

Variational Monte Carlo methods for trapped electrons

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- Electrons in a harmonic oscillator potential
- Quantum Monte Carlo
- Trial Wave Function
- Optimization Techniques

Electrons trapped in a harmonic oscillator potential

One Particle System

- The hamiltonian of the one particle system is

$$\hat{H} = -\frac{1}{2}\nabla^2 + \frac{1}{2}\omega^2(x^2 + y^2 + z^2)$$

- The solution to the stationary Schrödinger equation

$$\hat{H}\Phi_{n_x, n_y, n_z} = E_{n_x, n_y, n_z} \Phi_{n_x, n_y, n_z} \text{ is}$$

$$\Phi_{n_x, n_y, n_z}(x, y, z) \propto e^{-\omega(x^2+y^2+z^2)} H_{n_x}(\sqrt{\omega}x) H_{n_y}(\sqrt{\omega}y) H_{n_z}(\sqrt{\omega}z)$$

- The energy eigenvalues are $E_{n_x, n_y, n_z} = \omega(\frac{3}{2} + n_x + n_y + n_z)$
- Degeneracy is $g_N = (N + 1)(N + 2)$ when including spin degree of freedom

Electrons trapped in a harmonic oscillator potential

Many Body System

- The hamiltonian of the many body particle system is

$$\hat{H} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 \sum_{i=1}^N (x_i^2 + y_i^2 + z_i^2) + \sum_{i=1}^N \sum_{i<j}^N \frac{1}{r_{ij}}$$

- There exist in general no closed form solution to this problem. If we remove the correlation part in the hamiltonian, the solution is a slater determinant

$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix}$$

General Properties Of Monte Carlo Methods

- A statistical simulation method in the sense that a sequences of random numbers is used to perform the simulation.
- Particluarly suited for studying physical systems that can be described by a probability distribution function (PDF).
- The numerical efficiency scales nicely with the systems dimensionality

Random Walk And The Metropolis Algorithm

- Markov Chain - A random walk where the transition probability only depends on the current state of the system.
- Need to reach a distribution that is independent of time - equilibrium distribution
- Necessary condition for equilibrium:
 - Ergodicity
 - Detailed Balance
- Solution - Metropolis Algorithm
 - Choosing the transition probabilities in such a way that the sequence of states generated by the random walk sample the PDF
 - One choice is the Accept/Reject algorithm

$$A(\mathbf{R}_y, \mathbf{R}_x) = \min\left(1, \frac{\rho(\mathbf{R}_y)}{\rho(\mathbf{R}_x)}\right)$$

Quantum Monte Carlo

The basis for QMC is the Variational principle which states that given a hamiltonian H and a parameterized wave function Ψ_α , $\alpha = (\alpha_1, \dots, \alpha_N)$, the expectation value of $\langle H \rangle$, defined through

$$E_\alpha[H] = \langle H \rangle = \frac{\int d\mathbf{R} \Psi_\alpha^*(\mathbf{R}) H(\mathbf{R}) \Psi_\alpha(\mathbf{R})}{\int d\mathbf{R} \Psi_\alpha^*(\mathbf{R}) \Psi_\alpha(\mathbf{R})},$$

is an upper bound to the ground state energy E_0 of the hamiltonian H , that is

$$E_0 \leq \langle H \rangle.$$

Quantum Monte Carlo

Our PDF is of course

$$P(\mathbf{R}) = \frac{|\psi_T(\mathbf{R})|^2}{\int |\psi_T(\mathbf{R})|^2 d\mathbf{R}}$$

and by defining a new quantity

$$E_L(\mathbf{R}) = \frac{1}{\psi_T(\mathbf{R})} H\psi_T(\mathbf{R}),$$

called the local energy, we can rewrite the energy expectation value as

$$E[H] = \langle H \rangle = \int P(\mathbf{R}) E_L(\mathbf{R}) d\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^N P(\mathbf{R}_i) E_L(\mathbf{R}_i)$$

with N being the number of Monte Carlo samples.

The statistical uncorrelated variance which is defined by

$$\sigma^2 = \langle H^2 \rangle - \langle H \rangle^2$$

will be zero for the exact wave function. This is because

$$\langle H^n \rangle = \frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) H^n(\mathbf{R}) \Psi_T(\mathbf{R})}{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})} = \text{constant}$$

The goal is then to find the set of parameters that gives the lowest energy and/or variance.

Importance sampling

- The random walk is calculated by $\mathbf{R}_y = \mathbf{R}_x + r \times \delta s$
- To improve the algorithms efficiency we want to have a biased walk towards states of high probability. This is accomplished by using importance sampling.
- The new random walk is now given by $\mathbf{R}_y = \mathbf{R}_x + D\mathbf{F}(\mathbf{R}_x)\delta t + r_g$ where $\mathbf{F} = 2\Psi^{-1}\nabla\Psi$ is a quantum force that directs the walkers towards states of high probability.
- The acceptance probability becomes

$$A(\mathbf{R}_y, \mathbf{R}_x) = \min\left(1, \frac{P(\mathbf{R}_x, \mathbf{R}_y; \delta t)\rho(\mathbf{R}_y)}{P(\mathbf{R}_y, \mathbf{R}_x; \delta t)\rho(\mathbf{R}_x)}\right)$$

where $P(\mathbf{R}_y, \mathbf{R}_x; \delta t) = N \exp[-(\mathbf{R}_y - \mathbf{R}_x - D\delta t\mathbf{F}(\mathbf{R}_x))^2/4D\delta t]$ is the marginal transition probability

Trial Wave Function

- My trial wave function will be $\Psi_T = \Psi_{SD}\Psi_J$
- Because I only use the spatial part of the Slater determinant the rows will be pairwise equal and this results in a zero determinant
- This is solved by approximating the Slater determinant as

$$\Psi_{SD}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \propto \Psi_{SD\uparrow}(\mathbf{r}_1, \dots, \mathbf{r}_{N/2})\Psi_{SD\downarrow}(\mathbf{r}_{N/2+1}, \dots, \mathbf{r}_N)$$

- This ansatz is not antisymmetric under the exchange of electrons with opposite spins but it can be shown (see for example Moskowitz and Kalos, Int. J. Quantum Chem. **20** (1981) 1107) that it gives the same expectation value for the energy as the full Slater determinant. As long as the Hamiltonian is spin independent, the above is correct.

Pade-Jastrow Correlation Function

- To account for the correlation between the electrons I use the Pade-Jastrow function

$$\Psi_{J,\gamma}(r_{ij}) = \exp \left(\sum_{i=1}^N \sum_{i<j}^N U_{\beta,\gamma}(r_{ij}) \right)$$

where $U(r_{ij})$ is given by

$$U_{\beta,\gamma}(r_{ij}) = \frac{\sum_{k=1}^n \gamma_k r_{ij}^k}{1 + \sum_{k=1}^n \beta_k r_{ij}^k}$$

Cusp Condition

- Because of the $1/r_{ij}$ term in the hamiltonian, the columb potential diverges when to particles collide. Thus we need an compensating divergence in the kinetic energy so that the total energy remains finite
- The advantage of the Jastrow function is that it satisfies the electron-electron cusp condition if one choose special values for γ_1
- One can show that in 3D $\gamma_1 = 1/4$ for equal spin electrons and $\gamma_1 = 1/2$ for opposite spin electrons. In the 2D case the values are $\gamma_1 = 1/3$ and $\gamma_1 = 1$.

Stochastic Gradient Method (SGA)

- SGA is an optimization method for multidimensional functions with statistical variance
- Ari Harju presented, in an arXiv paper from 1997, a way to use the SGA method to optimize wave functions.
- The idea is to use the fluctuations in the local energy/variance to find the global minima and not get stuck in the an local one.
- The basic idea is to use an recursive algorithm

$$\alpha_{i+1} = \alpha_i - \ell_i \nabla_{\alpha} E(\alpha)$$

where ℓ_i is a set of weighting factors that should satisfy

$$\sum_{i=1}^{\infty} \ell_i^2 < \sum_{i=1}^{\infty} \ell_i = \infty$$

Stochastic Gradient Method (SGA)

- The energy gradient can be written as

$$\frac{\partial E}{\partial \alpha_i} = 2 \left\langle E_L \frac{\Psi'}{\Psi} \right\rangle - 2 \langle E_L \rangle \left\langle \frac{\Psi'}{\Psi} \right\rangle$$

- One choice of weight factor is $\ell_i = \frac{1}{i}$