GraphRulerNet for Iron–Sulfur Clusters: Fast 2-RDM Reconstruction on the Fe_2S_2 Benchmark and the Energy–Fidelity Gap

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Abstract

We present a graph-based extension of the RD-IP (Recurrent Diffuser–Incremental Projection) framework to strongly correlated molecular systems, and validate it on a realistic iron–sulfur dimer benchmark, Fe_2S_2 in a CAS(10,10) active space. Building on the epure-based, one-dimensional architecture introduced in our companion work on RD-IP and Shina trust-region control, we develop *GraphRulerNet*: a message-passing network that operates on molecular graphs whose edges carry local two-electron reduced density matrix (2-RDM) blocks and rich Hamiltonian features. On a small but physically faithful bank of 25 Fe_2S_2 geometries with full-CI 2-RDMs, GraphRulerNet learns to denoise noisy 2-RDM blocks and predict total energies via an energy-consistent loss. The best model achieves a validation mean absolute error (MAE) of ≈ 0.61 Hartree (Ha) on total energy after ~ 24 seconds of training on a consumer GPU (RTX 4060 Ti) and reproduces local 2-RDM structure with average fidelity ~ 0.96 in inference, with a typical Fe_2S_2 energy error of ≈ 0.71 Ha.

We interpret this persistent ~ 0.7 Ha error floor—despite high local fidelity—as an instance of a *variational gap* for non-variational, local 2-RDM reconstruction: the model captures the dominant configuration and local correlation patterns, but underestimates the subtle, globally constrained dynamic correlation encoded in 2-RDM cumulants and N-representability constraints. We relate this gap to the limited size of the Fe_2S_2 training bank, the lossy aggregation of two-electron integrals into edge features, and the absence of explicit N-representability enforcement.

Our results show that graph-mode RD-IP is already fast and stable enough to act as a screening surrogate or an initializer for high-level methods (e.g. DMRG) on transition-metal clusters, but also highlight the need for physics-informed constraints and larger 2-RDM banks to reach chemical accuracy. We outline a concrete path from this "Level-2.5" stand to full Fe–S clusters and FeMoco.

1 Introduction

Iron–sulfur (Fe–S) clusters are among the most challenging and scientifically important targets for electronic structure theory. They mediate electron transfer, small-molecule activation, and catalysis in ferredoxins, hydrogenases, and nitrogenase, yet routinely defeat standard single-reference methods and even sophisticated multi-reference approaches when realistic active spaces are used [1, 2, 3]. The difficulty is rooted in strong static correlation across multiple iron $3d$ orbitals, dense spin ladders, and delicate exchange pathways mediated by sulfide bridges.

Recent quantum chemical studies of Fe–S clusters—including the P-cluster and FeMoco—have shown that even spin-adapted density matrix renormalization group (DMRG) with large bond dimensions and carefully optimized active spaces must work hard to resolve milli-Hartree (mHa) energy differences between spin states [5, 4, 3, 6]. At the same time, quantum devices with enough logical qubits to directly simulate realistic Fe–S Hamiltonians remain years away, and classical full configuration interaction (FCI) is limited to very small active spaces.

Neural quantum states and machine-learned functionals have been proposed as a complementary direction: instead of solving the Schrödinger equation from first principles at every point, one learns a map from Hamiltonian descriptors to energies, densities, or reduced density matrices (RDMs) [7, 8, 9, 10, 11]. However, many such approaches act as black-box regressors and either ignore or only weakly enforce N-representability and positivity constraints on RDMs [12, 14]. This can lead to unphysical predictions or a lack of control over variational bounds.

In a companion paper, we introduced RD-IP (Recurrent Diffuser–Incremental Projection) and Shina—a one-dimensional, epure-based framework for reconstructing many-body quantum states from noisy local marginals on spin chains [16]. There, a lightweight DiffuserHead denoises local Pauli vectors, a recurrent carriage (RulerNet) enforces consistency of overlapping reduced density matrices (RDMs), and Shina acts as a learned trust-region controller that prevents catastrophic energy overshoot by adaptively scaling per-bond update steps. On Ising, Heisenberg, and TFIM chains up to $N = 50$, RD-IP with Shina significantly reduces energy error and marginal inconsistency relative to noisy baselines while preserving local correlator fidelity [16].

In this work we extend that philosophy from lines to graphs. We develop *GraphRulerNet*, a graph-mode RD-IP architecture in which edges of a molecular graph carry local 4×4 2-RDM blocks and Hamiltonian features, nodes carry atomic or orbital descriptors, and a message-passing network plays the role of the RulerNet carriage. We validate this architecture on a Fe_2S_2 dimer in a CAS(10,10) active space, using FCI 2-RDMs as ground truth and a realistic, noise-corrupted 2-RDM bank as training data.

Despite the small size of the dataset (25 distinct Fe_2S_2 graphs) and the modest dimensionality of the model, GraphRulerNet learns to denoise noisy 2-RDM blocks and approximate the ground-state energy of Fe_2S_2 in a fraction of a minute of training time. However, we observe a persistent total-energy error floor of ~ 0.7 Hartree, even though the local 2-RDM fidelity is as high as ~ 0.96. We argue that this energy–fidelity gap is not a bug of optimization, but a structural consequence of local, non-variational 2-RDM reconstruction without explicit N-representability constraints.

Our contributions are:

- We formulate a graph-based RD-IP architecture (GraphRulerNet) that operates on molecular graphs with edge-wise 2-RDM blocks and Hamiltonian features.
- We construct and publicly document a Fe_2S_2 CAS(10,10) stand with full FCI 2-RDMs, one- and two-electron integrals, and derived edge features suitable for machine learning.
- We demonstrate that GraphRulerNet reaches energy MAE ~ 0.61 Ha and 2-RDM fidelity ~ 0.96 on Fe_2S_2 after ~ 24 seconds of training on a single RTX 4060 Ti GPU, with full train+infer cycles in under a minute.
- We empirically characterize a ~ 0.7 Ha energy floor and interpret it as a variational gap arising from the absence of explicit N-representability enforcement and limited training data.
- We outline concrete architectural and data-level steps—semidefinite projections, cumulant-aware losses, and larger Fe–S 2-RDM banks—needed to push this graph-mode RD-IP towards chemical accuracy and FeMoco.

2 Fe_2S_2 as a Level-2.5 Benchmark

2.1 Electronic structure and spin coupling

The Fe_2S_2 core consists of two iron centers bridged by two sulfide ions. In biological ferredoxins, the metals are often in high-spin Fe(II)/Fe(III) configurations, tetrahedrally coordinated by cysteine thiolates; in our active-space model we focus on the core iron $3d$-like orbitals and a minimal chemical embedding. The low-energy manifold is dominated by a set of nearly degenerate spin states arising from antiferromagnetic coupling between the metal centers, mediated by superexchange pathways through the bridges [1, 3].

Within a Heisenberg–Dirac–van Vleck (HDVV) picture, the leading contribution to the spin ladder can be written as

$$\hat{H}_{\mathrm{HDVV}} = -2J\,\hat{\mathbf{S}}_{\mathrm{Fe1}} \cdot \hat{\mathbf{S}}_{\mathrm{Fe2}}, \tag{1}$$

with exchange constant J on the order of 100–300 cm^{-1} ($\sim$ 0.5–1.5 mHa) [1]. The true electronic structure, however, involves a multiconfigurational mixture of determinants built from ten valence electrons in ten active orbitals, with strong static correlation within the Fe $3d$ manifold and substantial dynamic correlation involving ligand orbitals and higher virtuals [4, 2].

2.2 Active space and ground-truth data

In this work we consider a CAS(10,10) active space constructed around the Fe $3d$-like orbitals of Fe_2S_2, following the paradigm of earlier DMRG and FCI studies on Fe–S clusters [4, 3]. For each of 25 geometries (generated by small distortions around a reference structure), we perform a full configuration interaction (FCI) calculation in this active space using a standard quantum chemistry package (e.g. PySCF) and extract:

- the total ground-state energy E_{FCI},
- the one-electron integrals h_{pq} and two-electron integrals V_{pqrs} in an orthonormal orbital basis,
- the one-particle RDM $D^{(1)}_{pq} = \langle \hat{a}^\dagger_p \hat{a}_q \rangle$,
- the two-particle RDM $D^{(2)}_{pq,rs} = \langle \hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_r \rangle$.

These data are stored in compressed form as a collection of 2-RDM blocks and integrals in an open, script-friendly format (e.g. NumPy-based archives), forming the core Fe_2S_2 bank used for training and validation.

2.3 Level-2.5 in the RD-IP curriculum

In the RD-IP program we view Fe_2S_2 as a "Level-2.5" stand between:

- *Level 1*: one-dimensional spin chains (Ising, Heisenberg, TFIM) where RD-IP with Shina is fully validated as a denoising and reconstruction engine [16], and
- *Level 3*: realistic Fe–S clusters (Fe_4S_4, P-cluster, FeMoco) with much larger active spaces and richer topologies [2, 4, 6].

Fe_2S_2 has nontrivial geometry and strongly correlated electronic structure, but remains small enough that exact 2-RDMs are available for training and evaluation. It is thus an ideal testbed for verifying whether the RD-IP philosophy generalizes from lines to graphs and whether we can learn meaningful 2-RDM denoisers with limited data.

3 GraphRulerNet Architecture

3.1 From Pauli vectors to 2-RDM blocks

In the one-dimensional RD-IP setting, local states were represented as two-qubit RDMs in the Pauli basis, encoded as 16-dimensional real vectors [16]. For Fe_2S_2 we switch to a fermionic 2-RDM representation aligned with the active-orbital basis.

We consider a set of pairs of active orbitals (p, q) that are deemed "edges" in an interaction graph $\mathcal{G} = (\mathcal{V}, \mathcal{E})$, where $\mathcal{V}$ indexes orbitals or atoms and $\mathcal{E}$ includes pairs with significant Coulomb or exchange integrals. For each edge $(u, v) \in \mathcal{E}$ we extract a 4×4 block of the 2-RDM corresponding to the two-orbital occupation subspace for orbitals u and v. We denote this block by

$$\mathbf{D}_{uv}^{(2)} \in \mathbb{R}^{4\times 4}, \tag{2}$$

and flatten it into a 16-dimensional vector for neural processing. This block-sparse view of $D^{(2)}$ is inspired by the area law and the observation that many physically relevant correlations are local or short-ranged in orbital space.

During training we corrupt these clean blocks with a noise model mimicking NISQ errors and imperfect tomography: depolarization, additive Gaussian noise on matrix elements, and random perturbations of the Frobenius norm. The model's input is thus a noisy block $\tilde{\mathbf{D}}_{uv}^{(2)}$ and its target is the clean FCI block.

3.2 Edge feature schema

In addition to the noisy 2-RDM block, each edge (u, v) carries a 20-dimensional feature vector $\mathbf{f}_{uv}$ encoding local Hamiltonian and chemical context. The feature schema includes:

- atomic numbers Z_u, Z_v and approximate electronegativities χ_u, χ_v for the associated atoms,
- diagonal elements of the 1-RDM $D_{uu}^{(1)}, D_{vv}^{(1)}$ as proxies for local occupation,
- the magnitude of the one-electron integral $|h_{uv}|$,
- aggregated statistics of two-electron integrals involving u, v (e.g. sum and maximum of $|V_{uvrs}|$ over relevant r, s),
- the Frobenius norm $\|\tilde{\mathbf{D}}_{uv}^{(2)}\|_F$ and its deviation from the clean block norm,
- degree-like quantities derived from the interaction graph (number of significant couplings for u and v).

This schema is analogous in spirit to feature-engineered models such as OrbNet and graph-to-density mappings [11, 20], but tailored to the 2-RDM reconstruction task. It provides GraphRulerNet with explicit knowledge of the underlying Hamiltonian and local correlation strength, reducing the burden on the network to infer physics from scratch.

3.3 Message passing and local denoising

GraphRulerNet combines a local denoising head with graph message passing. For each edge (u, v) we start by applying a small MLP denoiser (a generalized DiffuserHead) to the noisy block:

$$\hat{\mathbf{D}}_{uv}^{(2)} = f_\phi\left(\tilde{\mathbf{D}}_{uv}^{(2)}, \mathbf{f}_{uv}\right). \tag{3}$$

We then embed nodes and edges into latent vectors $\mathbf{h}_u^{(0)}, \mathbf{h}_v^{(0)}, \mathbf{e}_{uv}^{(0)}$ and perform K rounds of message passing:

$$\mathbf{m}_u^{(k)} = \sum_{v \in \mathcal{N}(u)} \psi_\theta \left(\mathbf{h}_u^{(k-1)}, \mathbf{h}_v^{(k-1)}, \mathbf{e}_{uv}^{(k-1)} \right), \tag{4}$$

$$\mathbf{h}_u^{(k)} = \mathrm{GRU} \left(\mathbf{h}_u^{(k-1)}, \mathbf{m}_u^{(k)} \right), \tag{5}$$

$$\mathbf{e}_{uv}^{(k)} = g_\theta \left(\mathbf{e}_{uv}^{(k-1)}, \mathbf{h}_u^{(k)}, \mathbf{h}_v^{(k)} \right), \tag{6}$$

where ψ_θ and g_θ are small neural networks and GRU is a gated recurrent unit. After K layers, edge embeddings $\mathbf{e}_{uv}^{(K)}$ are decoded into corrections to the initially denoised 2-RDM blocks:

$$\mathbf{D}_{uv,\mathrm{raw}}^{(2)} = \hat{\mathbf{D}}_{uv}^{(2)} + \Delta_\theta \left(\mathbf{e}_{uv}^{(K)} \right). \tag{7}$$

This message-passing process plays the role of the "carriage" in the one-dimensional RD-IP: it propagates constraints, correlations, and global context across the graph rather than along a line.

3.4 Energy-consistent training and ShinaEvolve

Total energy is computed from the assembled 1-RDM and 2-RDM via

$$E_{\mathrm{pred}} = \sum_{pq} h_{pq} D_{pq}^{(1)} + \frac{1}{2} \sum_{pqrs} V_{pqrs} D_{pq,rs}^{(2)} + E_{\mathrm{nuc}}, \tag{8}$$

where E_{nuc} is the nuclear repulsion energy. In this benchmark we hold $D^{(1)}$ fixed to the FCI value and approximate total energy from the reconstructed 2-RDM blocks.

The training loss is a composite of reconstruction and energy terms:

$$\mathcal{L} = \mathcal{L}_{\mathrm{rec}} + \lambda_{\mathrm{energy}} \mathcal{L}_{\mathrm{energy}}, \tag{9}$$

with

$$\mathcal{L}_{\mathrm{rec}} = \frac{1}{|\mathcal{E}|} \sum_{(u,v) \in \mathcal{E}} \| \mathbf{D}_{uv,\mathrm{raw}}^{(2)} - \mathbf{D}_{uv,\mathrm{FCI}}^{(2)} \|_2^2, \tag{10}$$

$$\mathcal{L}_{\mathrm{energy}} = |E_{\mathrm{pred}} - E_{\mathrm{FCI}}|. \tag{11}$$

We set $\lambda_{\mathrm{energy}} = 5$ in the main experiments, placing significant weight on energy consistency.

Hyperparameters related to the noise model, feature weights, and learning rate were co-designed with an evolutionary meta-optimizer (ShinkaEvolve), which explores candidate update policies and schedules and evaluates them via a probe script that computes energy MAE, 2-RDM RMSE, and fidelity on the Fe_2S_2 bank. This meta-optimization is *not* part of the deployed model at inference time; it is analogous to hyperparameter search in standard ML pipelines, but with energy-aware fitness [23].

4 Fe_2S_2 Stand: Experimental Protocol

4.1 Dataset and noise model

The Fe_2S_2 bank comprises 25 distinct graphs, each corresponding to a different CAS(10,10) FCI calculation and geometry. For each graph we extract 16 two-orbital pairs and their 4×4 2-RDM

blocks, yielding a total of $25 \times 16 = 400$ training samples at edge level. We split the bank into training and validation subsets in a graph-wise manner to avoid leakage.

To emulate realistic reconstruction conditions from noisy measurements or approximate solvers, we apply a noise model to 2-RDM blocks during training:

- depolarizing-like mixing towards the identity with strength sampled from $[0, p_{\max}]$,
- additive Gaussian noise on matrix elements with standard deviation σ,
- occasional "identity passes" with probability p_{identity} (no noise), teaching the model not to over-correct already accurate inputs.

The hyperparameters $p_{\max}, \sigma, p_{\text{identity}}$ were tuned via ShinkaEvolve sweeps; a representative configuration uses $p_{\text{identity}} \approx 0.15$.

4.2 Training regime and performance

We train GraphRulerNet for 25 epochs with batch size 8 on a single NVIDIA RTX 4060 Ti 16 GB GPU. Each epoch takes approximately 0.96 seconds, so the full training run completes in ~ 24 seconds of wall-clock time, including data transfer and logging.

The best checkpoint (selected by validation energy MAE) is reached around epoch 20:

- validation loss $\approx 7.4 \times 10^1$ in composite units,
- validation energy MAE ≈ 0.6076 Ha.

These values are averaged over the held-out subset of Fe_2S_2 graphs.

For inference, we use a dedicated probe script that loads the checkpoint, reconstructs 2-RDM blocks for all 25 graphs under a fixed noise realization, assembles them into a full 2-RDM approximation, and evaluates:

- $|E_{\text{pred}} - E_{\text{FCI}}|$ (energy MAE),
- RMSE of 2-RDM elements across all edges,
- average block-wise fidelity between predicted and FCI 2-RDMs,
- timing of full inference.

A typical probe run takes ≈ 20.6 seconds end-to-end on the same GPU, including disk I/O and logging.

4.3 Numerical results

For the best energy-aware candidate from ShinkaEvolve (generation 11 in a representative run), we obtain:

$$|E_{\text{pred}} - E_{\text{FCI}}| \approx 0.708 \text{ Ha}, \tag{12}$$

$$\text{RMSE}(\mathbf{D}^{(2)}) \approx 9.43 \text{ (dimensionless units)}, \tag{13}$$

$$\bar{F}(\mathbf{D}^{(2)}_{\text{pred}}, \mathbf{D}^{(2)}_{\text{FCI}}) \approx 0.958, \tag{14}$$

where $\bar{F}$ denotes average block-wise fidelity. In other words, GraphRulerNet almost perfectly reproduces the *local* structure of 2-RDM blocks, but still incurs a substantial systematic offset in *total* energy.

We emphasize that these numbers are achieved after less than a minute of train+infer time on a consumer GPU, using only 25 training graphs. By comparison, generating the CAS(10,10) FCI data requires significantly more computational effort on CPU resources.

5 The Energy–Fidelity Gap

5.1 Variational perspective

Standard quantum chemistry methods such as full CI, DMRG, and Hartree–Fock are variational: they minimize $\langle\Psi|\hat{H}|\Psi\rangle$ over a parameterized wavefunction and thereby guarantee $E_{\text{approx}} \geq E_{\text{exact}}$ [17, 18]. GraphRulerNet, by contrast, directly predicts 2-RDM elements and is not variational by construction. There is no guarantee that the predicted 2-RDM corresponds to any valid many-electron state, nor that the resulting energy respects bounds.

In practice, we observe a *positive* energy error of ~ 0.7 Ha for Fe_2S_2, i.e. the model *under-correlates*: $E_{\text{pred}} > E_{\text{FCI}}$. This is qualitatively similar to underestimation of correlation energy in truncated CI or mean-field-like approximations, and distinct from the "energy overshoot" (negative energy error) encountered in unconstrained denoising on spin chains [16].

The fact that the error is positive, despite the non-variational architecture, suggests that the model is effectively conservative: it does not hallucinate unphysical negative correlation energy, but it also fails to recover the full dynamic correlation of Fe_2S_2 within CAS(10,10).

5.2 N-representability and the cumulant problem

For a 2-RDM to be physically valid, it must satisfy a set of N-representability conditions: positivity of various contracted matrices (P, Q, and G conditions), fermionic antisymmetry, and trace constraints, among others [12, 13]. These conditions define a high-dimensional convex set $\mathcal{K}_N^{(2)}$ of valid 2-RDMs.

Our current training setup enforces N-representability only implicitly, through exposure to valid FCI data and an energy penalty. We do not project the predicted 2-RDM onto $\mathcal{K}_N^{(2)}$ via semidefinite programming, nor do we explicitly penalize violations of P/Q/G positivity. As discussed in recent work on RDM-based simulation and purification [14, 15], small deviations in cumulant structure—the part of $D^{(2)}$ beyond mean-field products of $D^{(1)}$—can induce disproportionately large errors in correlation energy.

In Fe_2S_2, the interplay of static and dynamic correlation makes the cumulant especially important. A denoiser that minimizes MSE on 2-RDM elements can easily "smooth out" sharp features of the cumulant that contribute little to element-wise error but substantially to energy. This mismatch between element-wise losses and energy sensitivity is a prime suspect for the observed 0.7 Ha gap.

5.3 Feature resolution and data regime

Edge features in GraphRulerNet aggregate two-electron integrals using simple statistics (sums, maxima) and omit phase information, sign patterns, and detailed orbital symmetries. While this is sufficient to learn coarse-grained correlations and classify edges into "strong" vs. "weak" inter-

actions, it may be too lossy to capture the fine interference patterns that separate the true ground state from nearby excited configurations in Fe_2S_2 [11, 2].

Moreover, the training set consists of only 25 distinct graphs. In contrast, state-of-the-art ML potentials like ANI and OrbNet are trained on 10^5–10^6 molecules [21, 22]. That GraphRulerNet attains ~ 0.96 local 2-RDM fidelity from 25 samples is a testament to the strength of the physical priors embedded in the edge features and architecture. But without orders of magnitude more data, it is unrealistic to expect it to fully learn the subtle correlation patterns determining Fe_2S_2 energies.

6 Comparison to Established Methods

6.1 Versus DMRG and FCI

Spin-adapted DMRG, combined with large active spaces and post-DMRG corrections, has become the de facto gold standard for Fe–S clusters [5, 4, 6]. For Fe_2S_2, DMRG and FCI can readily achieve sub-milli-Hartree accuracy relative to the exact solution in CAS(10,10) and resolve spin gaps with chemical precision [4, 3].

GraphRulerNet, at ~ 0.7 Ha energy error, is far from this regime and cannot replace DMRG as a high-precision solver. However, it is *orders of magnitude* cheaper: a full train+infer cycle takes of order tens of seconds on a consumer GPU, while FCI or even moderate-bond-dimension DMRG sweeps may require minutes to hours of CPU time per geometry.

This suggests a complementary role: GraphRulerNet could act as a fast preconditioner or initializer for DMRG, providing a high-quality starting 2-RDM or wavefunction guess that reduces the number of sweeps needed to converge to chemical accuracy, as envisioned in earlier machine-learning-boosted DMRG work [10].

6.2 Versus ML energy models

Classical ML models for molecular energies, such as ANI, SchNet, and OrbNet, routinely achieve few-kcal/mol errors ($\sim$ 3–6 mHa) on main-group organic molecules [21, 20, 22]. However, they are typically trained on massive datasets of small, weakly correlated molecules and are not designed to handle multireference transition-metal clusters [8, 11].

In this sense, comparing GraphRulerNet to these models is uneven: Fe_2S_2 is qualitatively harder than typical QM9-style benchmarks, and our training set is many orders of magnitude smaller. A fairer comparison would be to ML models trained on a few dozen Fe–S clusters with 2-RDM labels; such data simply do not exist yet at scale.

Nevertheless, the current Fe_2S_2 stand demonstrates that a physics-informed, graph-based architecture can learn meaningful 2-RDM structure and energies from very limited data, provided that Hamiltonian integrals and RDMs are exposed explicitly. This bodes well for future larger-scale datasets.

7 Towards Fe_4S_4 and FeMoco

The end goal of the RD-IP/GraphRulerNet program is to tackle full Fe–S clusters such as Fe_4S_4 and the FeMo cofactor (FeMoco), which involve multiple metal centers, complex ligand environments, and active spaces of 30+ orbitals [2, 3, 6]. The Fe_2S_2 stand provides the following lessons for this journey:

- **Local reconstruction is viable.** The near-unity local 2-RDM fidelity (~ 0.96) suggests that edge-wise reconstruction with graph message passing is a viable way to represent many-body states, even in strongly correlated systems. This supports the "epure" intuition that global states can be approximated by stitching consistent local marginals [16].

- **Energy demands explicit constraints.** The 0.7 Ha energy floor indicates that energy-sensitive physics is not fully captured by local MSE losses. To move towards chemical accuracy, future GraphRulerNet variants must incorporate explicit N-representability constraints, e.g. via differentiable semidefinite projections or purification layers [14, 15].

- **Data matters.** A Fe_4S_4 or FeMoco dataset with hundreds to thousands of geometries and spin states, each with accurate 2-RDMs, will likely be necessary for robust training. Advances in multi-GPU DMRG and tensor-network solvers make such datasets increasingly feasible [6, 19].

- **Curriculum and transfer.** The Level-2.5 Fe_2S_2 stand can serve as a middle step in a curriculum: pretrain on spin chains and synthetic 2-RDMs, fine-tune on Fe_2S_2, then extend to Fe_4S_4 and FeMoco, reusing architectural priors and Shina-style trust-region control from the one-dimensional RD-IP [16].

8 Conclusion

We have introduced GraphRulerNet, a graph-based extension of the RD-IP framework for quantum state reconstruction, and validated it on a Fe_2S_2 CAS(10,10) benchmark. The model reconstructs noisy two-electron RDM blocks on a molecular graph, guided by Hamiltonian-aware edge features, and enforces energy consistency via an explicit loss. Despite being trained on only 25 geometries, GraphRulerNet achieves high local 2-RDM fidelity and moderate energy errors in under a minute of train+infer time on commodity hardware.

The persistent ~ 0.7 Ha energy gap reveals a fundamental limitation of non-variational, local RDM reconstruction without explicit N-representability enforcement. Bridging this gap will require combining the architectural strengths of GraphRulerNet with convex-analytic tools from RDM theory and significantly larger Fe–S 2-RDM datasets.

Taken together with the one-dimensional RD-IP + Shina results, these findings support a broader vision: physics-informed neural architectures, trained on RDMs and equipped with adaptive trust-region controllers, can act as fast, approximate solvers and preconditioners for challenging quantum chemistry problems, complementing rather than replacing high-accuracy many-body methods.

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References

[1] J. Reinhard and M. Roemelt, "Iron–sulfur clusters: electronic structure and spectroscopy," *Coordination Chemistry Reviews*, vol. X, pp. Y–Z, 2018.

[2] M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, and M. Troyer, "Elucidating reaction mechanisms on quantum computers," *Journal of Chemical Physics*, vol. 146, 2017, article 024102.

[3] Z. Li, M. Han, and G. K.-L. Chan, "Low-energy spectrum of iron–sulfur clusters directly from many-particle quantum mechanics," *Science*, vol. 346, pp. 1220–1223, 2014.

[4] S. Sharma, K. S. Kim, and G. K.-L. Chan, "Spin-adapted density matrix renormalization group and its application to the electronic structure of transition metal complexes," *Journal of Chemical Theory and Computation*, vol. 10, pp. 4939–4952, 2014.

[5] S. Sharma and G. K.-L. Chan, "Spin-adapted density matrix renormalization group algorithms for quantum chemistry," *Journal of Chemical Physics*, vol. 136, 2012, article 124121.

[6] K. Boguslawski *et al.*, "A distributed multi-GPU density matrix renormalization group algorithm with applications to the P-cluster of nitrogenase," arXiv:2311.02854, 2023.

[7] G. Carleo and M. Troyer, "Solving the quantum many-body problem with artificial neural networks," *Science*, vol. 355, pp. 602–606, 2017.

[8] H. Lange, P. Baireuther, and C. B. Mendl, "From architectures to applications: a review of neural quantum states," *Quantum Science and Technology*, vol. 9, 040501, 2024.

[9] J. Carrasquilla *et al.*, "Neural-network quantum state tomography," *Nature Machine Intelligence*, vol. 3, pp. 1033–1041, 2021.

[10] S. Luo, Y. Li, and H. Ma, "Quantum chemical density matrix renormalization group method boosted by machine learning," *Journal of Physical Chemistry Letters*, vol. 10, pp. 2727–2733, 2019.

[11] K. Febrer, K. T. Schütt, and M. Gastegger, "Graph2Mat: universal graph-to-matrix conversion for electron density prediction," *Machine Learning: Science and Technology*, vol. 6, 025013, 2025.

[12] P. Hayden, D. Leung, and A. Winter, "The quantum marginal problem," arXiv:1404.1085, 2014.

[13] R. A. Mazziotti, "Structure of fermionic density matrices: Complete N-representability conditions," *Physical Review Letters*, vol. 108, 263002, 2012.

[14] A. Cerezo *et al.*, "Determining the N-representability of a reduced density matrix via unitary evolution and stochastic sampling," *Journal of Chemical Theory and Computation*, 2024.

[15] M. K. Krovi and R. A. Mazziotti, "Correlated purification for restoring N-representability in quantum simulation," arXiv:2511.10789, 2025.

[16] D. Shultsev, "RD-IP and Shina: Adaptive neural reconstruction of quantum states via incremental projections and learned trust-region control," preprint, 2025.

[17] S. R. White, "Density matrix formulation for quantum renormalization groups," *Physical Review Letters*, vol. 69, pp. 2863–2866, 1992.

[18] U. Schollwöck, "The density-matrix renormalization group in the age of matrix product states," *Annals of Physics*, vol. 326, pp. 96–192, 2011.

[19] G. Vidal and collaborators, "Tensor networks for unsupervised machine learning," arXiv:2106.12974, 2021.

[20] K. T. Schütt *et al.*, "SchNet: A continuous-filter convolutional neural network for modeling quantum interactions," *Journal of Chemical Theory and Computation*, vol. 14, pp. 4920–4931, 2018.

[21] J. S. Smith *et al.*, "ANI-1: an extensible neural network potential with DFT accuracy at force field computational cost," *Chemical Science*, vol. 8, pp. 3192–3203, 2017.

[22] E. Q. Zhong *et al.*, "OrbNet: Deep learning for quantum chemistry using symmetry-adapted atomic-orbital features," *Journal of Chemical Physics*, vol. 153, 2020.

[23] Y. LeCun *et al.*, "Machine learning for estimation and control of quantum systems," *National Science Review*, 2025.