

UCSB, Physics 129L, Computational Physics

Lecture notes, Week 10

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1 Quantum Monte Carlos

1.1 variational principle and trial wavefunctions

The **variational principle** states, any expectation value with a trial wavefunction $|\Psi_T\rangle$ has larger or equal energy with respect to the ground state energy,

$$E_T = \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \geq E_0$$

where E_0 is the true ground state energy.

This implies that: if E_T is **close to the exact energy**, Ψ_T is a good approximation. On the other hand, if E_T is **far from the exact energy**, we need a better wavefunction.

The **local energy** is defined as:

$$E_L(\mathbf{R}) = \frac{H\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}.$$

If Ψ_T is an exact eigenstate of H , then $E_L(\mathbf{R})$ is a **constant** (zero variance). In reality, the variance is **not zero** due to imperfections in Ψ_T .

$$\sigma^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2.$$

If we have **low variance**, the trial wavefunction Ψ_T is close to an eigenstate.

1.2 Importance sampling on trial wavefunctions

Suppose we wish to compute the expectation value of an operator $O[R]$, (such as differential (∂_R) or function ($f(R)$) operators), with respect to a wavefunction $\Psi(R)$ (which we do not know exactly). The expectation value is

$$\langle O[R] \rangle = \frac{\int dR \Psi^*(R) O[R] \Psi(R)}{\int dR |\Psi(R)|^2}.$$

In Monte Carlo integration, we introduce a probability density $P(R)$ and, using the **importance sampling**, we rewrite the integrals as,

$$\langle O[R] \rangle = \frac{\int dR \frac{\Psi^*(R) O[R] \Psi(R)}{P(R)} P(R)}{\int dR \frac{|\Psi(R)|^2}{P(R)} P(R)}.$$

Then, if we **sample configurations** R_i from $P(R)$, we approximate the integrals by the following sum,

$$\langle O[R] \rangle \approx \frac{\frac{1}{N} \sum_{i=1}^N \frac{\Psi^*(R_i) O[R] \Psi(R_i)}{P(R_i)}}{\frac{1}{N} \sum_{i=1}^N \frac{|\Psi(R_i)|^2}{P(R_i)}}.$$

A common and practical choice is to set,

$$P(R) = \frac{|\Psi_T(R)|^2}{\int dR |\Psi_T(R)|^2},$$

where $\Psi_T(R)$ is the **trial wave function** used as an approximation to the true (and unknown) wave function $\Psi(R)$.

We define the **local estimator** for $O[R]$ with respect to the trial wavefunction, and define the expectation value as the sum of local estimators,

$$O_L(R) = \frac{\Psi_T^*(R) O[R] \Psi_T(R)}{|\Psi_T(R)|^2} = \frac{O[R] \Psi_T(R)}{\Psi_T(R)}, \quad \langle O[R] \rangle \approx \frac{1}{N} \sum_{i=1}^N O_L(R_i),$$

with the configurations R_i drawn from $P(R) = |\Psi_T(R)|^2 / \int dR |\Psi_T(R)|^2$.

When you sample from $|\Psi_T(R)|^2$, you are generating many-body configurations R (i.e., electron positions) that follow the probability distribution $P(R)$ given by the trial wavefunction $\Psi_T(R)$.

This gives a very big problem for fermions: $P(R) \sim |\Psi_T(R)|^2$ is symmetric under particle exchange, therefore it is equal likely to have one configuration R_i and another configuration R_j under an odd number of particle swaps, such that the trial wavefunction $\Psi_T(R_i) = -\Psi_T(R_j)$ since the fermion wavefunction is antisymmetric.

Since we are sampling the symmetric probability, the configurations R_i drawn from this probability are used to calculate the expectation value via the sum of local estimators,

$$O_L(R) = \frac{O[R] \Psi_T(R)}{\Psi_T(R)}, \quad \langle O[R] \rangle \approx \frac{1}{N} \sum_{i=1}^N O_L(R_i).$$

We can see that **if the numerator $O[R] \Psi_T(R)$ does not perfectly agree with the sign change with respect to $\Psi_T(R)$ under odd number particle swaps,**

$$\Psi_T(R_i) = -\Psi_T(R_j) \Rightarrow O[R_i] \Psi_T(R_i) = -O[R_j] \Psi_T(R_j) \Rightarrow \langle O[R] \rangle = \text{oscillate}, \quad (1)$$

we will experience the fermionic sign problem: the expectation value estimation has large variance and oscillate (does not stabilize) regardless how many samples we have. In particular, if the numerator is symmetric under particle swap, the expectation value oscillates around zero regardless of the estimation,

$$\Psi_T(R_i) = -\Psi_T(R_j) \Rightarrow O[R_i] \Psi_T(R_i) = O[R_j] \Psi_T(R_j) \Rightarrow \langle O[R] \rangle \approx 0. \quad (2)$$

This leads to severe cancellation errors in Monte Carlo simulations.

Let's consider the kinetic energy operator,

$$O = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2.$$

We use a simple antisymmetric trial wavefunction for two fermions:

$$\Psi_T(x_1, x_2) = \sin(kx_1) - \sin(kx_2).$$

This ensures antisymmetry under exchange $x_1 \leftrightarrow x_2$. The kinetic energy operator for one particle is:

$$T = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}.$$

Applying this to the trial wavefunction, we have:

$$\frac{d^2}{dx_1^2} \Psi_T(x_1, x_2) = -k^2 \sin(kx_1), \quad \frac{d^2}{dx_2^2} \Psi_T(x_1, x_2) = -k^2 \sin(kx_2).$$

The total kinetic energy estimator is,

$$O_L(x_1, x_2) = -\frac{\hbar^2}{2m} \frac{\sum_{i=1}^2 \nabla_i^2 \Psi_T(x_1, x_2)}{\Psi_T(x_1, x_2)} = -\frac{\hbar^2 k^2}{2m} \frac{\sin(kx_1) + \sin(kx_2)}{\sin(kx_1) - \sin(kx_2)}.$$

The denominator $\sin(kx_1) - \sin(kx_2)$ changes sign when $x_1 \approx x_2$. This causes large fluctuations in $O_L(x_1, x_2)$.

If we sample positions x_1, x_2 using the probability distribution $|\Psi_T(x_1, x_2)|^2$, we get equal probabilities of getting (x_1, x_2) and (x_2, x_1) , leading to positive and negative values of the estimator. The sign problem naturally appears in kinetic energy evaluations due to the antisymmetric nature of $\Psi_T(x_1, x_2)$.

2 Density Functional Theory

Density Functional Theory (DFT) is used to determine the electronic structure of many-body systems (e.g., atoms, molecules, and solids). Instead of working with the many-electron wavefunction, which depends on $3N$ spatial coordinates, DFT reformulates the problem in terms of the **electron density** $\rho(\mathbf{r})$, which depends only on three spatial coordinates.

DFT has its mathematical foundations based on two theorems established by Hohenberg and Kohn in 1964. The first Hohenberg–Kohn theorem states that: **The ground-state electron density $\rho(\mathbf{r})$ uniquely determines the external potential $V_{\text{ext}}(\mathbf{r})$** (up to an additive constant), and hence all properties of the system. Mathematically, this means there is a one-to-one mapping:

$$\rho(\mathbf{r}) \longleftrightarrow V_{\text{ext}}(\mathbf{r}),$$

which implies that the ground-state many-electron wavefunction Ψ_0 and all observables are functionals of $\rho(\mathbf{r})$. It **does not** imply that $\rho(\mathbf{r})$ is only induced by external potential.

The first Hohenberg–Kohn theorem states that: There exists **a universal energy functional $E[\rho]$ such that the ground-state energy E_0 is the minimum of this functional** when evaluated at the true ground-state density $\rho_0(\mathbf{r})$:

$$E_0 = \min_{\rho} \{E[\rho]\},$$

with

$$E[\rho] = F[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}),$$

where $F[\rho]$ is a universal functional of the density containing the kinetic energy and electron–electron interactions. In other words, for any trial density $\rho(\mathbf{r})$ that is N -representable (i.e., it integrates to the number of electrons N),

$$E[\rho] \geq E_0.$$

3 Kohn–Sham Formalism

Since the exact form of $F[\rho]$ is unknown, Kohn and Sham introduced a practical approach. They **map the interacting system onto a fictitious non-interacting system that yields the same ground-state density**. The Kohn–Sham energy functional is written as:

$$E[\rho] = T_s[\rho] + E_{\text{ext}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho],$$

where:

- $T_s[\rho]$ is the kinetic energy of non-interacting electrons:

$$T_s[\rho] = -\frac{\hbar^2}{2m} \sum_{i=1}^N \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}),$$

with $\{\phi_i(\mathbf{r})\}$ being the Kohn–Sham orbitals.

- $E_{\text{ext}}[\rho]$ is the interaction energy with the external potential:

$$E_{\text{ext}}[\rho] = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}).$$

- $E_{\text{H}}[\rho]$ is the classical electrostatic (**Hartree**) energy:

$$E_{\text{H}}[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

- $E_{\text{xc}}[\rho]$ is the exchange–correlation energy functional, which includes all the many-body effects (exchange and correlation) not captured by the previous terms:

$$E_{\text{xc}}[\rho] = (T[\rho] - T_s[\rho]) + (V_{\text{ee}}[\rho] - E_{\text{H}}[\rho]).$$

For example, in LDA, we use the **exchange interaction from the free electron gas, rather than the true (non-local) exchange interaction** (Fock contribution). This can be incorporated via nonlocal Fock exchange energy calculated from the **Kohn–Sham orbitals**.

The Kohn–Sham orbitals are obtained by solving the **self-consistent Kohn–Sham equations**:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}),$$

where the effective potential is given by

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}(\mathbf{r}),$$

with the exchange–correlation potential defined as the functional derivative:

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}.$$

4 Exchange–Correlation Approximations

Since the exact form of $E_{\text{xc}}[\rho]$ is unknown, various approximations are used:

4.1 Local Density Approximation (LDA)

In LDA, the exchange–correlation energy is approximated by assuming that the system locally behaves like a homogeneous electron gas:

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{\text{xc}}(\rho(\mathbf{r})),$$

where $\varepsilon_{\text{xc}}(\rho)$ is the exchange–correlation energy per particle of a uniform electron gas. To calculate the exchange correlation potential $V_{\text{xc}}(\mathbf{r})$, we use the standard property of the functional derivative that:

$$\frac{\delta}{\delta \rho(r)} (\rho(r') \varepsilon_{\text{xc}}(\rho(r'))) = \delta(r - r') \varepsilon_{\text{xc}}(\rho(r')) + \rho(r') \frac{d}{d\rho(r')} \varepsilon_{\text{xc}}(\rho(r')).$$

Applying this to the integrand, we have,

$$V_{\text{xc}}(r) = \varepsilon_{\text{xc}}(\rho(r)) + \rho(r) \frac{d}{d\rho(r)} \varepsilon_{\text{xc}}(\rho(r)).$$

Generalized Gradient Approximation (GGA) improves upon LDA by including the gradient of the density:

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int d\mathbf{r} f(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})),$$

where f is a function of both density and its gradient.

4.2 Self-Consistent Field (SCF) Procedure

The Kohn–Sham equations are solved self-consistently:

1. **Initialize the Density:** Begin with an initial guess $\rho^{(0)}(\mathbf{r})$.
2. **Compute Effective Potential:** Evaluate $V_{\text{eff}}^{(0)}(\mathbf{r})$ using the guessed density.
3. **Solve Kohn–Sham Equations:** Solve

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}^{(0)}(\mathbf{r}) \right] \phi_i^{(0)}(\mathbf{r}) = \varepsilon_i^{(0)} \phi_i^{(0)}(\mathbf{r})$$

to obtain the Kohn–Sham orbitals.

4. **Update the Density:** Construct a new density from the occupied orbitals:

$$\rho^{(1)}(\mathbf{r}) = \sum_i^{\text{occupied}} |\phi_i^{(0)}(\mathbf{r})|^2.$$

5. **Iterate Until Convergence:** Repeat steps 2–4 until the density and energy converge within a chosen tolerance.

Approximating $\varepsilon_{xc}(\rho)$ Using Quantum Monte Carlo

In the Local Density Approximation (LDA) of Density Functional Theory (DFT), the exchange–correlation energy of an inhomogeneous electron system is approximated by assuming that locally the system behaves like a homogeneous electron gas (HEG). In mathematical terms, the LDA exchange–correlation energy functional is given by

$$E_{xc}^{\text{LDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})),$$

where $\varepsilon_{xc}(\rho)$ is the exchange–correlation energy per electron for a homogeneous electron gas of density ρ .

1. The Role of Quantum Monte Carlo in Determining $\varepsilon_{xc}(\rho)$

For the homogeneous electron gas, the total ground-state energy per electron can be expressed as

$$\varepsilon(\rho) = T_s(\rho) + \varepsilon_x(\rho) + \varepsilon_c(\rho),$$

where:

- $T_s(\rho)$ is the kinetic energy per electron for a non-interacting (free) electron gas,
- $\varepsilon_x(\rho)$ is the exchange energy per electron, which can be derived analytically,
- $\varepsilon_c(\rho)$ is the correlation energy per electron.

Quantum Monte Carlo methods—especially Diffusion Monte Carlo (DMC)—are employed to compute the total energy $\varepsilon(\rho)$ for a given electron density ρ (or equivalently, as a function of the parameter r_s , the radius of a sphere containing one electron on average).

2. Analytical Expression for the Exchange Energy

For a homogeneous electron gas, the exchange energy per electron is given by the well-known analytical expression:

$$\varepsilon_x(\rho) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \rho^{\frac{1}{3}}.$$

Alternatively, in terms of the Wigner–Seitz radius r_s , defined by

$$\frac{4\pi}{3}r_s^3 = \frac{1}{\rho},$$

this expression is often written as

$$\varepsilon_x(r_s) = -\frac{0.458}{r_s} \quad (\text{in Hartree units}).$$

3. Extracting the Correlation Energy from QMC

The total energy per electron $\varepsilon(\rho)$ obtained from QMC includes all contributions:

$$\varepsilon(\rho) = T_s(\rho) + \varepsilon_x(\rho) + \varepsilon_c(\rho).$$

Since both $T_s(\rho)$ and $\varepsilon_x(\rho)$ are known exactly for the homogeneous electron gas, the correlation energy per electron is isolated by subtracting these known terms from the total QMC energy:

$$\varepsilon_c(\rho) = \varepsilon(\rho) - T_s(\rho) - \varepsilon_x(\rho).$$

In practice, QMC simulations are performed at several densities (or values of r_s), and $\varepsilon(\rho)$ is computed with high accuracy. Then, using the known analytic expressions for $T_s(\rho)$ and $\varepsilon_x(\rho)$, one obtains numerical values for $\varepsilon_c(\rho)$.

4. Parameterization of $\varepsilon_{xc}(\rho)$

Once the QMC data provides the numerical values of $\varepsilon_c(\rho)$ (and hence the full $\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$) for a range of densities, this data is fitted to an analytical function. One popular parameterization is due to Perdew and Zunger (1981), which provides an explicit form for ε_c (and ε_{xc}) as a function of r_s . For example, for the unpolarized electron gas, one common parameterization is:

$$\varepsilon_c(r_s) = -\frac{0.1423}{1 + 1.0529\sqrt{r_s} + 0.3334 r_s} \quad (\text{in Hartree units}),$$

so that

$$\varepsilon_{xc}(r_s) = \varepsilon_x(r_s) + \varepsilon_c(r_s).$$

This analytic function can then be used in practical DFT calculations within the LDA.