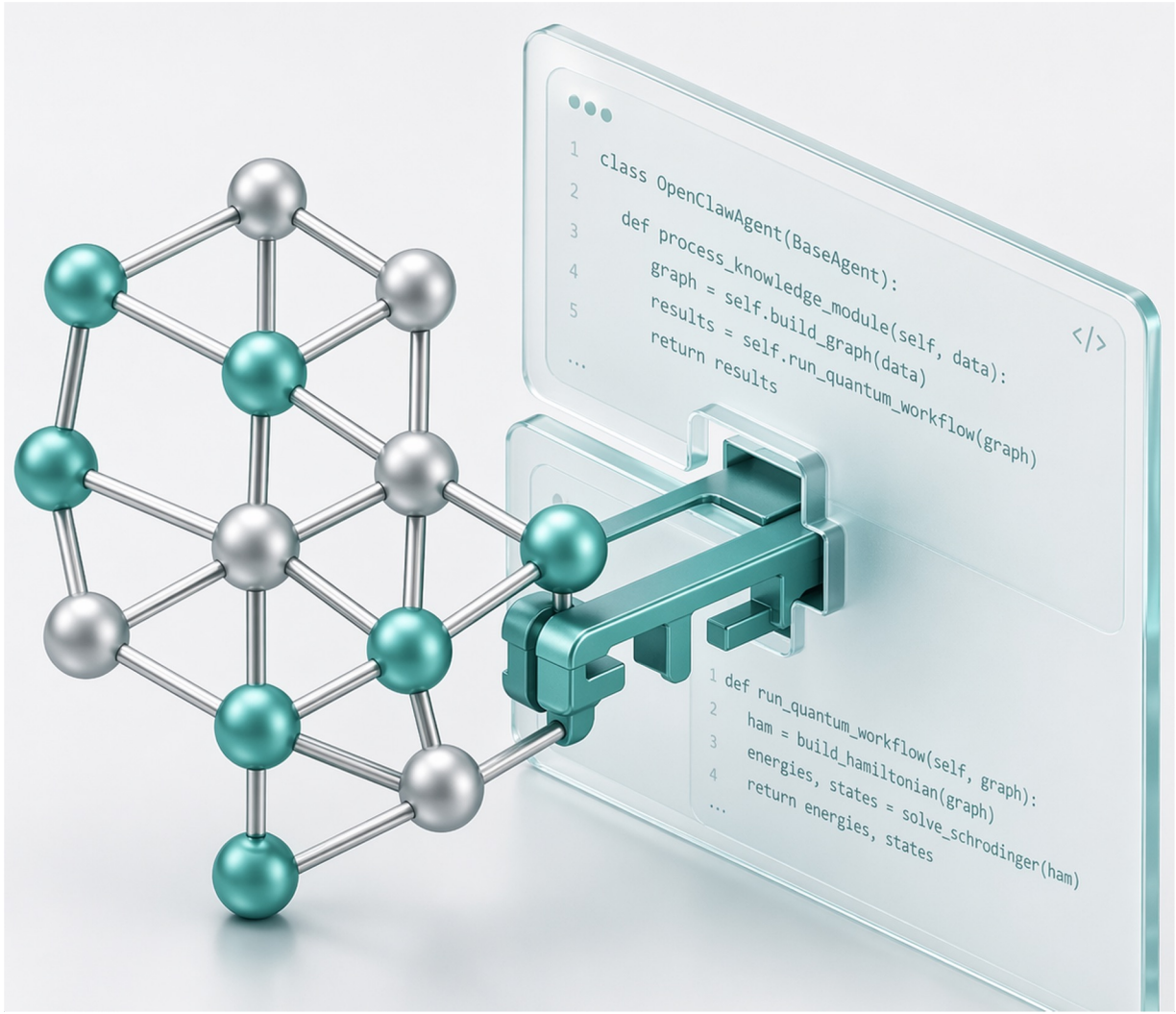
中国科学院大学 University of Chinese Academy of Sciences
前沿交叉科学学院 School of Advanced Interdisciplinary Sciences

Full Differentiable TDDFT Code for Neural Network XC Functional, Learning Hamiltonian form Natural SCF, Auto-Research Agent for Materials Discovery

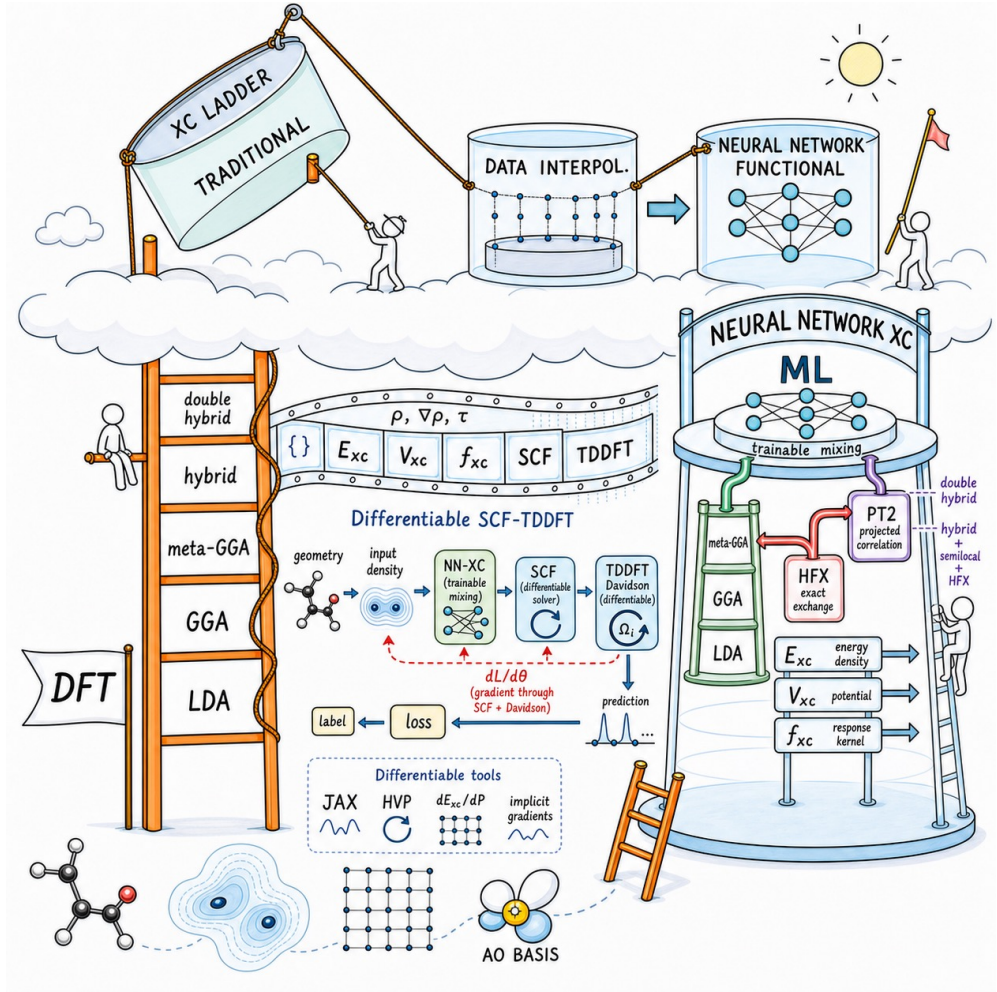
Yuan Jiao

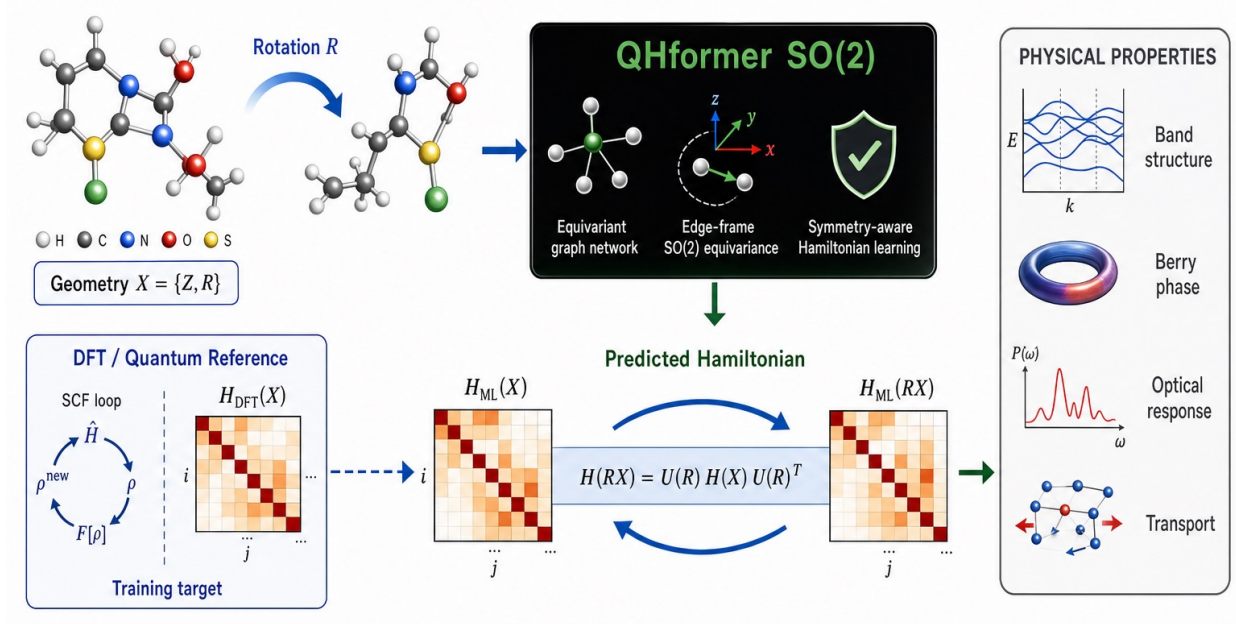
School of Advanced Interdisciplinary Sciences, SAIS

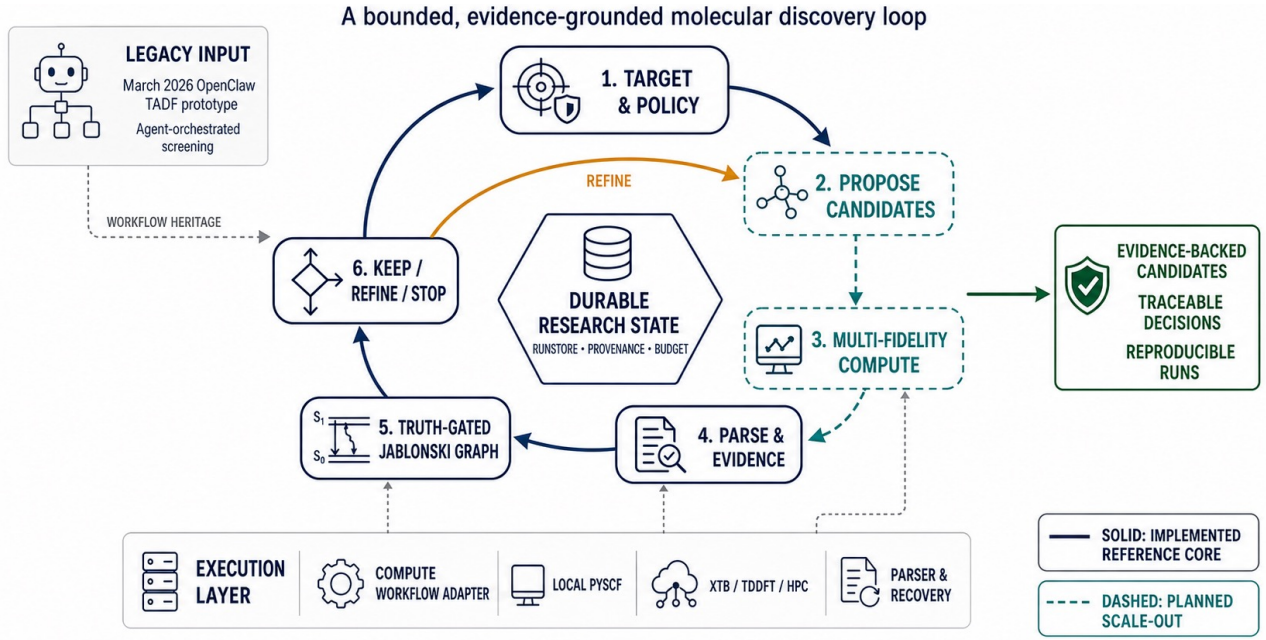
University of Chinese Academy of Sciences



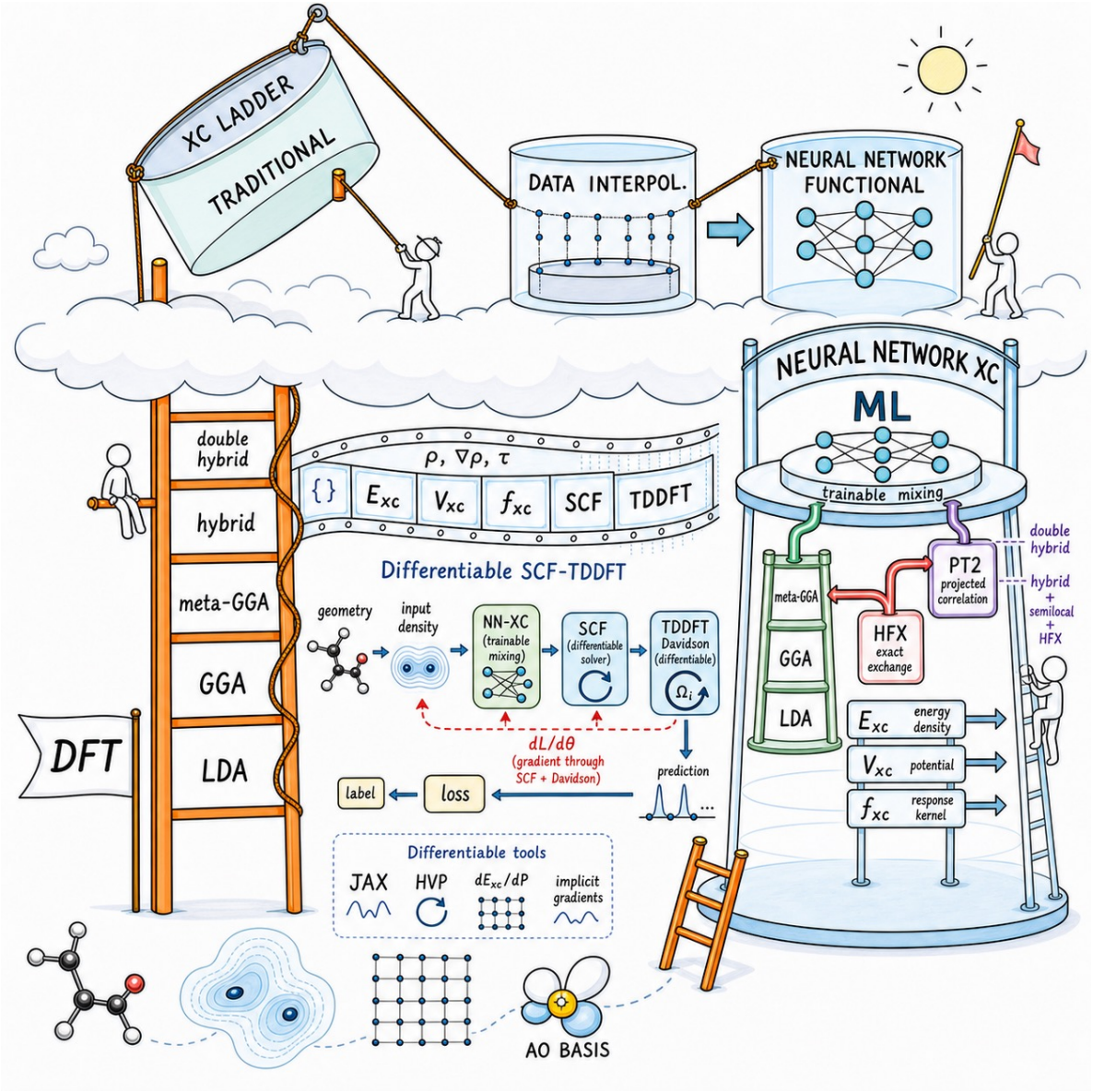
- **Full Differentiable TDDFT Code for Neural Network XC Functional**
- **Learning Hamiltonian form Natural SCF**
- **Auto-Research Agent for Materials**





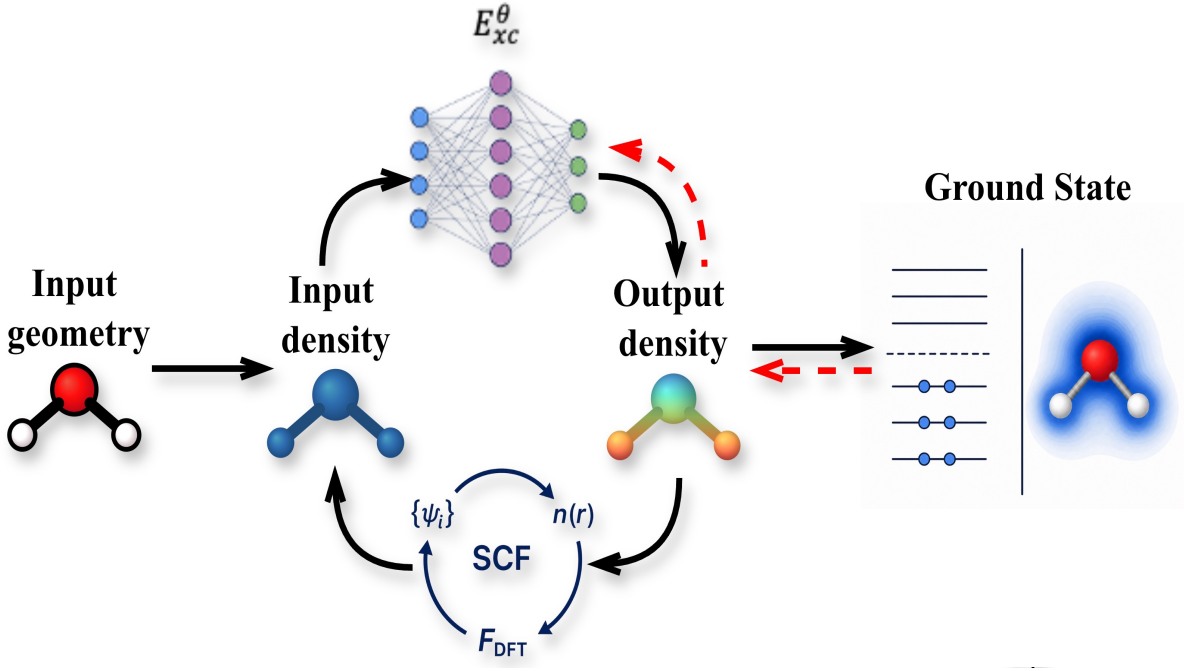


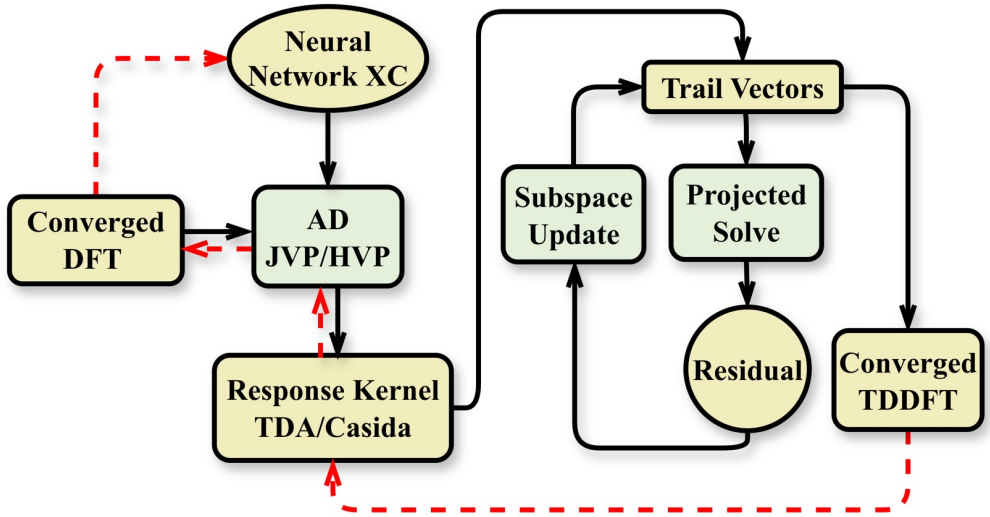
■ Full Differentiable TDDFT Code for Neural Network XC Functional




```python
def point_energy(variables: Array) -> Array:
    rho_point = jnp.maximum(variables[0],
density_floor_value)
    if kind_norm == "LDA":
        grad_point = jnp.zeros((3,),
dtype=variables.dtype)
        tau_point = jnp.asarray(0.0,
dtype=variables.dtype)
    elif kind_norm == "GGA":
        grad_point = variables[1:4]
        tau_point = jnp.asarray(0.0,
dtype=variables.dtype)
    elif kind_norm == "MGGA":
        grad_point = variables[1:4]
        tau_point = jnp.maximum(variables[4], 0.0)
    ...
    return eval_xc_energy_density(spec_norm, features)

return jax.jit(jax.vmap(jax.hessian(point_energy)))
```

■ Full Differentiable TDDFT Code for Neural Network XC Functional





- **SCF Implicit Differentiation**

$$L = L(\theta, D_\theta) \quad \text{with } D_\theta = T_{SCF}^{K}(D_0)$$

$$R(D_\theta, \theta) = F_\theta(D_\theta)D_\theta S - SD_\theta F_\theta(D_\theta) = 0$$

$$\nabla_\theta L(\theta, D_\theta) = \partial_\theta L + \partial_{\rho_\theta} L \frac{\partial_\theta R}{\partial_{D_\theta} R}$$

- **Davidson Solver Implicit Differentiation**

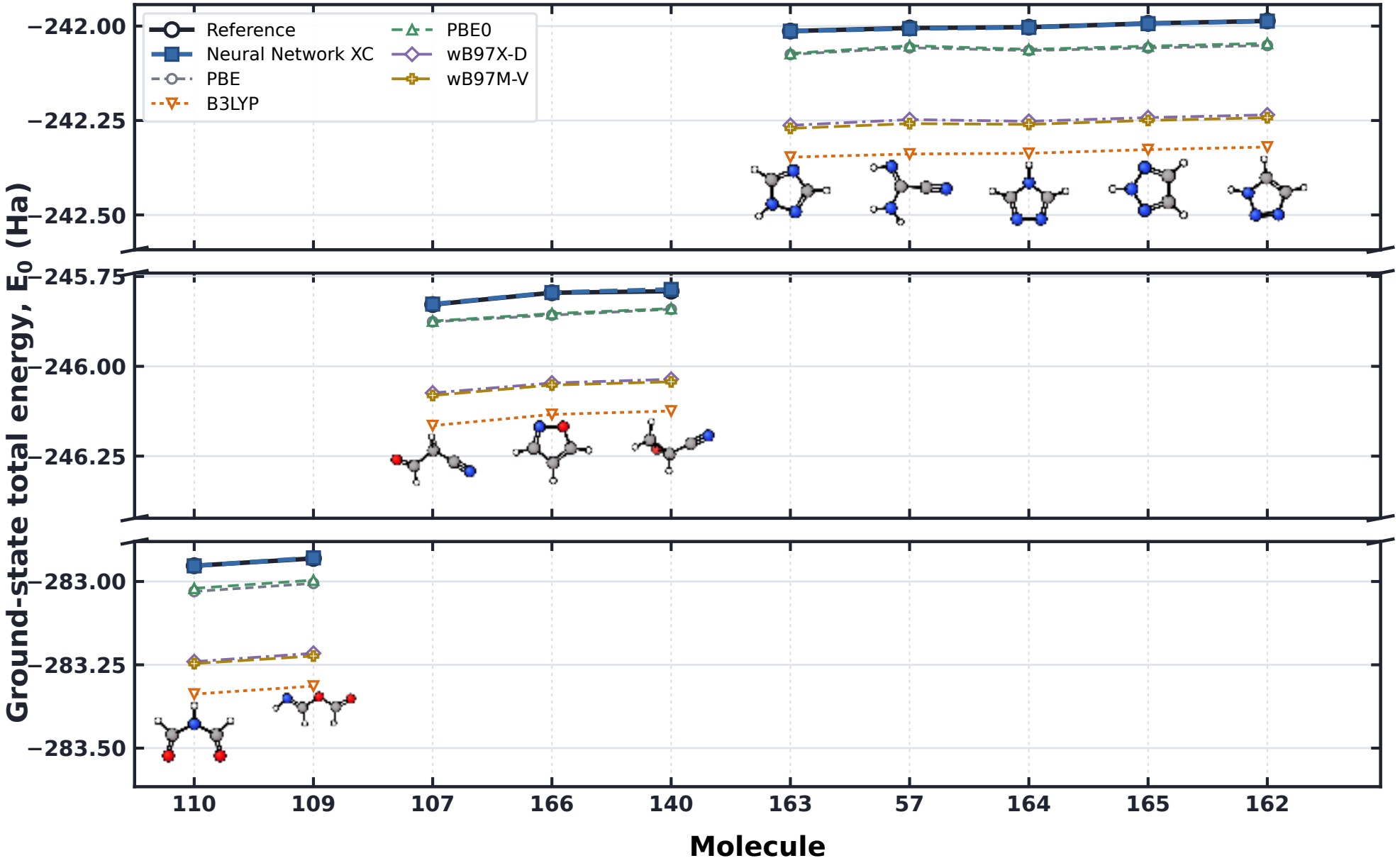
$$L = L(\theta, D_\theta, \Omega_n, f_n) \quad \text{with } D_\theta = T_{SCF}^{K}(D_0)$$

$$AX_n = \Omega_n X_n \quad f_n = \frac{1}{3}\Delta\varepsilon\mu_{if}^2$$

$$\nabla_\theta L(\theta, D_\theta, \Omega_n, f_n) = \partial_\theta L + \partial_{\rho_\theta} L \frac{\partial_\theta R}{\partial_{D_\theta} R} + \bar{\theta}$$

■ Full Differentiable TDDFT Code for Neural Network XC Functional

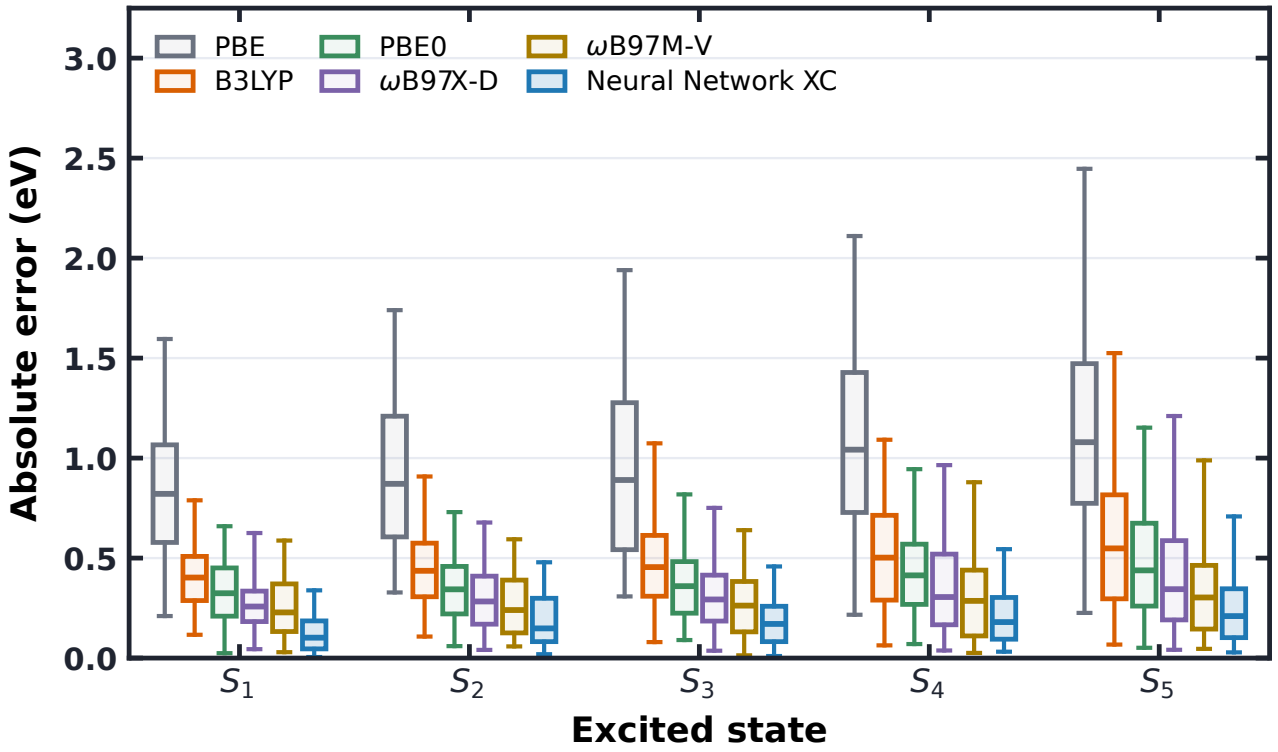
- Implicit SCF for CCSD(T)/aug-cc-pVTZ Ground State with def2-TZVP, grid level = 2



■ Full Differentiable TDDFT Code for Neural Network XC Functional

- **Implicit SCF/Davidson Solver for qsGWBSE@QM9 Excited State S_1**

Calculation	S_1	S_2	S_3	S_4	S_5
def2-SVP calculations, training set					
B3LYP	0.315	0.374	0.451	0.452	0.526
Neural Network XC, SCF-32	**0.059**	**0.227**	**0.252**	**0.228**	**0.300**
def2-SVP calculations, validation set					
B3LYP	0.396	0.438	0.367	0.552	0.518
Neural Network XC, SCF-32	**0.101**	**0.246**	**0.196**	**0.307**	**0.219**
def2-TZVP calculations, training set					
B3LYP	0.377	0.482	0.587	0.576	0.718
Neural Network XC, SCF-32	**0.076**	**0.166**	**0.231**	**0.248**	**0.330**
Neural Network XC, SCF-64	0.080	0.180	0.240	0.251	0.337
def2-TZVP calculations, validation set					
B3LYP	0.389	0.428	0.480	0.566	0.632
Neural Network XC, SCF-32	0.111	**0.295**	**0.216**	**0.331**	0.190
Neural Network XC, SCF-64	**0.104**	0.298	0.229	0.360	**0.189**



■ Full Differentiable TDDFT Code for Neural Network XC Functional

- **Functional**
  - **Differential SCF code and implicit differential Davidson solver code for TDDFT**
  - **HF and PT2 local energy density hybrid and CIS(D) based TDDFT for Double Hybrid Functional**
  - **GPU/CPU Integral Modules for DFT/TD-DFT**
  - **General XC Functional Library based on JAX-XC and General Base Set Library form PySCF**
  - **Fractional charge evaluation and differential unrestricted SCF code**

- **Outlook**

☐ **Long-Term(next vision):**

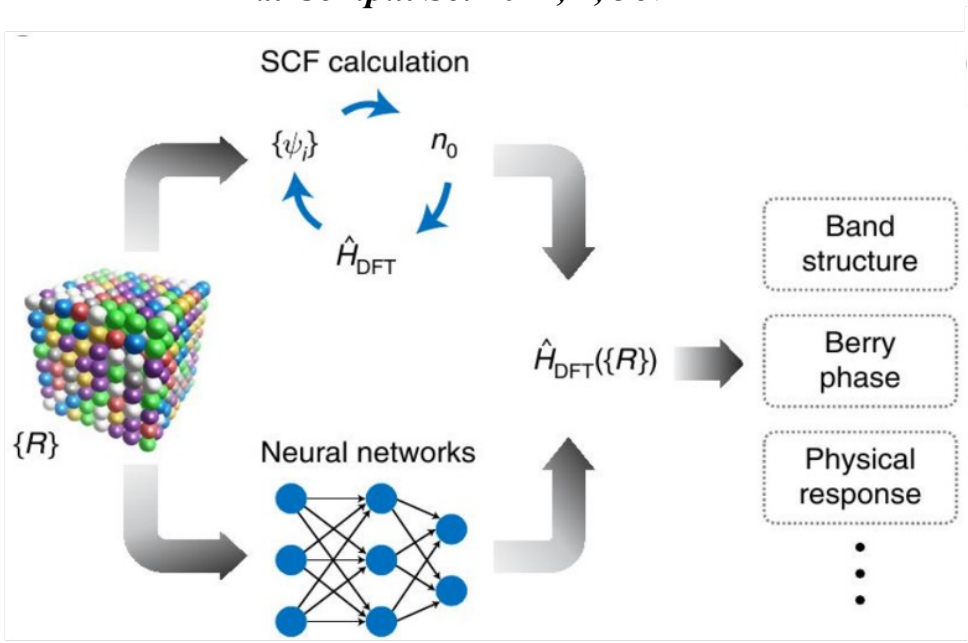
- **Lower GPU Memory Usage for Large Systems!**
- **Application on Materials Research**

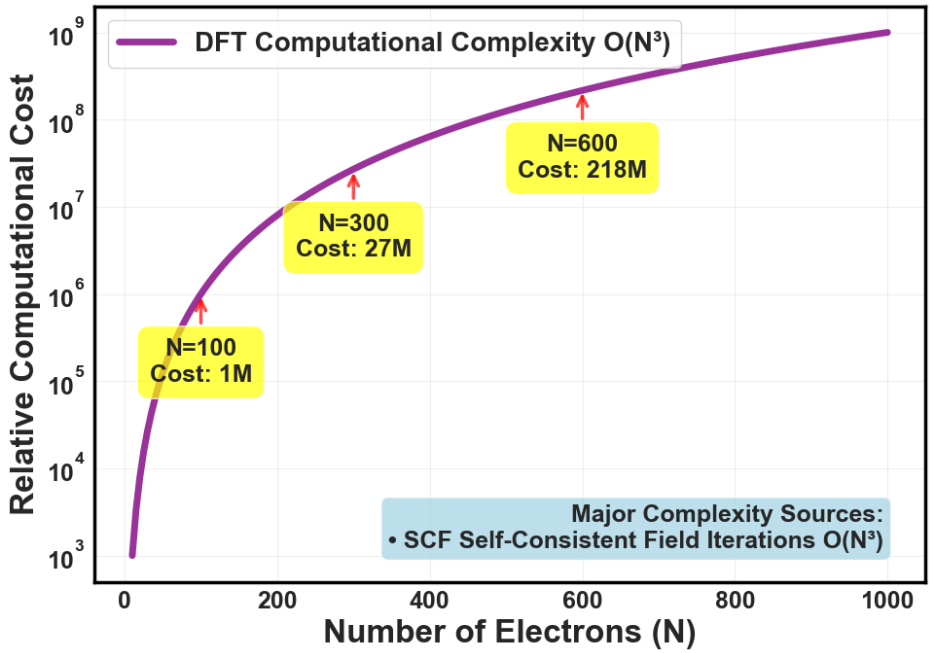
✅ **Short-Term(pre-release):**

- **Accurate Excitation Reference(qsGW-BSE@QM9)**
- **New Reference of all kinds of heavy atoms and Benchmark of popular XC functionals**

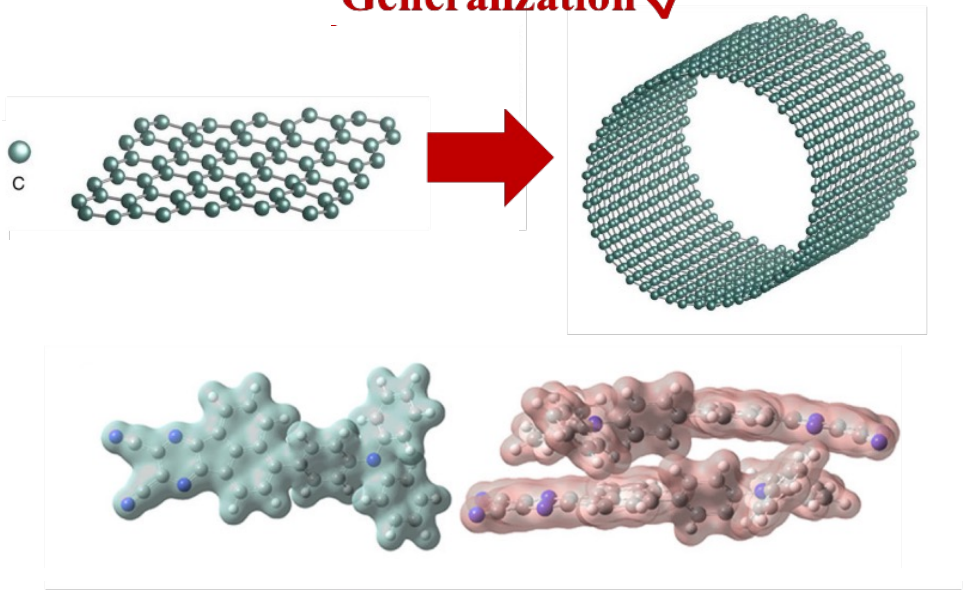
■ Learning Hamiltonian form Natural SCF

Nat Comput Sci 2022, 2, 367

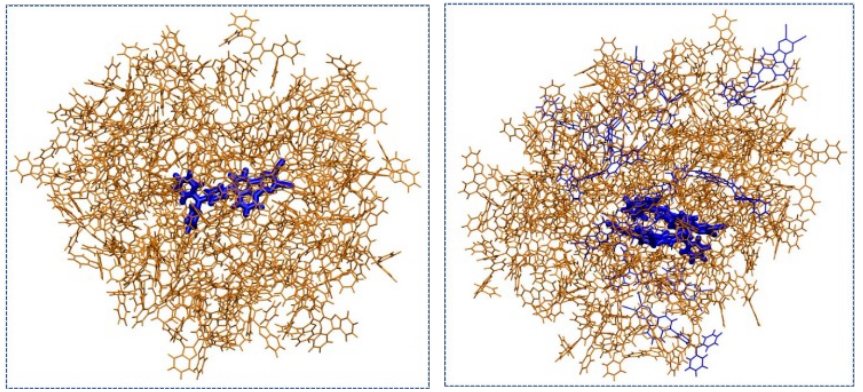




Generalization ✓

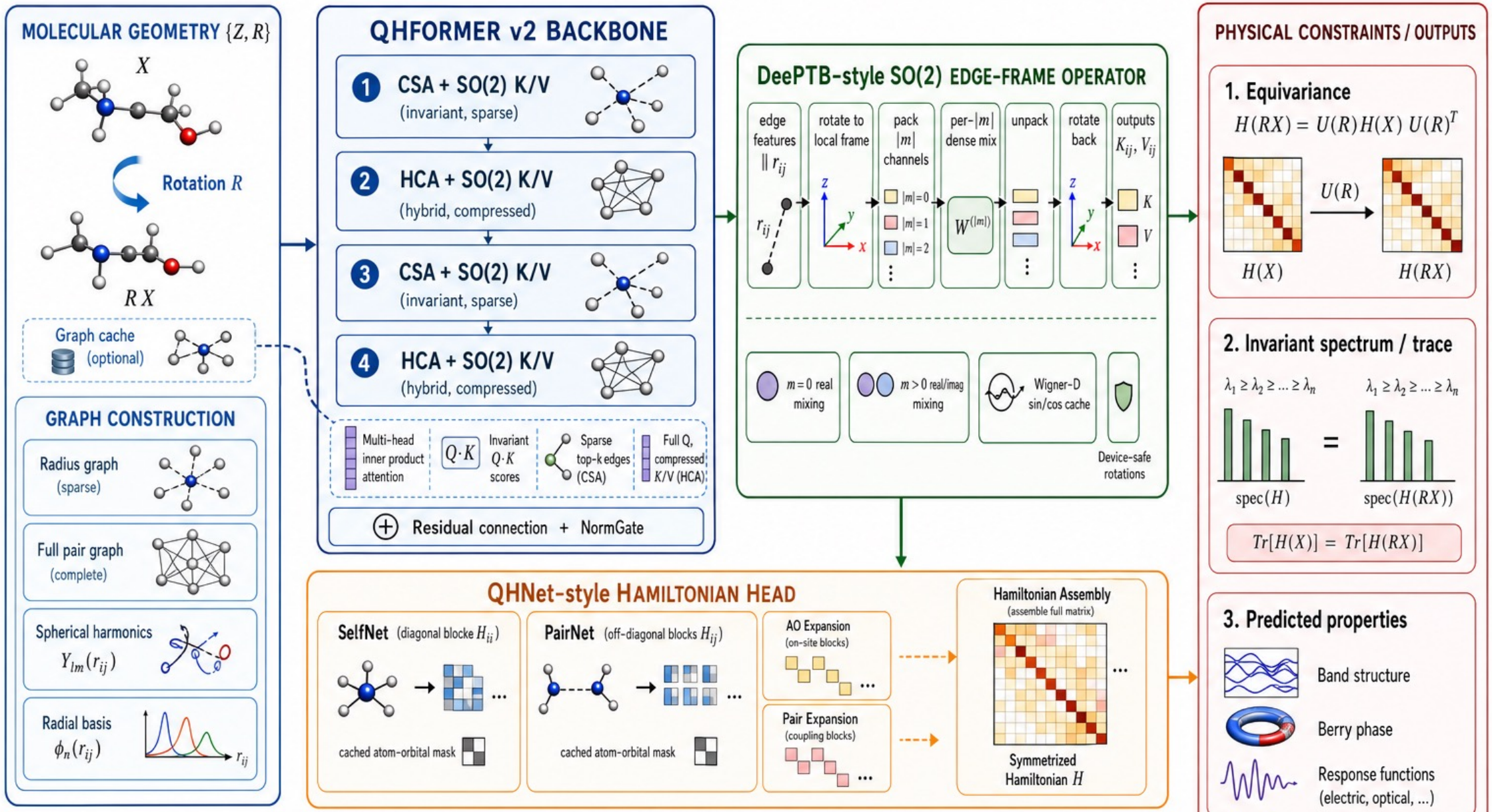


Generalization ?



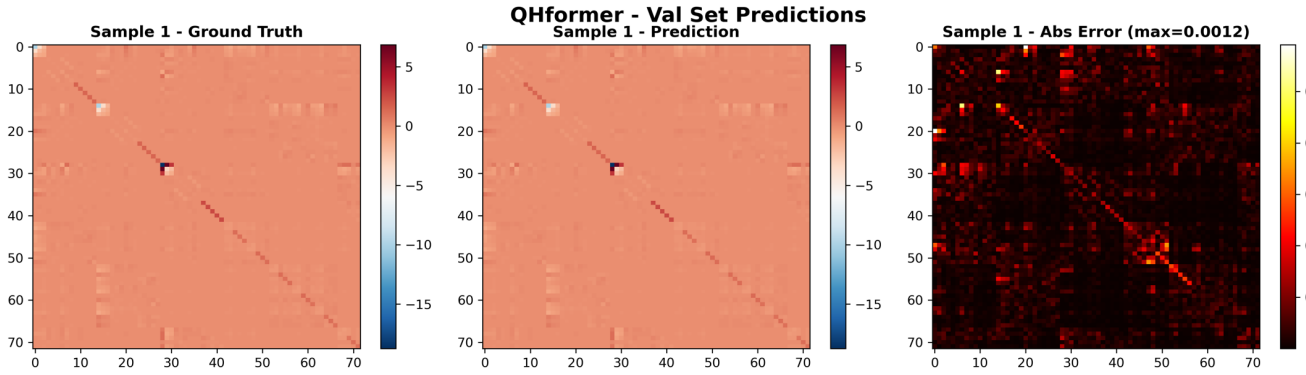
Phys Chem Chem Phys. 2024;26(26):18418-18425

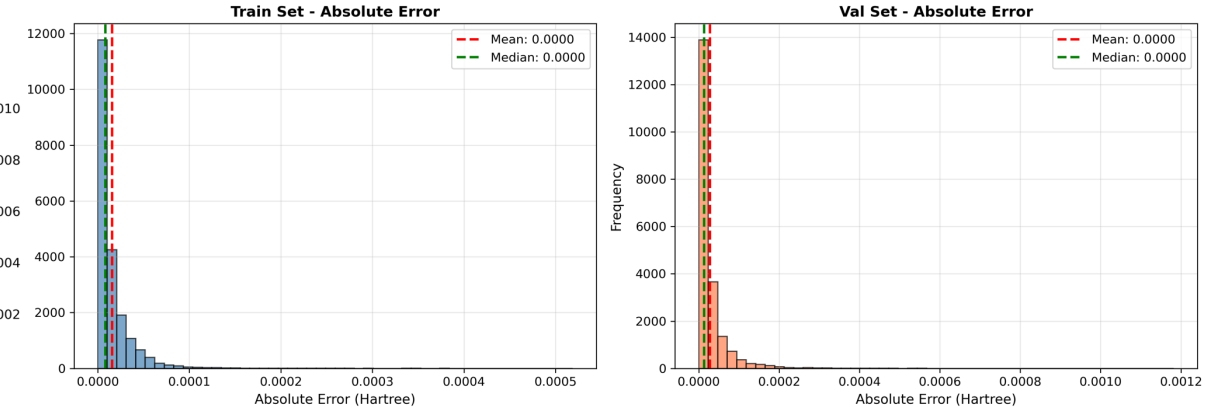
■ Learning Hamiltonian form Natural SCF



Github.com/STOKES-DOT/QHformer

■ Learning Hamiltonian form Natural SCF



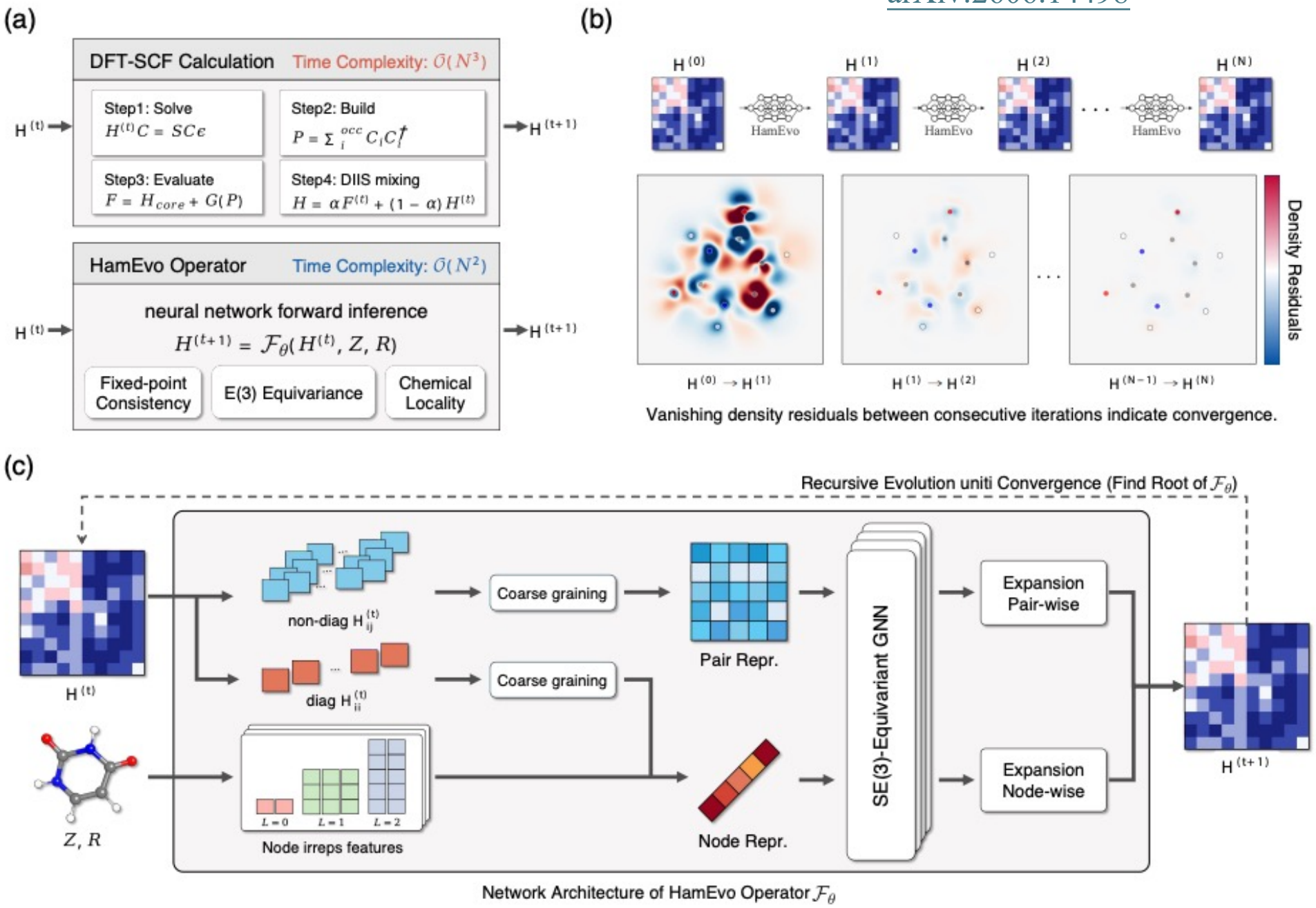


Config	Dense TP	SO(2)	Speedup	Peak memory
Operator only	2.25 ms	2.10 ms	1.07x	216 MB -> 151 MB
Full attention	10.39 ms	10.17 ms	1.02x	583 MB -> 380 MB

Variant	Runtime	Speedup vs dense TP attention	Peak memory ratio
Dense TP	11.16 ms	1.00x	100%
CSA + TP	10.53 ms	1.06x	33.1%
CSA + SO(2)	9.65 ms	1.16x	24.0%
HCA + TP	10.61 ms	1.05x	27.1%
HCA + SO(2)	9.53 ms	1.17x	24.4%

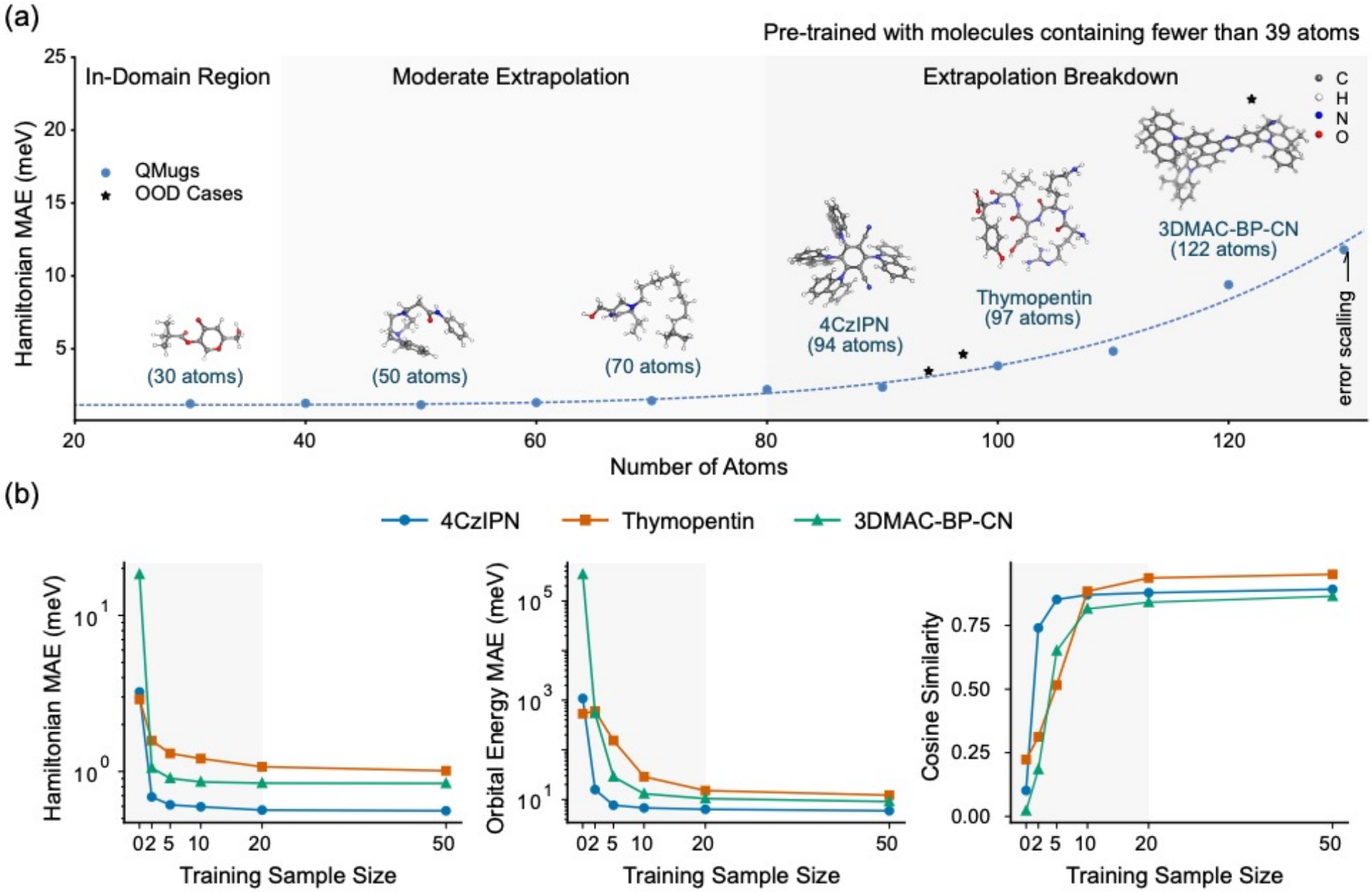
■ Learning Hamiltonian form Natural SCF

arXiv:2606.14498



■ Learning Hamiltonian form Natural SCF

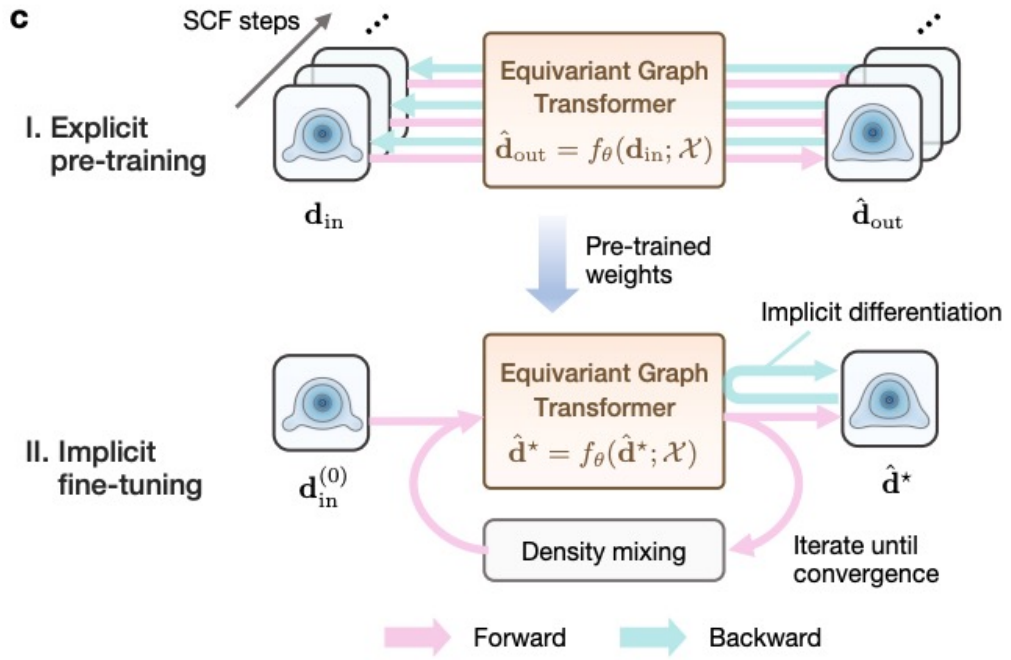
arXiv:2606.14498



■ Learning Hamiltonian form Natural SCF

arXiv:2406.15873

- Functional
  - Qhformer-Based SE(3) Equivariant Graph Transformer
  - Accurate Hamiltonian Prediction on MD Trajectory
  - Lower GPU Memory and Trade-off Accuracy



- Outlook

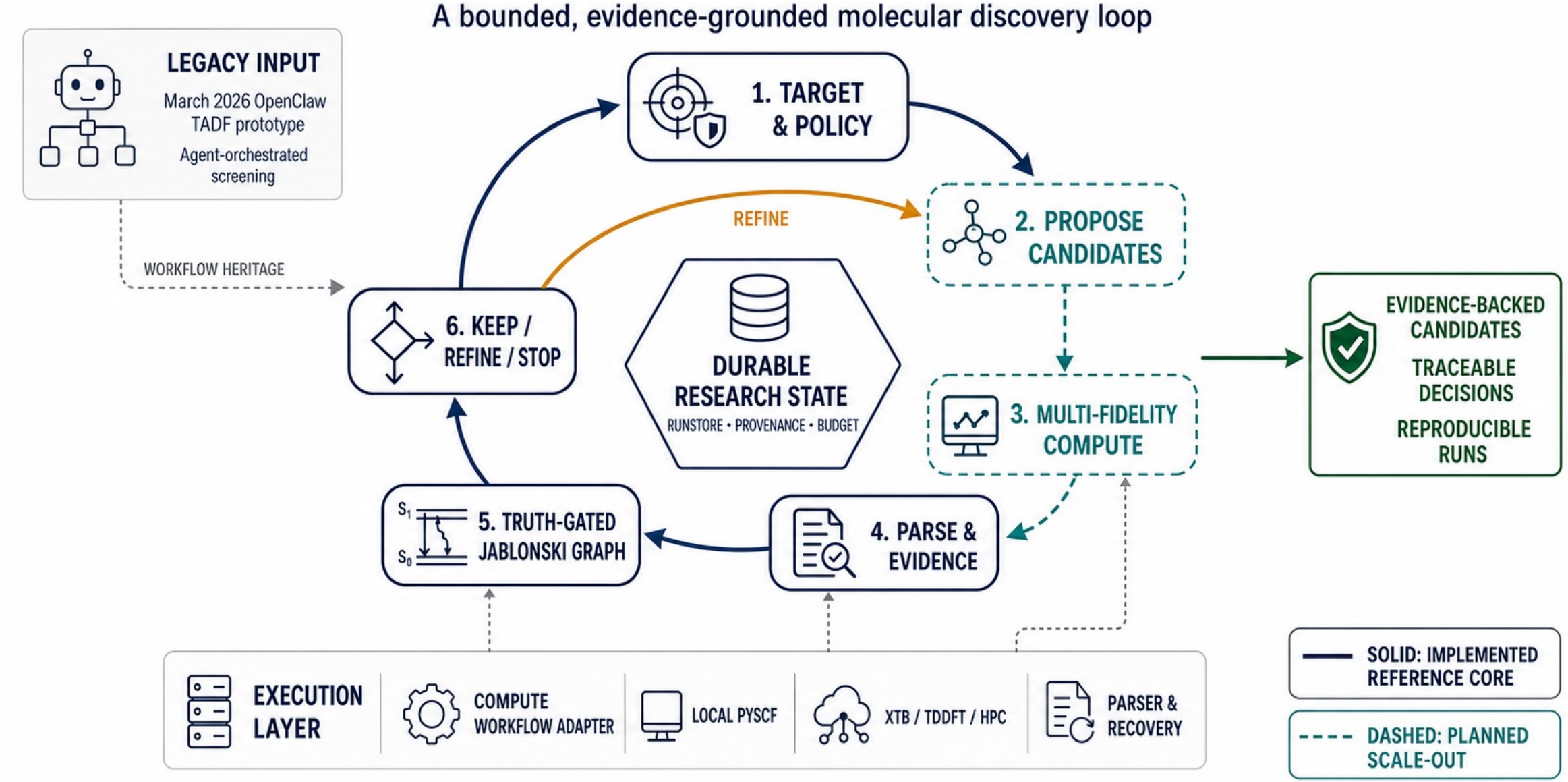
☐ Long-Term(next vision):

- Application on Transportation of Organic System
- Band-like, Hoping-like, Temperature Dependence

☐ Short-Term(pre-release):

- Learning Hamiltonian form Natural SCF
- Form SE(3)-Transformer to Equiformer_v2

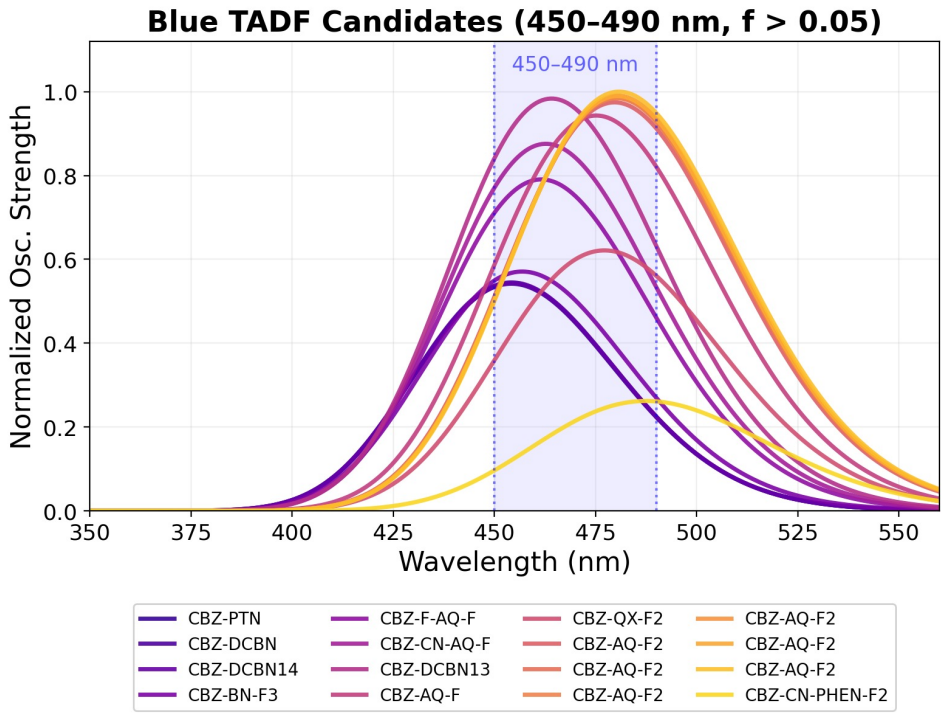
■ Auto-Research Agent for Materials Discovery

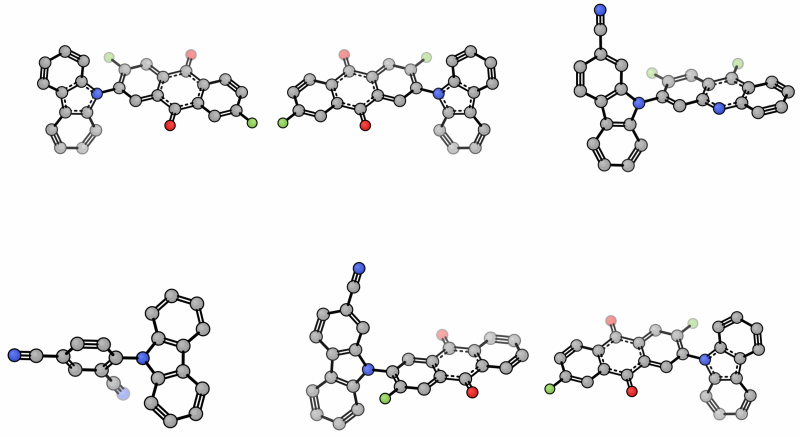


github.com/silico-quantum/tadf-screening & github.com/QPengGroup/ChemAgent

■ Auto-Research Agent for Materials Discovery

```
Stage 0: Initialization
  └ screening_workflow_initializer.py
     └ Confirm: topology, sample count (default 10k), interaction mode

Stage 1: Candidate Generation
  ├ build_da_topology_library.py  (D-A, D-A-D, A-D-A, D-pi-A...)
  └ SMILES → .xyz structure generation (export to manifest.csv)

Stage 2: xTB Pre-screening
  ├ Input: manifest.csv (idx, name, xyz_path)
  └ run_xtb_batch_manifest.py → xtb_progress.csv
      Required columns: idx, name, xyz_path, status, detail,
                        total_energy_eh, homo_lumo_gap_ev, normal_termination
  ⚠ If xTB ok=0 → STOP and diagnose

Stage 2B: TDDFT-xTB Wavelength Filter (optional)
  └ run_tddft_xtb_filter.py
      Filter: emission in target range, f ≥ threshold

Stage 3: TDDFT Validation (remote)
  ├ S0 optimization
  ├ Excited-state optimization (S1 for TADF/Fluorescence; T1 for Phosphorescence)
  ├ Vertical emission
  └ Gate: ΔE_ST < 0.10 eV, f ≥ 0.05, k_TADF > 10⁴ s⁻¹

Stage 4: Elite Candidates → downstream analysis
```





■ Auto-Research Agent for Materials Discovery

github.com/QPengGroup/ChemAgent

OpenChem
~

› Hello! Please introduce yourself

Thinking: The user is asking me to introduce myself. According to my system prompt, I should call myself OpenChem and describe myself as an interactive computational photophysics and organic optoelectronic-materials research agent.

你好！我是 **OpenChem**，一个专注于计算光物理与有机光电材料研究的交互式智能体。

我的核心研究方向包括：

- **有机光电材料**：TADF（热活化延迟荧光）、OLED 发光材料、激子动力学等
- **激发态机制**：吸收/发射光谱、内转换（IC）、系间窜越（ISC）、反向系间窜越（RISC）、电荷转移态等
- **分子设计与筛选**：高通量虚拟筛选、光物理性质预测、结构-性能关系分析
- **计算工作流**：基态 DFT → TDDFT 激发态计算 → 自旋轨道耦合/非辐射速率 → 速率常数提取（如 MOMAP 光物理服务适配器）

我也熟悉你在做的研究工作——等变图神经网络、range-separated hybrid 泛函优化、Hamiltonian 预测——并且可以协助：

- 计算化学输入文件的准备与验证（Gaussian、ORCA、Q-Chem、ABACUS 等）
- 结果解析与 Jablonski 图构建
- 文献与数据驱动的光物理机制解读
- 本地 PySCF 光物理工作流的执行（openchem_photophysics）

有什么光物理或材料计算方面的问题，随时可以开始！😊

■ Auto-Research Agent for Materials Discovery

一、关键能量数据 (ωB97X-D/def2-TZVP)

```
S₁ ─── 5.016 eV   (247 nm)   f = 0.0444   ππ* (HOMO→LUMO)
  │                    ΔE_ST = 0.931 eV = 7508 cm⁻¹
T₁ ─── 4.085 eV   (304 nm)   <S²> = 2.01   UKS
  │
S₀ ─── 0.000 eV
```

二、辐射速率 k_r (荧光)

参数	值
振子强度 f	0.0444
k_r	**7.46 × 10^8 s^{-1}**
τ_r (自然辐射寿命)	**1.34 ns**

> *^{1}Lb 态是弱允许的（对称性近禁阻），但由于激发能高（∝E^2），辐射速率仍然可观。*

三、系间窜越速率 k_ISC (S_1→T_1)

ΔE_ST = 0.93 eV　← 很大！TADF 要求 <0.1 eV

SOC 情景	SOC (cm^{-1})	λ=0.20 eV 时 k_ISC	结论
$^1ππ^*$→$^3nπ^*$ (El-Sayed 允许)	3	~7 × 10^{-18} s^{-1}	可忽略
$^1ππ^*$→$^3ππ^*$ (禁阻)	0.3	~7 × 10^{-20} s^{-1}	可忽略
N 原子极限 (73 cm^{-1})	73	~4 × 10^{-15} s^{-1}	可忽略

> *ISC 被 ΔE_ST = 0.93 eV 的 Marcus 势垒 (>1.4 eV) 完全抑制。苯胺不是 TADF 分子。*

四、内转换速率 k_IC (S_1→S_0)

能量间隙定律估算受制于大 ΔE 的指数衰减。实验上，苯胺的荧光寿命为：

- 气相 τ_f ≈ 4–10 ns → k_total ≈ 1.0–2.5 × 10^8 s^{-1}
- 与我们的 k_r = 0.75 × 10^8 s^{-1} 对比：
  - **k_nr(实验) ≈ 0.3–1.8 × 10^8 s^{-1}**
  - **荧光量子产率 Φ_f ≈ 0.3–0.75 (气相)**

五、磷光速率 k_ph (T_1→S_0)

参数	典型值
T_1 能量	4.09 eV (32950 cm^{-1})
k_ph (无重原子)	0.1–10 s^{-1}
τ_ph	0.1–10 s
实际 Φ_ph	<10^{-3} (极弱)

六、JablonskiGraph – 速率版

```
          k_r = 7.5×10⁸ s⁻¹  (τ=1.3 ns)
S₁  ──────────────────────────────→  S₀ + hν (247 nm)
 │
 │  k_ISC ≈ 0 (ΔE_ST=0.93 eV, 被 Marcus 势垒阻断)
 │
 ↓          k_ph ~ 0.1-10 s⁻¹
T₁  ──────────────────────────────→  S₀ + hν' (极弱)
 │
 │  k_nr(IC) ≈ 1-2×10⁸ s⁻¹ (实验估计)
 │
 ↓
S₀
```

■ Auto-Research Agent for Materials Discovery

✅ 苯胺光物理研究 – 完整报告已生成

报告保存在 /Users/jiaoyuan/aniline_report/REPORT.md。

📁 项目产出总览

```
aniline_report/
├── REPORT.md                ← 完整研究报告（本文）
├── wb97xd/
│   ├── results_wb97xd_tzvp.json    ωB97X-D 激发态数据
│   └── run.log                     计算日志
├── solvent/
│   ├── results.json                PCM 溶剂效应数据
│   └── run.log
├── rates/
│   └── run.log                     速率计算日志
└── aniline_photophysics_out/
    └── results_corrected.json      B3LYP/STO-3G 预览
```

📊 三阶段研究总结

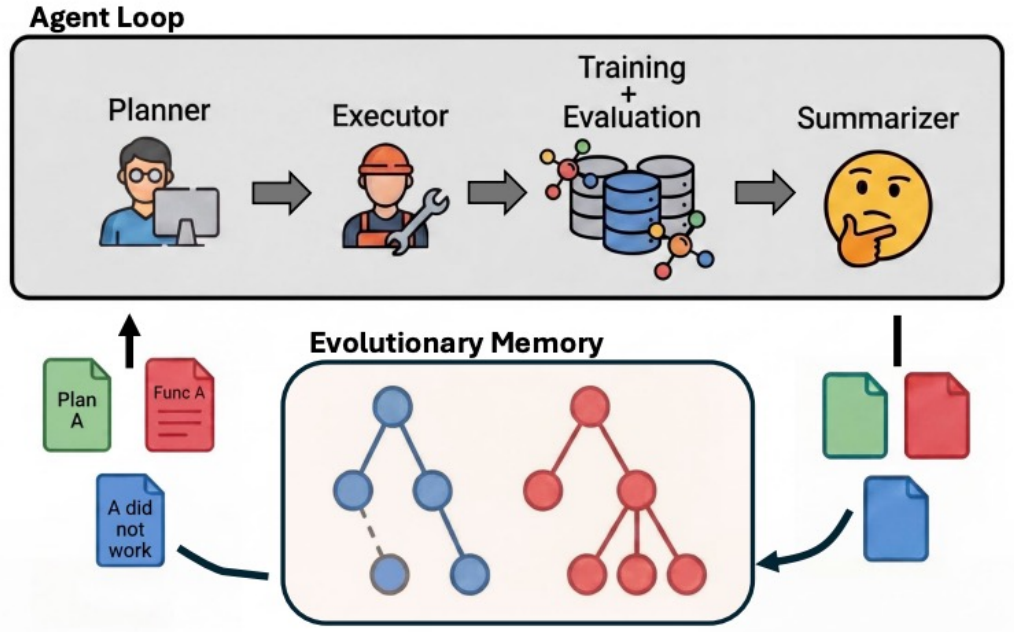
阶段	内容	关键结果
1. 激发态	B3LYP/STO-3G → ωB97X-D + CAM-B3LYP/TZVP	S_1=5.02 eV (^{1}Lb), S_2=5.92 eV (^{1}La), Δ vs exp ~0.8 eV
2. 溶剂	LR-PCM: Gas → cyclohexane → MeCN → H_2O	PCM 红移 ~0.07 eV; H 键效应缺失导致与实验蓝移符号相反
3. 速率	k_r, k_ISC, k_IC, k_ph	τ_r=1.3 ns, ISC 被 ΔE_ST=0.93 eV 阻断, IC 主导非辐射

🎯 核心结论

> *苯胺 $S_1 \to T_1$ 间隙为 0.93 eV, ISC 在动力学上完全阻断, 不适合独立作为 TADF 分子。但作为富电子给体, 可构建 D-A 型 TADF 候选物——这是下一步分子设计的自然延伸。*

■ Auto-Research Agent for Materials Discovery

- **Functional**
  - Computation Task Management
  - Organic Materials Screening
  - Simple Computational Error Correction
  - Only Skills Based



- **Outlook**

☐ Long-Term(next vision):

- Standard of HPC for Both Human user and Agent user
- Git tools for Code Management for Both Human and Agent
- LLM-Wiki for Knowledge Data Set

☐ Short-Term(pre-release):

- Auto-Research for New Materials Discovery
- Experience and Knowledge form Auto-Research Loop
- Standard Workflow in Materials Discovery