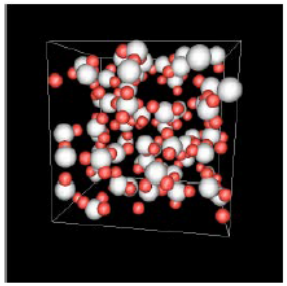
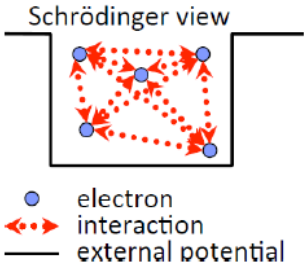
First-Principles/ab-initio Methods for HEDP

➢ Density-Functional Theory (DFT)

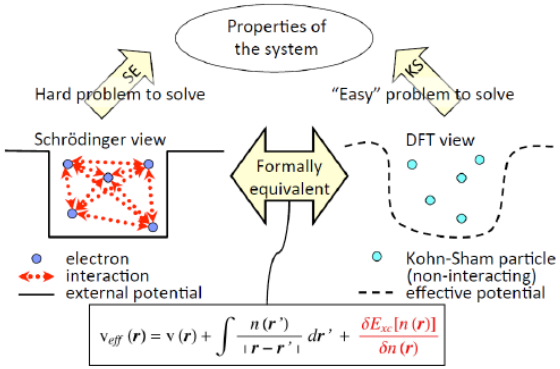




Quantum many-body Schrödinger Equation:

$$\left[-\frac{\hbar^2}{2m}\sum_i \nabla^2 + V(r_1, r_2, \ldots, r_n)\right]\Psi(r_1, r_2, \ldots, r_n) = E\Psi(r_1, r_2, \ldots, r_n)$$

DFT versus the Schrödinger Equation



All many-body effects are included in the effective potential via the Exchange-Correlation functional, $E_{xc}[n(r)]$.

The Kohn-Sham DFT equation can be *iteratively* solved once the exchange-correlation functional is known

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\boldsymbol{r})\right)\psi_\nu(\boldsymbol{r}) = \epsilon_\nu \psi_\nu(\boldsymbol{r}) \quad \nu = 1, 2, \ldots, N$$

$$n(\boldsymbol{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\boldsymbol{r})|^2$$

$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

AM05, LDA, GGA, Meta-GGA, Hybrids

The form of the divine exchange-correlation functional is unknown.
We need to find good approximations.

➢ Path-Integral Monte-Carlo (PIMC)

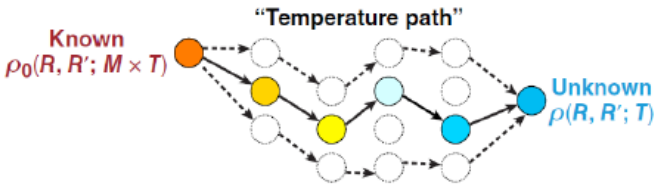
PIMC,* based on the convolution of the density matrix, uses the Monte Carlo method to efficiently evaluate multidimensional integrations

- The density matrix $\rho(R, R'; T)$, introduced by J. von Neumann in 1927, describes the statistical distribution of a quantum system in thermal equilibrium

$$\rho(R,R';T) = \left\langle R \left| e^{-\hat{H}/kT} \right| R' \right\rangle = \sum_n \varphi_n(R)\varphi_n(R')e^{-E_n/kT}$$

- The convolution property of $\rho(R, R'; T)$ can be written as

$$\rho(R,R';T) = \left\langle R \left| e^{-\hat{H}/KT} \right| R' \right\rangle = \int dR_1 \rho(R,R_1;2T)\rho(R_1,R';2T)$$



*D. M. Ceperley, Rev. Mod. Phys. 67, 279 (1995);
B. Militzer, Ph.D. thesis, University of Illinois at Urbana-Champaign, 2000.

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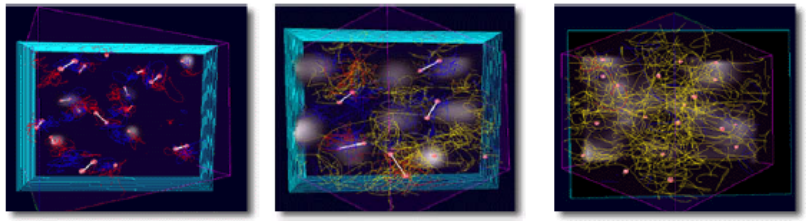
PIMC allows simulations of quantum systems without any assumptions beyond the Schrodinger equation at finite temperature

- Once we knew ρ(R,R';β), we can calculate the thermodynamic properties of the system with the corresponding operators ô:

$$< \hat{O} >= \frac{\int dR\, dR' \left\langle R \left| \hat{O} \right| R' \right\rangle \langle R'|\rho|R\rangle}{\int dR \langle R|\rho|R\rangle}$$



Molecular liquid | Molecular metallic liquid | Metallic liquid

➢ Quantum Monte-Carlo (QMC)

Many-electron wave functions

- Hartree product

$$\Psi_{\mathcal{H}} = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\ldots\psi_N(\mathbf{x}_N)$$

- Slater determinant

$$\Psi_{\mathcal{D}} = \frac{1}{\sqrt{N_e}}\begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & \ldots & \psi_1(\mathbf{x}_{N_e}) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & & \\ \vdots & & \ddots & \\ \psi_{N_e}(\mathbf{x}_1) & & & \psi_{N_e}(\mathbf{x}_{N_e}) \end{vmatrix}$$

- Single determinant Slater-Jastrow function

$$\Psi_{\mathcal{DJ}} = \Psi_{\mathcal{D}}\Psi_{\mathcal{J}}$$

where the Jastrow factor $\Psi_{\mathcal{J}}$ could be (for example)

$\Psi_{\mathcal{J}} = \exp(\mathcal{J})$,

$\mathcal{J} = \sum_{i\neq j}^{N_e}\left[-U_0(r_{ij}) - U(r_{ij}) + \sum_n^{N_n} S^n(\mathbf{r}_i, \mathbf{r}_j, r_{ij})\right]$,

and $U_0(r_{ij}) = \frac{A}{r_{ij}}\left(1 - \exp\left(-\frac{r_{ij}}{F}\right)\right)$.

Variational Monte Carlo

Trial many-body wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \equiv \Psi(\mathbf{R})$

$$E_{\mathrm{VMC}} = \frac{\int \Psi\hat{H}\Psi\, d\mathbf{R}}{\int \Psi^2\, d\mathbf{R}} = \frac{\int \Psi^2(\Psi^{-1}\hat{H}\Psi)\, d\mathbf{R}}{\int \Psi^2\, d\mathbf{R}} \left(\equiv \int p(x)f(x)\, dx\right)$$

with

$$f(x) \equiv E_{\mathrm{L}} = \frac{\hat{H}\Psi}{\Psi} \quad (\text{"local energy"}) \text{ and } p(x) = \Psi^2 \text{ (close to optimal)}$$

Generate M points distributed according to Ψ^2

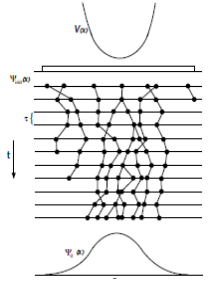
$$E_{\mathrm{VMC}} \simeq \frac{1}{M}\sum_i E_{\mathrm{L}}(\mathbf{R}_i)$$

Zero variance principle - as Ψ tends to the exact wave function, the fluctuations in E_{L} tend to zero.

Diffusion Monte Carlo

- So use distribution (ensemble) of Brownian particles ('walkers') to represent $\Psi(\mathbf{R}, \tau)$. The Green's function $G(\mathbf{R}, \mathbf{R}', \delta\tau)$ is then interpreted as the probability of a walker moving from point $\mathbf{R}'$ to $\mathbf{R}$ in a time $\delta\tau$. Branching factor determines population of walkers: In regions of high V, walkers will be killed off; in low V regions, walkers will multiply.

- Propagate distribution defined by Green's function in imaginary time. At long times, excited states will decay away. Can then continue propagation and accumulate averages of observables.



Diffusion Monte Carlo

- How do we propagate solution in imaginary time?

$$\Psi(\mathbf{R}, \tau + \delta\tau) = \int G(\mathbf{R}, \mathbf{R}', \delta\tau)\Psi(\mathbf{R}', \tau)\, d\mathbf{R}'$$

- How do we find Green's function $G(\mathbf{R}, \mathbf{R}', \delta\tau)$? Consider Schrödinger equation in two parts:

$$-\frac{1}{2}\nabla^2_{\mathrm{R}}\Psi = -\frac{\partial\Psi}{\partial\tau} \quad \text{diffusion equation}$$

$$V\Psi = -\frac{\partial\Psi}{\partial\tau} \quad \text{rate equation}$$

- Green's function for diffusion equation known: $3N$ dimensional Gaussian with variance $\delta\tau$ in each dimension.

$$G(\mathbf{R}, \mathbf{R}', \delta\tau) = (2\pi\delta\tau)^{-\frac{3N}{2}} \exp\left(-\frac{|\mathbf{R} - \mathbf{R}'|^2}{2\delta\tau}\right)$$

- Extra branching factor from rate equation.

$$\times \exp\left[-\delta\tau\left(\frac{V(\mathbf{R}) + V(\mathbf{R}') - 2E_{\mathrm{T}}}{2}\right)\right]$$

Diffusion Monte Carlo

onsider imaginary time behaviour of time-dependent Schrödinger equation

$$\left(\hat{H} - E_T\right)\Psi(\mathbf{R}, t) = -\frac{\partial\Psi(\mathbf{R}, t)}{i\partial t}$$

or eigenstate, general solution is clearly

$$\phi(\mathbf{R}, t) = \phi(\mathbf{R}, 0)e^{-i(\hat{H} - E_T)t}$$

hen expand arbitrary $\Psi(\mathbf{R}, t)$ in eigenfunctions of $\hat{H}$

$$\Psi(\mathbf{R}, t) = \sum_{n=0}^{\infty} c_n\phi_n(\mathbf{R})e^{-i(E_n - E_T)t}$$

ubstitute $it \to \tau$ (imaginary time). Oscillatory behaviour becomes xponential.

$$\Psi(\mathbf{R}, \tau) = \sum_{n=0}^{\infty} c_n\phi_n(\mathbf{R})e^{-(E_n - E_T)\tau}$$

et time independence by choosing E_T to be ground state eigenvalue E_0. s $\tau \to \infty$, $\Psi \to$ ground state ϕ_0.

$$\Psi(\mathbf{R}, \tau) = c_0\phi_0 + \sum_{n=1}^{\infty} c_n\phi_n(\mathbf{R})e^{-(E_n - E_T)\tau}$$