中国科学院大学
University of Chinese Academy of Sciences

Deep Learning-Based Electronic Structure Calculation Methods for Organic Functional Systems

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School of Advanced Interdisciplinary Sciences, UCAS

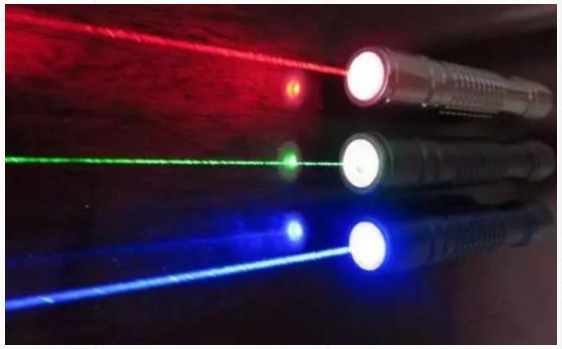
University of Chinese Academy of Sciences

CONTENTS

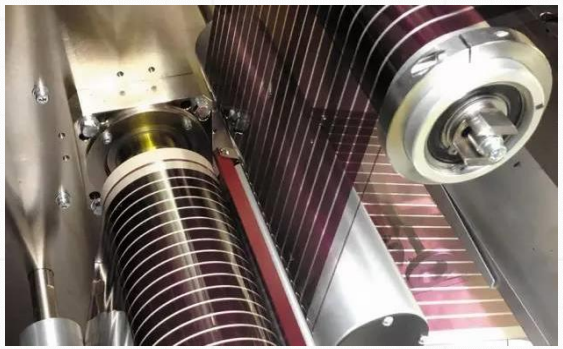
Background: Organic Functional Materials

OLED screen

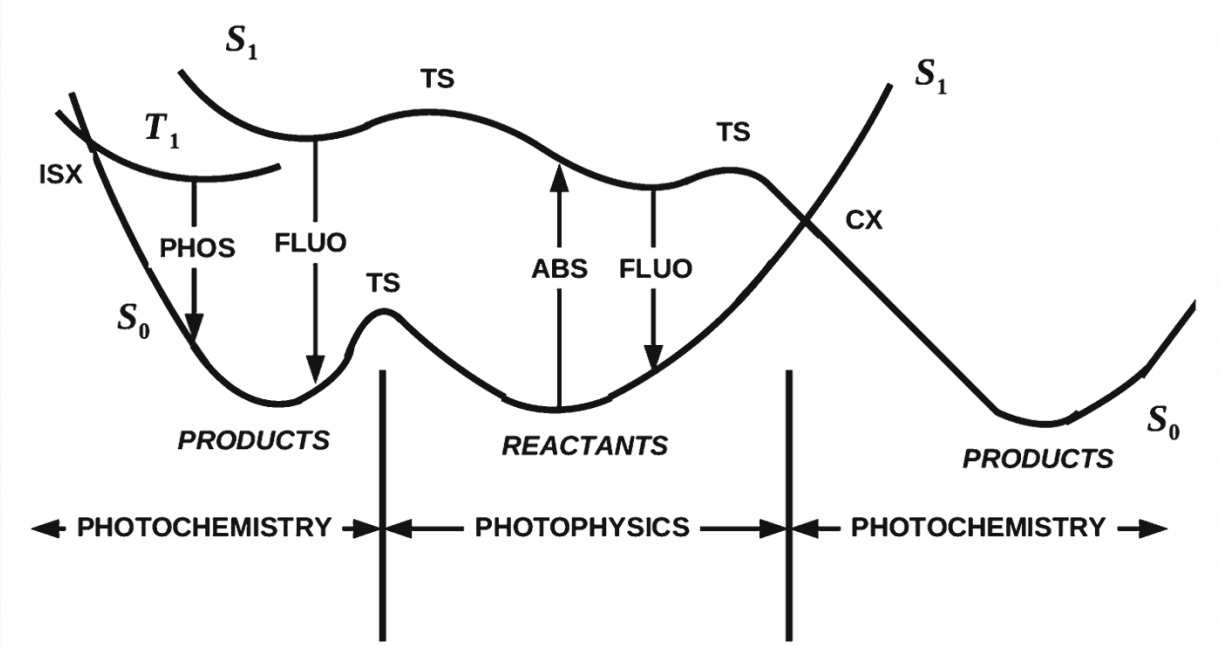
Lighting

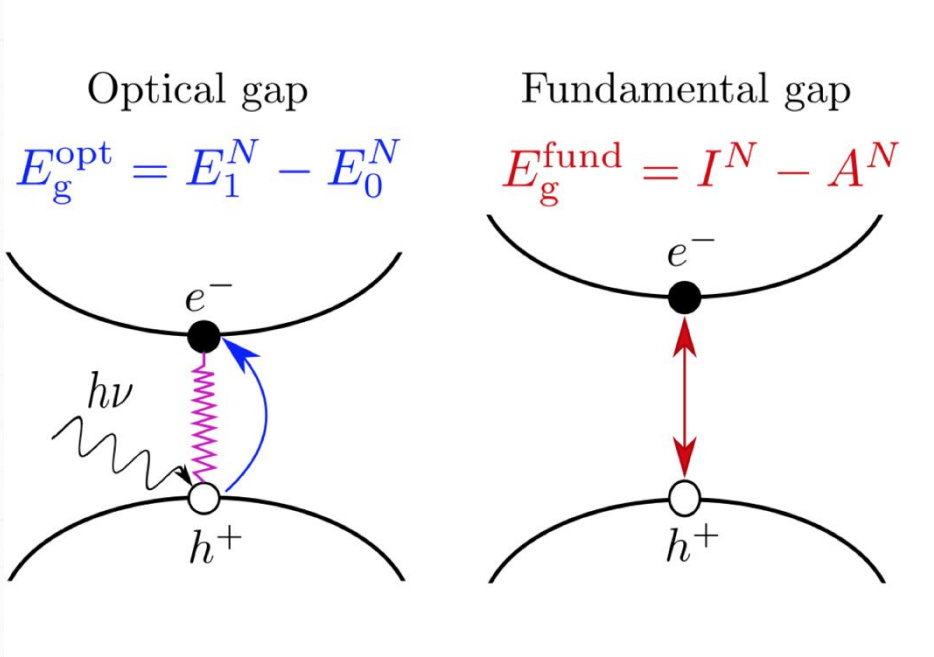


Organic laser



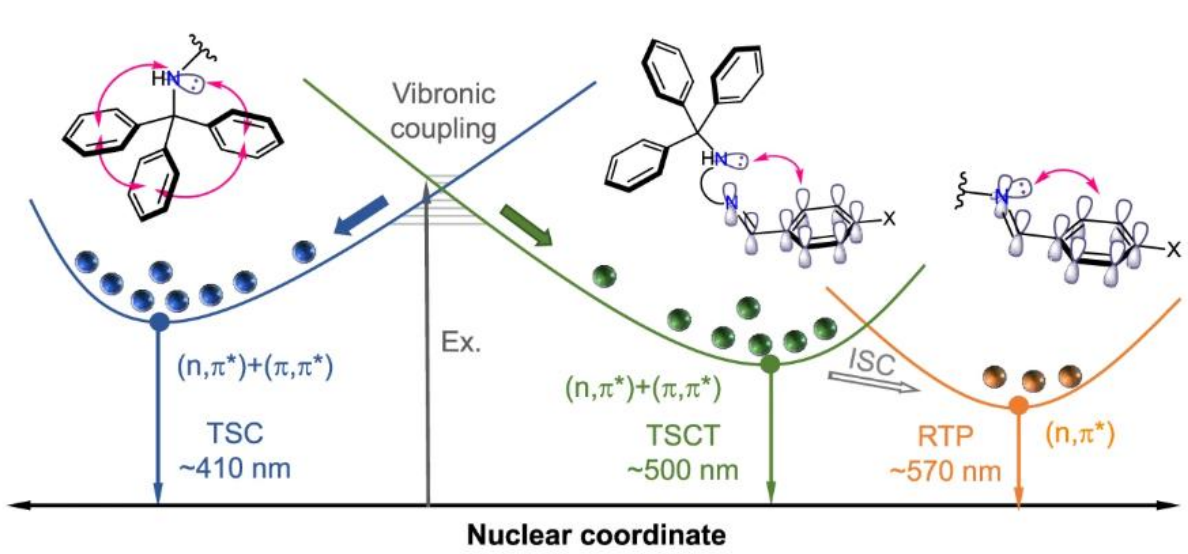
Flexible electronics

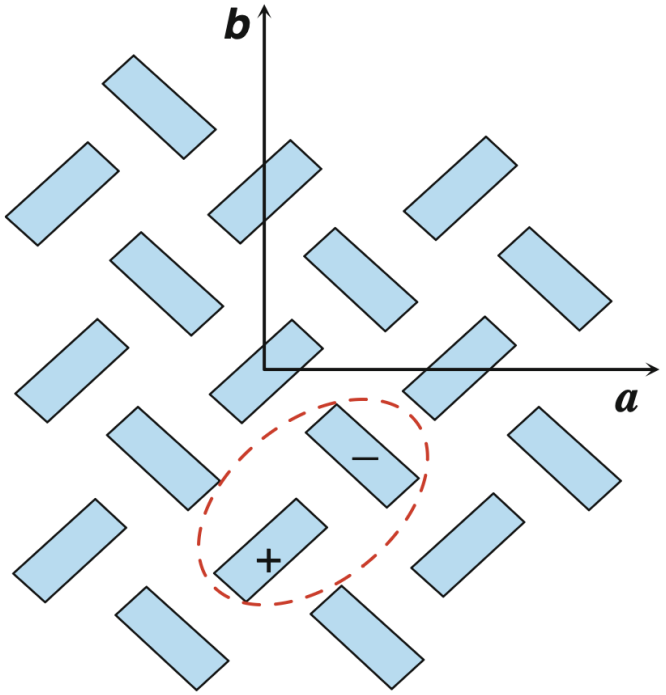


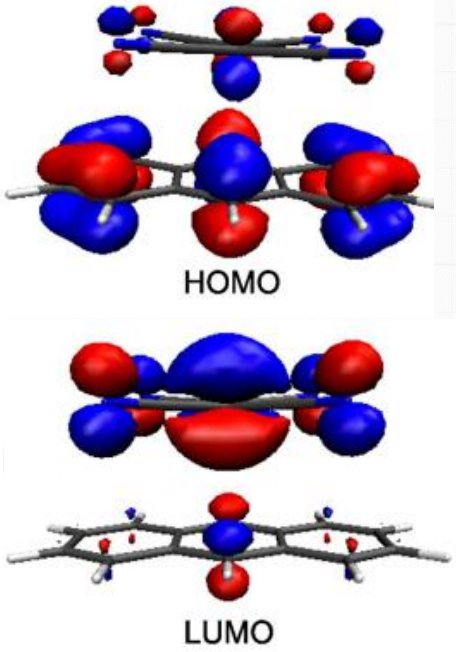


Background: Clusteroluminescence

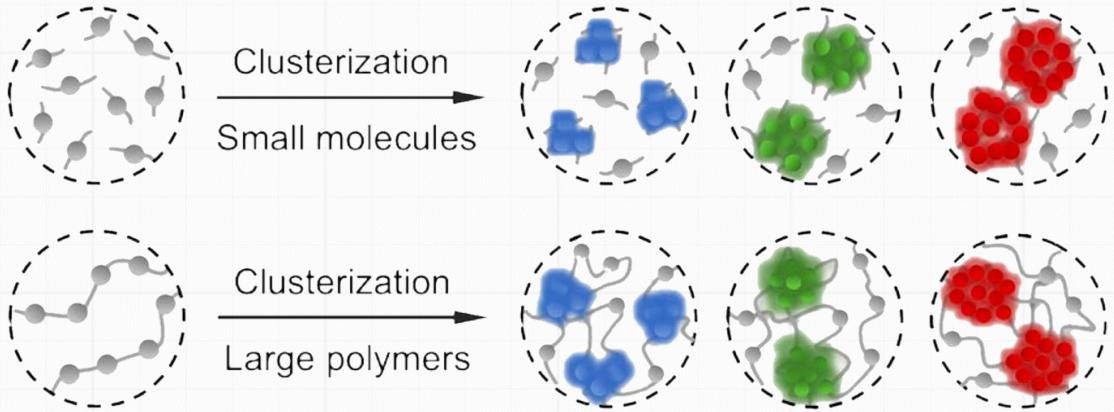
Nat Commun 16, 3910 (2025)

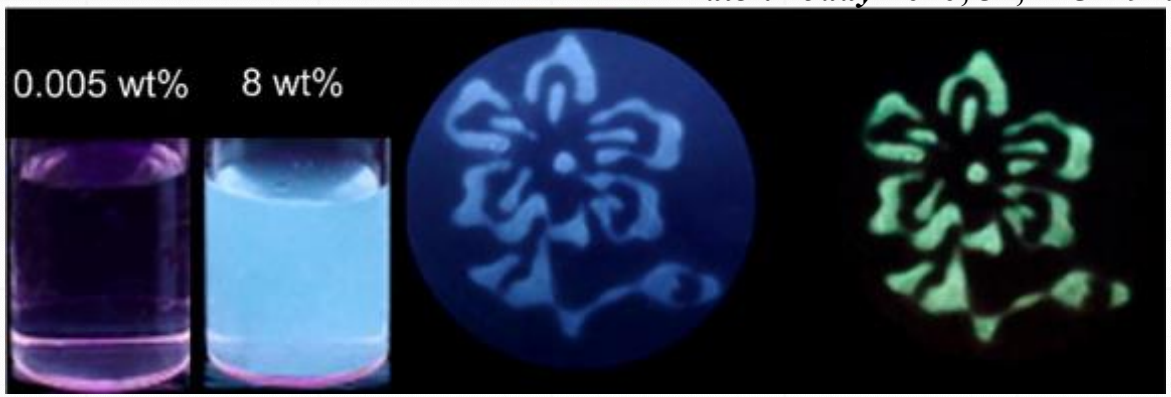






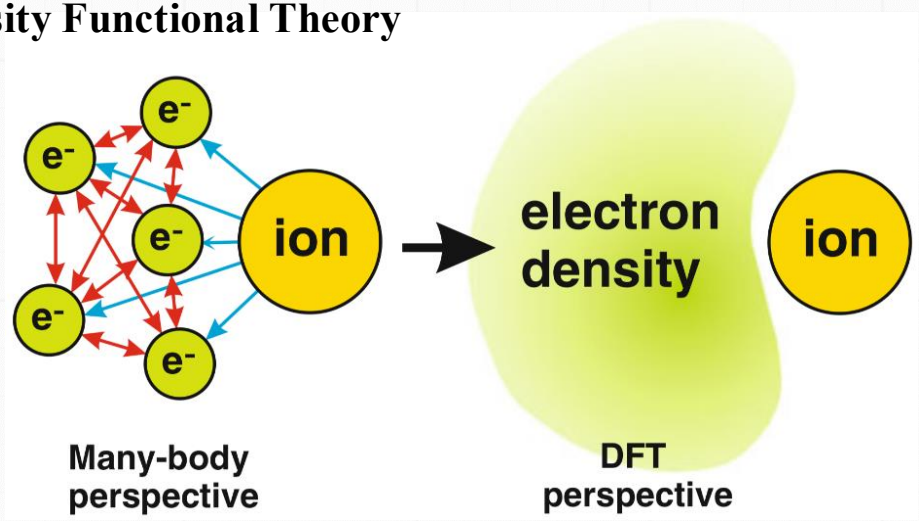
Mater. Today 2020, 32, 275–292.





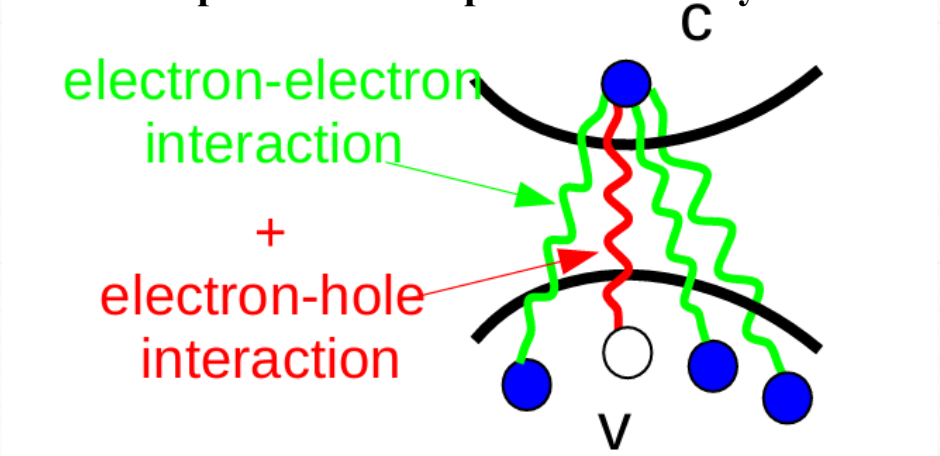
Background: DFT and TDDFT

Density Functional Theory

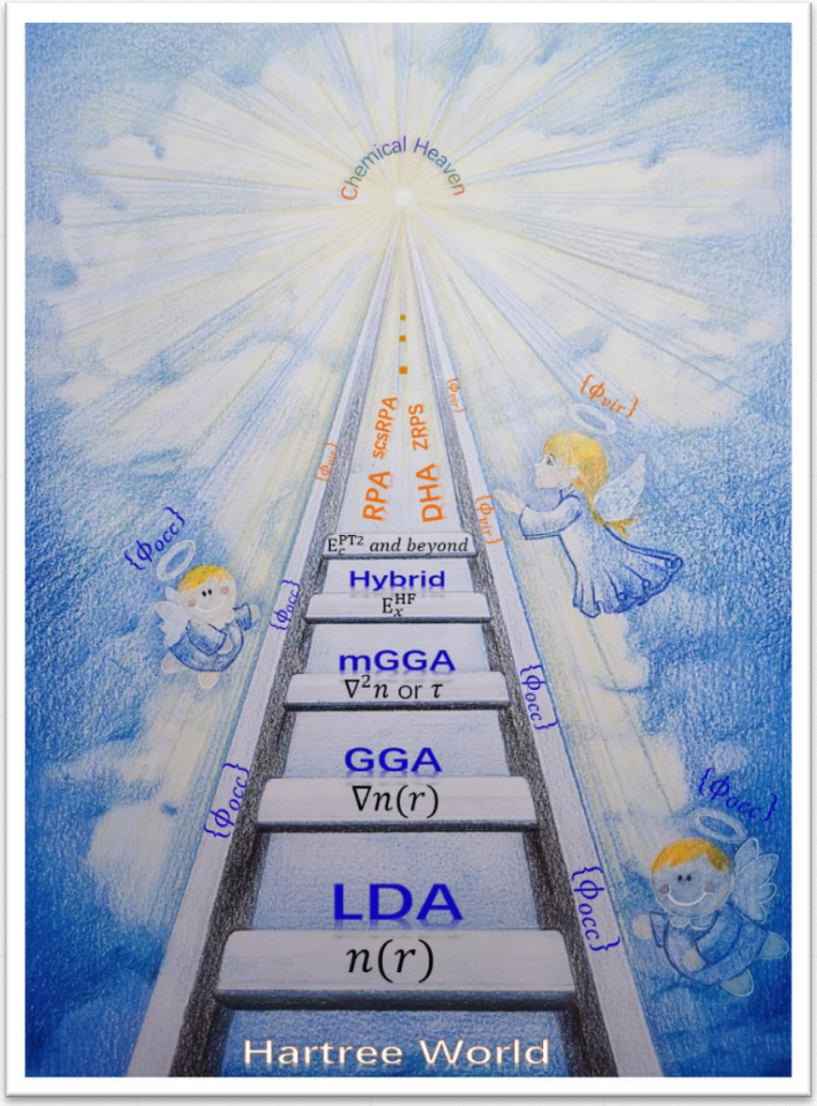


Linear-Response → **Runge-Gross Theorem**

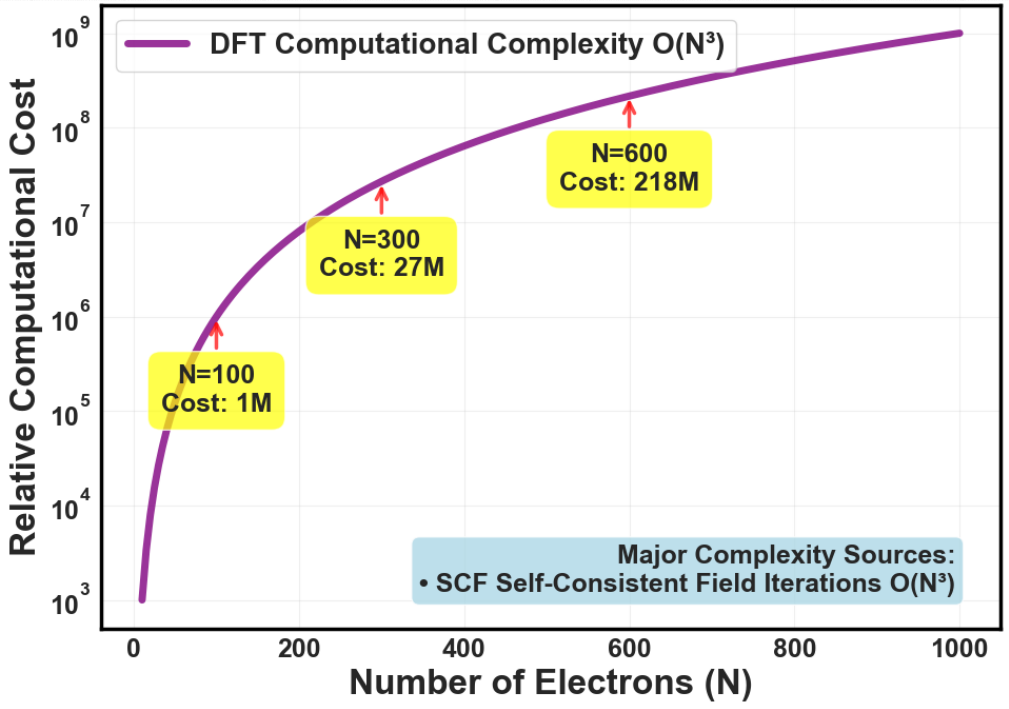
Linear-Response Time Dependent Density Functional Theory

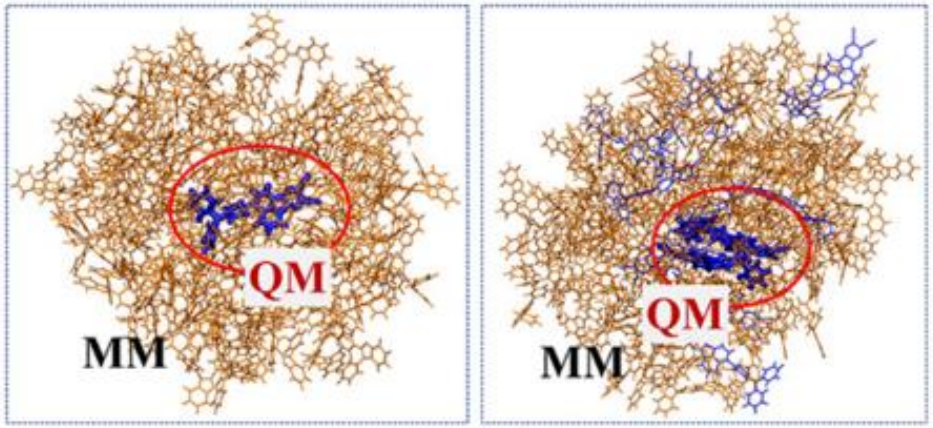


WIREs Comput Mol Sci. 2023;13(2):e1631



Background: Difficulties !

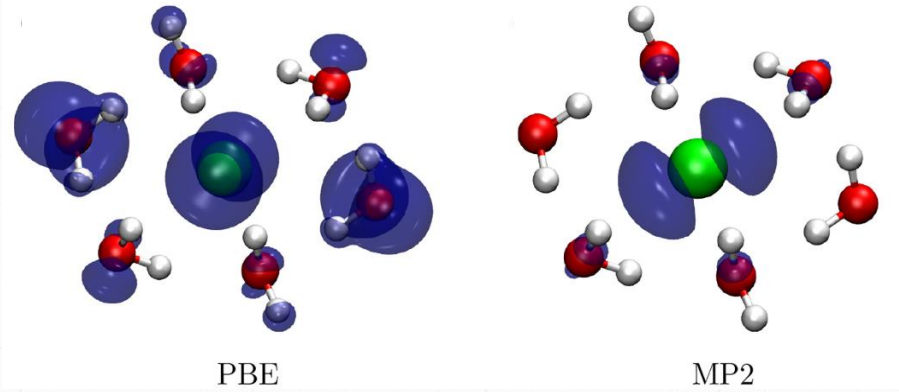




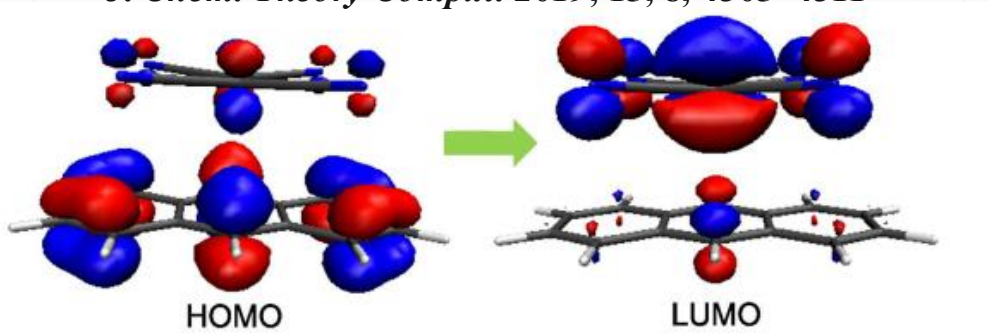
QM-monomer/MM QM-dimer/MM

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

WIREs Comput Mol Sci. 2023;13(2):e1631



J. Chem. Theory Comput. 2019, 15, 8, 4305–4311



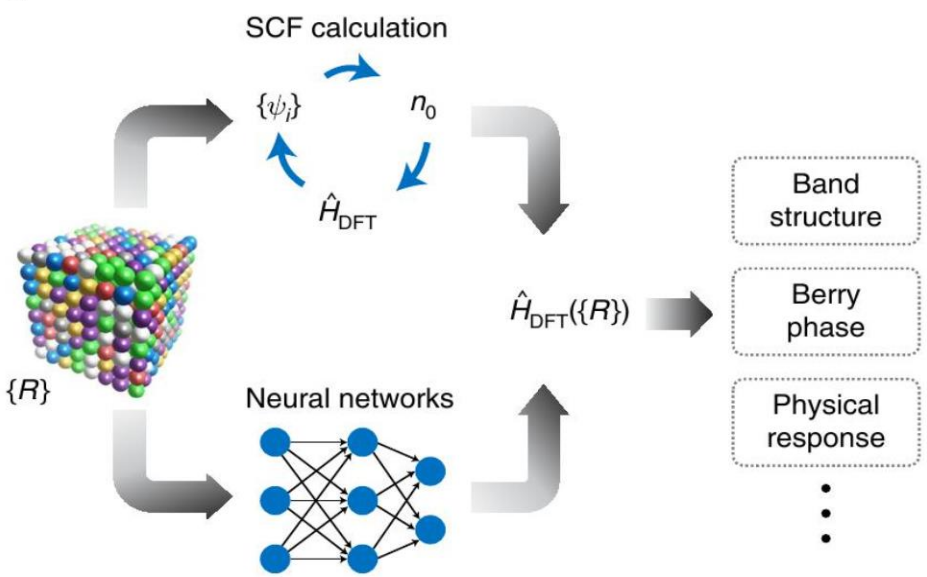
N-electron system

$$v_{eff}(\boldsymbol{r},\boldsymbol{R}) = v_{ext}(\boldsymbol{R}) + \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + v_{xc}(\boldsymbol{r})$$

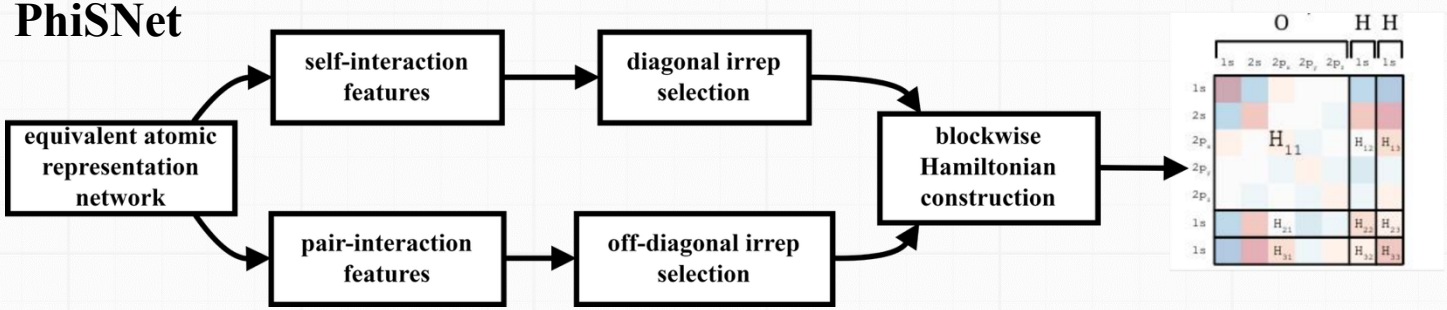
One-electron system($|\boldsymbol{r}| \to \infty$)

$$v_{eff}(\boldsymbol{r},\boldsymbol{R}) = v_{ext}(\boldsymbol{R}) + \frac{1}{|\boldsymbol{r}|} + v_{xc}(\boldsymbol{r})$$

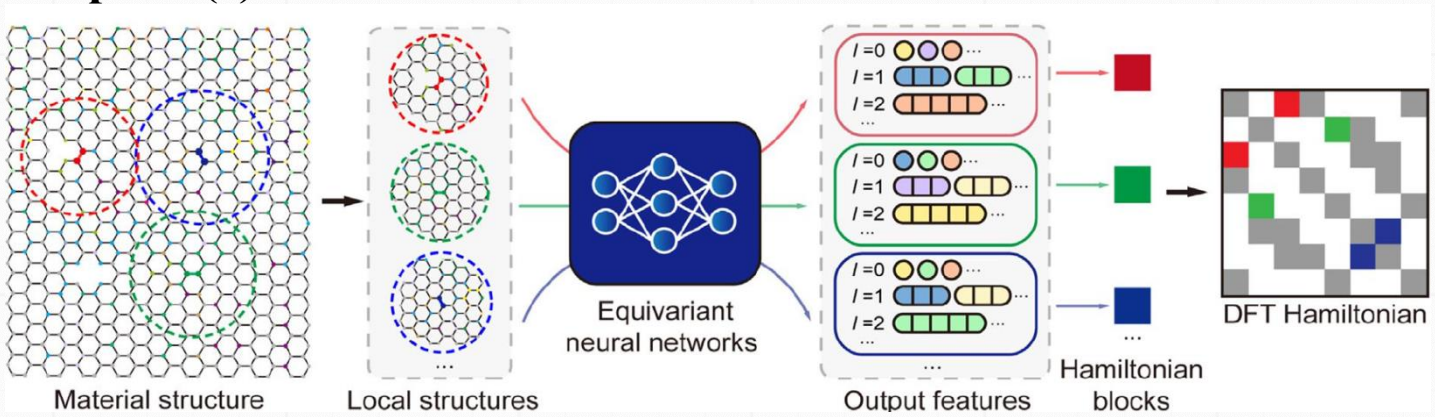
Background: Hamiltonian Learning



PhiSNet



DeepH-E(3)



Nat Commun. 2024;15(1).

Hamiltonian Matrix in Atomic Basis Function

$$\psi_i(\boldsymbol{x}) = \sum_a C_{ai}\chi_a(\boldsymbol{x}) \qquad HC = \varepsilon SC$$

$$H = H_{ij} = \int d\boldsymbol{x}\, \chi_i^*(\boldsymbol{x})\hat{H}\chi_j(\boldsymbol{x})$$

$$\chi_i(\boldsymbol{x}) = R_{nl}(r_i)Y_{lm}(\theta_i, \phi_i)$$

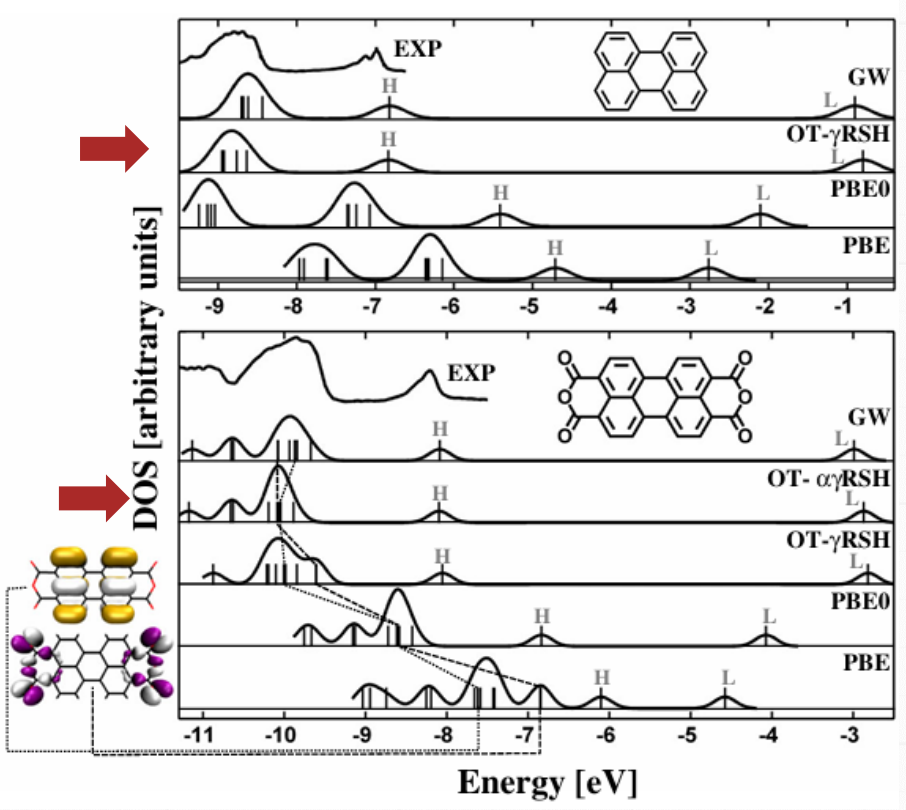
$$(H_{ij})^{l_1,l_2}_{m_1,m_2} = \sum_{m_1,m_2} D^{l1}_{m_1 n_1} D^{l2}_{m_2 n_2} (H_{ij})^{l_1,l_2}_{n_1,n_2}$$

SchNet+H, HamGNN, DeepTB,

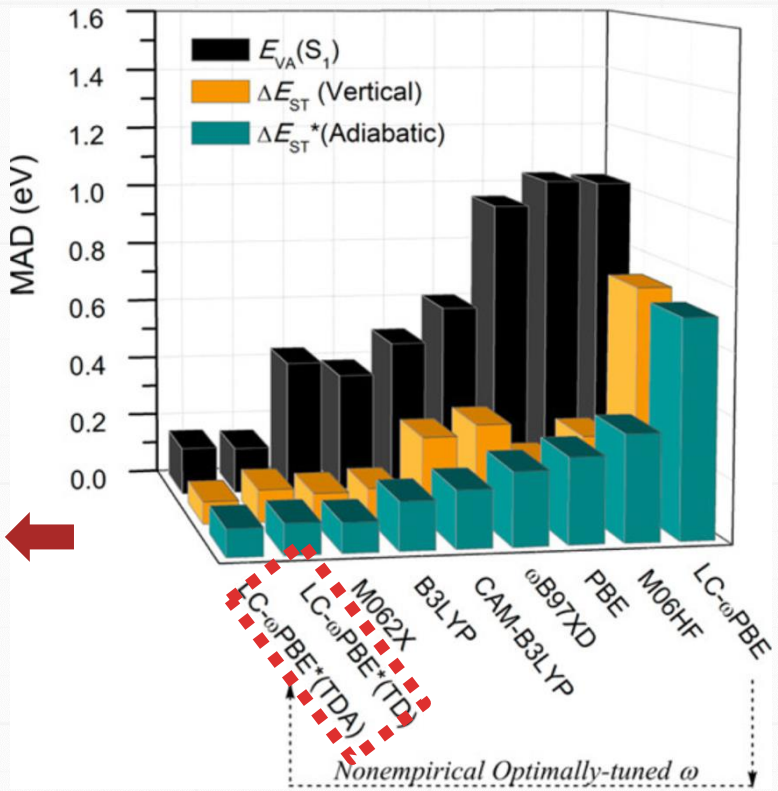
DHNet and other Works…

Background: Exchange-Correlation Functional Optimization

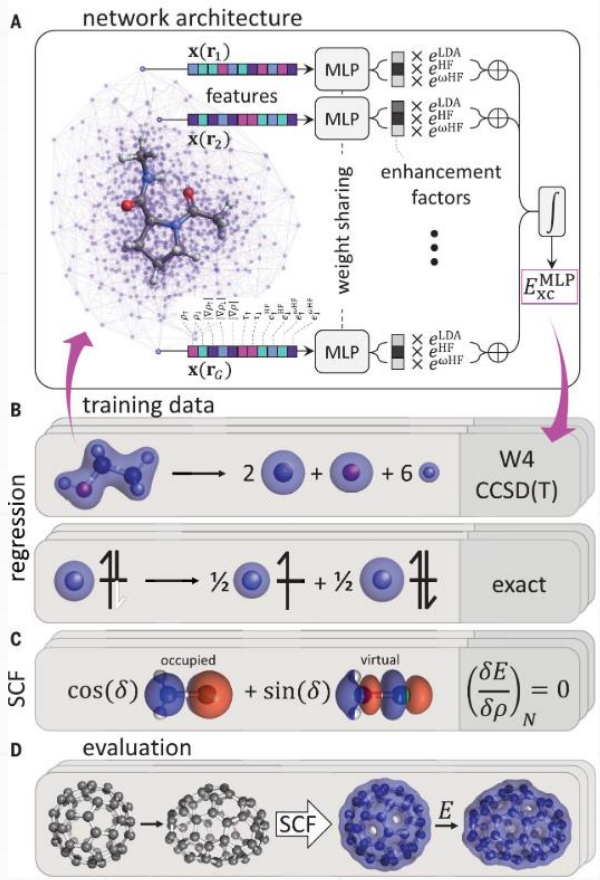
Phys Rev Lett. 2012;109(22):226405.



J Chem Theory Comput. 2015;11(8):3851-3858.



Science. 2021;374(6573):1385-1389



Range-Separated Hybrid Functionals

$$E_{xc} = \alpha E_x^{SR-HF}(\omega) + (1-\alpha)E_x^{SR-DFT}(\omega) + \beta E_x^{LR-HF}(\omega) + (1-\beta)E_x^{LR-DFT}(\omega) + E_c^{DFT}$$

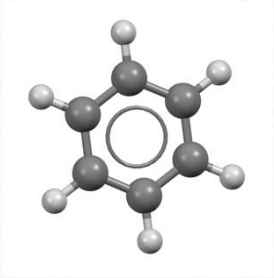
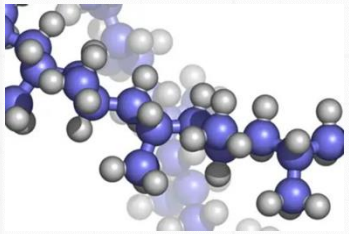
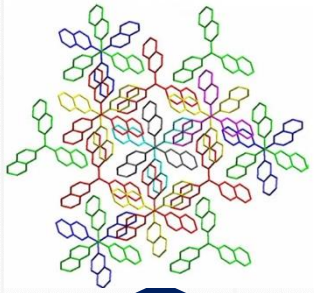
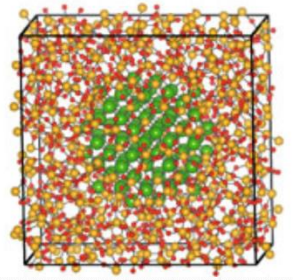
Janak Theorem

$$J(\omega) = J_N(\omega) + J_{N+1}(\omega) \rightarrow \text{argmin}[J^2(\omega)]$$

$$J_N(\omega) = |\varepsilon_{HOMO}^{\omega}(N) + IP(N)|$$

$$J_{N+1}(\omega) = |\varepsilon_{HOMO}^{\omega}(N+1) + IP(N+1)|$$

Motivation: Efficient Deep-Learning DFT method

System

Monomer → Polymer → Oligomer → Crystal

CAS ORCA Molpro Q-CHEM PySCF

Deep Learning +DFT !

VASP (b-initio Vienna Package Simulation) QUANTUMESPRESSO

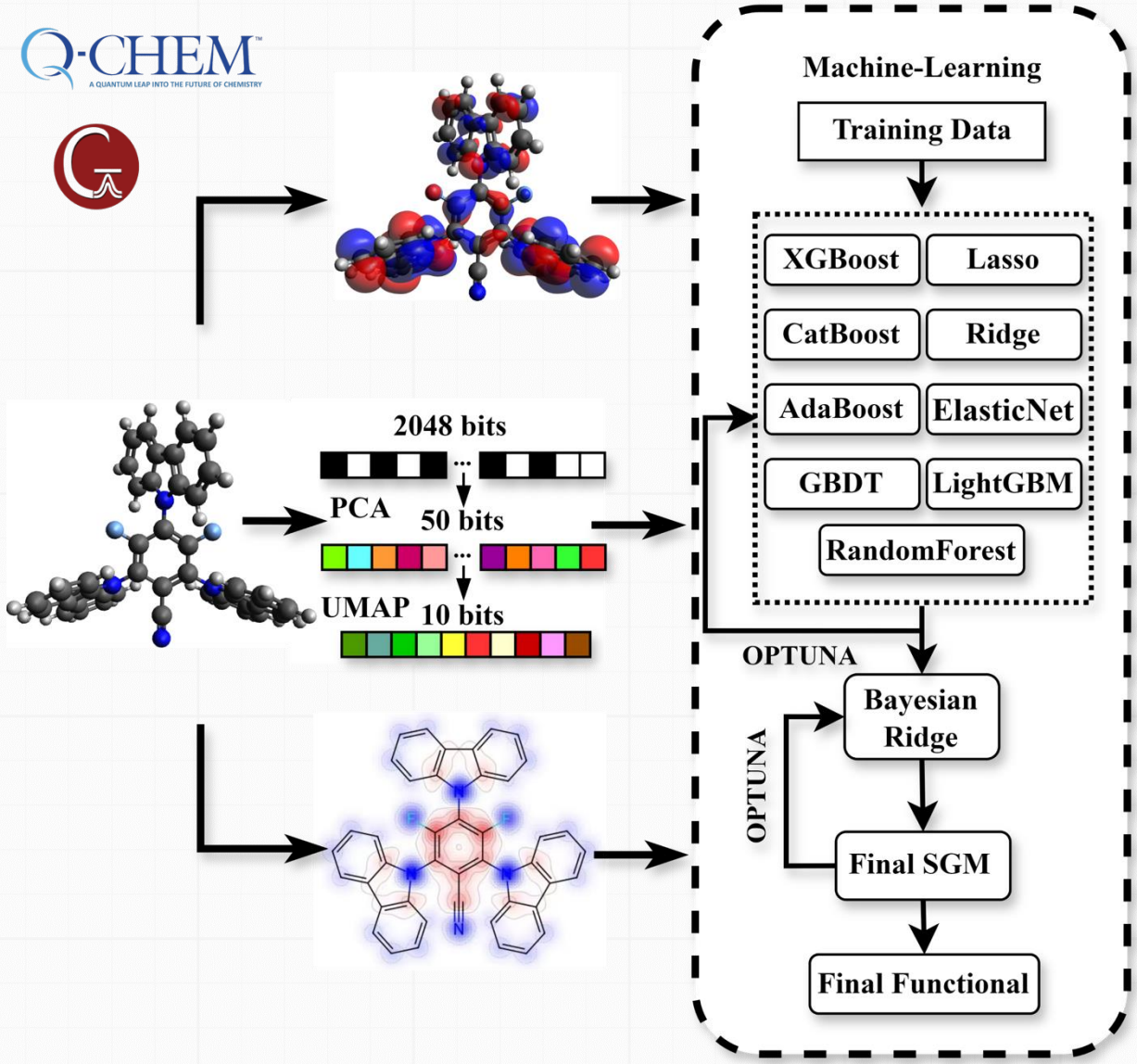
Size

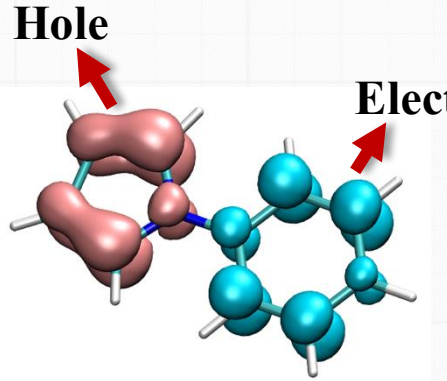
WFM → DFT → Full Quantum Mechanics ? → DFT

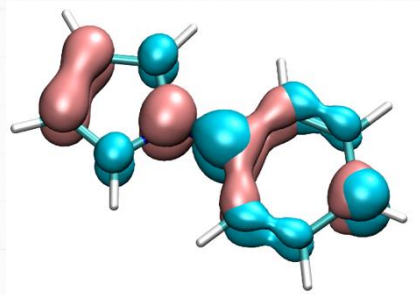
$N \sim 10^1 \rightarrow 10^2$ $N \sim 10^2 \rightarrow 10^3$ $N \sim 10^3 \rightarrow 10^5$ $N \sim 10^{23}$

- Accurate electronic structure calculations for the systems with complex structure and serious SIE – Aggregate or Cluster Systems
  - SIE correction for complex organic systems
  - Efficient calculation method for complex organic systems

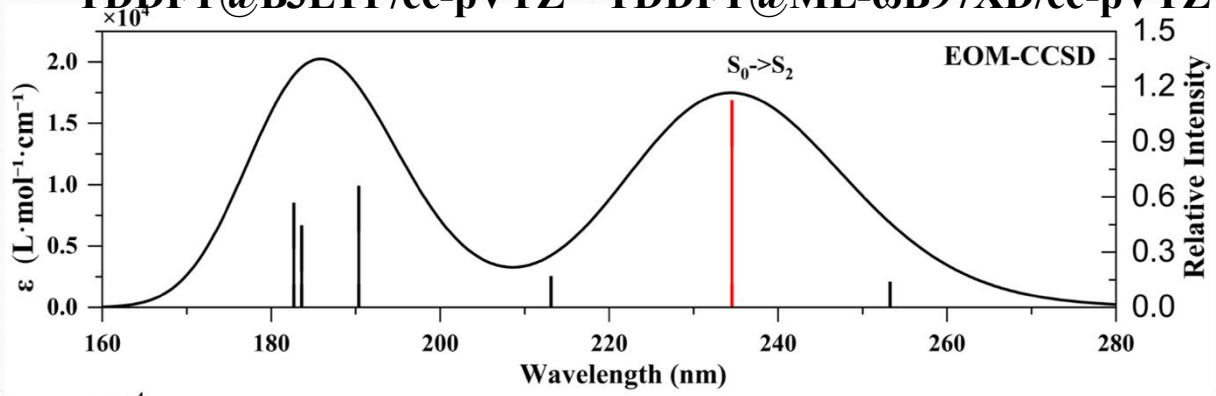
Technical Approach: Preparatory Work OPTXC

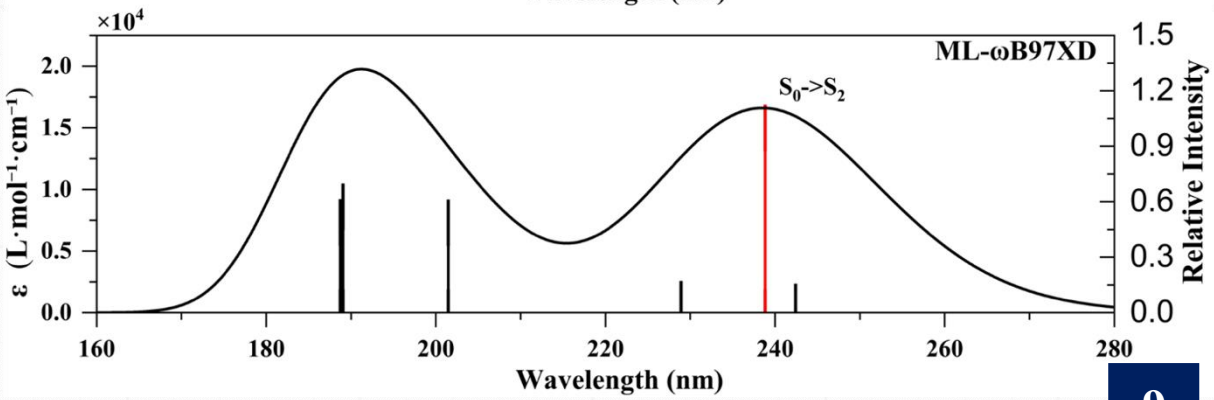




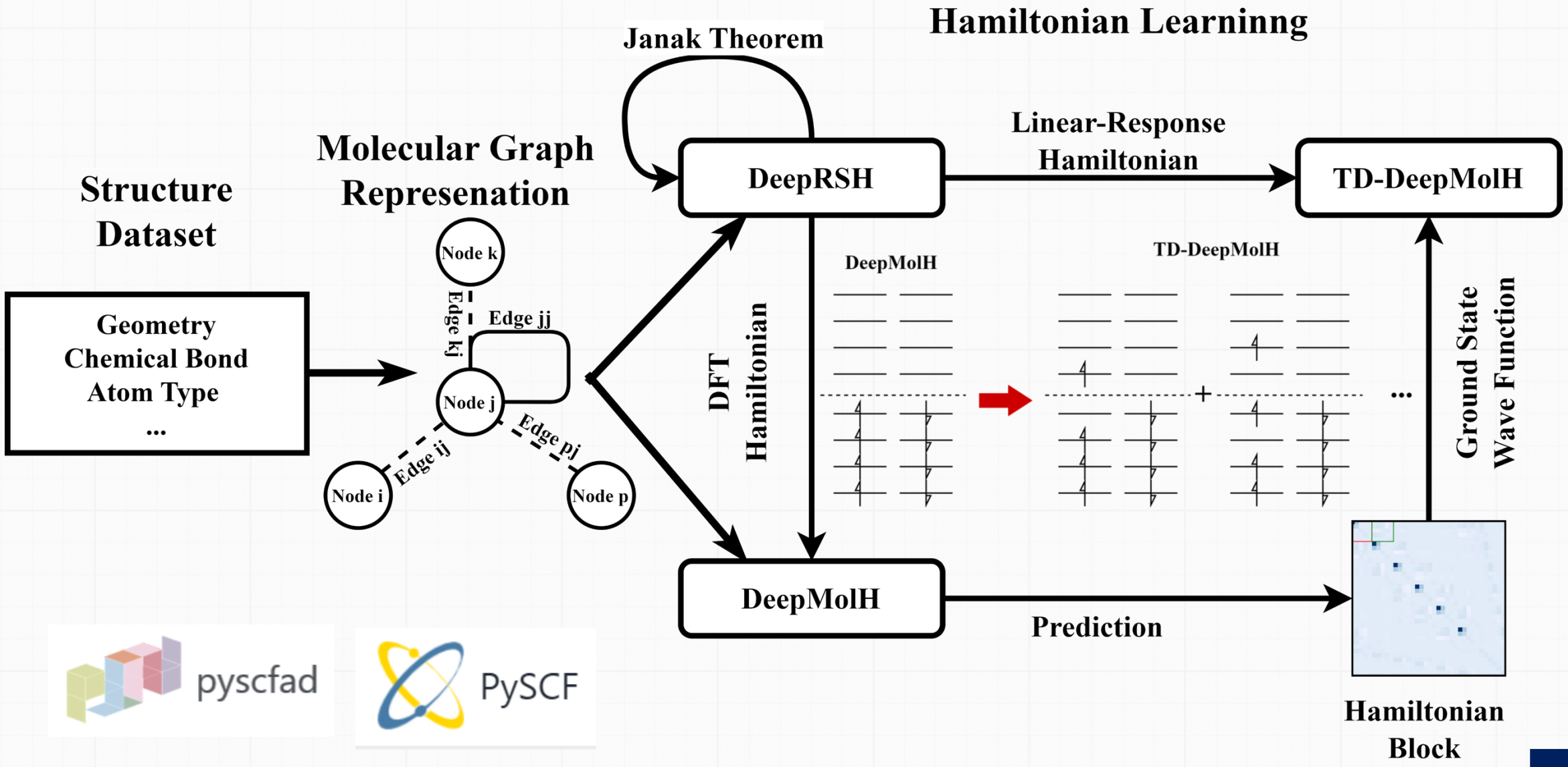


TDDFT@B3LYP/cc-pVTZ TDDFT@ML-ωB97XD/cc-pVTZ



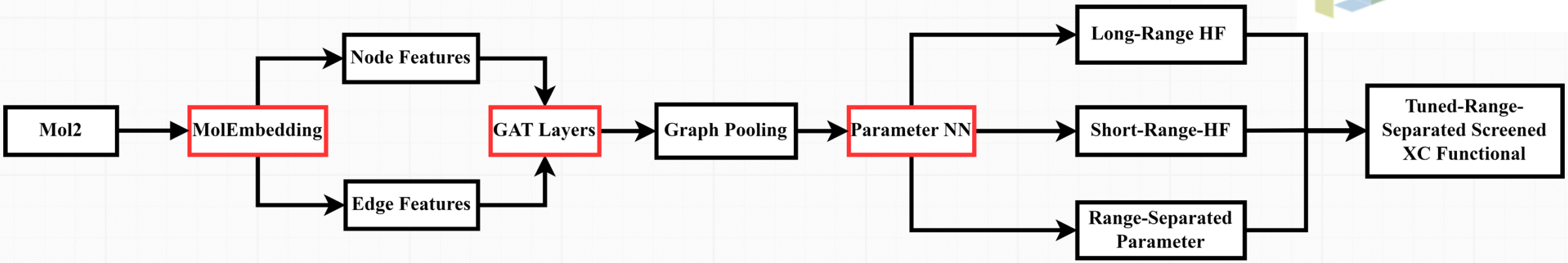


Technical Approach: DeepRSH, DeepMolH and TD-DeepMolH

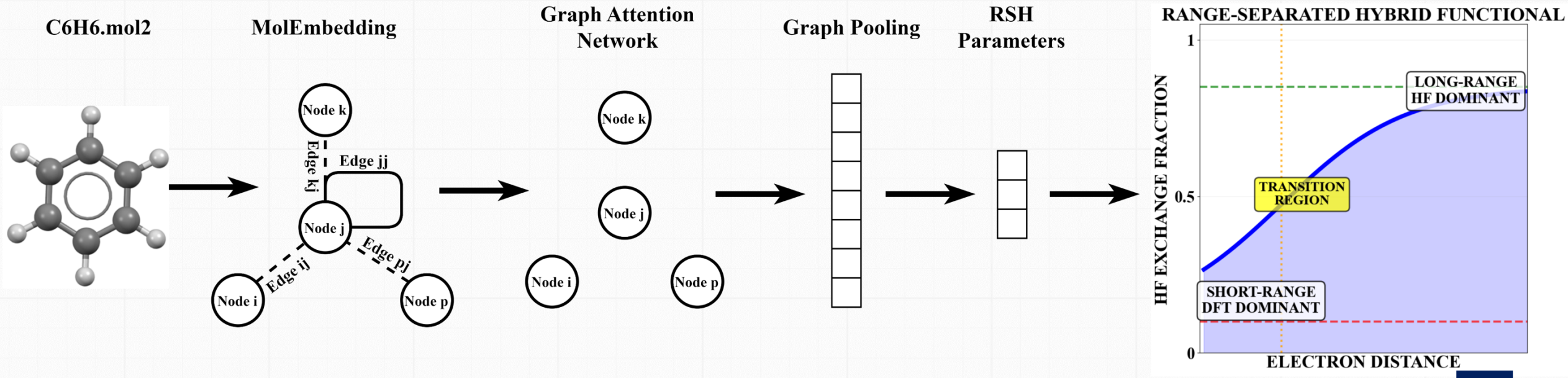


Technical Approach: GNN Based Optimization Method

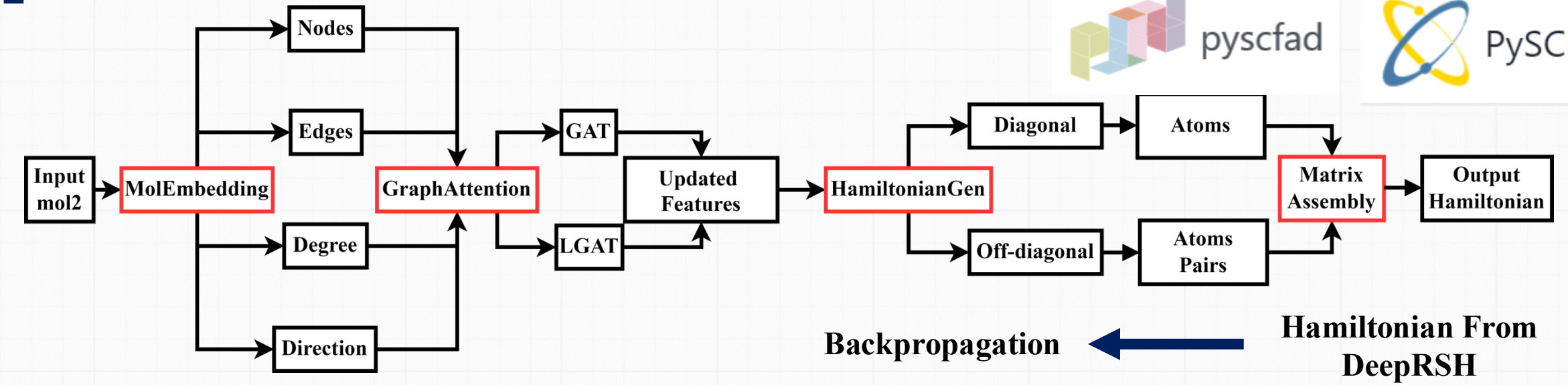
pyscfad

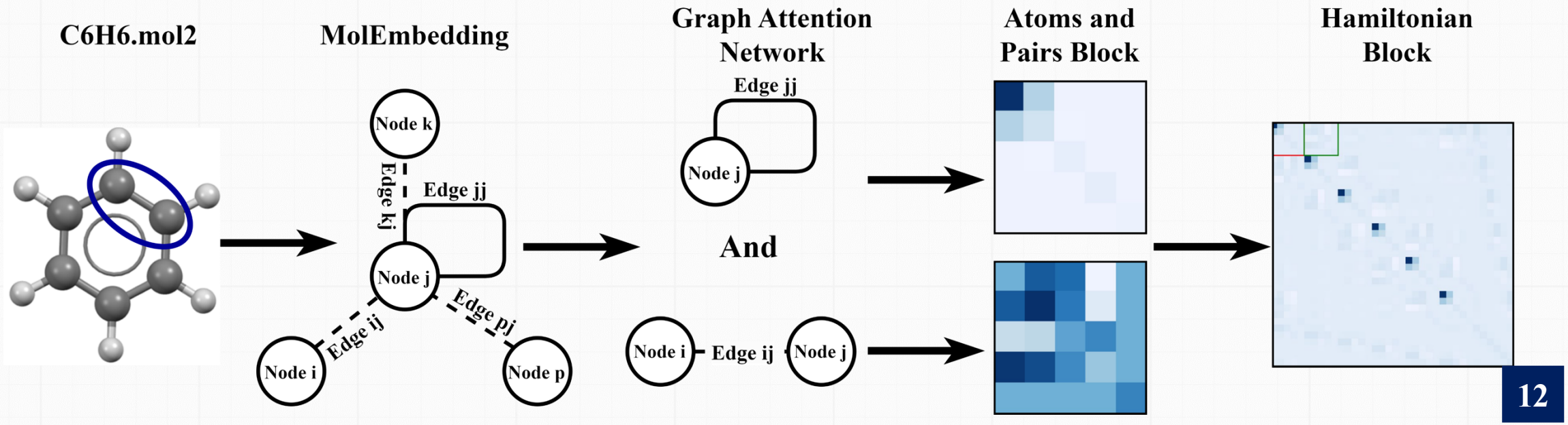


Backpropagation ← **Janak Theorem**



Technical Approach: Hamiltonian Learning Method -DeepMolH





Technical Approach: Excited State Method – TD-DeepMolH

?

Casida Equation

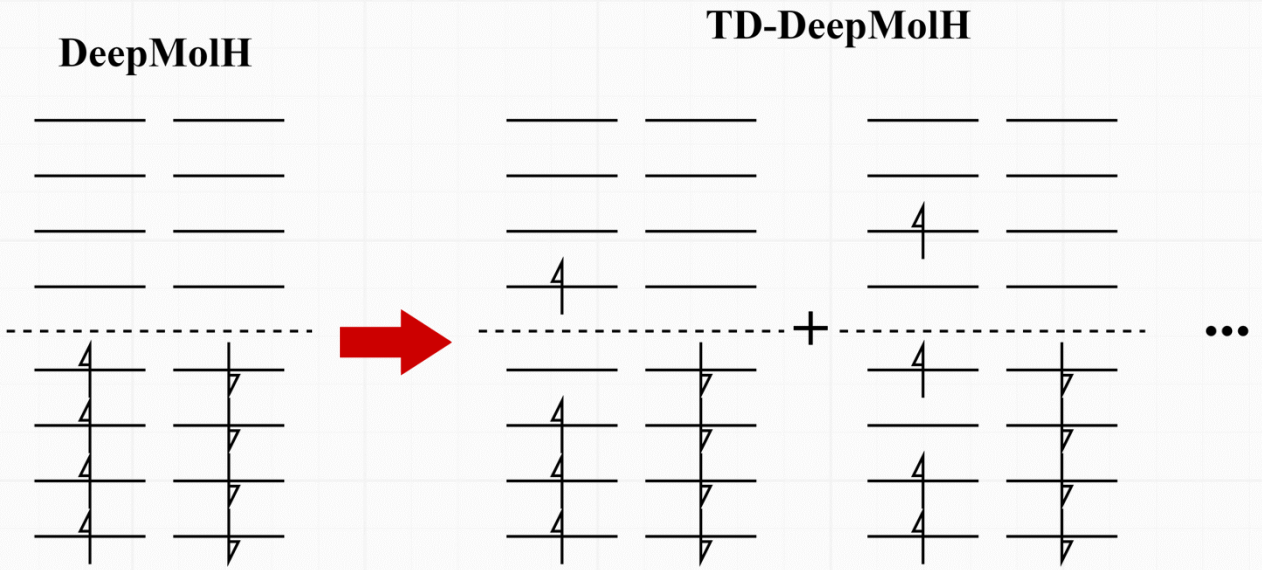
$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix}$$

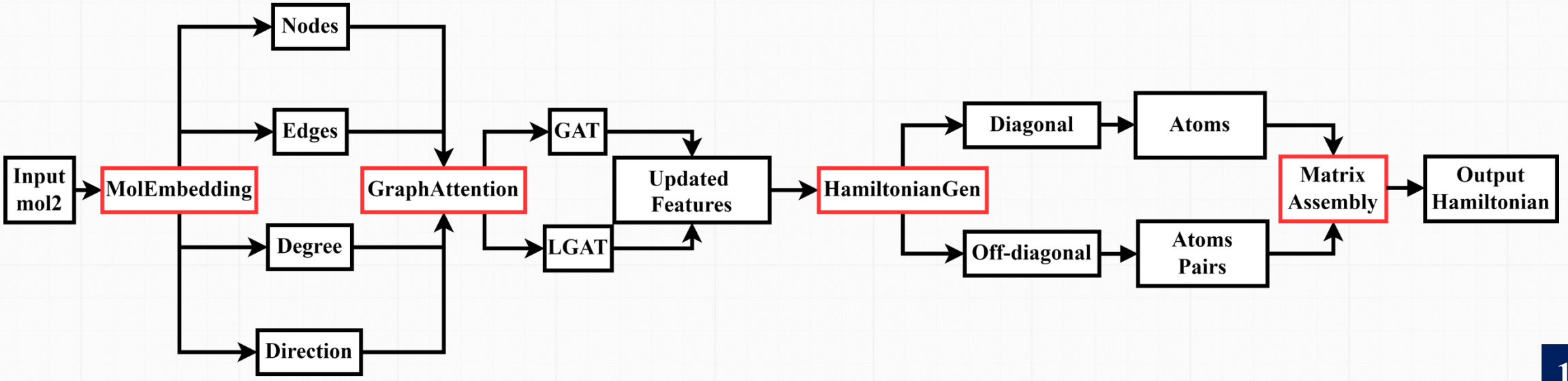
$$\psi_{ex} = \sum_{ai} x_{ai}\phi_{ai}$$

$$\psi_{di} = \sum_{ai} y_{ai}\phi_{ai}$$

$$A_{ia.jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + \int d\boldsymbol{r}\int \boldsymbol{r}'\phi_i(\boldsymbol{r})\phi_a^*(r)\left\{\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + f_{xc}\right\}\phi_b^*(r')\phi_j(\boldsymbol{r}')$$

$$B_{ia,jb} = \int d\boldsymbol{r}\int \boldsymbol{r}'\phi_i(\boldsymbol{r})\phi_a^*(r)\left\{\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + f_{xc}\right\}\phi_b^*(r')\phi_j(\boldsymbol{r}')$$





Timeline

Ground States:

- **2025.09-2025.12:** Optimization of DeepMolH and DeepRSH modules
- **2026.01-2026.02:** Expanding DeepMolH from monomers to oligomers
- **2026.03-2026.08:** Photophysics properties of clusteroluminescence based on DeepMolH

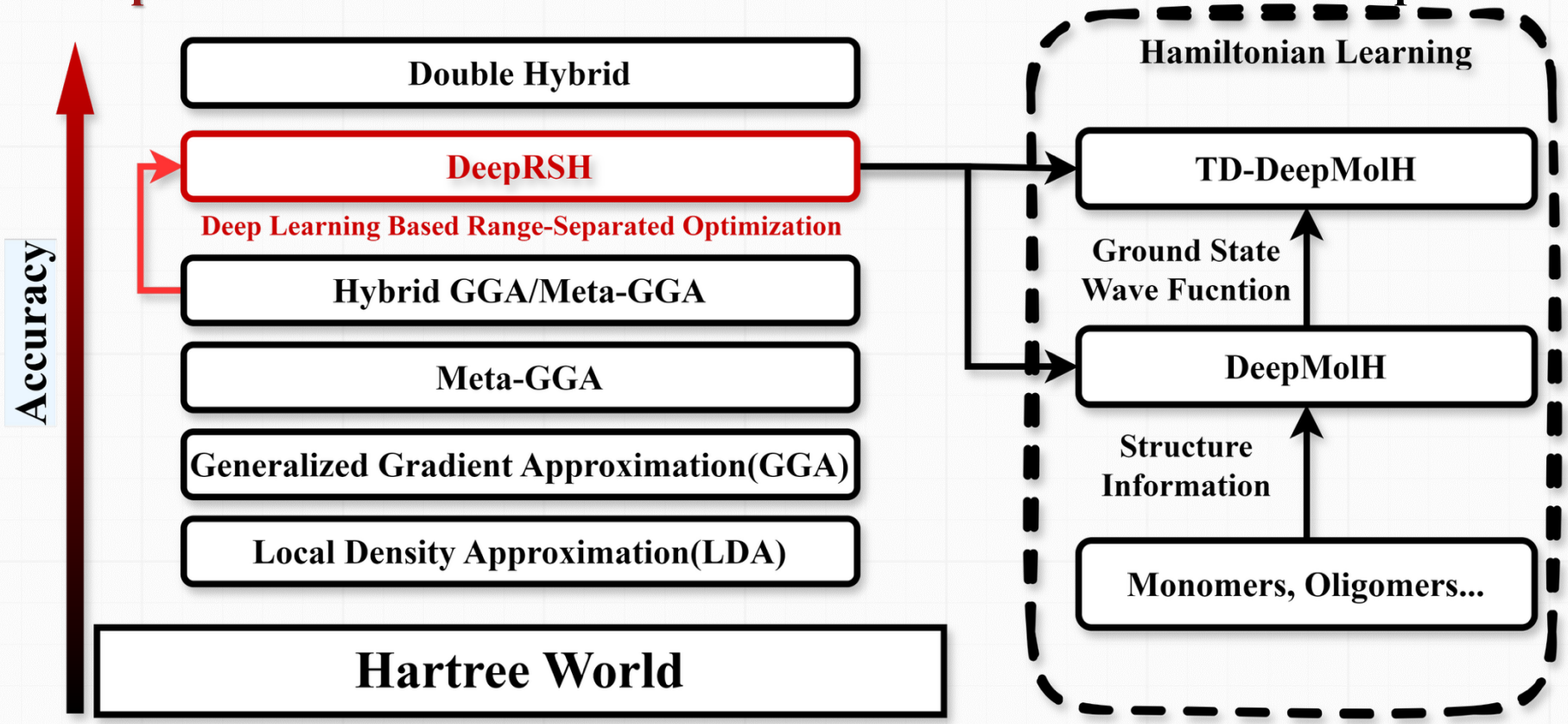
Excited States:

- **2026.09-2027.02:** Discussion of excited states theory and construction of TD-DeepMolH
- **2027.03-2027.08:** Expanding TD-DeepMolH from monomers to oligomers
- **2027.09-2027.12:** Rigorous interpretation of the photophysical mechanisms in clusteroluminescence

Expected Outcomes: Electronic Structure Theory

Electronic Structure Methods:

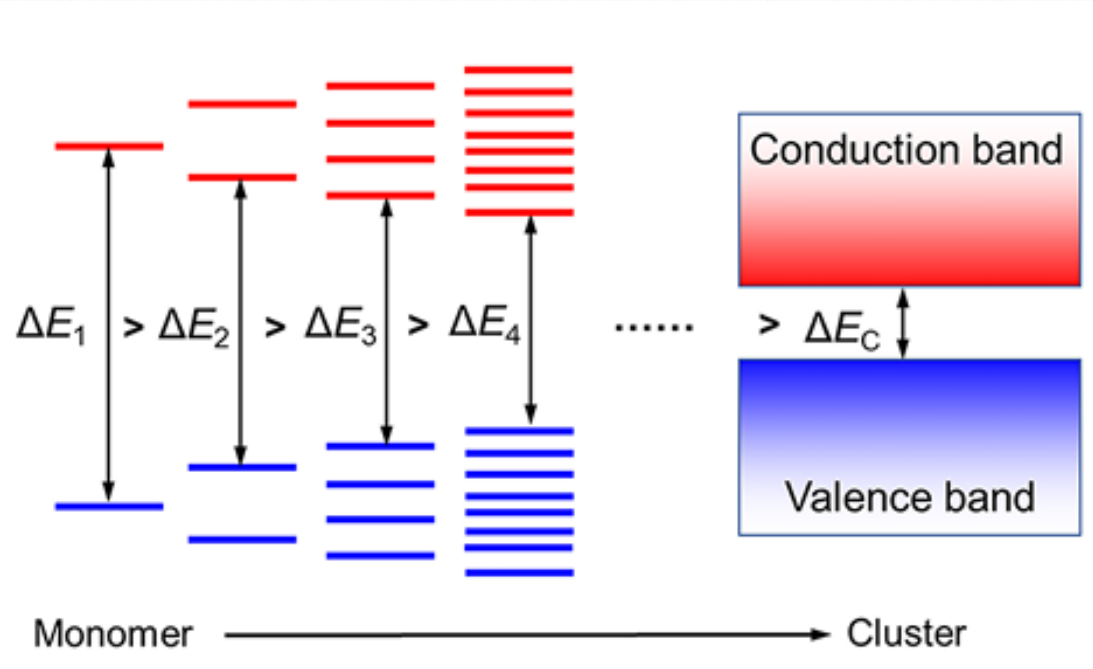
- **DeepRSH:** Range-Separated Hybrid functional optimization module
- **DeepMolH:** Deep learning DFT Hamiltonian method for complex organic system
- **TD-DeepMolH:** Efficient excited states calculation method based on DeepMolH

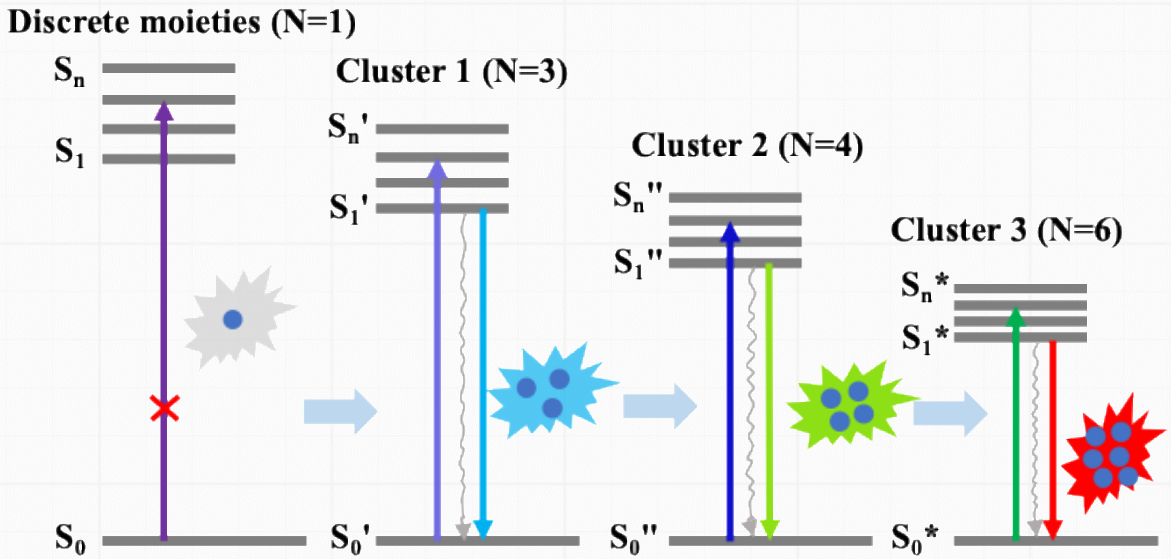


Expected Outcomes: Organic Functional Materials

Organic Photoelectric Materials:

- Basic photophysics mechanism of Clusteroluminescence for energy gap
- Accurate excited state information of Clusteroluminescence
- Structure-Property Relationship of Clusteroluminescence





Acknowledgments

School of Chemical Science, UCAS

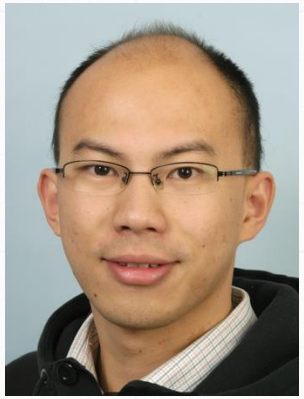
Prof. Qian Peng

Discussion on basis picture and calculation detail of organic functional materials

Dr. Juanjuan Wang

Dr. Juanfang Yang

Institute of Physics, CAS



Prof. Lei Wang

Assoc. Prof. Xinyang Dong

Discussion on basis theory of Hamiltonian learning and ab initio methods

中国科学院大学
University of Chinese Academy of Sciences

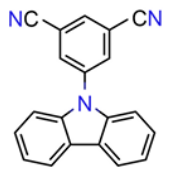
Thank you for your criticism and correction !

Yuan Jiao
School of Advanced Interdisciplinary Sciences, UCAS

Q&A

Appendix: Calculation results of OPTXC

(a) carbazole (Cz)



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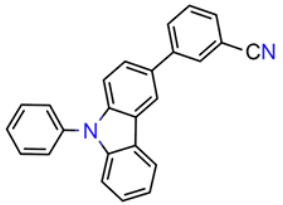

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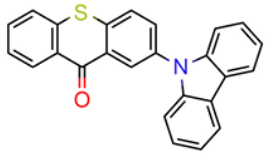

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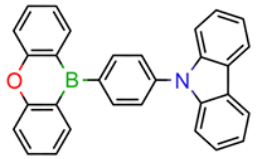
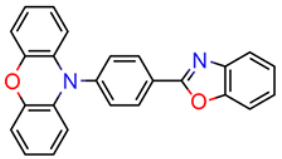
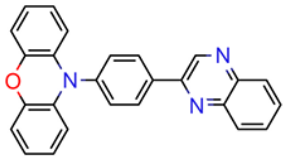


4, %HL=8.9%

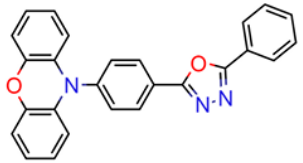
(b) phenoxazine (PXZ) and phenothiazine (PTZ)



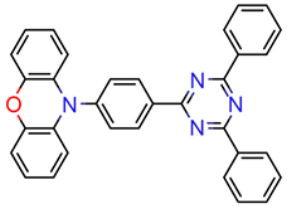
5, %HL=81.5%



6, %HL=61.1%

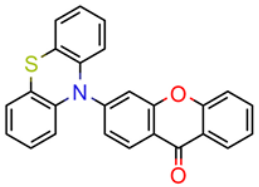


7, %HL=65.0%

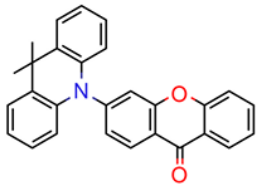


8, %HL=74.6%

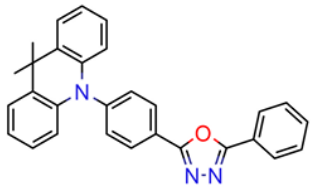
(c) 9,9-dimethyl-9,10-dihydroacridine (DMAC)



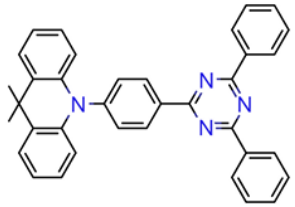
9, %HL=61.5%



10, %HL=70.4%

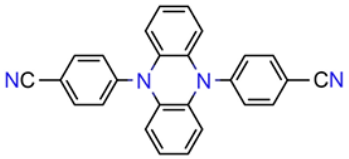


11, %HL=62.9%

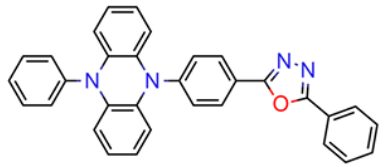


12, %HL=73.9%

(d) 5,10-dihydrophenazine (DHPZ)

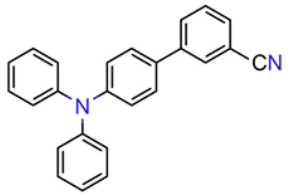


13, %HL=89.8%

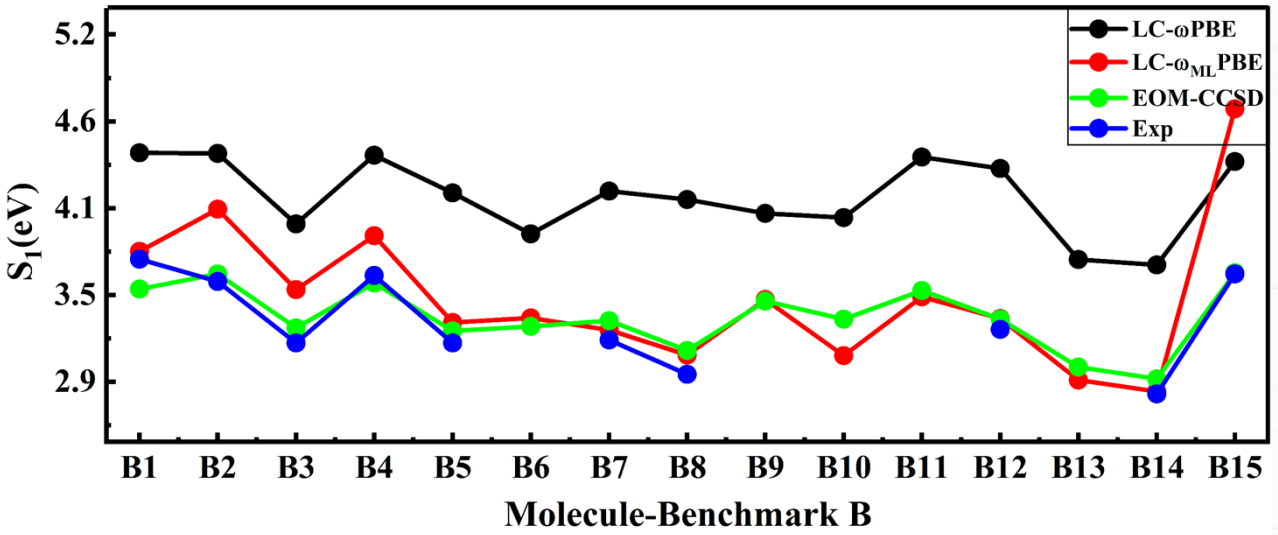


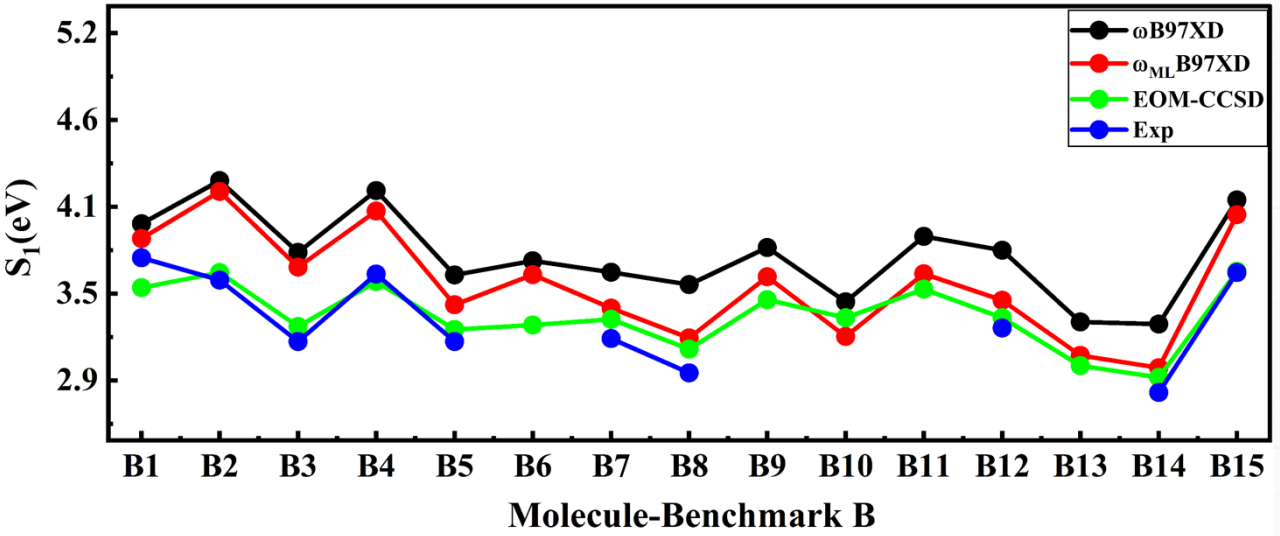
14, %HL=63.8%

(e) triphenylamine (TPA)



15, %HL=47.7%





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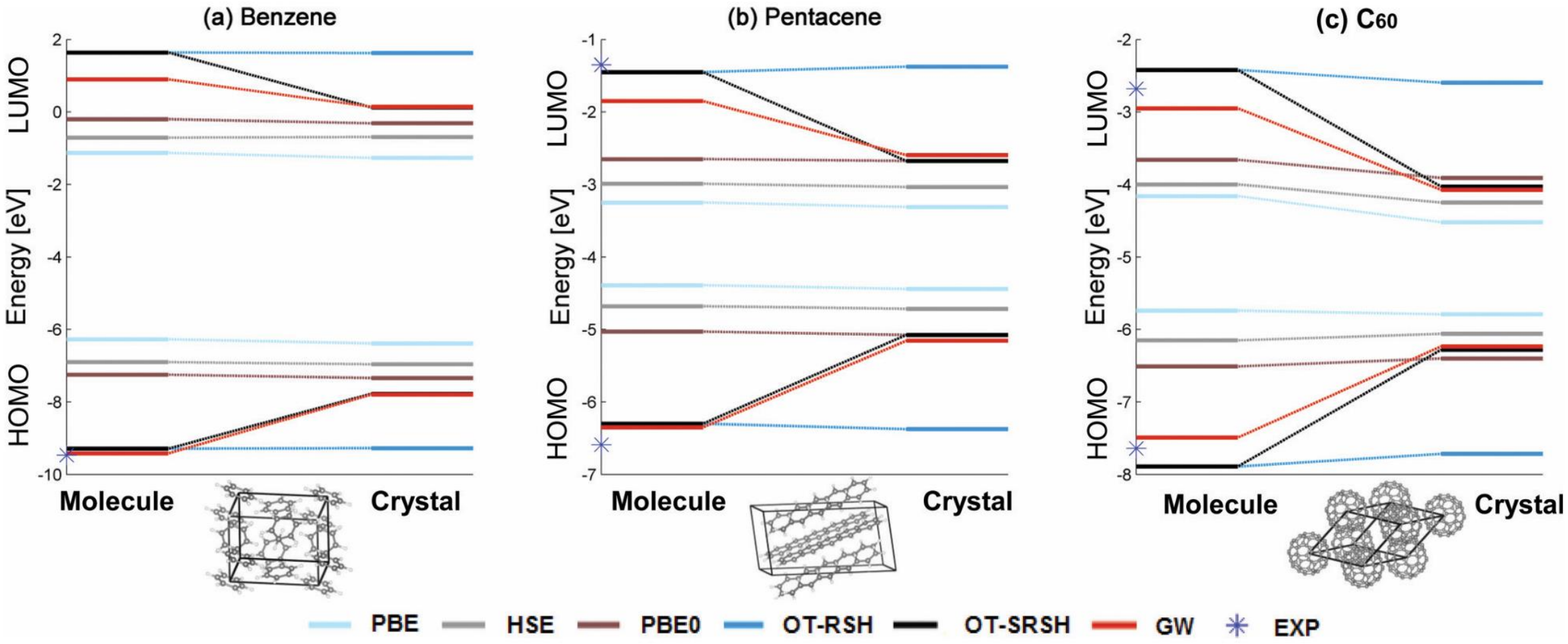
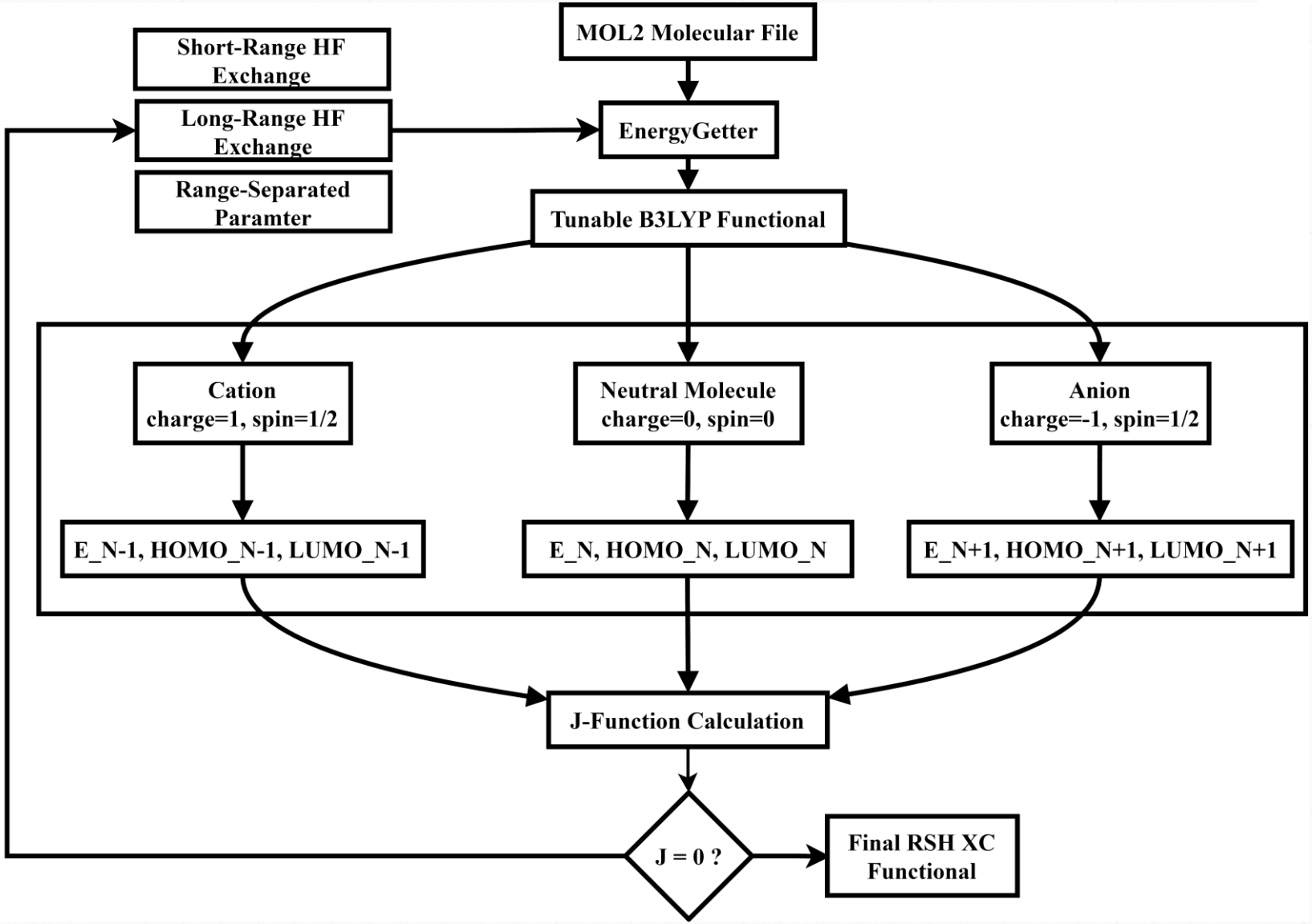
Appendix: Screened Range-Separated Hybrid Functionals

Phys. Rev. B 88, 081204(R)

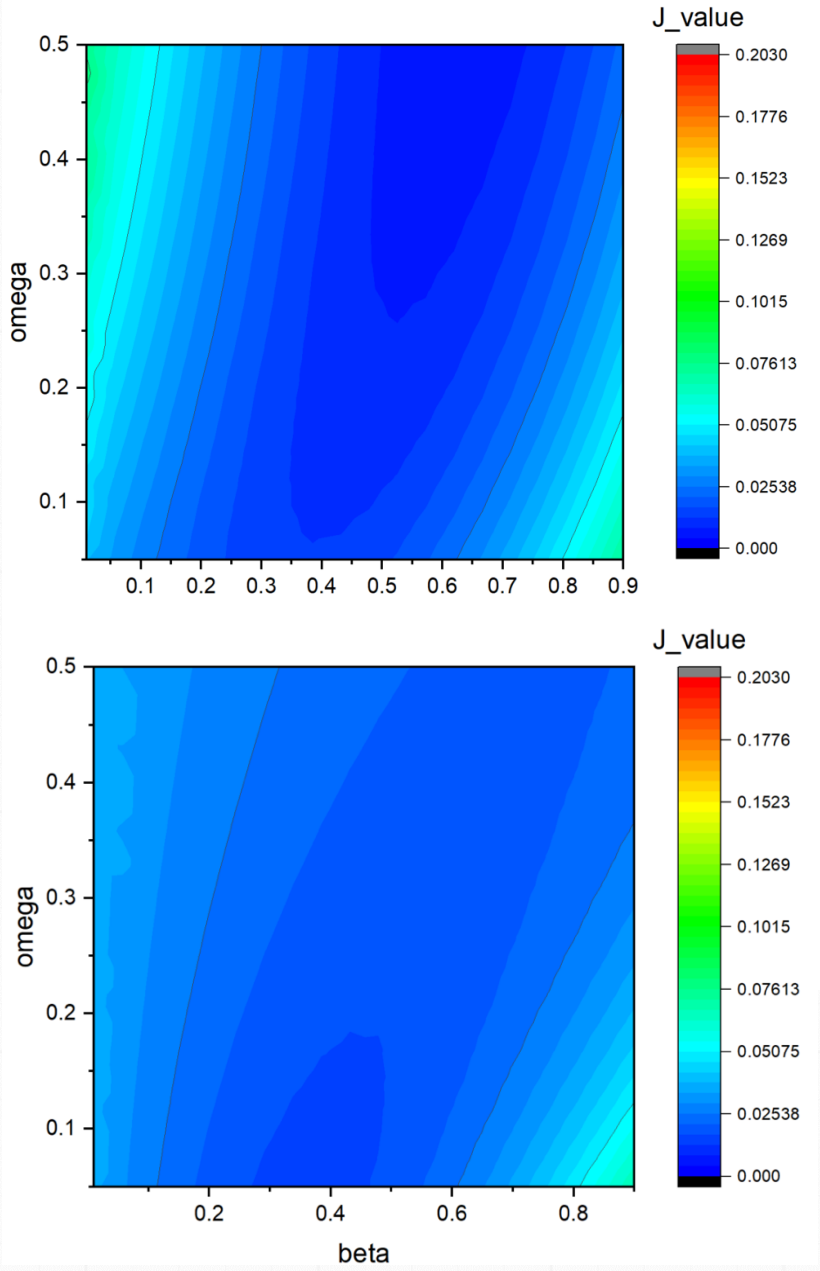


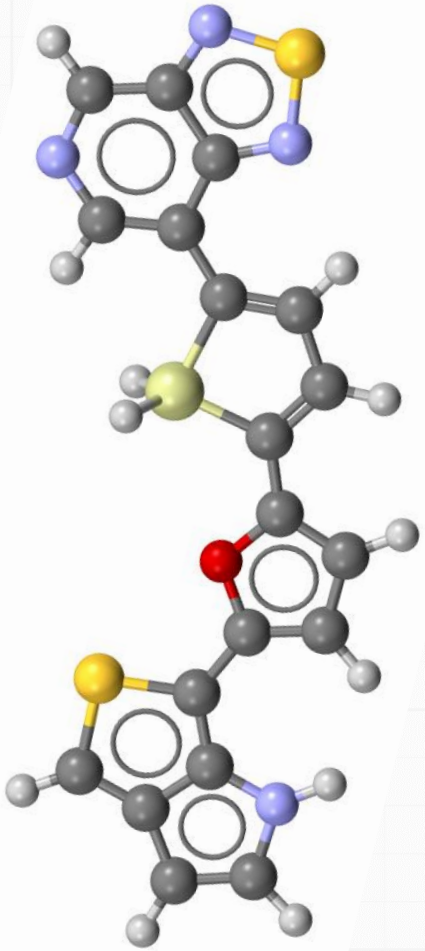
Appendix: Optimization method of DeepRSH

pyscfad



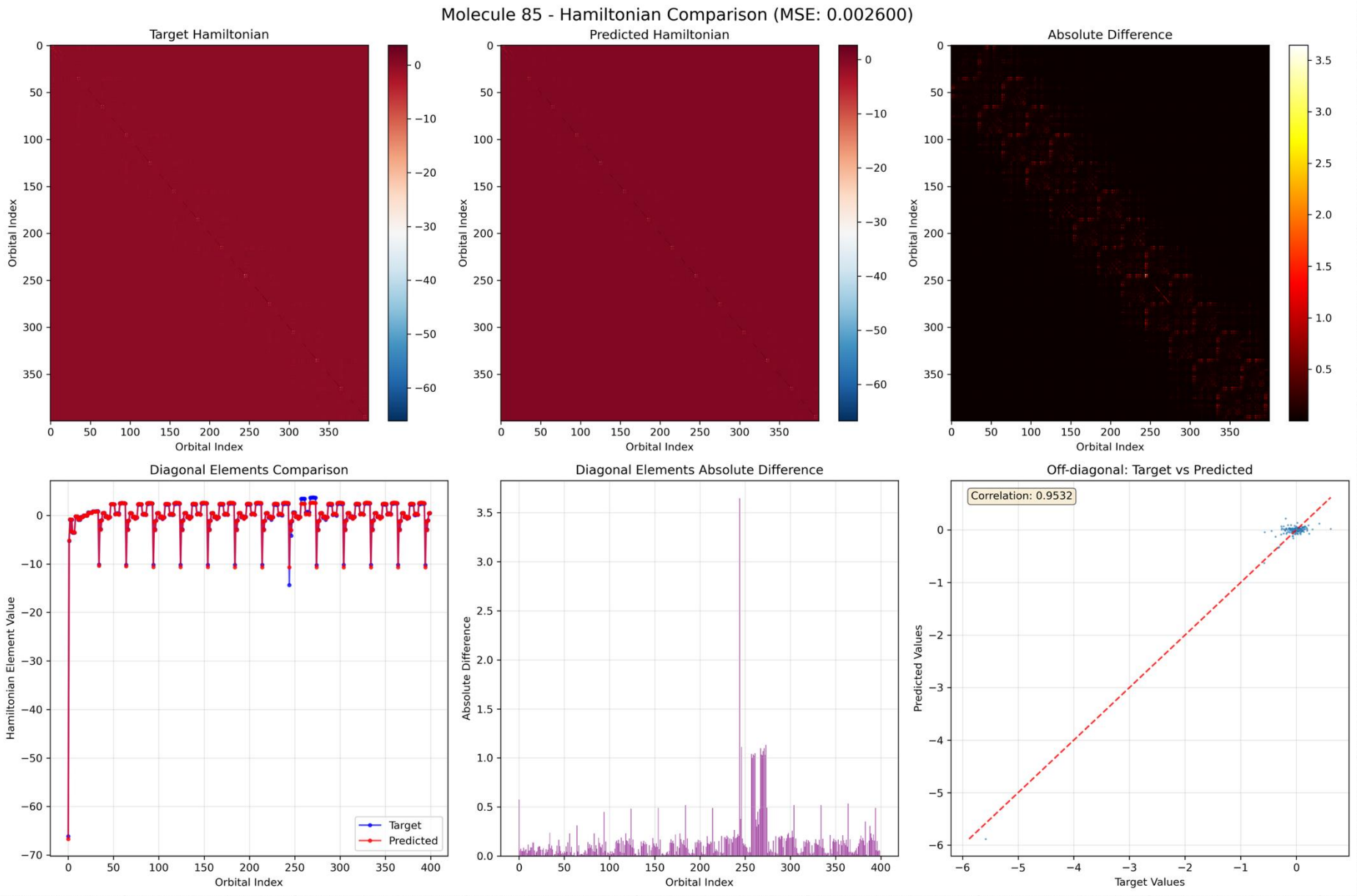
Appendix: Optimization method of DeepRSH

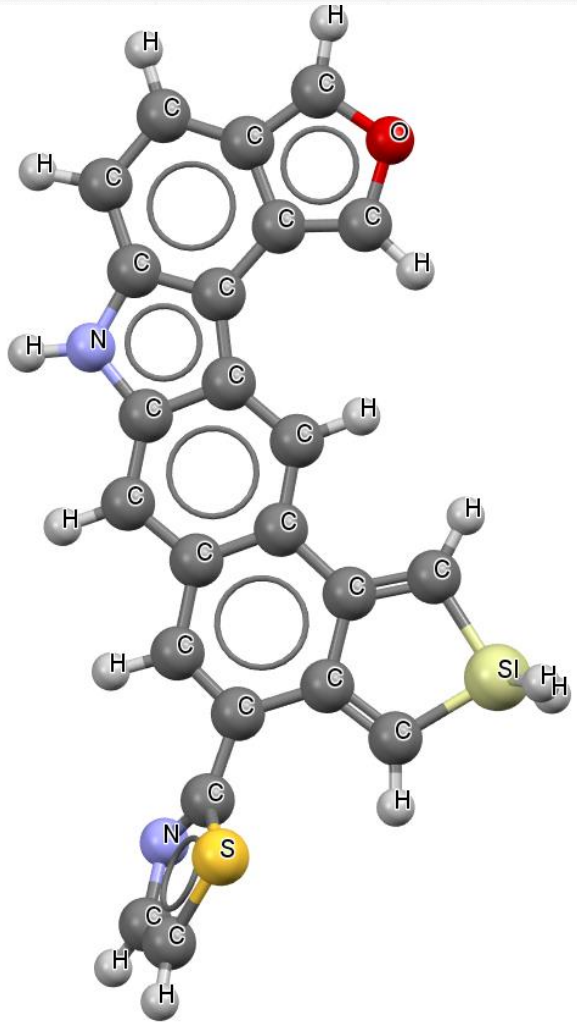




Scaned-CAM-B3LYP/cc-pVDZ

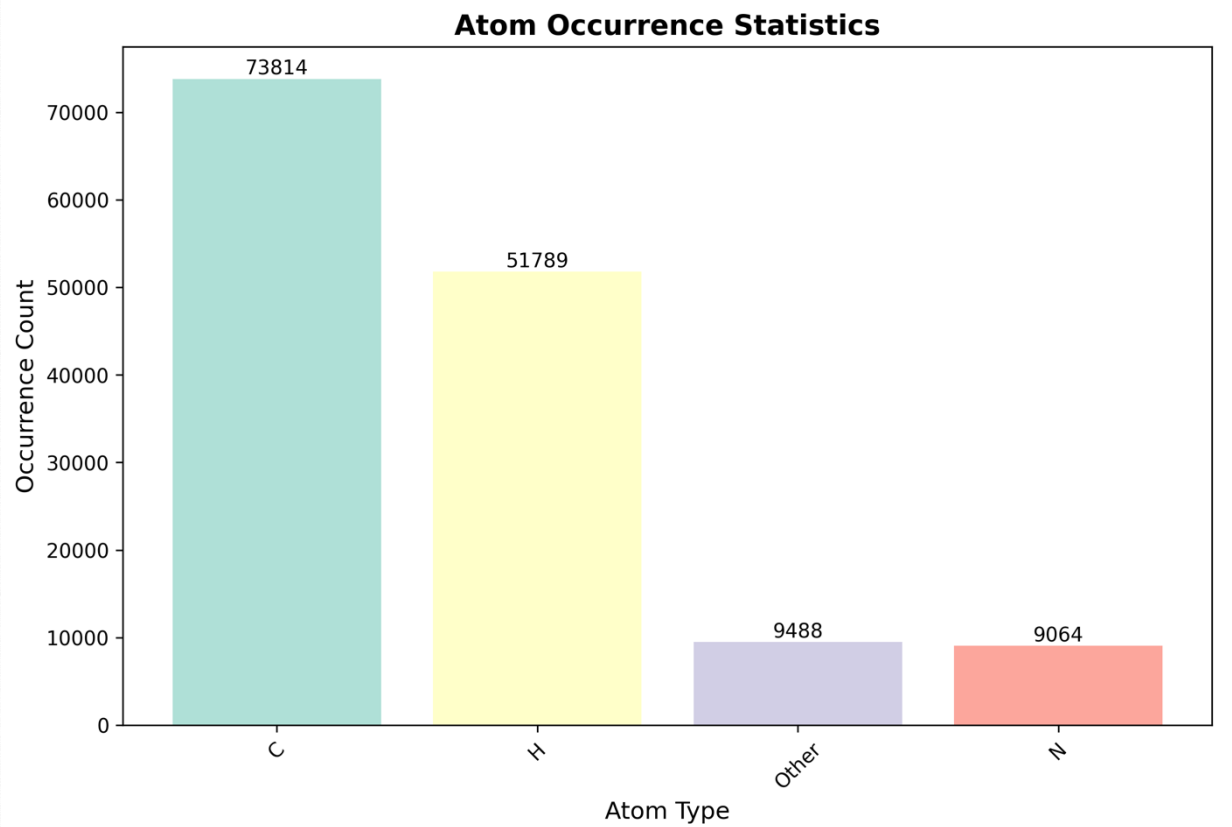
Appendix: Test of DeepMolH trained on 270 molecules

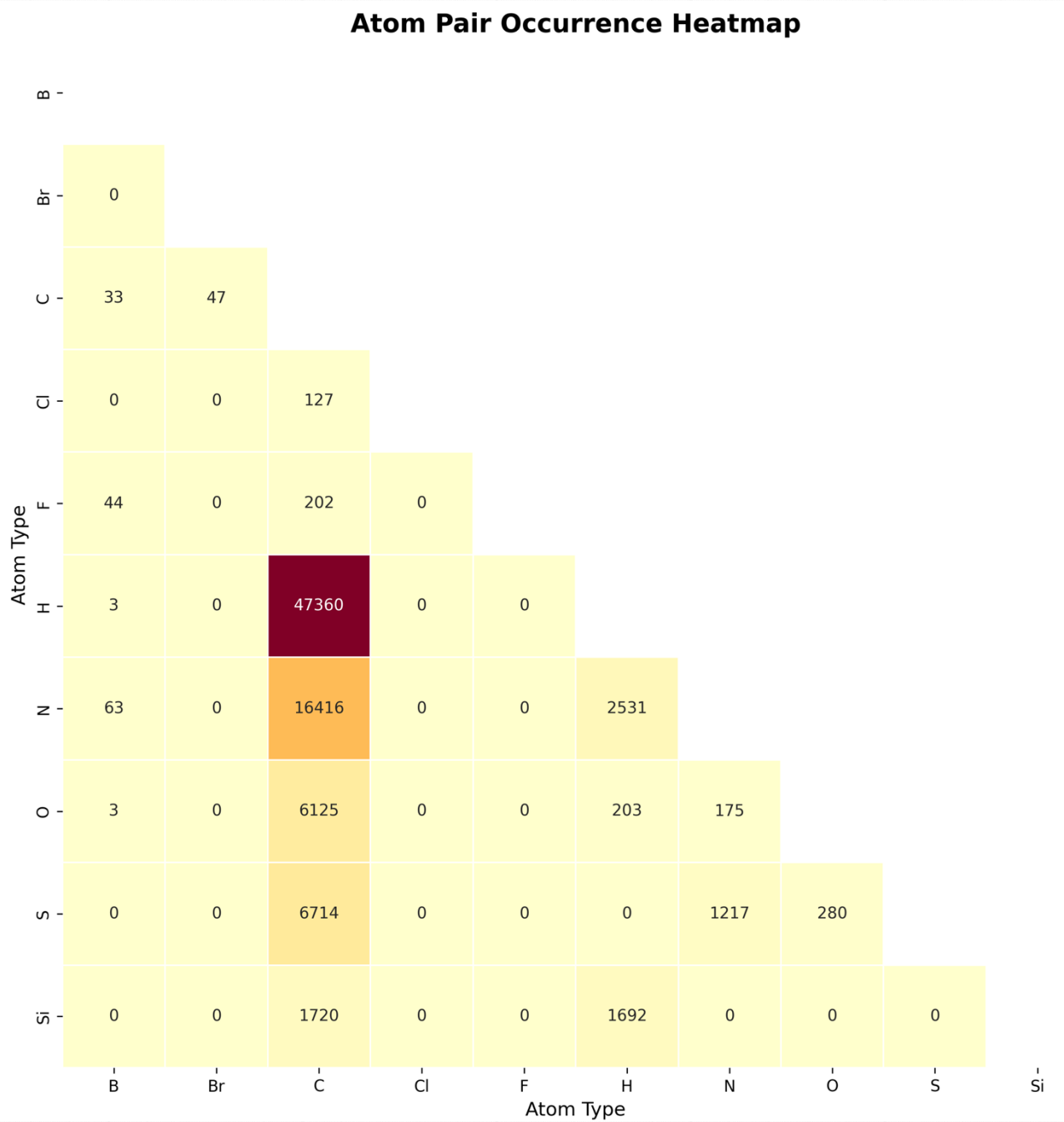




B3LYP/cc-pVTZ

Appendix: Dataset





Appendix: Matrix Size of Hamiltonian in DFT and TDDFT

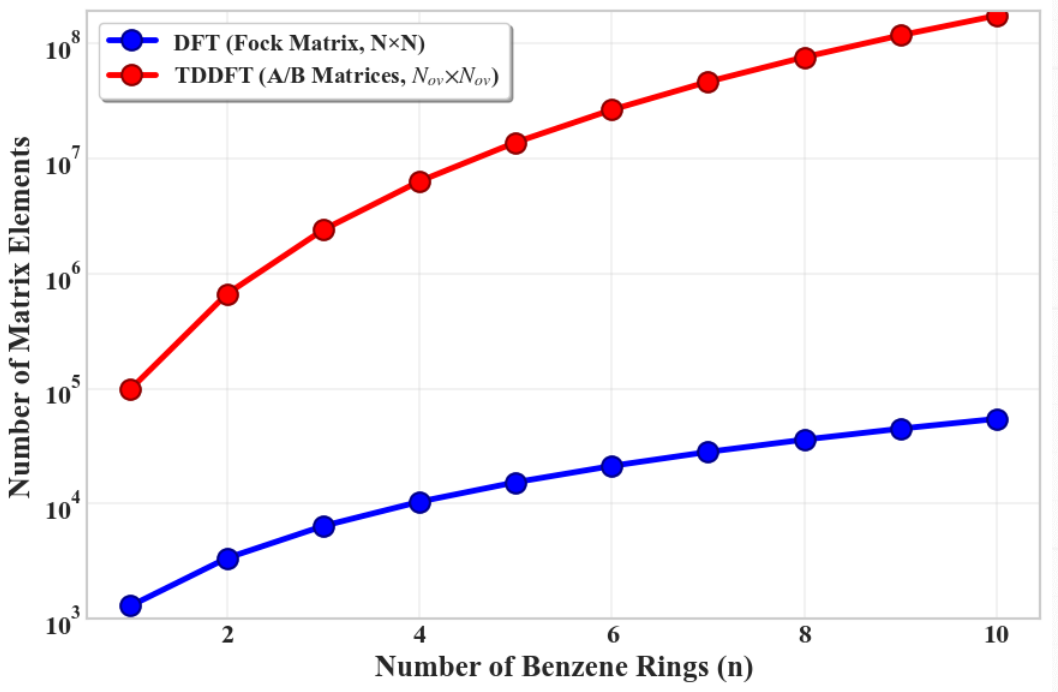
Casida Equation

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} \qquad \psi_{ex} = \sum_{ai} x_{ai}\phi_{ai}$$

$$\psi_{di} = \sum_{ai} y_{ai}\phi_{ai}$$

$$A_{ia.jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + \int d\boldsymbol{r}\int \boldsymbol{r}'\phi_i(\boldsymbol{r})\phi_a^*(r)\left\{\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + f_{xc}\right\}\phi_b^*(r')\phi_j(\boldsymbol{r}')$$

$$B_{ia,jb} = \int d\boldsymbol{r}\int \boldsymbol{r}'\phi_i(\boldsymbol{r})\phi_a^*(r)\left\{\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + f_{xc}\right\}\phi_b^*(r')\phi_j(\boldsymbol{r}')$$



Ground State Hamiltonian Matrix: ~$O(N_e^3)$for calculation

- $(N_{occ}+N_{virt}) \times (N_{occ}+N_{virt})$

Excited State AB Matrix: ~$O(N_e^5)$ for calculation ~$O\left(N_e^4\right)$ for memory

- $(2N_{occ}\times N_{virt}) \times (2N_{occ}\times N_{virt})$
- $(N_{occ}\times N_{virt}) \times (N_{occ}\times N_{virt})$ **in Tamm-Dancoff Approximation**

Appendix: Equivariant Graph Neural Network

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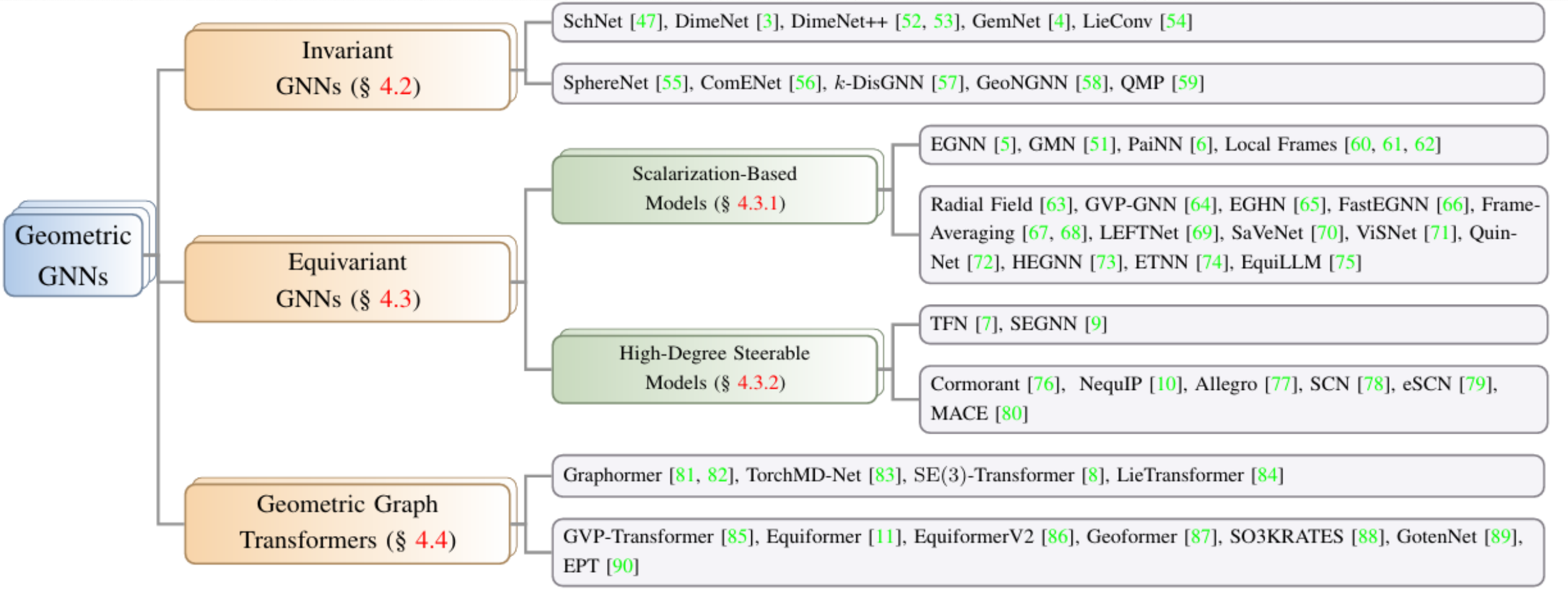

Appendix: Application of Graphormer-M-OFDFT

Nat Comput Sci 4, 210–223 (2024).