Solving the Many-Electron Schrödinger Equation

With a Transformer Architecture

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Outline

The Schrödinger equation

On 1926 Schrodinger derived the Time Dependent Form.(TDSE)

$$i\,\hbar\,\partial_t \Psi = \hat{H}\,\Psi, \tag{1}$$

- $\Psi \in \mathcal{H}$ is a complex value function called **wave function**.
- $\hat{H}$ is called the **Hamiltonian Operator** , encodes all the information of the energy of the system.
- Depends on the position $\vec{\mathbf{r}}$ of a particle and the temporal evolution (t).
- Ψ encodes all information about the system; $|\Psi|^2$ gives a probability density that integrates to 1.

Hamiltonian

In the position basis:

$$\hat{H} = \frac{\hat{\vec{P}}^2}{2m} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V} \tag{2}$$

Time Dependent Form

When the wave function could be written as:

$$\psi(\vec{\mathbf{r}}, t) = R(\vec{\mathbf{r}})T(t) \tag{3}$$

TDSE returns you that:

$$T(t) = e^{-iEt/\hbar} \wedge \hat{H}R(\vec{\mathbf{r}}) = ER(\vec{\mathbf{r}}) \tag{4}$$

Where E is the total energy of the system. The eigen-problem becomes obtain R solving:

Find a Ψ, such that:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right]\psi(\vec{\mathbf{r}}) = E\psi(\vec{\mathbf{r}}) \tag{5}$$

Find the potential V of the system.

Wave Function as Probability Density

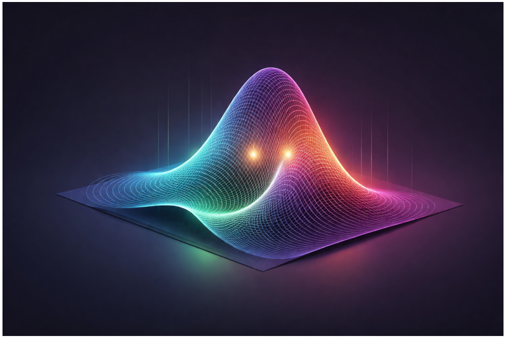


Figure 1: $|\Psi(\mathbf{R})|^2$ represent the probability to find a particle near the position $\mathbf{R}$.

Many-Body System

When considering a many-body system, we need to consider the position of each electron like also the spin of it. When considering n bodies, we have:

$$\hat{H}\psi(\mathbf{x}_1, \ldots, \mathbf{x}_n) = E\psi(\mathbf{x}_1, \ldots, \mathbf{x}_n) \quad (6)$$

With $\mathbf{x}_i = \{\mathbf{r}_i, \sigma\}$, where $\mathbf{r}_i \in \mathbb{R}^3$ is the position of each particle and $\sigma \in \{\uparrow . \downarrow\}$ is the so called spin.

Considerations

- Each particle interact with all the another particles in specific ways.
- For atoms, consider all the protons, electrons and neutrons.
- Solution obey physical laws.

Setting up the Hamiltonian

The first step is obtain a practical form of the **Hamiltonian**.

- Kinetic energy: $T = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2$.
- Electron-nuclear attraction: $V_{en} = -\sum_{i,I} \frac{Z_I}{r_{iI}}$.
- Electron-electron repulsion: $V_{ee} = \sum_{i<j} \frac{1}{r_{ij}}$.

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{I=1}^{M} \frac{1}{2M_I}\nabla_I^2 - \sum_{i=1}^{N}\sum_{I=1}^{M} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{1\leq i<j\leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{1\leq I<J\leq M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{7}$$

Borh Oppenheimer approximation helps with.

Fermi-Dirac statistics

All the fermions follow the Fermi-Dirac Statistics, this is.

- Electrons are indistinguishable fermions.
- Exchanging two electrons flips the wavefunction's sign: $\Psi(\dots i, j \dots) = -\Psi(\dots j, i \dots)$.
- Pauli exclusion: no two electrons can occupy the same

Slater Determinant

We can enforce this using a determinant to enforce an antisymmetric Ψ.

$$\psi = \begin{vmatrix} \phi_1^k(\mathbf{x}_1) & \dots & \phi_1^k(\mathbf{x}_n) \\ \vdots & & \vdots \\ \phi_n^k(\mathbf{x}_1) & \dots & \phi_n^k(\mathbf{x}_n) \end{vmatrix} \tag{8}$$

Where ϕ are called spin orbitals

Kato cusp conditions, Jastrow Factor

When two electrons

- Coulomb potentials cause a sharp cusp in Ψ when particles overlaps.
- Electron–nucleus cusp: $\left.\dfrac{\partial \Psi}{\partial r_{iI}}\right|_{r_{iI}=0} = -\, Z_I \, \Psi(0).$
- Electron–electron cusp: $\left.\dfrac{\partial \Psi}{\partial r_{ij}}\right|_{r_{ij}=0} = \dfrac{1}{2}\, \Psi(0).$

Jastrow Factor $\exp(\mathcal{J})$

In this work we are going to use this specific form:

$$\mathcal{J}_\theta(x) = \sum_{i<j;\sigma_i=\sigma_j} -\frac{1}{4}\frac{\alpha_{par}^2}{\alpha_{par} + |\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,j;\sigma_i\neq\sigma_j} -\frac{1}{2}\frac{\alpha_{anti}^2}{\alpha_{anti} + |\mathbf{r}_i - \mathbf{r}_j|} \tag{9}$$

Loss: Variational Principle

Variational principle states:

$$E[\Psi] = \frac{\langle \Psi \mid H \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} \geq E_0$$

Minimizing $E[\Psi]$ drives the ansatz toward the ground state.

$$E[\Psi] = \mathcal{L}(\Psi_\theta) = \frac{\langle \Psi_\theta | \hat{H} | \Psi_\theta \rangle}{\langle \Psi_\theta | \Psi_\theta \rangle} = \frac{\int d\mathbf{R} \Psi^*(\mathbf{R}) \hat{H} \Psi(\mathbf{R})}{\int d\mathbf{R} \Psi^*(\mathbf{R}) \Psi(\mathbf{R})}$$

Define:

$$p_\theta(\mathbf{R}) = |\Psi_\theta(\mathbf{R})|^2 \frac{1}{\int d\mathbf{R}' \Psi_\theta^2(\mathbf{R}')} \wedge E_L(\mathbf{R}) = \frac{\hat{H}\Psi_\theta(\mathbf{R})}{\Psi_\theta(\mathbf{R})}$$

Then:

$$\mathcal{L}_\theta = \mathbb{E}_{\mathbf{R} \sim |\Psi_\theta|^2} [E_L(\mathbf{R})] \tag{10}$$

Variational Monte Carlo

Quantum Monte Carlo

With the samples $\mathbf{R}_1, \dots, \mathbf{R}_M \sim |\Psi|^2_\theta(\mathbf{R})$ we can make:

$$\mathcal{L}_\theta = \mathbb{E}_{\mathbf{R}\sim\Psi^2_\theta}[E_L(\mathbf{R})] \approx \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{R}_k) \tag{11}$$

With:

$$E_L(\mathbf{R}_k) = \frac{\hat{H}\psi(\mathbf{R}_k)}{\psi(\mathbf{R}_k)} = -\frac{1}{2}\frac{\nabla^2\psi(\mathbf{R_k})}{\psi(\mathbf{R}_k)} + V(\mathbf{R}_k)$$

Obtain $\mathbf{R}_k \rightarrow$ Metropolis-Hastings Algorithm

Metropolis-Hastings Algorithm

Goal: Generate many samples $\mathbf{R} \sim \rho$, Requirement: $C\rho$

1. $\mathbf{R}_0 \in E$ random.
2. Propose $\mathbf{R}' = \mathbf{R}_0 + \eta$,where $\eta \sim q(\eta)$, (Normal Gaussian)
3. Compute the quantity:

$$A(\mathbf{R_0}, \mathbf{R}') = \min\left(1, \frac{\rho(\mathbf{R}')}{\rho(\mathbf{R}_0)}\right)$$

4. Generate a uniform number $U \in [0,1]$. If: $U < A(\mathbf{R}_0, \mathbf{R}')$ then $\mathbf{R_1} = \mathbf{R}'$, otherwise try another $\mathbf{R}'$. Accept or decline.

Metropolis-Hastings

In each sample generates $E_L(\mathbf{R}_k)$ then average to obtain $\mathbb{E}(E_L)$ and begin the back propagation step.

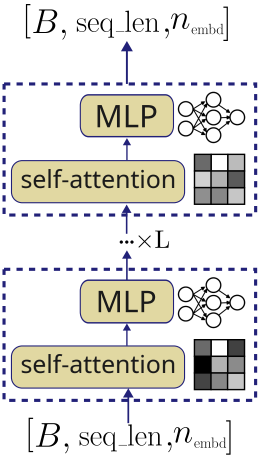
Gradients of the Loss

Using calculus you obtain:

$$\nabla_\theta \mathcal{L} = 2\mathbb{E}_{x\sim\Psi^2}[(E_L(x) - \mathbf{E}_p(E_L)) \log \psi] \tag{12}$$

This expectation is calculated in the same way.

Transformer Architecture



$[B, \text{seq\_len}, n_{\text{embd}}]$
MLP
self-attention
$\cdots \times L$
MLP
self-attention
$[B, \text{seq\_len}, n_{\text{embd}}]$

Figure 2: Tranformer backbone

Multi Head Attention → Self Attention

- n_{embd} the embedding dimension
- n_h the number of attention heads
- d_h the dimension per head
- $\mathbf{h}_t \in \mathbb{R}^{n_{\text{embd}}}$ the hidden dimension.

Attention on the room

The learnable matrices are:

$$W^Q, W^K, W^V \in \mathbb{R}^{n_{\text{embd}} \times n_{\text{embd}}}$$

$$\mathbf{k}_i = \mathbf{W}^k \mathbf{h}_i, \mathbf{q}_i = \mathbf{W}^q \mathbf{h}_i, \mathbf{v}_i = \mathbf{W}^v \mathbf{h}_i$$

$$[\mathbf{q_1}, \mathbf{q_2}, \ldots, \mathbf{q_{n_h}}] = \mathbf{q}$$

$$[\mathbf{k_1}, \mathbf{k_2}, \ldots, \mathbf{k_{n_h}}] = \mathbf{k}$$

$$[\mathbf{v_1}, \mathbf{v_2}, \ldots, \mathbf{v_{n_h}}] = \mathbf{v}$$

In the $i-th$ head:

$$\mathbf{o}_{t,i} = \sum_{j=1}^{t} \text{Softmax}\left(\frac{\mathbf{q}_{t,i}^T \mathbf{k}_{j,i}}{\sqrt{d_h}}\right) \mathbf{v}_{j,i} \tag{13}$$

W^O the output projection matrix.

$$\mathbf{u}_t = W^O [\mathbf{o}_{t,1}; \mathbf{o}_{t,2}; \ldots; \mathbf{o}_{t,n_h}]$$

Outline

Psiformer Ansatz

Ansatz: Proposal model that you propose guided by intuition and that you optimize.

- be *antisymmetric* under particle exchange,
- capture strong *electron–electron correlations.*

Proposed ansatz

Motivated by these constraints, we propose a Slater–Jastrow form:

$$\Psi_\theta(\mathbf{R}) = \underbrace{\exp\left(\mathcal{J}_\theta(\mathbf{R})\right)}_{\text{Coulomb correlations}} \times \underbrace{\sum \omega_k \det\left[\boldsymbol{\phi}_\theta^k(\mathbf{R})\right]}_{\text{antisymmetry}}$$

Psi Former Architecture

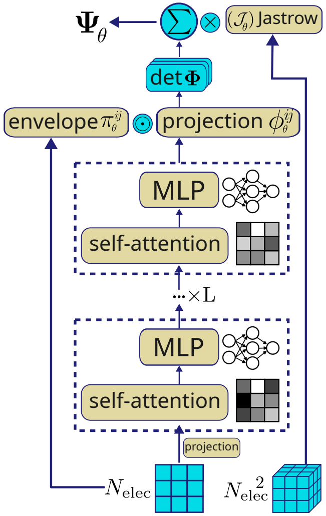
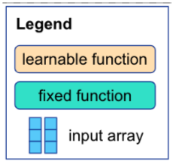


Figure 3: Psi Former Architecture



- The envelope is a matrix with learned exponential decay as elements.
- Learn the Jastrow factor only have two parameters.
- In practice we use logarithm scale.

Psiformer Shapes

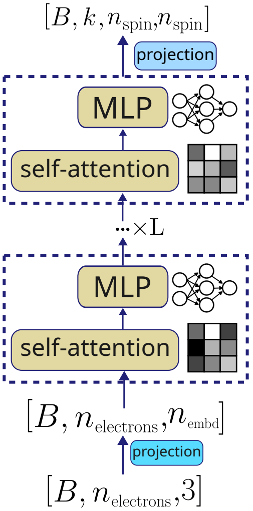

$[B, k, n_{\text{spin}}, n_{\text{spin}}]$
projection
MLP
self-attention
$\cdots \times \text{L}$
MLP
self-attention
$[B, n_{\text{electrons}}, n_{\text{embd}}]$
projection
$[B, n_{\text{electrons}}, 3]$

Figure 4: Psiformer shapes handling

Methodology

Hyperparameter	Small	Large
Layers L	2	4
Heads H	4	8
Model Dim d	256	512
MLP Dim d_{ff}	1024	2048
Determinants K	1	2
MCMC walkers N_w	1024	2048
MCMC steps / iter	10	10
Learning rate	2×10^{-4}	1×10^{-4}
Total parameters	50441	$3M$

Figure 5: Psiformer Torch Small and Large

Goal: Obtain accurate ground state-energies using an Ansatz created with **Torch** library

Training Loop:

Set the spins and electron number

1.Sample configurations $\mathbf{R}_k$

2.Estimate local energy E_L

3.Backpropagation using **A.D**

4.Update parameters θ using **AdamGrad**.

5. Track metrics with **Wandb.**

Implementation : Laplacian Computation

The kinetic energy requires the Laplacian: $\nabla^2\Psi(\mathbf{R}) = \sum_i \frac{\partial^2\Psi}{\partial R_i^2}$

```
R = R_o.requires_grad_(True)      # particle coordinates
psi = model(R)                   # neural wavefunction
# first derivative: gradient
grad_psi = torch.autograd.grad(
    psi, R,
    create_graph=True,
    # retain_graph=True
)[0]
# second derivative: Laplacian
laplacian = 0.0
for i in range(R.shape[-1]):
    laplacian += torch.autograd.grad(
        grad_psi[..., i], R,
        # create_graph=True,
        retain_graph=True
    )[0][..., i]
```

Determinant Stability in Psiformer

$$\Psi_\theta(\mathbf{R}) \propto \det[\mathbf{\Phi}_\theta(\mathbf{R})]$$

Derivative of a determinant.

$$\frac{\partial \det(\mathbf{A})}{\partial \mathbf{A}} = \det(\mathbf{A})\mathbf{A}^{-T}$$

Key instability. If $\mathbf{\Phi}$ becomes singular or nearly singular:

$$\det \mathbf{A} \to 0 \quad \Rightarrow \quad [a_{ii}^{-1}] \to \infty$$

so the gradient can explode even when the wavefunction itself is small.

Fix: Custom Operation

Idea: Use SVD ($A = U\Sigma V^T$) to compute $\nabla \log \det A = A^{-T}$ without explicit inversion (Appendix D).

```
import torch

class StableLogDet(torch.autograd.Function):
    @staticmethod
    def forward(ctx, A):
        # Decompose A: S are singular values
        U, S, Vh = torch.linalg.svd(A)
        ctx.save_for_backward(U, S, Vh)
        return S.log().sum()

    @staticmethod
    def backward(ctx, g):
        U, S, Vh = ctx.saved_tensors
        # Reconstruct A^{-T} = U * diag(1/S) * Vh
        inv_S = torch.diag_embed(1.0 / S)
        grad_A = U @ inv_S @ Vh
        return g * grad_A
```

Optimizer: Adam vs. AdamW

Core Difference: AdamW *decouples* weight decay from the gradient update to fix regularization on adaptive optimizers.

1. Adam (Entangled L2 Regularization)

- Decay is added to the gradient, so it gets scaled by the adaptive variance.

$$
\begin{aligned}
g_t &= \nabla \mathcal{L} + \lambda \theta_t \\
\theta_{t+1} &= \theta_t - \text{AdamStep}(g_t)
\end{aligned}
$$

2. AdamW (Decoupled Weight Decay)

- Decay is applied directly, bypassing the adaptive scaling mechanism.

$$
\begin{aligned}
g_t &= \nabla \mathcal{L} \\
\theta_{t+1} &= \theta_t - \text{AdamStep}(g_t) - \eta \lambda \theta_t
\end{aligned}
$$

Keeping the GPU Busy: Batched Energy Evaluation

Naive training issue. Initial training evaluated energies step-by-step over MCMC samples.

$$\text{GPU utilization} \approx 30\%$$

Solution: batched evaluation. MCMC samples are reshaped and flattened:

$$(\text{mc\_steps}, B, n_e, 3) \;\rightarrow\; (\text{mc\_steps} \times B, n_e, 3)$$

Result.

$$\text{GPU utilization} \approx 99\%$$

Results: Convergence Curve

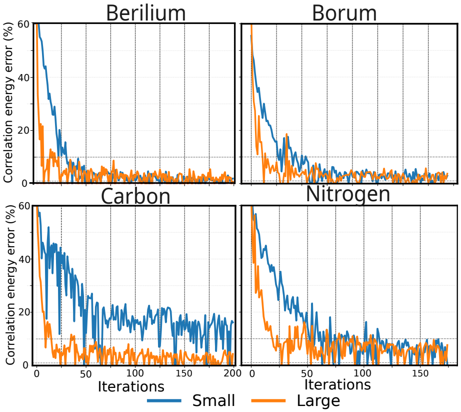


Figure 6: Convergence Curve

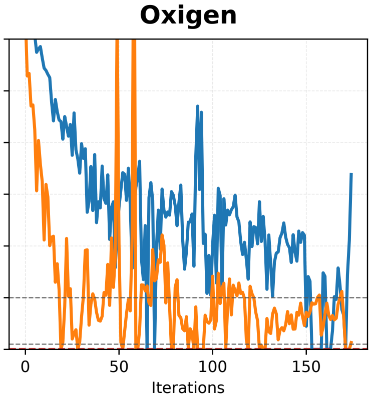


Figure 7: Oxigen Convergence

Results: Energy Estimates

Atom	E_b	E_s	E_l	Δ_s	Δ_l	Δ_{l-s}
H	-0.500	-0.492	**-0.498**	0.008	0.002	**-0.006**
He	-2.903	-2.801	**-2.893**	0.102	0.010	**-0.092**
Li	-7.478	-7.097	**-7.243**	0.381	0.235	**-0.146**
Be	-14.667	-13.901	**-14.237**	0.766	0.430	**-0.336**
B	-24.653	-24.042	**-24.567**	0.611	0.086	**-0.525**
C	-37.845	-35.492	**-36.457**	2.353	1.388	**-0.965**
N	-54.589	-50.492	**-51.700**	4.097	2.889	**-1.208**
O	-75.067	-63.492	**-72.139**	11.575	2.928	**-8.647**

Figure 8: Ground state energies (Ha) for H-O, baseline vs Psiformer

Comments

- Pretraining using external data.
- Laplacian Bottleneck
- KFCA Optimizer (Natural Gradient Descent)
- Flash Attention
- Learning transferability
- Scaling Laws

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Thanks!

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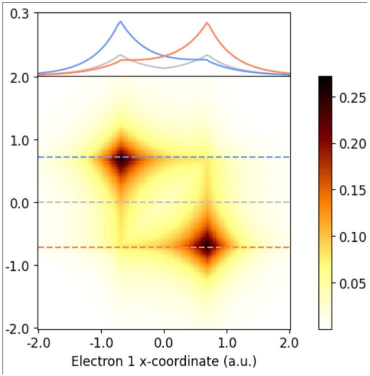
Electron 1 x-coordinate (a.u.)