Quantum Monte Carlo Simulation

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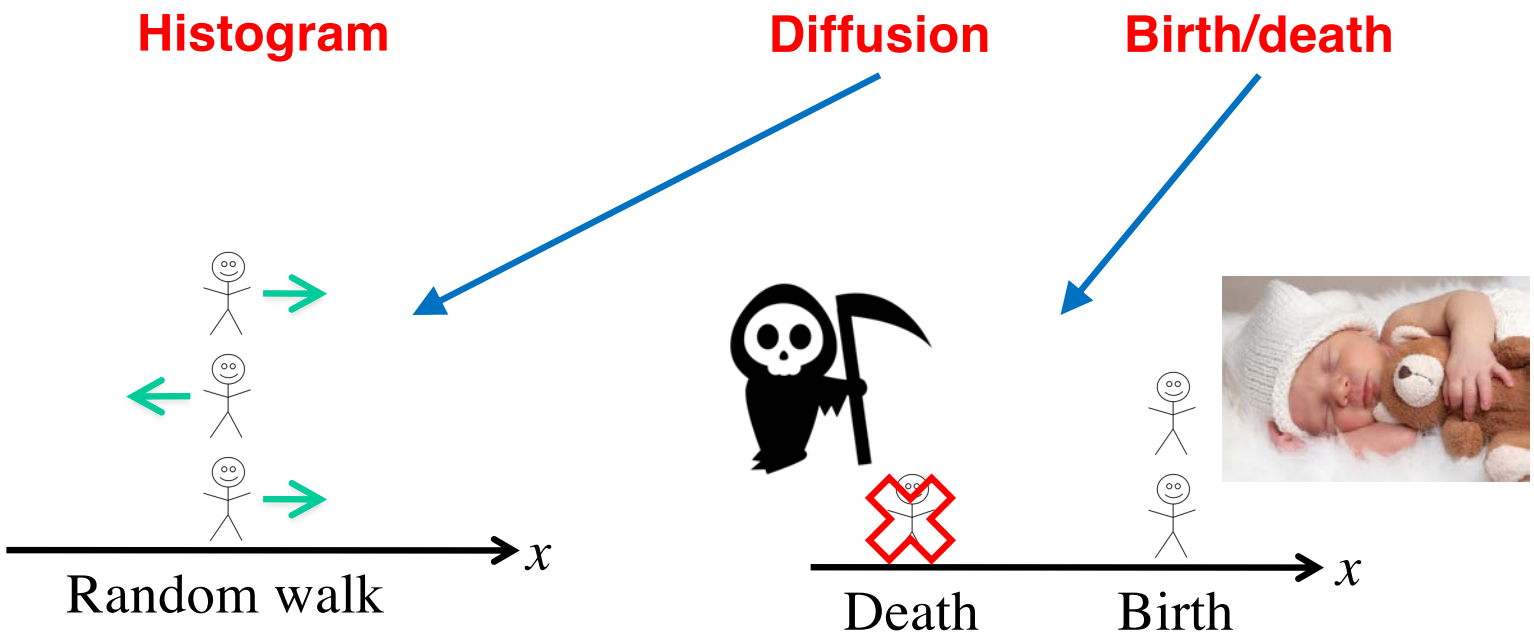
Random walk to solve quantum eigenvalue problem

Imaginary-time Schrödinger Equation

- $\tau = it$

$$\frac{\partial}{\partial \tau}\psi(x,\tau) = -\frac{H}{\hbar}\psi(x,\tau) = \frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi(x,\tau) - \frac{V(x)}{\hbar}\psi(x,\tau)$$



$$D_{\mathrm{QMC}} = \frac{\hbar}{2m} = 58\ \mathrm{m}^2/\mathrm{s} \gg D_{\mathrm{water}} = 10^{-9}\ \mathrm{m}^2/\mathrm{s}$$

Ground-State Filter

$$\psi(x,\tau) = \exp(-H\tau/\hbar)\psi(x,0) = \sum_n c_n \phi_n(x)\exp(-E_n\,\tau/\hbar)$$

$$c_n = \int dx \phi_n(x)\psi(x,0)$$

Completeness: $|\psi\rangle = \overbrace{\sum_n |n\rangle\langle n|}^{=1}\psi\rangle$

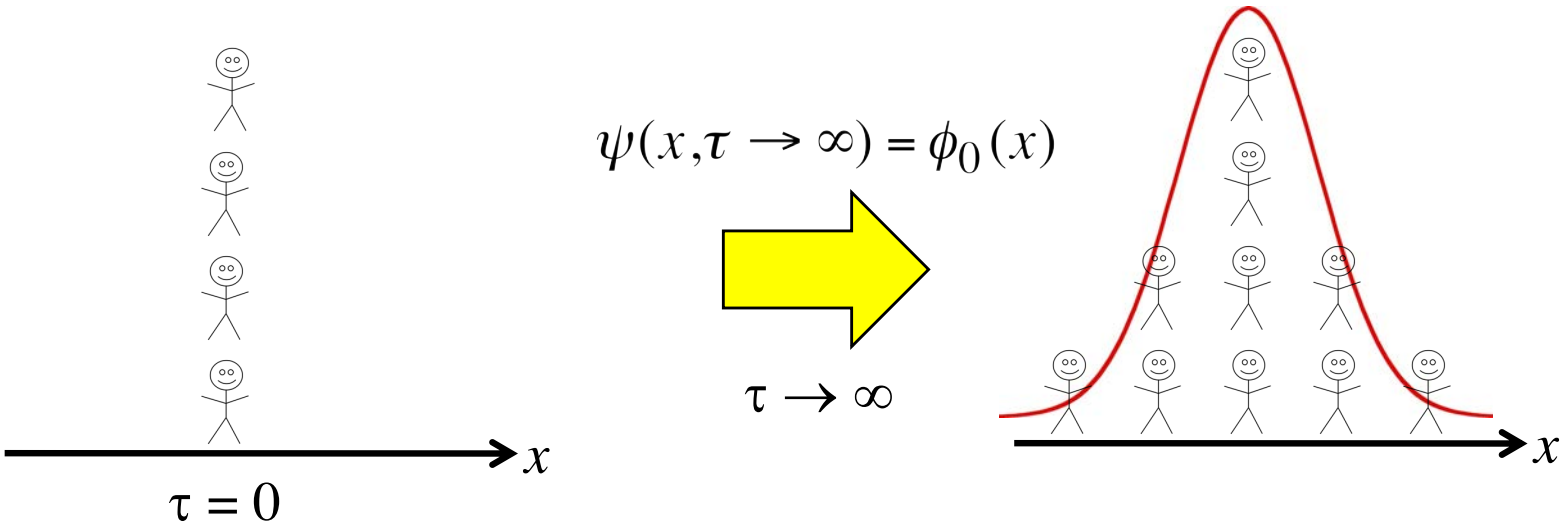
$\langle 0|H|0\rangle = E_0 < E_1 < \cdots$

$$\lim_{\tau\to\infty}\psi(x,\tau) = c_0\phi_0(x)\exp(-E_0\,\tau/\hbar)$$

- **Energy estimate**

It's not $\psi^*(x,\tau)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x,\tau)$

$$E_0 = \langle V\rangle = \frac{\int_{-\infty}^{\infty} V(x)\psi(x,\tau)dx}{\int_{-\infty}^{\infty}\psi(x,\tau)dx} \cong \frac{1}{N}\sum_{i=1}^{N} V(x_i)$$



Reference Energy

- **Energy measured relative to reference energy to achieve stationary population**

$$\frac{\partial}{\partial\tau}\psi(x,\tau) = \frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi(x,\tau) - \frac{V(x) - V_{\text{ref}}}{\hbar}\psi(x,\tau)$$

$$\int_{-\infty}^{\infty}\frac{\partial}{\partial\tau}\psi(x,\tau)dx = \left[\frac{\hbar}{2m}\frac{\partial}{\partial x}\psi(x,\tau)\right]_{-\infty}^{\infty} - \int\frac{V(x)}{\hbar}\psi(x,\tau)dx + \frac{V_{\text{ref}}}{\hbar}\int\psi(x,\tau)dx$$

$$= -\int\frac{V(x)}{\hbar}\psi(x,\tau)dx + \frac{V_{\text{ref}}}{\hbar}\int\psi(x,\tau)dx$$

$$\int_{-\infty}^{\infty}\frac{\partial^2}{\partial x^2}\psi(x) = \left[\frac{\partial}{\partial x}\psi(x)\right]_{-\infty}^{\infty} = 0$$

- **For $\tau \to \infty$,**

$$\psi(x,\tau) \approx c_0\phi_0(x)\exp\left(-(E_0 - V_{\text{ref}})\,\tau/\hbar\right)$$

$$\therefore \frac{\partial}{\partial\tau}\psi(x,\tau) \approx \frac{V_{\text{ref}} - E_0}{\hbar}\psi(x,\tau)$$

$$\int\frac{V_{\text{ref}} - E_0}{\hbar}\psi(x,\tau)dx = -\int\frac{V(x)}{\hbar}\psi(x,\tau)dx + \frac{V_{\text{ref}}}{\hbar}\int\psi(x,\tau)dx$$

$$\therefore \frac{E_0}{\hbar}\int\psi(x,\tau)dx = \int\frac{V(x)}{\hbar}\psi(x,\tau)dx \quad \Rightarrow \quad E_0 = \frac{\int V(x)\psi(x,\tau)dx}{\int\psi(x,\tau)dx} = \langle V\rangle$$

Choice of Reference Energy

- **Number of random walkers:** $N(\tau) = \int_{-\infty}^{\infty} \psi(x,\tau)dx$

$$\frac{d}{d\tau}N = \frac{V_{\text{ref}} - \langle V \rangle}{\hbar} N(\tau)$$

$$\because \int_{-\infty}^{\infty} \frac{\partial}{\partial\tau}\psi(x,\tau)dx = -\int \frac{V(x)}{\hbar}\psi(x,\tau)dx + \frac{V_{\text{ref}}}{\hbar}\int_{-\infty}^{\infty}\psi(x,\tau)dx$$

- **Choose new V_{ref} to counter-balance the current population growth**

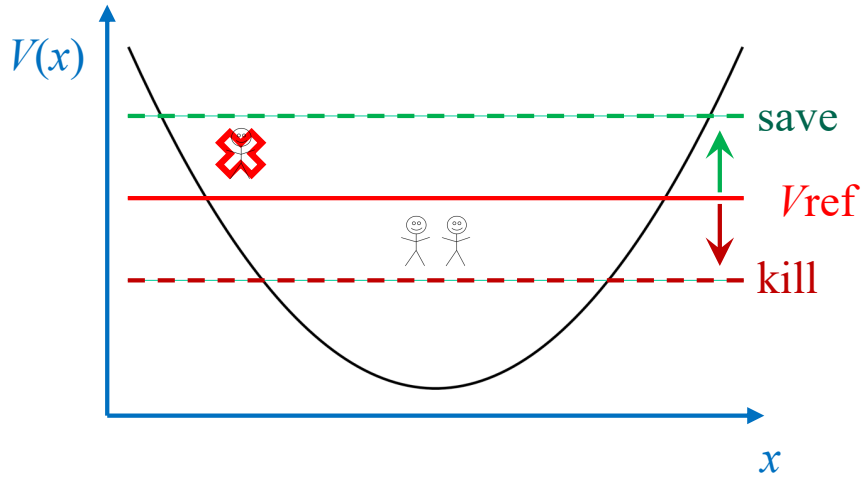
$$-\frac{d}{d\tau}N|_{\text{current}} = \frac{V_{\text{ref}}^{\text{new}} - \langle V \rangle}{\hbar} N(\tau)$$

$$\frac{V_{\text{ref}}^{\text{new}}}{\hbar} = \frac{\langle V \rangle}{\hbar} - \frac{dN/d\tau}{N(\tau)}$$

$$\therefore V_{\text{ref}} = \langle V \rangle - \frac{N(\tau+\Delta\tau) - \cancel{N(\tau)}}{N(\tau)\Delta\tau}$$

(N_0)

$\hbar = 1$ (atomic unit)



For numerical stability, replace N by $N(\tau = 0) = N_0$

Quantum Monte Carlo Algorithm

1. Place N_0 walkers at the initial set of positions x_i.
2. Compute the reference energy, $V_{\text{ref}} = \Sigma_i\, V(x_i)/N_0$.
3. For each walker,

   $$D = \frac{\hbar}{2m} = \frac{1}{2}(\text{a. u.}) = \frac{(\Delta s)^2}{2\Delta\tau}$$

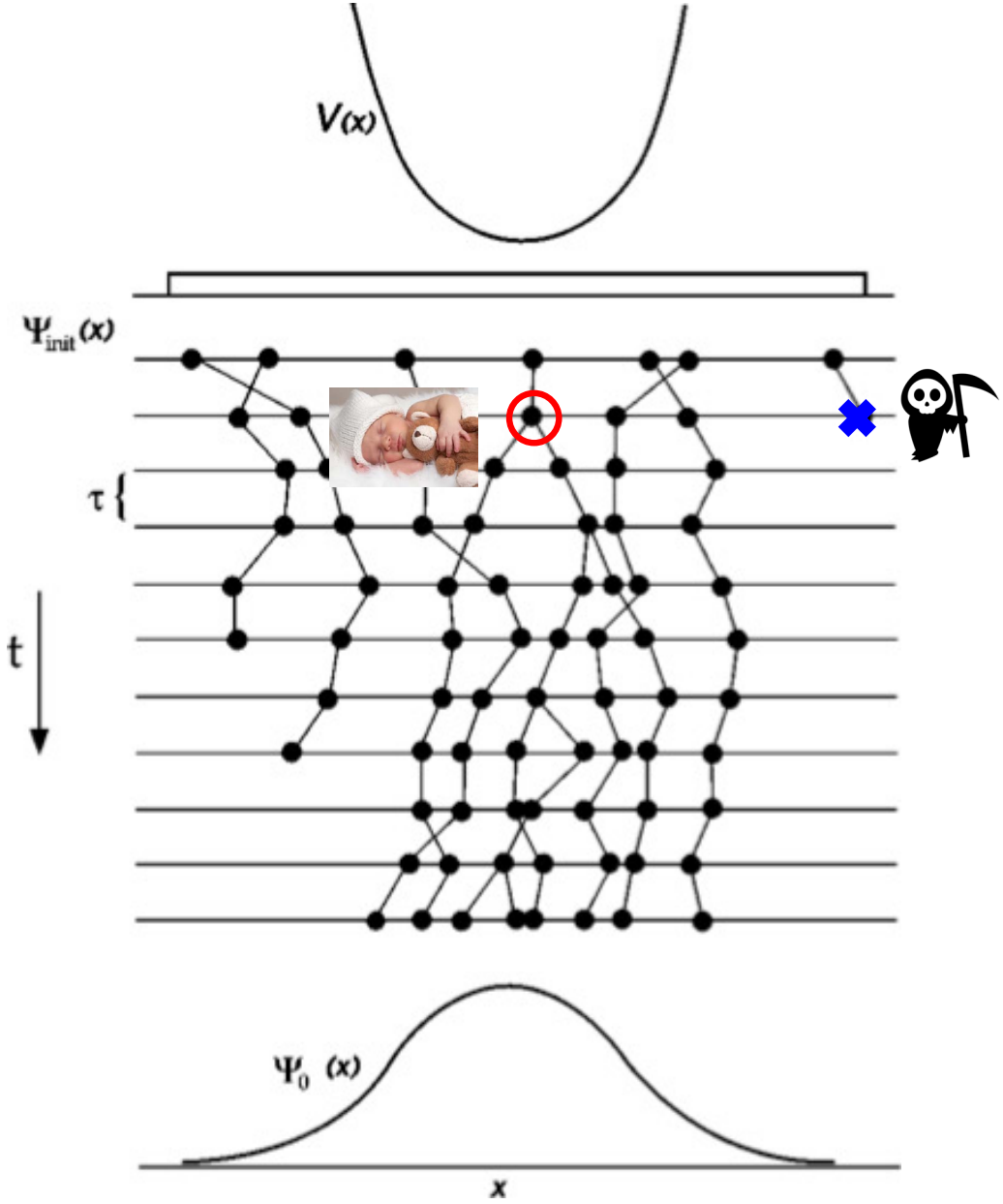
   a. Randomly move the walker to the right or left by a fixed step length Δs.

   b. Compute $\Delta V = V(x) - V_{\text{ref}}$ & a random number $r \in [0, 1]$. If $\Delta V > 0$ & $r < \Delta V \Delta\tau$ ($\Delta\tau = \Delta s^2$), then remove the walker. If $\Delta V < 0$ & $r < -\Delta V \Delta\tau$, then add another walker at x. Otherwise, just leave the walker at x.
4. Compute the mean potential energy $\langle V \rangle = \Sigma_i\, V(x_i)/N$ & the actual number of random walkers N. The new reference potential is given by

   $$V_{\text{ref}} = \langle V \rangle - \frac{N(\tau + \Delta\tau) - N(\tau)}{N(\tau)\Delta\tau} N_0$$

   The average $\langle V \rangle$ is an estimate of the ground state energy.
5. Repeat steps 3–4 until the estimates of the ground state energy $\langle V \rangle$ have reached a steady state value with only random fluctuations. Average $\langle V \rangle$ over many Monte Carlo steps to compute the ground state energy.

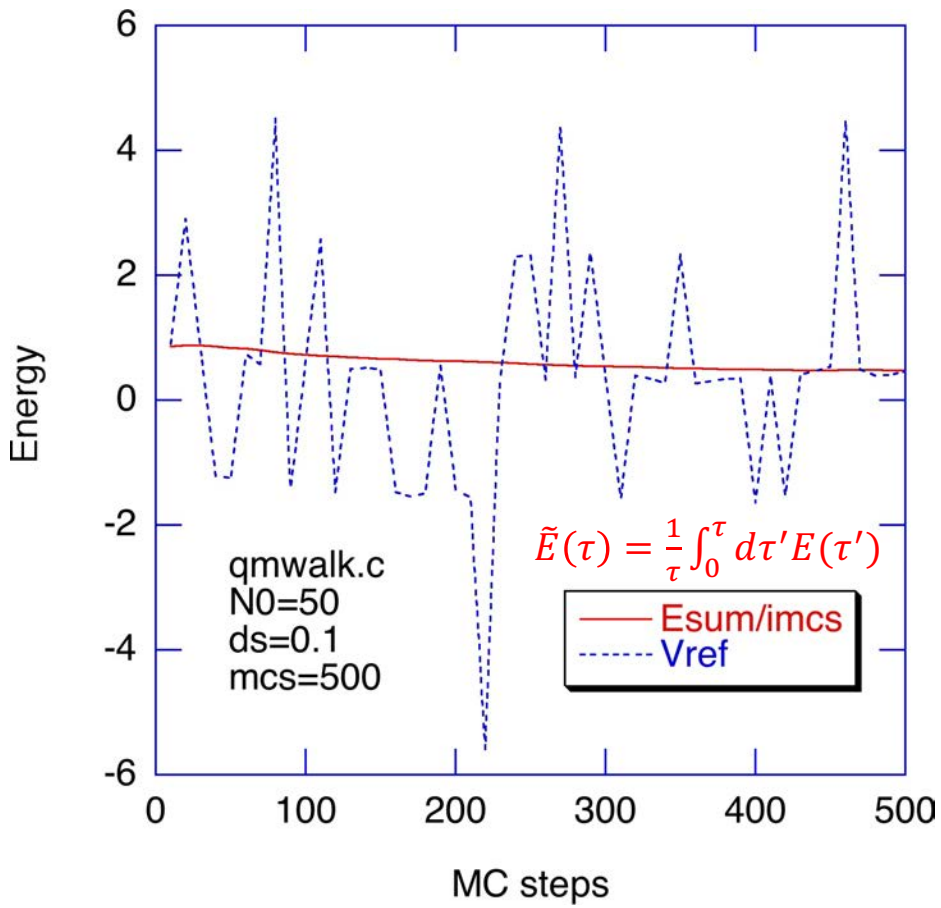
Random Walk + Birth/Death

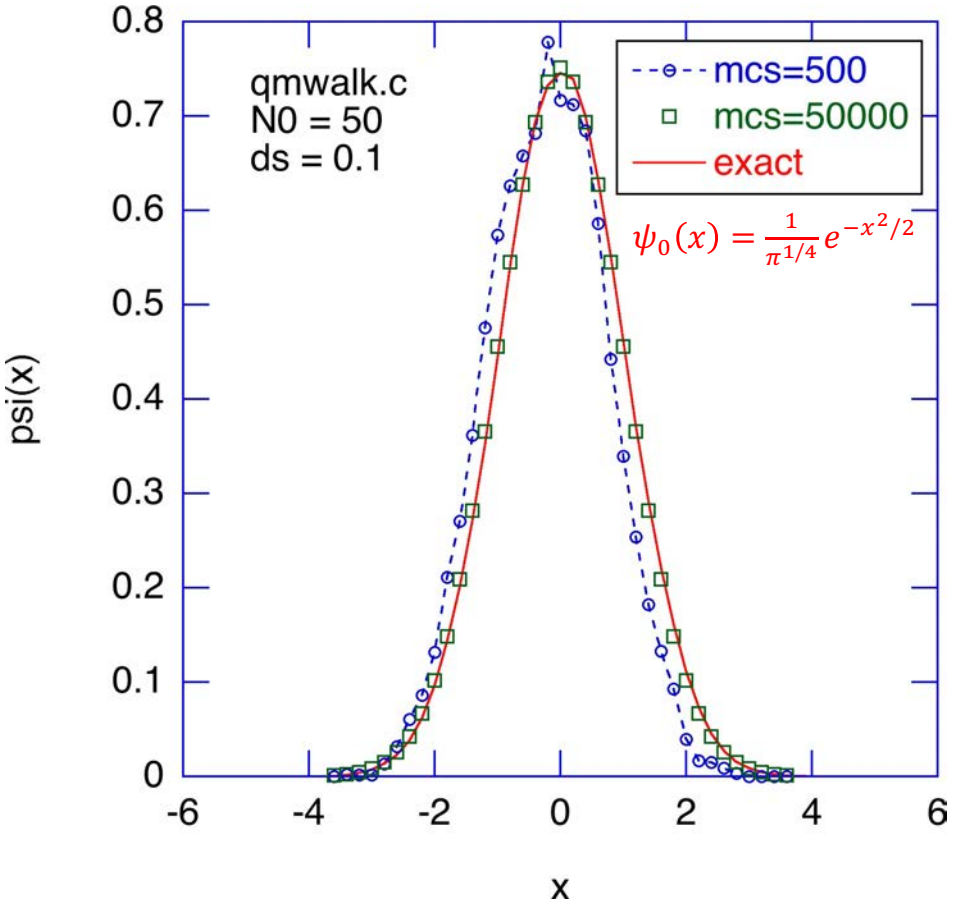


W. M. C. Foulkes *et al.*, *Rev. Mod. Phys.* **73**, 33 ('01)

Numerical Example

- $V(x) = x^2/2$ (in atomic unit)





(after 0.4×500 = 200 MC steps of thermalization)

$$D = \frac{\hbar}{2m} = \frac{1}{2}(\text{a.u.}) = \frac{(\Delta s)^2}{2\Delta\tau}$$

Where to Go from Here

- **Types of QMC for many electrons: diffusion MC & variational MC (zero temperature); path-integral MC (finite temperature)**

  Interacting Electrons, Martin, Reining & Ceperley (Cambridge Univ. Press, '16)

- **QMC for realistic materials**

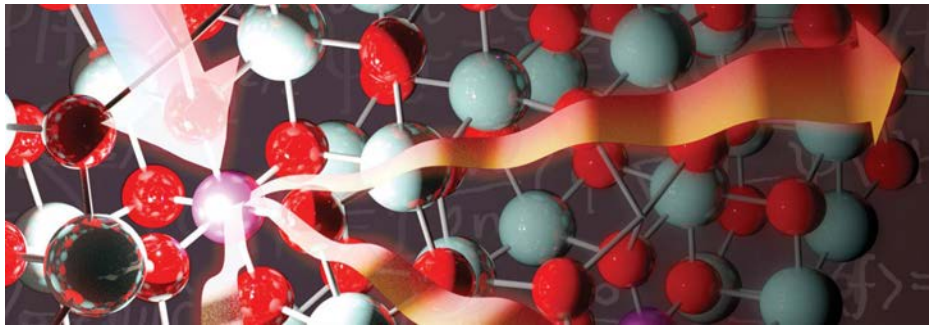
  Quantum Monte Carlo simulations of solids, Foulkes et al., *Rev. Mod. Phys.* **73**, 33 ('01)

- **QMC software (variational & diffusion)**

  ***QMCPACK*: http://qmcpack.org**

  ***QWalk*: http://qwalk.github.io/mainline**

  ***CASINO*: https://vallico.net/casinoqmc**



- **Neural networks to represent many-electron wave functions (~ variational QMC)**

  ***NetKet*: https://www.netket.org**