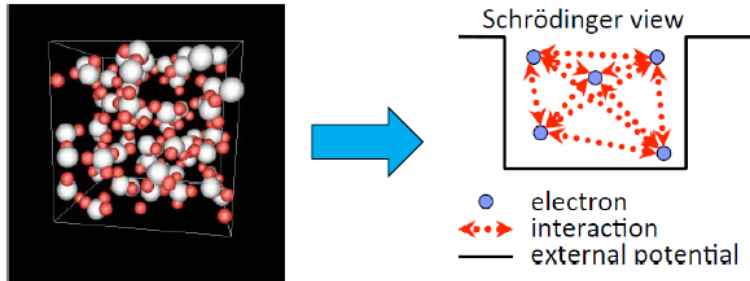


First-Principles/ab-initio Methods for HEDP

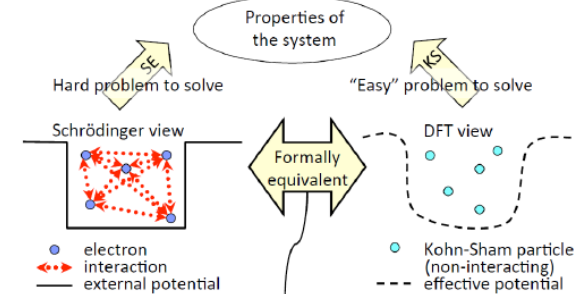
➤ Density-Functional Theory (DFT)



Quantum many-body Schrödinger Equation:

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

DFT versus the Schrödinger Equation



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

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

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



$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) \right) \psi_v(\mathbf{r}) = \epsilon_v \psi_v(\mathbf{r}) \quad v = 1, 2, \dots, N$$

$$n(\mathbf{r}) = \sum_{v=1}^N |\psi_v(\mathbf{r})|^2$$

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

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

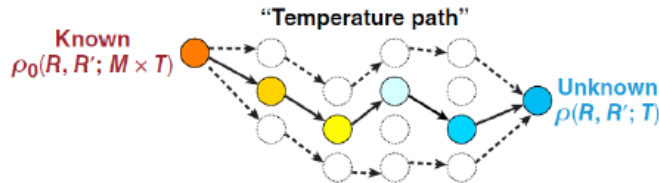


- The density matrix $\rho(R, R'; T)$, introduced by J. von Neumann in 1927, describes the statistical distribution of a quantum system in thermal equilibrium

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

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

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



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

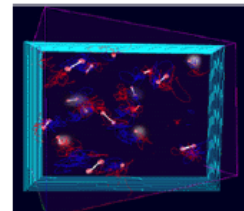
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PIMC allows simulations of quantum systems without any assumptions beyond the Schrodinger equation at finite temperature

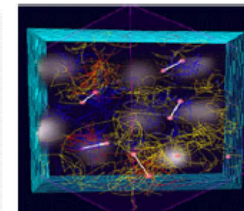


- Once we knew $\rho(R, R'; \beta)$, we can calculate the thermodynamic properties of the system with the corresponding operators \hat{o} :

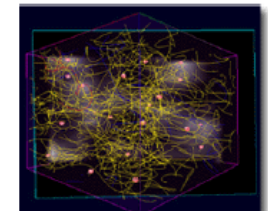
$$\langle \hat{o} \rangle = \frac{\int dR dR' \langle R | \hat{o} | R' \rangle \langle R' | \rho | R \rangle}{\int dR \langle R | \rho | R \rangle}$$



Molecular liquid



Molecular metallic liquid



Metallic liquid

➤ Quantum Monte-Carlo (QMC)

Many-electron wave functions

- Hartree product

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

- Slater determinant

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

- Single determinant Slater-Jastrow function

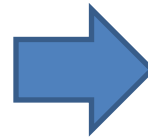
$$\Psi_{\mathcal{DJ}} = \Psi_{\mathcal{D}}\Psi_{\mathcal{J}}$$

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

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

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

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



Variational Monte Carlo

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

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

with

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

Generate M points distributed according to Ψ^2

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

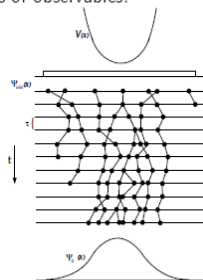
Zero variance principle - as Ψ tends to the exact wave function, the fluctuations in E_L tend to zero. ■



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?

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

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

$$\begin{aligned} -\frac{1}{2}\nabla_{\mathbf{R}}^2 \Psi &= -\frac{\partial \Psi}{\partial \tau} && \text{diffusion equation} \\ V\Psi &= -\frac{\partial \Psi}{\partial \tau} && \text{rate equation} \quad \blacksquare \end{aligned}$$

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

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

- Extra **branching factor** from rate equation.

$$\times \exp\left[-\delta\tau \left(\frac{V(\mathbf{R}) + V(\mathbf{R}') - 2E_T}{2}\right)\right]$$



Diffusion Monte Carlo

consider **imaginary time** behaviour of time-dependent Schrödinger equation

$$(\hat{H} - E_T)\Psi(\mathbf{R}, t) = -\frac{\partial \Psi(\mathbf{R}, t)}{\partial t} \quad \blacksquare$$

or eigenstate, general solution is clearly

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

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

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

substitute $it \rightarrow \tau$ (imaginary time). **Oscillatory** behaviour becomes **exponential**.

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

at time independence by choosing E_T to be ground state eigenvalue E_0 . as $\tau \rightarrow \infty$, $\Psi \rightarrow$ ground state ϕ_0 .

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