\Delta\mathbf{r}$ (large); also, move each link $\mathbf{r}_p$ by a small amount $\Delta\mathbf{r}_p$; the new configuration is called $\mathbf{r}'$.
2. Compute $U_{pot}(\mathbf{r}')$ and $\Delta U \equiv U_{pot}(\mathbf{r}') - U_{pot}(\mathbf{r})$.
3. Metropolis step: Draw ξ from an equidistribution in $[0, 1]$;
   if $\Delta U \leq 0$, put $\mathbf{r} = \mathbf{r}'$;
   if $\Delta U > 0$ and $\xi \leq e^{-\beta\Delta U}$, put $\mathbf{r} = \mathbf{r}'$ as well;
   if $\Delta U > 0$ and $\xi > e^{-\beta\Delta U}$, let $\mathbf{r}$ remain unchanged.
4. Return to (1).

Generalization to N quantum particles interacting by a pair potential $u(|\mathbf{r}_j - \mathbf{r}_i|)$:

Each of these particles has to be represented by a P-element ring chain. Denoting the position of element p in chain (=particle) i by $\mathbf{r}_{i,p}$, we have for the diagonal element of the total density matrix

$$\rho(\mathbf{r}_0, \mathbf{r}_0; \beta) =$$

$$A^{3NP/2} \int \ldots \int d\mathbf{r}_{1,1} \ldots d\mathbf{r}_{N,P-1} \, exp \left[-A\pi \sum_{i=1}^{N} \sum_{p=0}^{P-1} \left(\mathbf{r}_{i,p} - \mathbf{r}_{i,p+1} \right)^2 \right]$$

$$\cdot exp \left[-\frac{\beta}{P} \sum_{i=1}^{N} \sum_{j>i} \sum_{p=0}^{P-1} u(|\mathbf{r}_{j,p} - \mathbf{r}_{i,p}|) \right]$$

with $\mathbf{r}_0 \equiv \{\mathbf{r}_{1,0} \ldots \mathbf{r}_{N,0}\}$. Obviously, the pair potential acts only between *respective* links (p) of *different* chains.

Exercise: Write a PIMC program treating the case of one particle of mass m in a two-dimensional oscillator potential $U(\mathbf{r}) = kr^2/2$. Let the Trotter number vary between 2 and 10. Determine the positional probability $p(\mathbf{r})$ of the particle from the relative frequency of residence at r, averaged over all chain links. Noting that

$$p(\mathbf{r}) \quad \equiv \quad \rho(\mathbf{r}, \mathbf{r}; \beta)$$

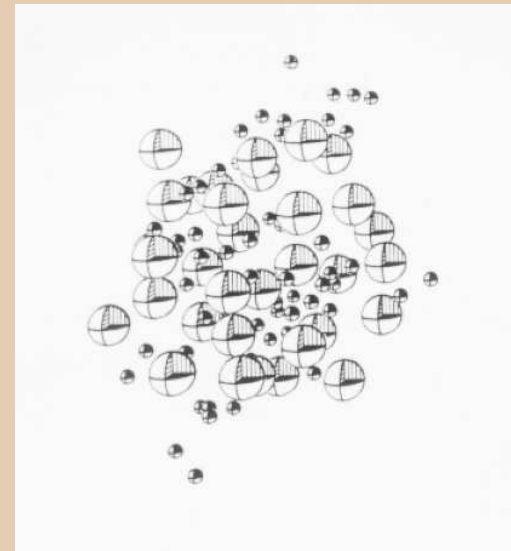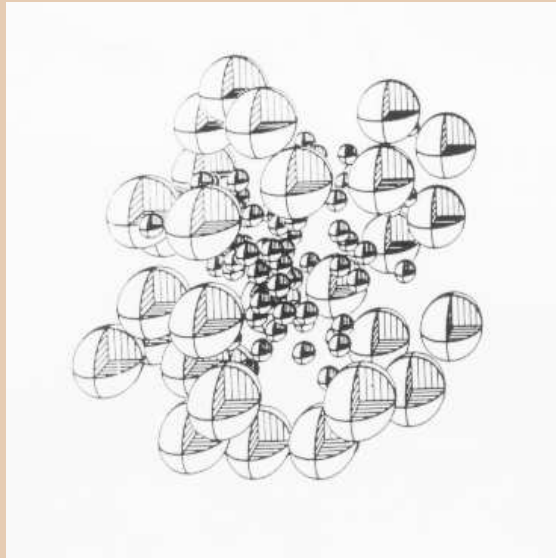we would expect for the two-dimensional harmonic oscillator (with $\omega_0^2 = k/m$)

$$p(r) \quad = \quad 2\pi r \left[\frac{A}{\pi}\right] e^{-Ar^2}, \quad \text{where} \quad A \equiv \frac{m\omega_0^2}{\hbar} tanh\frac{\beta\hbar\omega_0}{2}$$

(For convenience, put $\hbar = 1$.) Draw several configurations of the ring polymer that occur in the course of the simulation.

Sample Application:

Coker, D. F., et al., J. Chem. Phys. 86 (1987) 5689: solvation of electrons in simple fluids.

From Coker et al.: solvated electron a) in liquid helium: strongly localized. Shell of He is rigid and difficult to polarize, $\Longrightarrow$ repulsive cage.
b) in liquid xenon: extended positional probability. Shell of Xe polarizable $\Longrightarrow$ flat dipole potential.

Density Functional Molecular Dynamics (DFMD)

So far: time-independent calculations.
Now: Quantum molecular dynamics
Born-Oppenheimer approximation: Treat atomic cores (or ions, i.e. nucleus plus inner electrons) as classical particles, the outer electrons by QM.
$\Longrightarrow$Electronic wave functions assume least energy configuration.

$\Longrightarrow$Minimization problem!

− Let $\Psi_i(\mathbf{r})$ be the wave functions of the N electrons. The electron density at some position $\mathbf{r}$ is then given by

$$n(\mathbf{r}) \quad \equiv \quad \sum_{i=1}^{N} |\Psi_i(\mathbf{r})|^2$$

− Let $\{\mathbf{R}_l\}$ be the momentary configuration of the (classical) ions.

The ions produce a potential field $U(\mathbf{r}; \{\mathbf{R}_l\})$ which the electronic wave functions are invited to adjust to.

Total energy:

$$E(\{\Psi_i\}; \{\mathbf{R}_l\}) \;=\; E_1 + E_2 + E_3 + E_4$$

with

$$E_1 \;=\; \sum_{i=1}^{N} \int_V d\mathbf{r}\, \Psi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 \right] \Psi_i(\mathbf{r})$$

kinetic energy of the electrons

$$E_2 = \int_V d\mathbf{r}\, U(\mathbf{r}; \{\mathbf{R}_l\})\, n(\mathbf{r})$$

potential energy in the field created by the ions

$$E_3 \;=\; \frac{1}{2} \int_V \int_V d\mathbf{r}\, d\mathbf{r}' \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

electrostatic interaction between the electrons

$$E_4 \;=\; E_{xc}[n(\mathbf{r})]$$

exchange + correlation energy, e.g. by local density approximation, LDA

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Expand $\Psi_i(\mathbf{r})$ in plane waves,

$$\Psi_i(\mathbf{r}) \;=\; \sum_{\mathbf{k}} c_i(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

with up to several hundred terms per electron.

$\Longrightarrow$ Minimize $E(\{\Psi_i\}; \{\mathbf{R}_l\})$ with respect to $\{c_i(\mathbf{k})\}$, maintaining orthonormality,

$$\int_V \Psi_i^*(\mathbf{r}, t)\,\Psi_j(\mathbf{r}, t)\,d\mathbf{r} \;=\; \delta_{ij}$$

– Conventional method (Nobel prize winner): Apply variational calculus, solve iteratively. $\Longrightarrow$ Too slow for MD!

– But: *Simulated annealing* is fast! May be done either in its original version (MC), or by a sort of MD in configuration space, Car's and Parrinello's "dynamical simulated annealing":

Let M be the ion mass, and μ an abstract "mass" assigned to each electronic wave function Ψ_i, with $\mu \approx 1 AMU << M$. Then

$$
\begin{aligned}
\mu \ddot{\Psi}_i(\mathbf{r}, t) &= -\frac{\delta E}{\delta \Psi_i^*(\mathbf{r}, t)} + \sum_j \lambda_{ij} \Psi_j(\mathbf{r}, t) \\
M \ddot{\mathbf{R}}_l &= -\nabla_l E
\end{aligned}
$$

where the Lagrange multipliers λ_{ij} have been introduced to maintain orthonormality.

The first equation represents the abstract "motion" in the space of the electronic degrees of freedom, the second equation describes the classical motion of the heavy ions.

To keep the "kinetic energy" of Ψ_i small, use a thermostat!

Applications:

- Amorphous silicon
- Lithium
- microclusters of alkali metals
- molten carbon
- ionic melts
- etc.