Vandermonde Wave Function Ansatz for Improved Variational Monte Carlo

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Abstract—Solutions to the Schrödinger equation can be used to predict the electronic structure of molecules and materials and therefore infer their complex physical and chemical properties. Variational Quantum Monte Carlo (VMC) is a technique that can be used to solve the weak form of the Schrödinger equation. Applying VMC to systems with N electrons involves evaluating the determinant of an N by N matrix. The evaluation of this determinant scales as \( O(N^3) \) and is the main computational cost in the VMC process. In this work, we investigate an alternative VMC technique based on the Vandermonde determinant. The Vandermonde determinant is a product of pairwise differences and so evaluating it scales as \( O(N^2) \). Therefore, this approach reduces the computational cost by a factor of \( N \).

The Vandermonde determinant was implemented in PyTorch and the performance was assessed in approximating the ground state energy of various quantum systems against existing techniques. The performance is evaluated in a variety of systems, starting with the one-dimensional particle in a box, and then considering more complicated atomic systems with multiple particles. The Vandermonde determinant was also implemented in PauliNet, a deep-learning architecture for VMC. The new method is shown to be computationally efficient, and results in a speed-up as large as 5X. In these cases, the new ansatz obtains a reasonable approximation for wavefunctions of atomic systems, but does not reach the accuracy of the Hartree-Fock method that relies on the Slater determinant. It is observed that while the use of neural networks in VMC can result in highly accurate solutions, further work is necessary to determine an appropriate balance between computational time and accuracy.

Index Terms—Schrödinger equation, Vandermonde ansatz, Variational Monte Carlo

I. INTRODUCTION

Variational Monte Carlo (VMC) is an established technique for computing the ground-state energy of quantum systems. It is one algorithm provided by major HPC applications for quantum Monte Carlo such as QMCPACK [1]. Recently, a number of papers [2]–[4] have recognized that techniques from deep learning can be adopted naturally into the VMC setting. In VMC, the wavefunction of a quantum system is approximated as a parametric function, while modern neural networks make excellent function approximators.

When applying VMC to many-electron atomic and molecular systems, it is typical to use the Born-Oppenheimer approximation and assume the nuclei have fixed coordinates relative to the electrons; then a number of single-electron orbitals are modeled, with separate terms to account for the interactions of electrons.

A particularly important property to enforce is antisymmetry – under exchanges of same-spin electrons, the sign of the wavefunction must undergo flipping. The typical way to enforce antisymmetry is to arrange the single-electron wavefunctions in an aggregate Slater matrix, whose determinant is computed with a computational cost of \( O(N^3) \), this is seen in section III subsection B. This technique forms the basis of the neural architectures described in [2], [4], and asymptotically dominates the computational costs.

The Vandermonde determinant has been proposed as an alternative construction for enforcing antisymmetry [5]. Since the Vandermonde determinant can be written as a product of pairwise differences, it can be evaluated using only \( O(N^2) \) operations. In this paper, we investigate the use of the Vandermonde determinant as an alternative means of enforcing antisymmetry when solving Schrödinger’s equation and also implement it under the framework of the PauliNet architecture [4].

II. BACKGROUND

A. Variational Monte Carlo

Variational Monte Carlo (VMC) is a technique that can be used to estimate the ground state of a quantum system. We assume that we have access to the Hamiltonian \( H \) that characterizes the system. We would like to approximate the ground state wavefunction \( |\psi\rangle \), also written \( \psi \) when working in the dual space, which is the solution of the time-independent Schrödinger equation

\[
H |\psi\rangle = E |\psi\rangle
\]
for the lowest-energy state of the system. The variational principle of quantum mechanics states that all wavefunctions \( \phi \) other than the true ground state wavefunction \( \Psi_0 \) yield higher expectation values for the energy: \( \mathbb{E}_{\Psi_0}[E] \leq \mathbb{E}_\phi[E] \). Variational Monte Carlo uses this principle to estimate the ground state wavefunction and ground state energy. The procedure, roughly speaking, consists of the following steps (as described in [2]):

1) Start with some initial variational ansatz \( |\psi_\alpha(x)\rangle \) from some class of functions parameterized by \( \alpha \).

2) Using Markov-chain Monte Carlo (MCMC) techniques [6], [7], sample from the probability distribution implied by this wavefunction: \( \pi(x) \propto ||\psi_\alpha(x)||^2 \).

3) Minimize the expected value of the energy of the system

\[
\mathbb{E}[E] = \frac{\langle \psi_\alpha | H | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} = \int \psi_\alpha^*(x) H \psi_\alpha(x) dx / \int \psi_\alpha^*(x) \psi_\alpha(x) dx.
\]

Using the samples \( x_i \sim \pi(x) \), we can approximate this expected value by computing

\[
\frac{1}{N} \sum_{i=1}^{N} \psi_\alpha^*(x_i) H \psi_\alpha(x_i)
\]

and approximate the variance by computing

\[
\frac{1}{N} \sum_{i=1}^{N} \{ \psi_\alpha^*(x_i) H \psi_\alpha(x_i) - \mathbb{E}[E] \}^2
\]

and optimize the parameters \( \alpha \) of the ansatz to minimize some combination of these losses.

**B. Deep neural network ansatz**

PauliNet [4] is a neural network architecture for solving \( N \)-body electron systems (i.e., molecular and atomic systems). It uses deep learning techniques to approximate electronic wavefunctions. Although it uses neural networks, it is also physically inspired and borrows ideas from traditional techniques. In particular, it effectively incorporates the Hartree-Fock method which is a baseline analytic approximate solution to a simplified version of the appropriate Schrödinger equation

Below, we provide a high-level overview of the architecture of PauliNet, and the procedure for training it to minimize the ground-state energy. Then, we give more detailed explanations of specific important properties of its architecture.

PauliNet uses a Slater-Jastrow-backflow ansatz. Ansatzes of this general form have long been popular for variational Monte Carlo, and are widely used in the QMCPACK [1]. PauliNet follows this basic structure but replaces various parts of it with neural networks. It constructs the ansatz in the following form:

\[
\Psi_\theta(r) = e^{\gamma(r)+J_\theta(r)} \sum_p c_p \text{det}(\varphi_p^+(r)) \text{det}(\varphi_p^-(r))
\]

where

\[
\varphi_\mu(r) = \varphi_\mu(r_\mu) f_{\mu,\theta}(r)
\]

This expression is described in more detail below.

- The \( \mu \) denotes an index when there are multiple copies of certain basis sets or other functions.
- \( \varphi_\mu(r) \) are Hartree-Fock functions, a well-known approximate solution derived by making simplifying assumptions to the physical problem until it becomes analytically tractable; they are essentially treated as inputs. They are modified to enforce nuclear cusp constraints, and they naturally enforce decay of the wavefunction to zero as electrons stray far from the nucleus.
- The terms \( J_\theta \) and \( f_{\mu,\theta} \) are learnable neural networks; \( f_{\mu,\theta} \) are the backflow factors which model electron-electron interactions and scale the basis functions; the \( J_\theta \) is the Jastrow factor which models global correlations between electrons but does not affect antisymmetry.
- The \( \gamma \) are fixed, physical cusp constraints: as electrons approach each other the wavefunction must obey certain physical behavior.
- The rescaled \( \varphi \) are combined using Slater determinants, split according to spin up (\( \uparrow \)) or spin down (\( \downarrow \)) electrons (antisymmetry only applies to electrons with the same spin).
- There may be multiple copies of each Slater determinant, which are indexed by \( p \) and combined in a weighted sum. We focus on the single-determinant case for most of our work, however.
- Implicit in the implementation of Equation (1) is the use of SchNet [8] to transform electron coordinate inputs into a 128-dimensional vector for input into \( f_{\mu,\theta} \) and \( J_\theta \).

The architecture combines physically motivated inputs and architectural choices with flexible transformations represented by general function approximators.

**III. Vandermonde and Slater Ansatz on Simple Systems**

**A. Getting started**

As a testbed for comparing different ansatzes, we implemented our own variational Monte Carlo pipeline. This uses a simple Metropolis-Hastings sampler, and the standard “score function” stochastic gradient descent estimator, also used in PauliNet:

\[
\mathcal{L}(\theta) = \mathbb{E}_{r \sim \Psi_\theta} [E_{loc} | \Psi_\theta(r) |]
\]

\[
\nabla_\theta \mathcal{L}(\theta) = 2\mathbb{E}_{r \sim \Psi_\theta} [(E_{loc} \Psi_\theta(r) - \mathcal{L}(\theta)) \nabla_\theta \log |\Psi_\theta|]
\]

We experiment with a number of simple physical systems but primarily focus on systems where antisymmetry of the wave function is a concern.

**B. Antisymmetry: Slater and Vandermonde determinants**

Due to the Pauli exclusion principle, it is standard to require that the wavefunction \( \Psi \) for a system of fermions obey antisymmetry. The traditional way to enforce this is to employ a Slater determinant constructed from the components of a Hartree product [9, section 14.5] as presented below.

\[
\Psi_{HF}(r_1, r_2, ..., r_N) = \phi_1(r_1) \phi_2(r_2) ... \phi_N(r_N).
\]
The \( \phi_i \) are hydrogenic functions. And the Slater determinant is

\[
\Psi_{\text{Slater}} = \begin{vmatrix}
\phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_N(r_1) \\
\phi_1(r_1) & \phi_2(r_2) & \cdots & \phi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(r_N) & \phi_2(r_N) & \cdots & \phi_N(r_N)
\end{vmatrix}
\]

However, computing a determinant has a complexity of \( O(N^3) \), which is costly.

An alternate method of enforcing antisymmetry is the Vandermonde determinant. This has been proposed, for instance, in [5]. In brief, the Vandermonde determinant takes as input a map \((\phi(r_1), \phi(r_2), \cdots, \phi(r_N))\) and takes the determinant of the following matrix:

\[
\det_V = \begin{vmatrix}
1 & \phi(r_1)^1 & \phi(r_1)^2 & \cdots & \phi(r_1)^{N-1} \\
1 & \phi(r_2)^1 & \phi(r_2)^2 & \cdots & \phi(r_2)^{N-1} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
1 & \phi(r_N)^1 & \phi(r_N)^2 & \cdots & \phi(r_N)^{N-1}
\end{vmatrix}
\]

This is a determinant, and assuming the vector of \( \varphi \) is permutation equivariant (as it is in our applications), exchanging two inputs will exchange rows of the matrix, swapping signs of the determinant, so that antisymmetry is enforced.

The Vandermonde determinant has an advantageous property: one does not need to write out the full matrix and actually take its determinant; instead, it is possible to use the following expression, requiring only \( O(N^2) \) operations:

\[
\det_V = \prod_{i<j} (\varphi(r_i) - \varphi(r_j)).
\]

Thus the Vandermonde determinant is a potentially efficient technique for enforcing antisymmetry with a lower computational cost than the widely-used Slater determinant.

C. Deficiencies of the Vandermonde ansatz

When trading the Slater ansatz for the Vandermonde ansatz we constrained ourselves to the physical information carried by a single \( \phi_i \) in the array used to compute the Slater determinant. To overcome this loss of physical information, the Vandermonde determinant can be multiplied by an appropriate symmetric function in order to add more physical information to the ansatz such as the boundary conditions imposed by the system. See, for example, the ansatz for the two fermions in a box system in Equation (4).

D. Two fermions in a box

For our experiments, we considered the following physical systems:

- To verify our solutions, we considered the toy problem of two fermions in a box – a slight variation on a textbook problem in quantum mechanics.
- We also considered \( n \)-electron systems: Helium (2 electrons) and Lithium (three electrons).

We will return to these models in the experimental results section, for now we will develop the two fermions in a box system as a base for what is to come. The two fermions in a box system consists of two fermions (particles where the Pauli exclusion principle applies) in a box (finite volume infinite potential well) that the fermions are restricted to. The system is relatively simple and analytically tractable – in fact, for the most naturally defined ansatzes the local energy does not depend on the particle configuration, making variational Monte Carlo totally unnecessary. This model is nevertheless a good initial testing ground for VMC. As a concrete example, we consider the Schrödinger equation for the 1-D box case,

\[
-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) \Psi(x_1, x_2) = E \Psi(x_1, x_2).
\]

The time independent Schrödinger in this case amounts to the simple eigenvalue problem corresponding to the Laplacian. The Laplacian indeed has a discrete spectrum over a bounded domain. For a 1-dimensional box of length \( L \) and the particles bounded to the domain \([0, L] \), the eigenvalue/eigenvector pairs are the energies \( E_{\alpha_1, \alpha_2} = \frac{\hbar^2 \pi^2}{2mL^2} (\alpha_1^2 + \alpha_2^2) \) with the corresponding states \( \Psi_{\alpha_1, \alpha_2}(x_1, x_2) = \sqrt{\frac{2}{L}} \sin \left( \frac{\alpha_1 \pi x_1}{L} \right) \sqrt{\frac{2}{L}} \sin \left( \frac{\alpha_2 \pi x_2}{L} \right) \).

Let us now calculate the corresponding local energy:

\[
E_{\text{loc}} = \frac{1}{\Psi_{\alpha_1, \alpha_2}(x_1, x_2)} \left\{ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) \Psi_{\alpha_1, \alpha_2}(x_1, x_2) \right\}
\]

This local energy is independent of configuration, therefore structurally for an ansatz will yield trivial results: VMC would be completely superfluous as samples from the wavefunction would serve no purpose. The same issues arise even after implementing antisymmetry via a Slater determinant. In order to test VMC, in Section V-A, we devise a deliberately deficient ansatz, using both Slater and Vandermonde determinants. Below, we denote parameters by \( \alpha_1, \alpha_2 \), etc. After working through this toy model we will consider the Helium atom, Lithium, Beryllium and then finally Lithium hydride using the conventional Slater determinant techniques as well as our Vandermonde approach.

IV. VANDERMONDE ANSATZ IN PAULINET

A. Vandermonde determinants

The main motivation for replacing the Slater determinants with Vandermonde determinants in PauliNet is in reducing the computational cost of evaluating the local energy. In PauliNet, the cost of evaluating the wavefunction scales as \( O(N^3) \) where \( N \) is the number of electrons. This is because the cost of computing the Slater determinants is \( N^3 \) and the determinant calculations dominate the cost of evaluating the wavefunction. Due to the kinetic energy, evaluating the total energy scales as \( N \) times the complexity of evaluating the wavefunction. Therefore, the computational cost of PauliNet scales asymptotically as \( O(N^4) \).

In contrast, evaluating the Vandermonde determinants scales as \( O(N^2) \). Therefore, replacing the Slater determinants in PauliNet with Vandermonde determinants reduces the computational cost from \( O(N^4) \) to \( O(N^3) \).
In the next sections, we outline our implementation of the Vandermonde determinant in PauliNet. We compare performance on various atomic systems including Beryllium and Lithium hydride. Finally we provide a visual comparison of the wavefunctions obtained by using PauliNet with the Vandermonde determinant and PauliNet with the Slater determinant.

B. General approach

There are two Slater determinants in the PauliNet ansatz. Instead of taking a Slater determinant, our modification to PauliNet first takes a product of the \( \hat{\varphi}_\mu \) in eq. (1) and then takes the Vandermonde determinant of the product. That is, letting \( \hat{\varphi} = \prod_{\mu=1}^N \hat{\varphi}_\mu(r) \), we set

\[
\text{det}_V := \prod_{i<j}(\hat{\varphi}(r_i) - \hat{\varphi}(r_j)),
\]

and replace every Slater determinant in PauliNet with the corresponding Vandermonde determinant \( \text{det}_V \).

C. Enforcement of cusp and other conditions

In order for antisymmetry to be enforced, the \( \hat{\varphi} \) must be permutation equivariant. The same is true for the Vandermonde determinant: this motivates our use of the products \( \prod_{\mu=1}^N \hat{\varphi}_\mu(r) \), which incorporate information from the whole basis while ensuring permutation equivariance – exchanging two electrons will exchange only the positions of their respective \( \hat{\varphi} \) without changing values.

While this construction can ensure that antisymmetry is enforced, it has a drawback compared to the Slater determinant. If any electron violates the boundary conditions, its \( \hat{\varphi} \) goes to zero: then every term in the Slater determinant will go to zero, while the same is not true of the Vandermonde determinant. After observing and debugging unexpected samples of configurations with infinite or zero energy, we realized that it was necessary to have a separate term outside the Vandermonde determinants enforcing these properties.

Since the underlying Hartree-Fock functions \( \varphi_\mu \) enforce these conditions, we simply select a single \( \varphi_\mu \) and multiply the entire wavefunction by \( \prod_{\mu=1}^N |\varphi_\mu(r)| \) – thus ensuring that if any electron violates cusp or boundary conditions, the entire wavefunction still goes to zero. This term, which falls outside of the determinants, is a symmetric function as required.

V. EXPERIMENTAL RESULTS

A. VMC for simple systems

For two fermions in a box we must make sure that the wave function satisfies antisymmetric conditions. Recall that the Pauli exclusion principle tells us that two particles cannot occupy the same state. To enforce this we must find a function, \( \Psi_{\text{excited}}(x_1) \) for particle one, that has the same geometry as the second excited state and use this in conjunction with the first excited state wave function, \( \Psi_{\text{ground}}(x_2) \), to create a total ground state ansatz for our two particle system, \( \Psi_{\text{total}} = \Psi_{\text{excited}}(x_1)\Psi_{\text{ground}}(x_2) \). A possible pair of ansatz are \( \Psi_{\text{excited}}(x) = -(1-x^{2\alpha_1})x \) and \( \Psi_{\text{ground}}(x) = (1-x^{2\alpha_2}) \).

Finally, implementing a Slater determinant on the appropriate Slater matrix afforded by the above ansatz we may achieve antisymmetry.

Figure 1 shows the training results for the following ansatz, which is a 2-dimensional Slater determinant of the Slater matrix constructed from the ansatz \( \Psi_{\text{excited}} \) and \( \Psi_{\text{ground}} \) discussed above:

\[
\Psi(x_1, r_2) = (1 - x_1^{2\alpha_1})(1 - x_2^{2\alpha_2})x_2
- (1 - x_2^{2\alpha_1})(1 - x_1^{2\alpha_2})x_1 \tag{2}
\]

Figure 2 shows the training results for another Slater-based ansatz, with slightly different basis:

\[
\Psi(x_1, x_2) = (1 - x_1^{2\alpha_1})e^{-\alpha_2 x_2^2} - (1 - x_2^{2\alpha_1})e^{-\alpha_2 x_1^2} \tag{3}
\]

as well as the results for a basic Vandermonde-based ansatz:

\[
\Psi(x_1, x_2) = (1 - x_1^{2\alpha_1})(1 - x_2^{2\alpha_1})
\times (\sin(\alpha_2 x_1) - \sin(\alpha_2 x_2)). \tag{4}
\]

Both Slater ansatz cases achieve convergence to the true ground state energy as seen in plots on Figure 1 and Figure 2. Despite not fully converging to the ground truth, the Vandermonde ansatz allows for speed up in convergence. Figure 2 shows on the right a relatively rapid convergence in vicinity of the true ground state energy, on the other hand, the Gaussian-type Slater ansatz on the left of Figure 2 converges about 20 iterations after our Vandermonde type ansatz, Equation (4), has already converged. It is surprising nonetheless, that the ansatz used in the leftmost figure of Figure 2 converges. The Gaussian terms do not satisfy the necessary boundary conditions.
条件，但可变的参数会优化，以缓解这个问题。尽管范德蒙德变分式能够在最快收敛时提供最弱的近似能量，在这些模型中，这在两个粒子的盒情况中，由于相对较大的差异，使得近似的精确度和真实的地子状态能量和真实的地子状态能量有显著的差异。

我们考虑一些原子系统。由于波尔磁通规则，我们将需要力矩产生对称性通过一个物理上启发的变分式。

传统氦-斯莱特变分式是

$$\psi(r_1, r_2) = e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} - e^{-\alpha_1 r_2} e^{-\alpha_2 r_1}. \quad (5)$$

这个变分式使用氢型波函数，$\phi(r) = e^{-\alpha r}$，作为构建斯莱特行列式的基础。确实，如果两个电子环绕着氢原子的核，两个电子之间不会相互作用，每个电子都会表现为它是否是氢原子的一员。

在图3中，我们看到在使用斯莱特和范德蒙德变分式时，我们估计的局部能量对真实地子状态能量的收敛性。这两个变分式都使用了相同的参数。

$$\psi(r_1, r_2, r_3) = e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} e^{-\alpha_1 r_3} \times \sum_{l=1}^{2} \left( \prod_{i<j} e^{-\alpha_i r_i} - e^{-\alpha_i r_j} \right). \quad (7)$$

斯莱特行列式变分式在这一情况下是

$$\psi(r_1, r_2, r_3) = \begin{vmatrix} e^{-\alpha_1 r_1} & e^{-\alpha_2 r_2} & e^{-\alpha_1 r_3} \\ e^{-\alpha_2 r_1} & e^{-\alpha_2 r_2} & e^{-\alpha_2 r_3} \\ e^{-\alpha_3 r_1} & e^{-\alpha_3 r_2} & e^{-\alpha_3 r_3} \end{vmatrix}. \quad (8)$$

如图4所示，可以检测到更长的时间所需的蒙特卡尔运行。我们可以用更多的迭代来看到斯莱特行列式变分式收敛到真实的地子状态。

表1: 对于使用标准斯莱特行列式变分式和范德蒙德变分式（值是根据图2、3和4计算的）。范德蒙德变分式收敛速度更快。

<table>
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<th>表1: 对于使用标准斯莱特行列式变分式和范德蒙德变分式（值是根据图2、3和4计算的）。范德蒙德变分式收敛速度更快。</th>
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| 变分式 | 范德蒙德 | 斯莱特 | 速度差

在这一部分，我们分析了各种变分式的类型，其中有一些遵守波尔磁通规则。表1显示了速度的提升，对于所有的模型我们都使用了我们的软件。我们计算了表中显示的数值所花费的时间。我们在例子中看到了在使用斯莱特变分式和范德蒙德变分式时，前者需要的时间更长，但是当我们将斯莱特变分式进一步收敛到真实的地子状态能量时，这个结果没有测试到。它仍然需要测试是否在实际的时间内，变分式能够收敛到真实的地子状态能量。对于这些更复杂系统，如锂-氢化物和铍，我们使用了PauliNet软件。
B. VMC for atoms and molecules with PauliNet

We used the same architectural designs as the original PauliNet paper (see Table 2 in [4] for the full set of parameters), with a few exceptions. We only used a single determinant for both the Slater and Vandermonde cases. All network sizes and dimensionalities of feature representations remained the same, and we used the same basis functions. We found it necessary to lower the maximum learning rate to 0.005 from the default 0.01. We ran for 600 or 800 iterations, less than for the results collected originally in [4].

1) Results and Comparisons: With the Vandermonde determinants, convergence was achieved but to an energy relatively far from the correct answer – the Slater determinants reached much closer. To visualize the wavefunction during training, we made plots of the wavefunction sliced along a single coordinate of a single electron.

Figure 7 shows the evolution of the wavefunction for LiH, a system with four electrons (one for hydrogen and three for lithium). Figure 5 shows the same evolution for Beryllium, a single-atom system with four electrons.

In both of these systems, we find that the Slater determinant reaches a lower energy – much closer to the true values in both cases. The energies reached are listed in the captions of Figures 5 and 7.

We also make plots showing how the wavefunction changes after every 50 training iterations over the course of 800 total iterations. In particular, we train PauliNet using both the Slater determinant and the Vandermonde determinant, and every 50 training iterations, we estimate \( ||\Psi_x^2 - |\Psi_{x-1}|^2|| \) by evaluating \( \Psi_x \) and \( \Psi_{x-1} \) at 3000 random points, where \( \Psi_x \) is the wavefunction after 50x training iterations. This is a measure of how much the wavefunction changes during training. The results are shown in Figure 6. We find that PauliNet with the Slater determinant continues to train, while the Vandermonde determinant trains quickly at first but appears to get “stuck” in a local minimum far from the true ground state energy.

The relative accuracy of various methods is most readily understood by comparing the estimation of the ground-state energy. In particular, we compared our estimation of the ground state energy to the estimation obtained by the Hartree-Fock method and the original PauliNet. PauliNet uses the Hartree-Fock method as a baseline solution and as a starting point for the variational Monte Carlo method. It first performs a Hartree-Fock calculation to produce one electron orbitals \( \varphi_{\mu}(r_i) \) (see Equation (1)) which are then used as inputs to PauliNet. After performing variational Monte Carlo, PauliNet significantly surpasses the accuracy of Hartree-Fock. The authors of PauliNet demonstrate this in [4] by comparing the accuracy of their solution after 7000 training steps to the Hartree-Fock method and another deep learning based VMC method.

After 7000 training steps, our modification with the Vandermonde determinant in general does not exceed Hartree-Fock accuracy. Others who used similar constructions [3] also reported poor results. In order to present our method as a viable low-cost alternative to PauliNet, we would at least want to surpass the accuracy of Hartree-Fock for most systems. We believe that there may be other modifications that one could make in order to achieve this level of accuracy while still maintaining the \( N^3 \) asymptotic complexity.

VI. CONCLUSION

A possible limitation of our adaptations to PauliNet might be the use of the Hartree-Fock-derived basis functions as...
Fig. 7: Two slices of the PauliNet wavefunction for Lithium hydride. Two different slices of the wave function are plotted every 50 steps over the course of 800 total training steps. Thinner lines are earlier time steps, thicker are later. The ground state energy estimation at the final iteration is -7.1686 for PauliNet with the Vandermonde determinant, and -8.0619 for PauliNet with the Slater determinant. The true ground state energy is -8.07.

predetermined inputs to the ansatz. The core Hartree-Fock ansatz itself uses a Slater determinant, so the parameters of the basis functions might be particularly well-tuned for use in conjunction with Slater determinants. The flexible neural networks of the rest of the PauliNet architecture are still capable of learning, but when using the Vandermonde determinant they might have to overcome this limitation.

As such, one possible avenue for improvement might be replacing the basis functions \( \varphi \) with ones somehow better suited to the Vandermonde determinant. The authors of PauliNet claim that part of the success of their method is the fact that it begins with the physically plausible Hartree-Fock functions. It might be possible to initialize by solving some analogue to the Hartree-Fock wavefunction that uses a Vandermonde determinant instead of a Slater determinant, potentially yielding better performance.

Variational Monte Carlo is a widely-used algorithm for approximating the ground state energy of quantum systems. While more complex variations of Monte Carlo approaches can give better performance, VMC is widely used and implemented in many popular high-performance codes including QMCPACK [1]. Variational Monte Carlo relies on the use of a flexible parametric ansatz to represent the wavefunction.

Recently, several authors including [2], [4] have proposed to use deep-learning-based ansatzes in the variational Monte Carlo pipeline. These techniques show promise – using the relatively simple VMC algorithm, they are able to achieve performance commensurate with more complex algorithms. In this work, we focused on the PauliNet architecture from [4].

For many-electron systems, most common ansatzes (including both PauliNet and QMCPACK) use a construction known as the Slater determinant to enforce antisymmetry. For an \( N \)-electron system, this requires taking the determinant of an \( N \times N \) matrix, an \( O(N^3) \) operation which in some cases is the asymptotically dominant term for computational cost. There is however another possible construction known as the Vandermonde determinant. The authors of [5] show that the Vandermonde determinant can function as a universal approximator for antisymmetric functions, and [3] uses a Vandermonde-type construction, suggesting that in principle, it could work as well as the Slater determinant as part of a flexible deep-learning-based ansatz. Yet it is potentially only an \( O(N^2) \) operation.

To investigate the feasibility of replacing the Slater determinant with the Vandermonde determinant, we have followed two approaches:

- We implemented our own variational Monte Carlo pipeline on which we tested simple Slater and Vandermonde based ansatzes on simple physical systems.
- We proposed the use of the Vandermonde determinant in place of the Slater determinant in the PauliNet architecture.

In general, we found that the Vandermonde determinant does not work as well as the Slater determinant. In our own implementation, its performance is tolerable, suggesting that as systems scale up and the asymptotic difference in evaluation cost becomes relevant, the trade-off in computational cost could be reasonable. Within PauliNet, the use of the Vandermonde determinant results in a wavefunction that, while somewhat viable, performs significantly worse than PauliNet with Slater determinants.

With regards to PauliNet, a major challenge during development was ensuring the appropriate enforcement of physical boundary conditions – this falls out naturally when using the Slater determinant but required extra effort to guarantee using the Vandermonde determinant. It is possible that different techniques for enforcing these conditions might give better performance than the ones we used. Additionally, it is possible that the input Hartree-Fock basis functions are not well-adapted for the Vandermonde determinant, and that deriving new basis functions could also significantly enhance performance.

VII. ACKNOWLEDGEMENTS

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REFERENCES


