中国科学院大学 前沿交叉科学学院
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After Full Differentiable TDDFT Code for Neural Network XC Functional, Multi-Configuration Self-Consistent Field in Excited State

GradTDDFT
AI-native differentiable TDDFT in JAX

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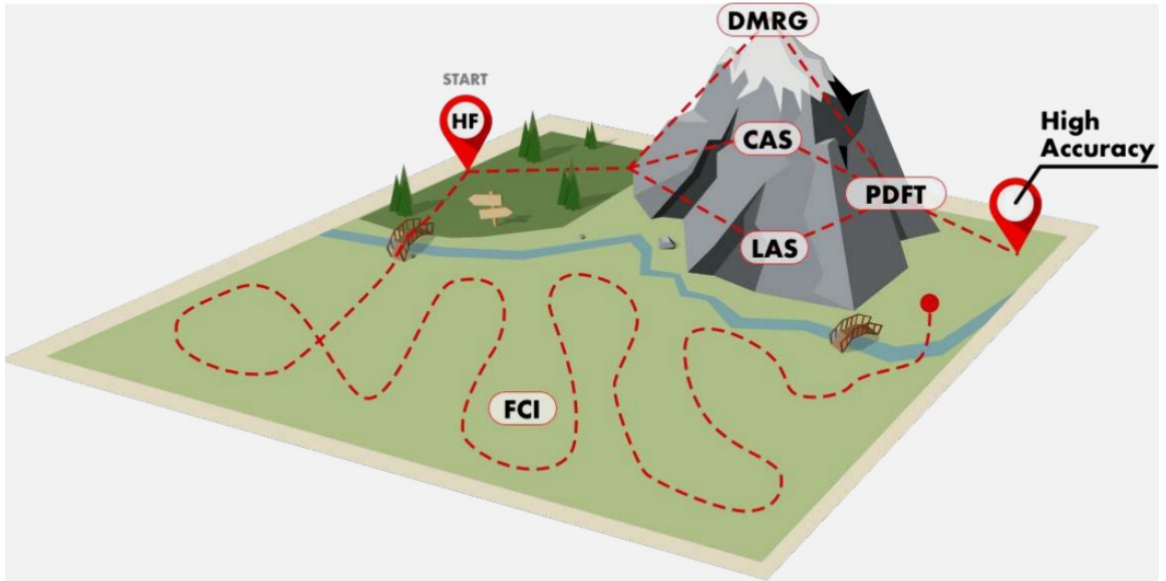
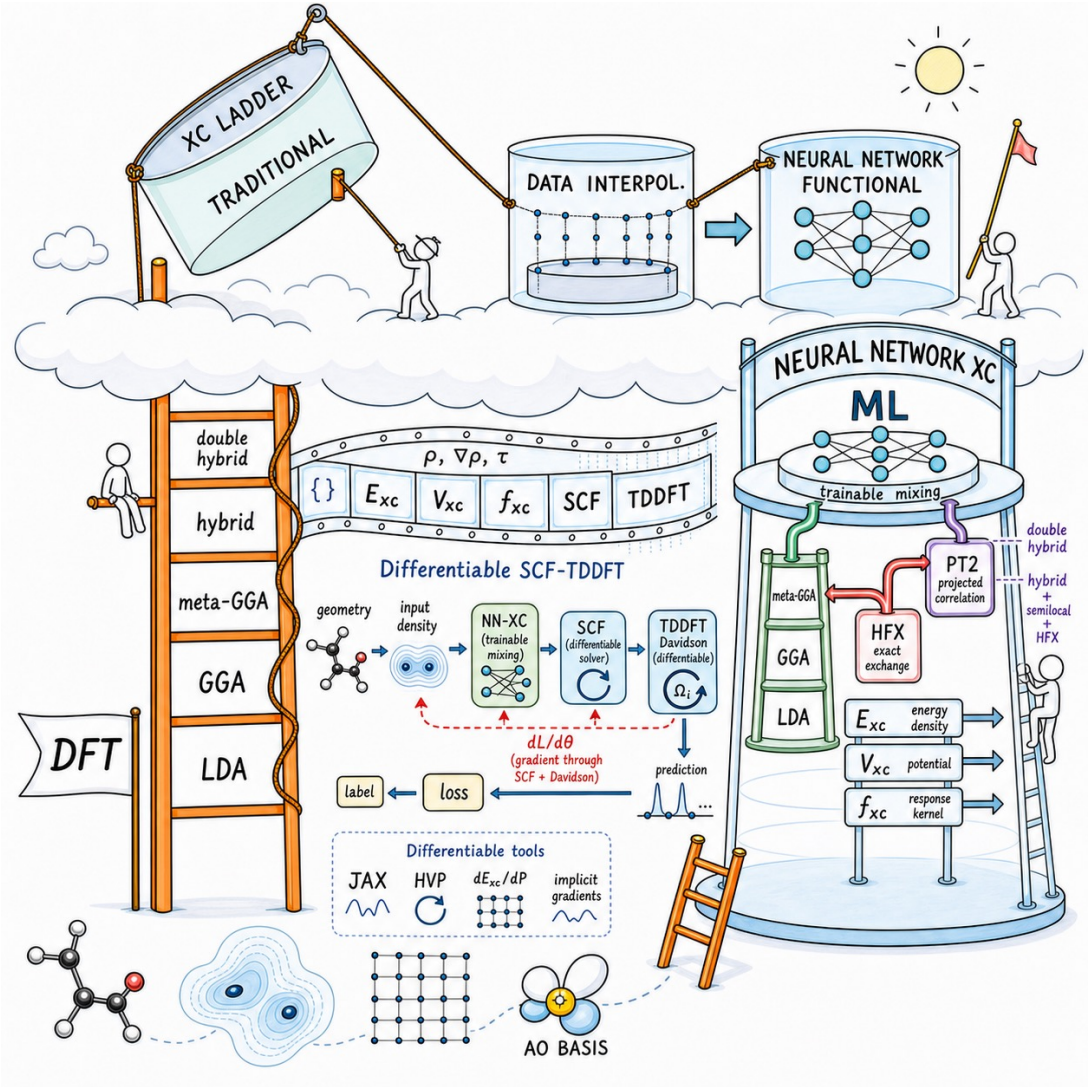
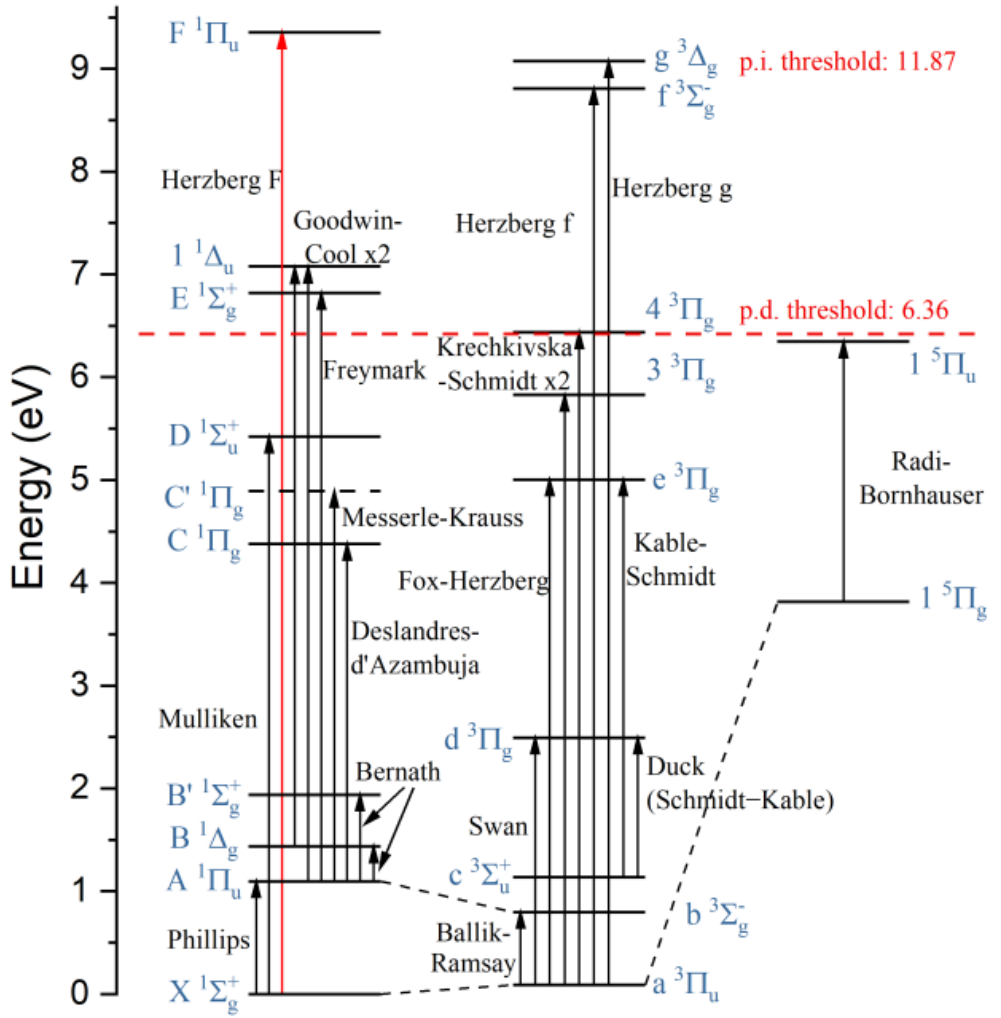


- **Full Differentiable TDDFT Code for Neural Network XC Functional and its Limitations**
- **Multi-Configuration Self-Consistent Field or Non-Adiabatic? Beyond LR-TDDFT**





Github.com/STOKES-DOT/GradTDDFT

FIG. 1. Electronic states and band systems of C_2.

■ Background –TDDFT

$$v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\}) \Leftrightarrow \rho(\boldsymbol{x}) \Leftrightarrow \{\psi_i(\boldsymbol{x})\}$$

The Time-Dependent of XC Functional Vanished !

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\}) + v_H(\boldsymbol{x}) + v_{xc}(\boldsymbol{x})\right]\psi_i(\boldsymbol{x}) = \varepsilon_i\psi_i(\boldsymbol{x})$$

Runge-Gross Theorem

$$v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\},\boldsymbol{t}) + \boldsymbol{C}(\boldsymbol{t}) \Leftrightarrow \rho(\boldsymbol{x},\boldsymbol{t}) \Leftrightarrow \{\psi_i(\boldsymbol{x},\boldsymbol{t})\boldsymbol{e}^{-\boldsymbol{i}\boldsymbol{\alpha}(\boldsymbol{t})}\}$$

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\},\boldsymbol{t}) + v_H(\boldsymbol{x},\boldsymbol{t}) + v_{xc}(\boldsymbol{x},\boldsymbol{t})\right]\psi_i(\boldsymbol{x},\boldsymbol{t}) = i\frac{\partial}{\partial t}\psi_i(\boldsymbol{x},\boldsymbol{t})$$

Linear-Response – Adiabatic Approximation

$$F_{aa}^{(0)}x_{ai} - x_{ai}F_{ii}^{(0)} + \sum_{bj}\left(\frac{\partial F_{ai}}{\partial P_{bj}}x_{bj} + \frac{\partial F_{ai}}{\partial P_{jb}}y_{bj}\right)P_{ii}^{(0)} = \omega x_{ia}$$

$$F_{aa}^{(0)}y_{ai} - y_{ai}F_{ii}^{(0)} - \sum_{bj}P_{ii}^{(0)}\left(\frac{\partial F_{ia}}{\partial P_{bj}}x_{bj} + \frac{\partial F_{ia}}{\partial P_{jb}}y_{bj}\right) = \omega x_{ia}$$

$$F_{aa}^{(0)} = \int d\boldsymbol{r}\psi_a^*(\boldsymbol{x},\boldsymbol{t})\left\{-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\},\boldsymbol{t}) + v_H(\boldsymbol{x},\boldsymbol{t}) + v_{xc}(\boldsymbol{x},\boldsymbol{t})\right\}\psi_a(\boldsymbol{x},\boldsymbol{t})$$

$$F_{ia} = \int d\boldsymbol{r}\psi_i^*(\boldsymbol{x},\boldsymbol{t})\left\{-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\},\boldsymbol{t}) + v_H(\boldsymbol{x},\boldsymbol{t}) + v_{xc}(\boldsymbol{x},\boldsymbol{t})\right\}\psi_a(\boldsymbol{x},\boldsymbol{t}) + g_{ai}(\omega) + \Delta F_{ia}^{(0)}$$

Casida-TDDFT

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

$$\psi_{ex} = \sum_{ai} x_{ai}\hat{a}_a^+\hat{a}_i\psi_{gr}$$

$$\psi_{di} = \sum_{ai} y_{ai}\hat{a}_a^+\hat{a}_i\psi_{gr}$$

TDA-TDDFT

$$AX = \omega X$$

$$\psi_{ex} = \sum_{ai} x_{ai}\hat{a}_a^+\hat{a}_i\psi_{gr}$$

■ Background –TDDFT

A, B Matrix and Response Kernel

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

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

$$f_{xc}[\rho] = \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}$$

TDA-TDDFT

$$AX = \omega X$$

$$\psi_{ex} = \sum_{ai} x_{ai}\hat{a}_a^+\hat{a}_i\psi_{gr}$$

Casida-TDDFT

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

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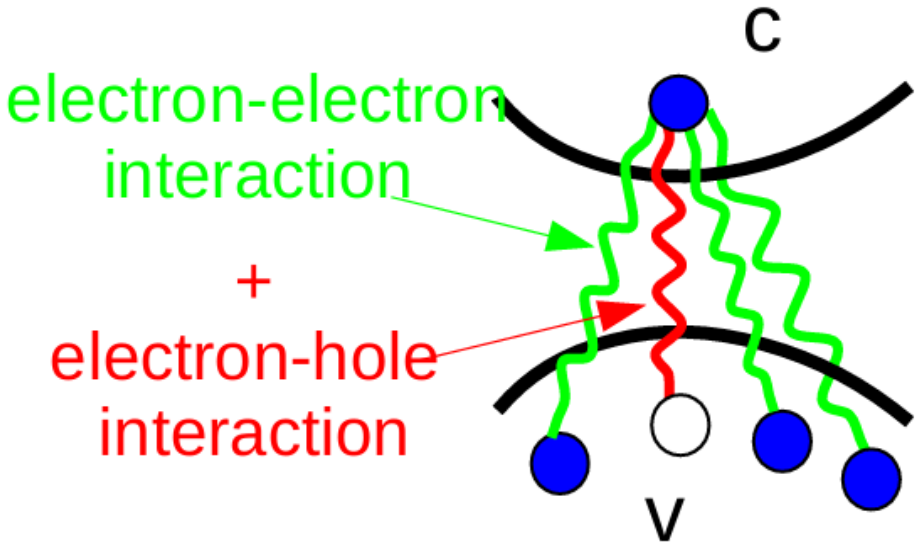


■ GradTDDFT – Functional and Comparation

Model/Software	Differentiable	XC Library	HF/PT2	Excited state
DM21	Fixed Density	Only LDA	HF(Frozen)	❎
GradDFT	Fixed Density Explicit SCF(unstable)	Write by hand	HF(Nograd)	❎
GradTDDFT	Fixed Density Explicit SCF Implicit SCF Implicit Davidson Solver	JAX-XC	HF/PT2(Differentiable/Nograd)	Only Small Molecules(RIS)

NOTE:

- SCF/Davidson Solver is hard to converge for random initialization
- GPU memory comes to 600GB for 29 atoms without any approximation with grid_level=2
- HF/PT2 part is hard to be differentiable

■ GradTDDFT– Response Kernel with Automatic Differentiation

- **HF Exchange Kernel**

$$E_x^{HF} = \int d\boldsymbol{r} c_x^{hf}[\rho(\boldsymbol{r})] e_x^{hf}[\phi(\boldsymbol{r})]$$

$$e_x^{hf}[\phi] = -\frac{1}{2}\sum_{pq} \phi_p^*(r)\phi_q(r) \int d\boldsymbol{r}' \frac{\phi_i^*(\boldsymbol{r}')\phi_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

In A matrix of Casida equation

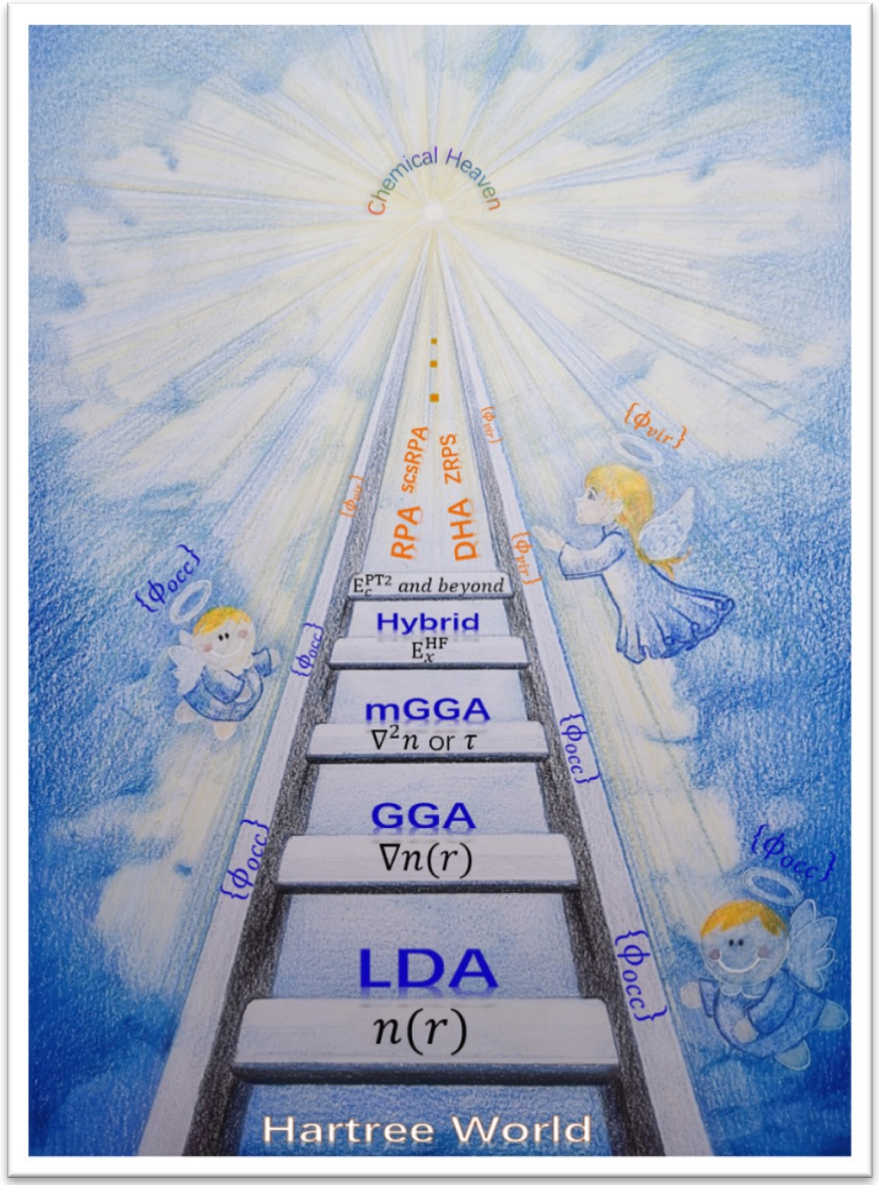
$$K_{ai,bj} = -\alpha_{eff}(ij|ab) \quad \text{with} \quad \alpha_{eff} = \frac{\int c_x^{hf}[\rho(\boldsymbol{r})]\rho(\boldsymbol{r})d\boldsymbol{r}}{\int \rho(\boldsymbol{r})d\boldsymbol{r}}$$

- **PT2 kernel**

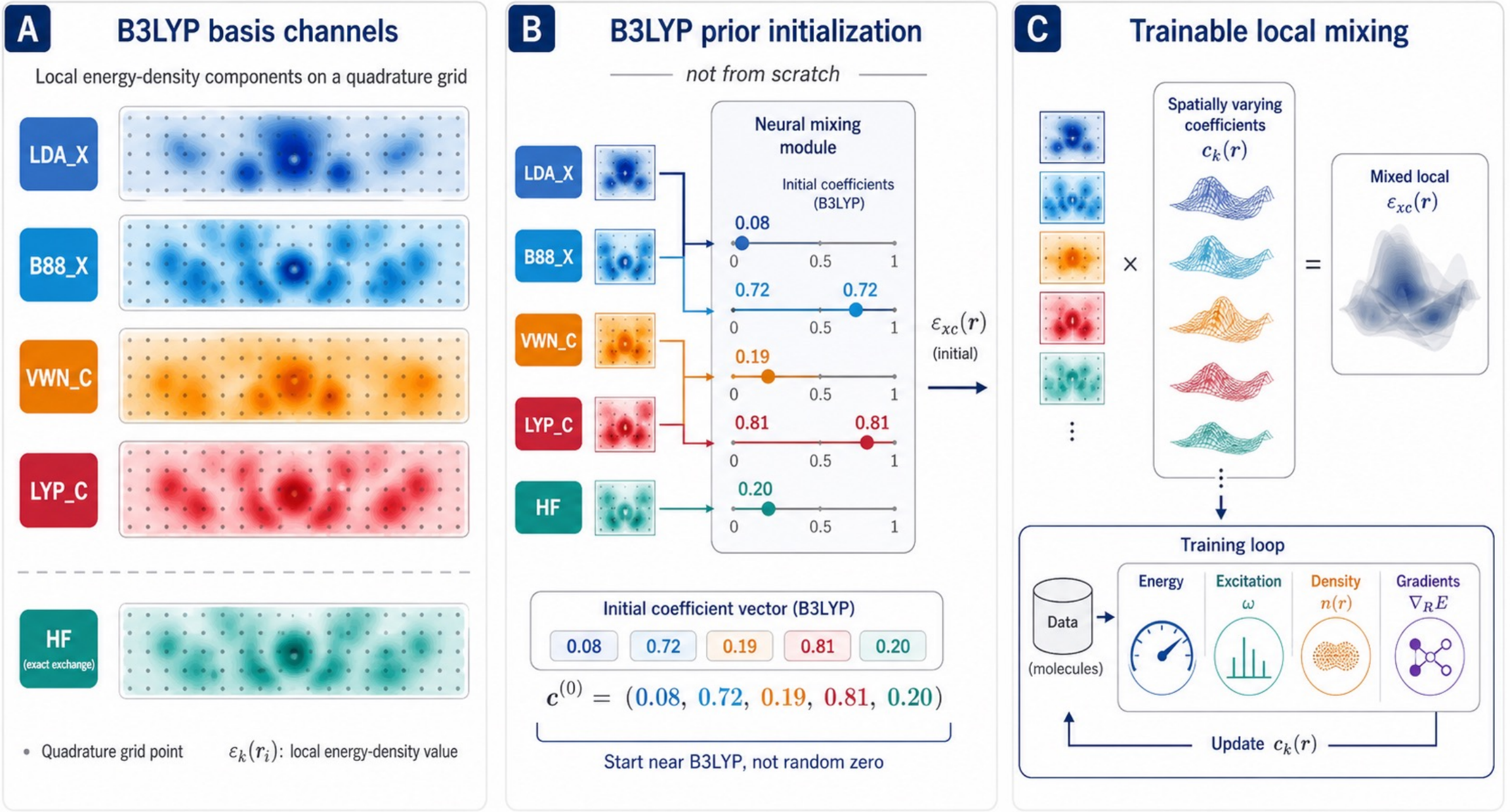
$$E_c^{PT2} = \sum_{ia,jb} \frac{(ai|jb)[2(ai|jb)-(ib|ja)]}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b} \rightarrow \int d\boldsymbol{r} c_c^{pt2}[\rho] e_c^{pt2}[\phi(\boldsymbol{r})]$$

$$e_c^{PT2} = \sum_{ia,jb} \rho_{ai} V_{jb}(\boldsymbol{r}) \frac{[2(ai|jb)-(ib|ja)]}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$$

$$f_{xc}^{pt2} = \frac{\partial^2 c_c^{pt2}[\rho]}{\partial u_\nu \partial u_\mu} e_c^{pt2}[\phi(\boldsymbol{r})] + \frac{\partial^2 e_c^{pt2}[\phi(\boldsymbol{r})]}{\partial u_\nu \partial u_\mu} c_c^{pt2}[\rho]$$



■ GradTDDFT – Training Modes in Neural Network XC Functional



■ GradTDDFT – Training Modes in Neural Network XC Functional

● **Implicit SCF/Fixed Density for H_2^+ Ground State with def2-TZVP, grid level = 2**

- **N-electron system**

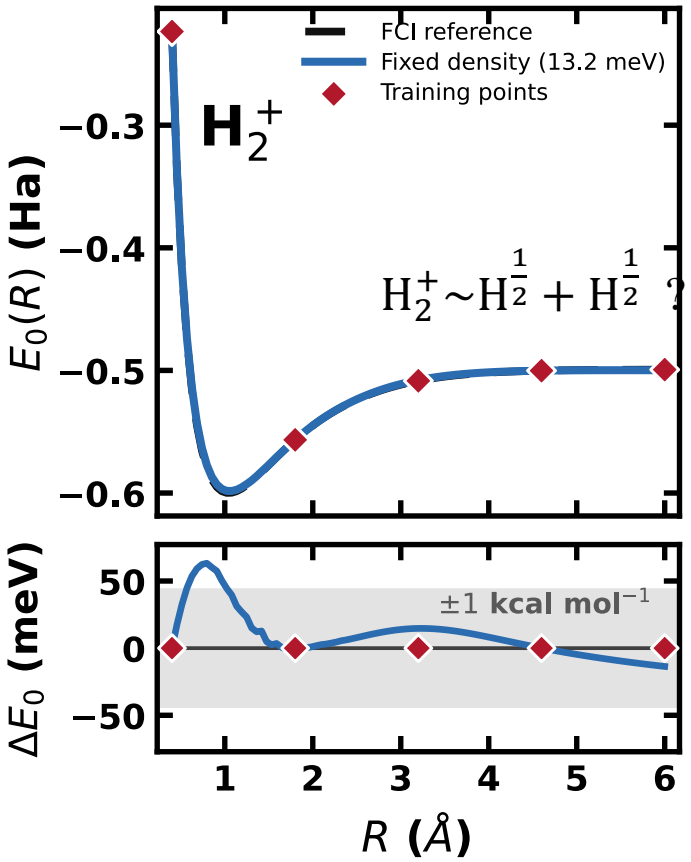
$$v_{eff}(\boldsymbol{r},\boldsymbol{R}) = v_{ext}(\boldsymbol{R}) + \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + v_{xc}(\boldsymbol{r})$$

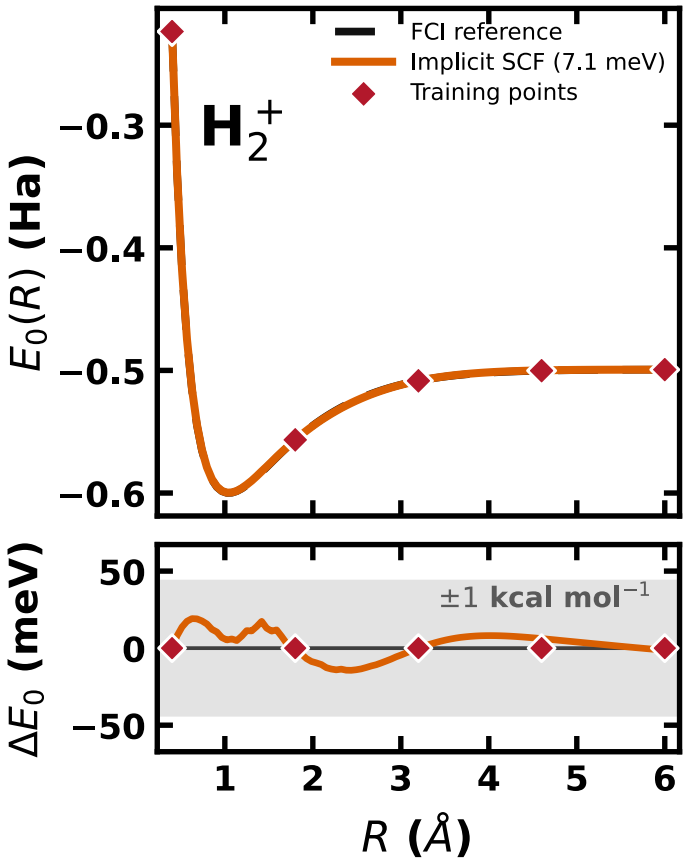
- **One-electron system($|\boldsymbol{r}| \to \infty$)**

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

- **Loss Function**

$$L = \frac{1}{N}\sum|E_{NN} - E_{FCI}| + \frac{1}{N^2}\sum(E_{NN} - E_{FCI})^2 + \frac{1}{N^2}\sum(\rho_{NN} - \rho_{FCI})^2$$





■ GradTDDFT – Training Modes in Neural Network XC Functional

● Implicit SCF for H_2 Ground State with def2-TZVP, grid level = 2

- **Static Correlation Error**

  σ_g^2 **Binding Orbital**

  σ_u^2 **Antibinding Orbital**

  - **MCSCF**

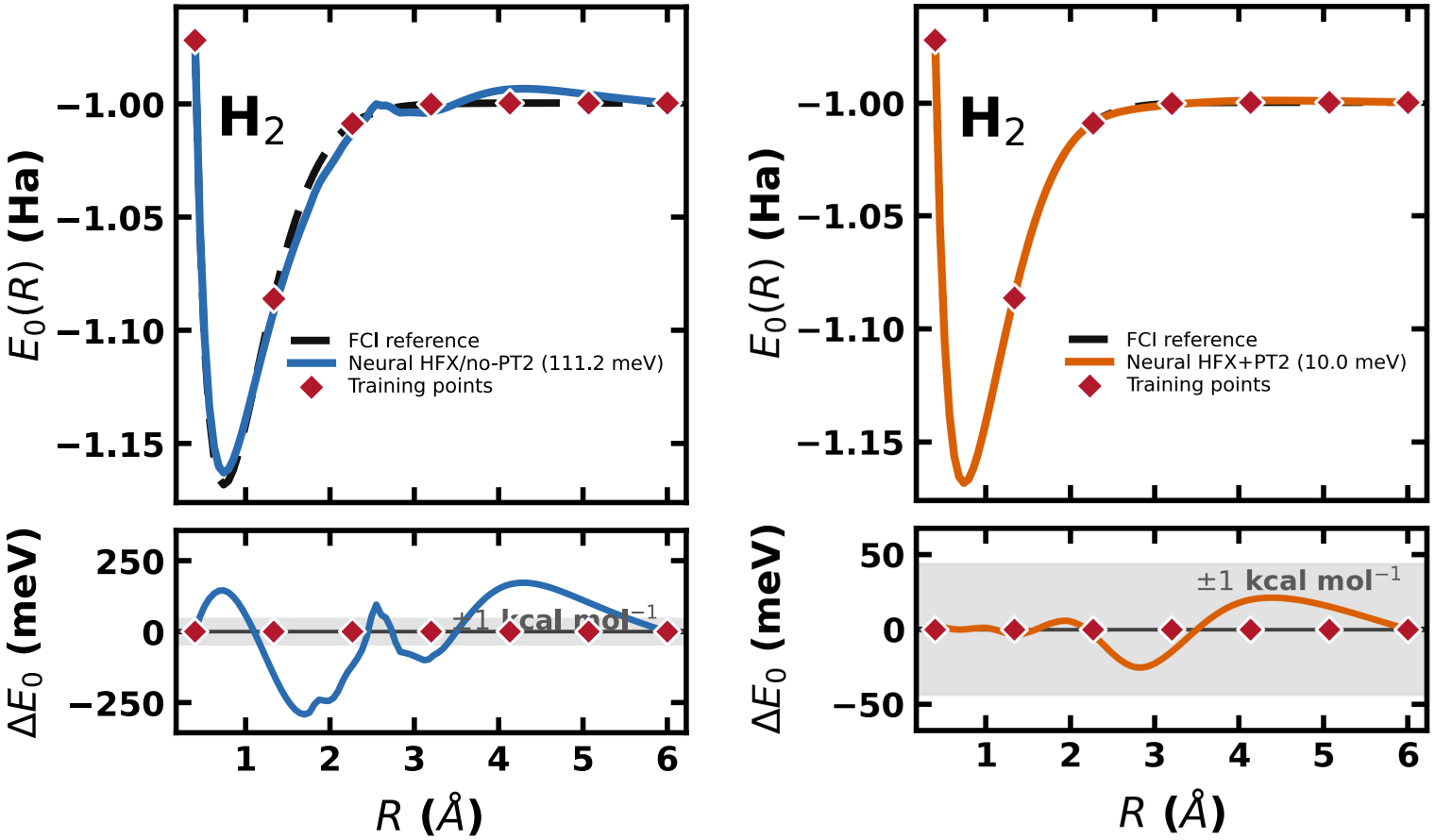
    $\psi = c_u\phi(\sigma_g^2) + c_u\phi(\sigma_u^2)$

  - **Hartree-Fock**

    $\psi_1 = \phi(\sigma_g^2) \quad \psi_2 = \phi(\sigma_u^2)$

- **Loss Function**

$$L = \frac{1}{N}\sum|E_{NN} - E_{FCI}| + \frac{1}{N^2}\sum(E_{NN} - E_{I}$$
$$+\frac{1}{N^2}\sum(\rho_{NN} - \rho_{FCI})^2$$



■ GradTDDFT – Training Modes in Neural Network XC Functional

● Implicit SCF/ Davidson Solver for H_2 Excited State S_1 with def2-TZVP, grid level = 2

- **Static Correlation Error**

  σ_g^2 **Binding Orbital**

  σ_u^2 **Antibinding Orbital**

  - **MCSCF**

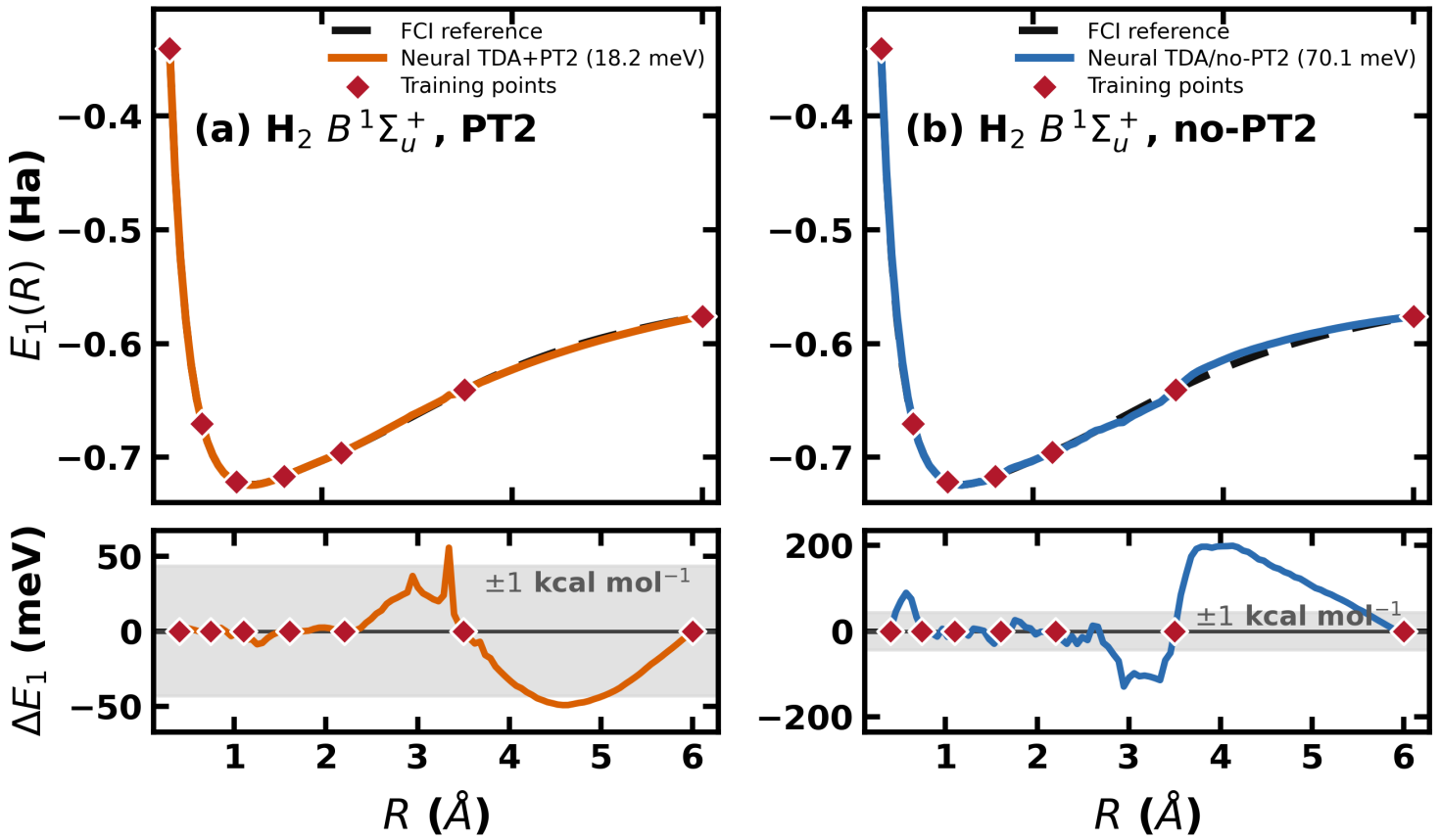
    $\psi = c_u\phi(\sigma_g^2) + c_u\phi(\sigma_u^2)$

  - **Hartree-Fock**

    $\psi_1 = \phi(\sigma_g^2) \quad \psi_2 = \phi(\sigma_u^2)$

- **Loss Function**

$$L = \frac{1}{N}\sum|E_{NN} - E_{FCI}| + \frac{1}{N^2}\sum(E_{NN} - E_{FCI})^2 + \frac{1}{N^2}\sum(\rho_{NN} - \rho_{FCI})^2$$



■ GradTDDFT – Training Modes in Neural Network XC Functional

● Implicit SCF for N_2 Ground State with def2-TZVP, grid level = 2

- **Static Correlation Error**

  $\sigma_g^2\ \pi_g$ **Binding Orbital**

  $\sigma_u^2\ \pi_u$ **Antibinding Orbital**

  - **MCSCF**

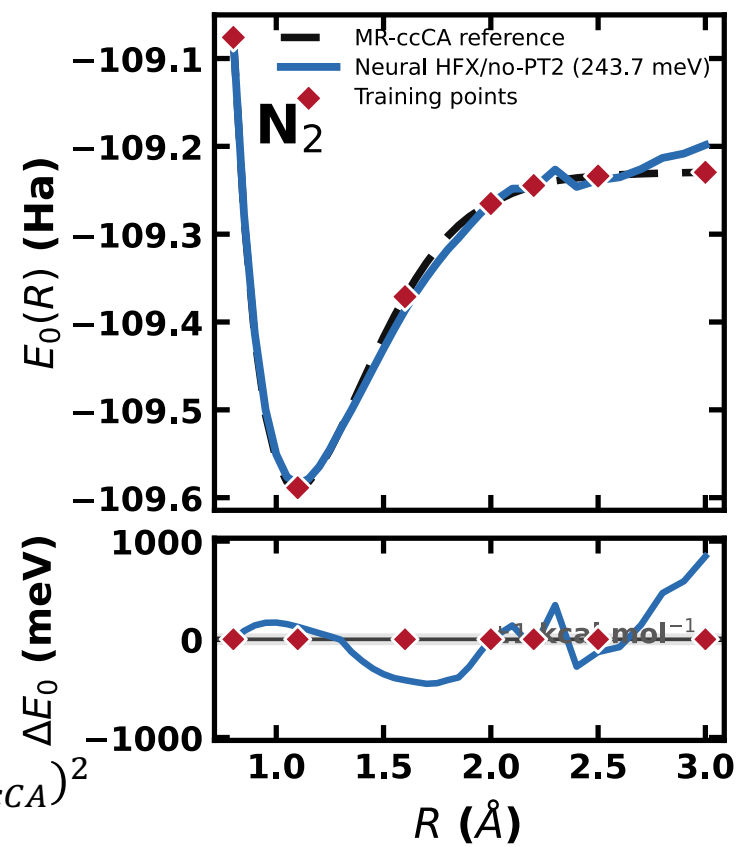
    $\psi = c_u\phi(\sigma_g^2) + c_u\phi(\sigma_u^2) + \cdots$

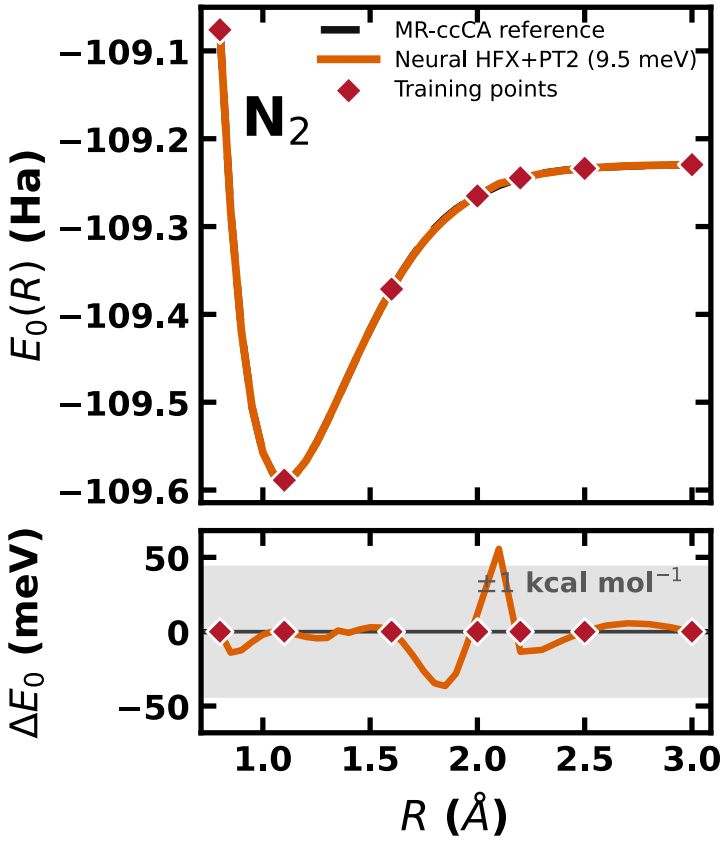
  - **Hartree-Fock**

    $\psi_1 = \phi(\sigma_g^2)\quad \psi_2 = \phi(\sigma_u^2)$

- **Loss Function**

$$L = \frac{1}{N}\sum|E_{NN} - E_{MR-ccCA}| + \frac{1}{N^2}\sum(E_{NN} - E_{MR-ccCA})^2$$





■ GradTDDFT – Training Modes in Neural Network XC Functional

- Implicit SCF/Davidson Solver for N_2 Excited State S_1 with def2-TZVP, grid level = 2

- **Static Correlation Error**

  $\sigma_g^2\ \pi_g$ **Binding Orbital**

  $\sigma_u^2\ \pi_u$ **Antibinding Orbital**

  - **MCSCF**

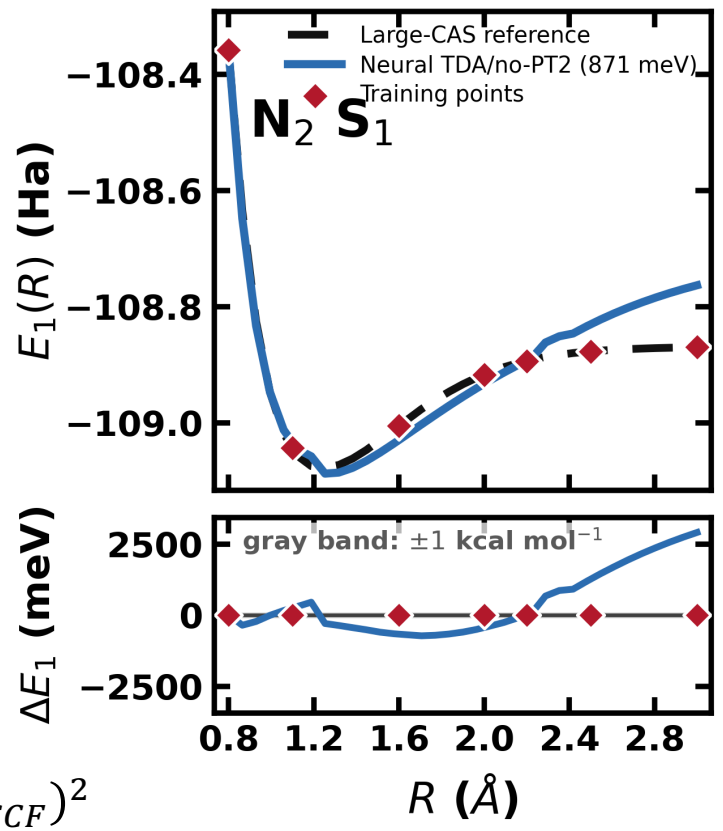
    $\psi = c_u\phi(\sigma_g^2) + c_u\phi(\sigma_u^2) + \cdots$

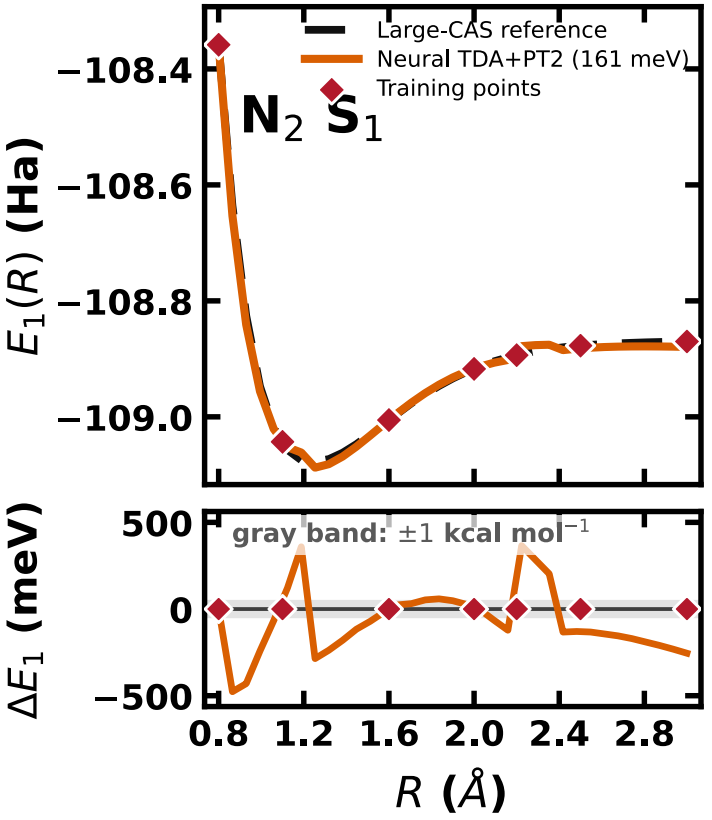
  - **Hartree-Fock**

    $\psi_1 = \phi(\sigma_g^2)\quad \psi_2 = \phi(\sigma_u^2)\ \cdots$

- **Loss Function**

$$L = \frac{1}{N}\sum|E_{NN} - E_{CASSCF}| + \frac{1}{N^2}\sum(E_{NN} - E_{CASSCF})^2$$

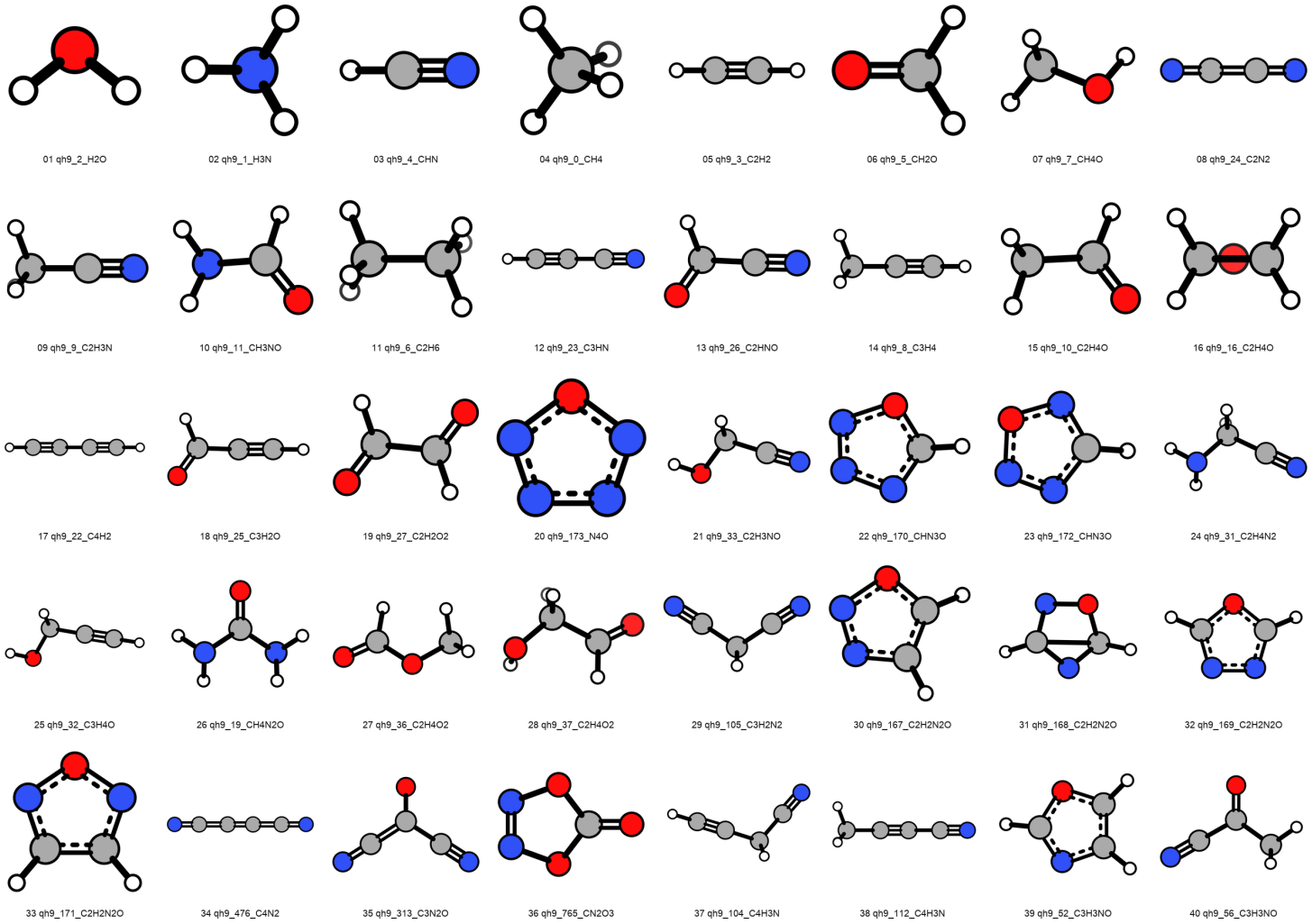




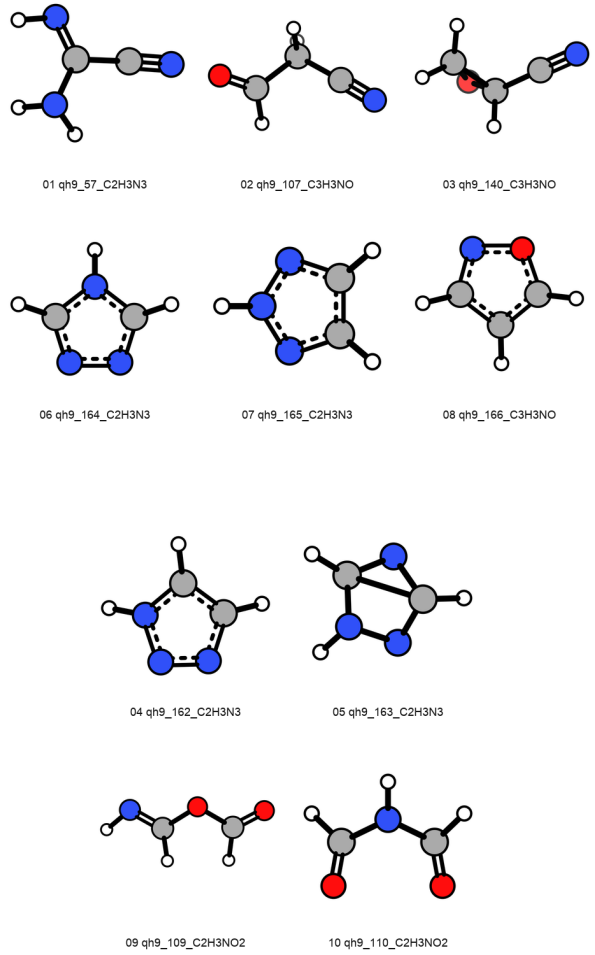
GradTDDFT – Training Modes in Neural Network XC Functional

- Implicit SCF/Davidson Solver for QH9

Training Set

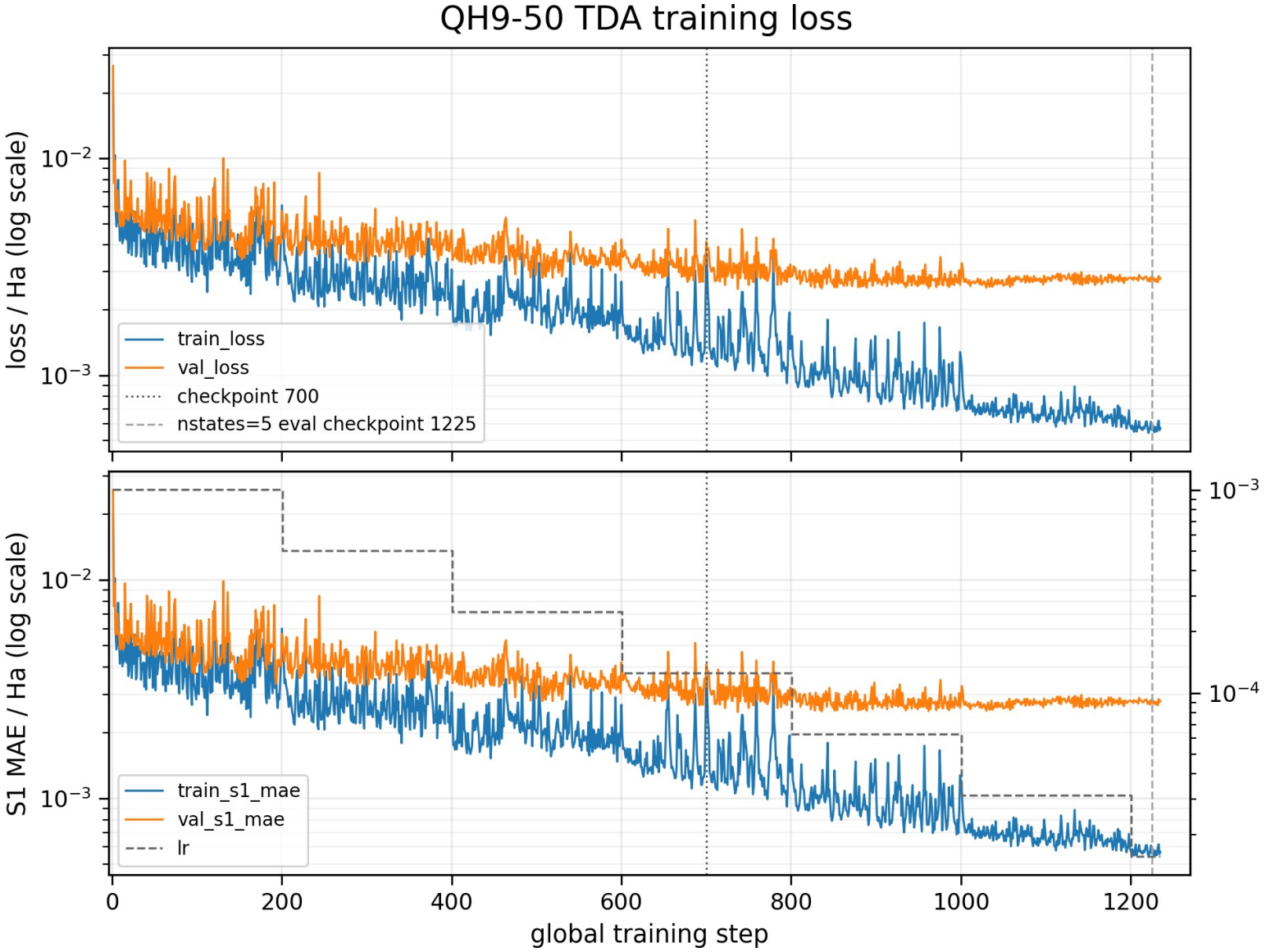


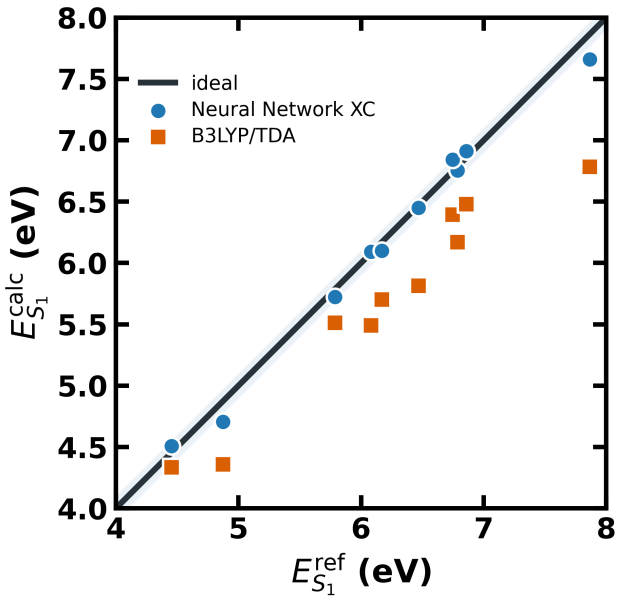
Validation Set

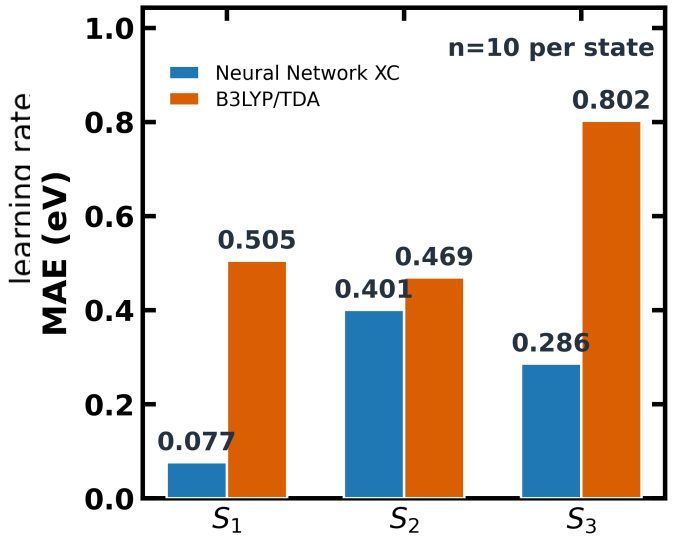


■ GradTDDFT – Training Modes in Neural Network XC Functional

- **Implicit SCF/Davidson Solver for QH9 Excited State S_1 with def2-SVP, grid level = 1**

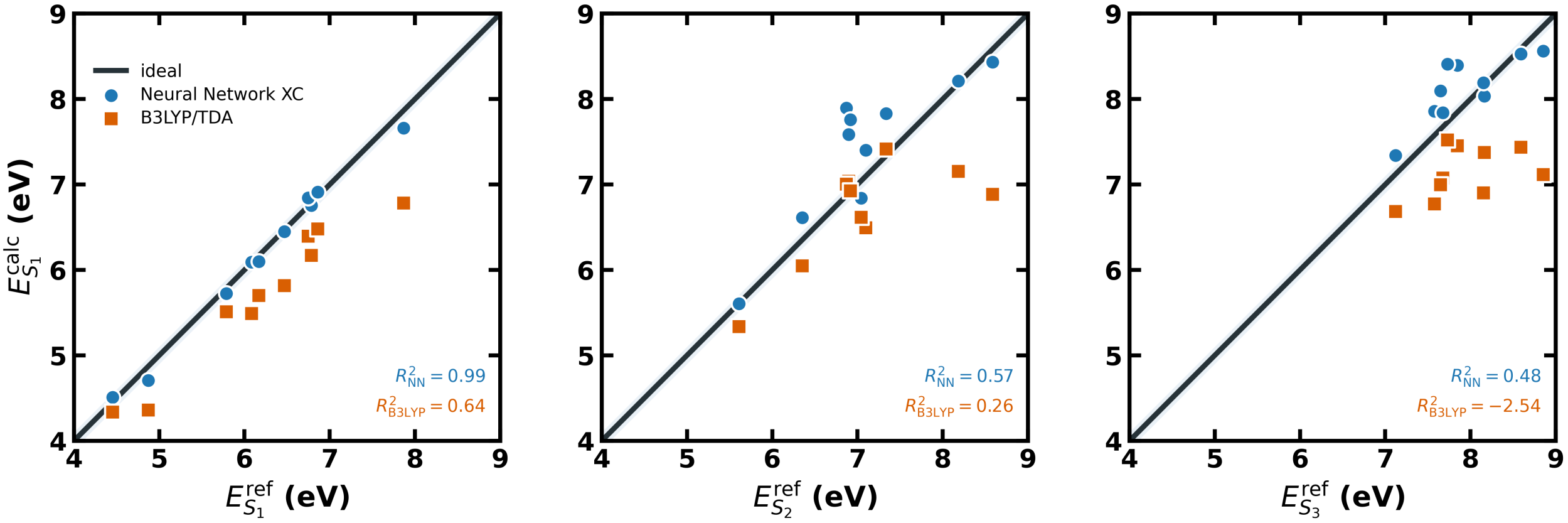






■ GradTDDFT – Training Modes in Neural Network XC Functional

- Implicit SCF/Davidson Solver for QM9 Excited State S_1 with def2-SVP, grid level = 1



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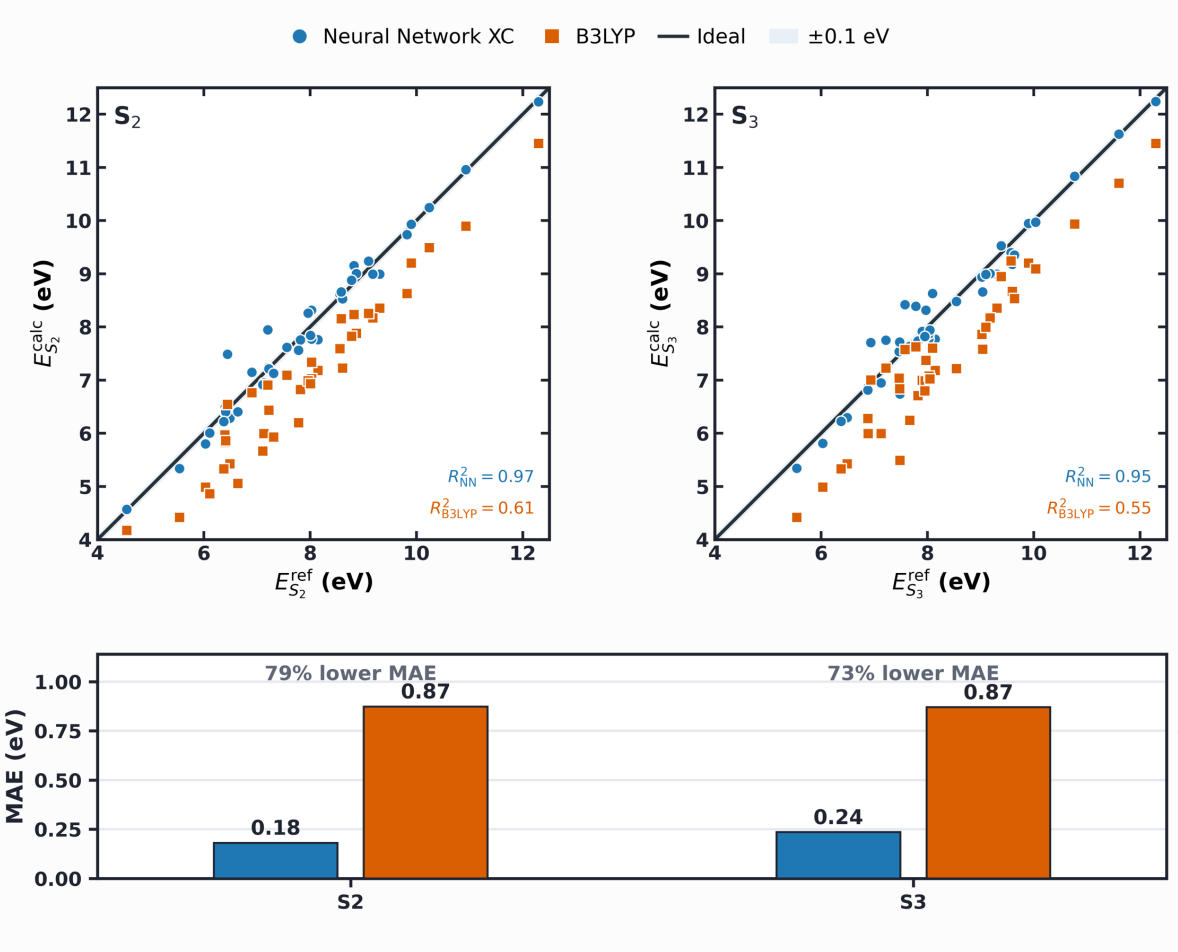
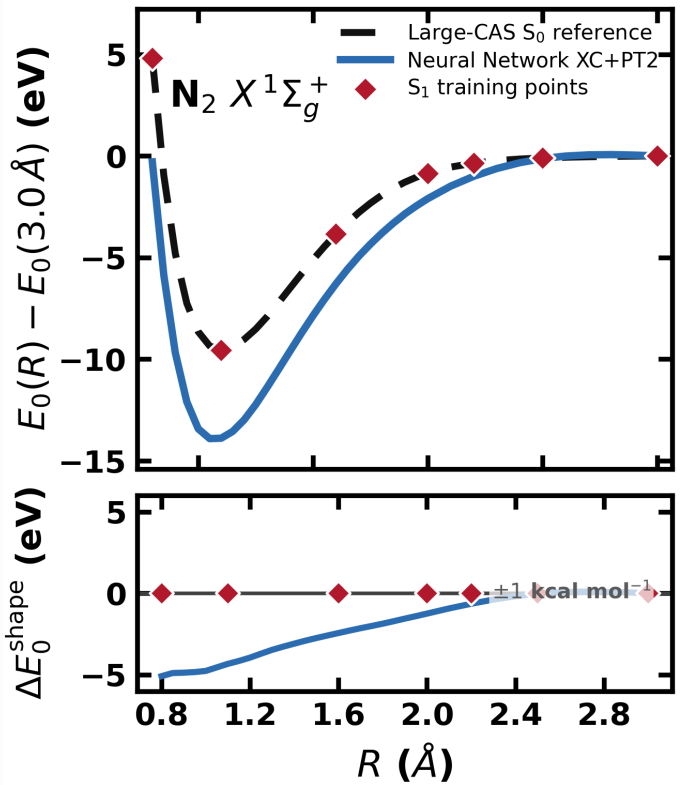
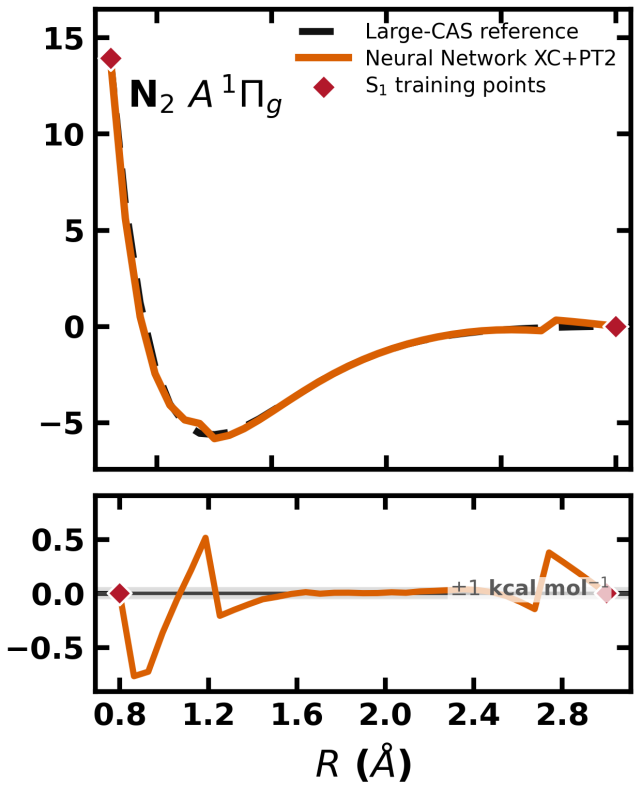
- **Implicit SCF/Davidson Solver for QH9 Excited State S_1 with def2-SVP, grid level = 1**

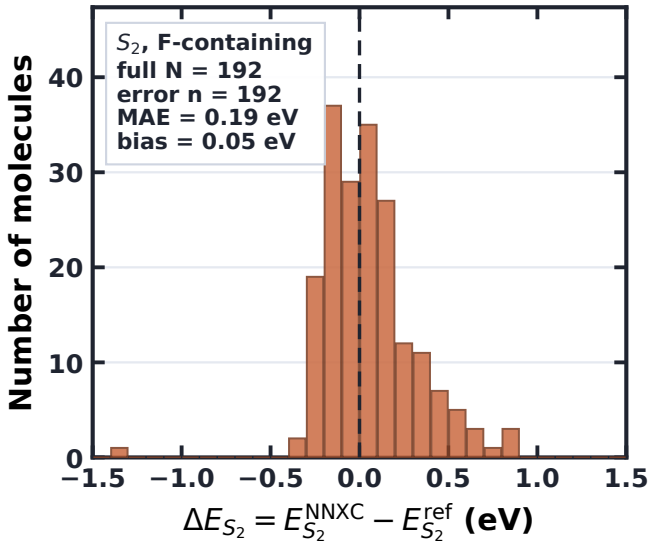


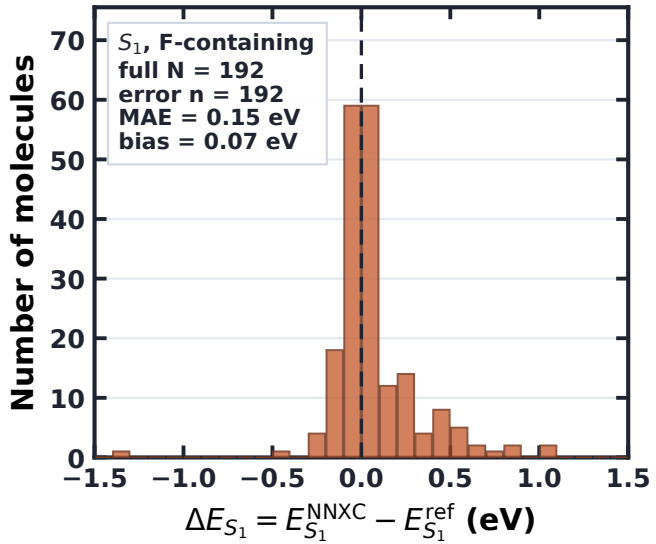


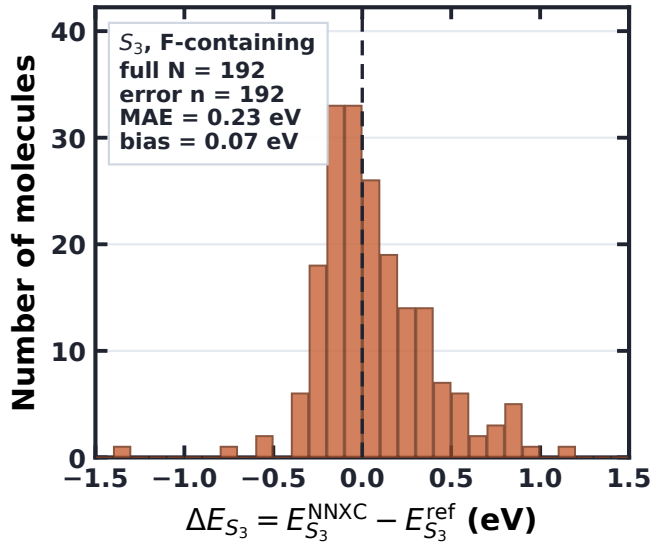


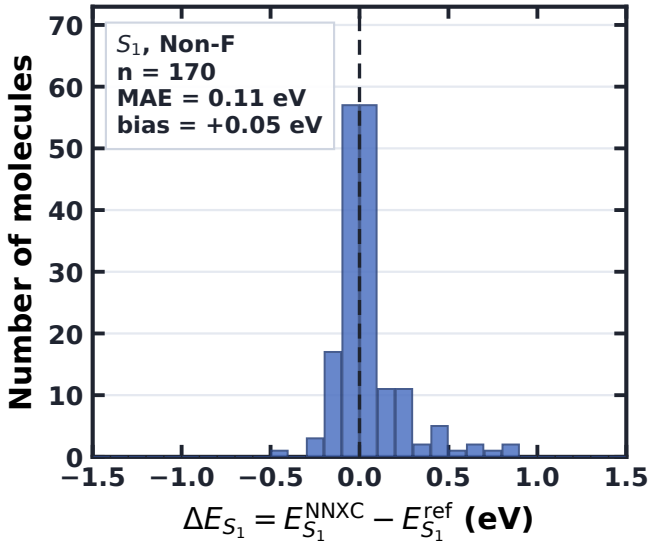
■ GradTDDFT – Training Modes in Neural Network XC Functional

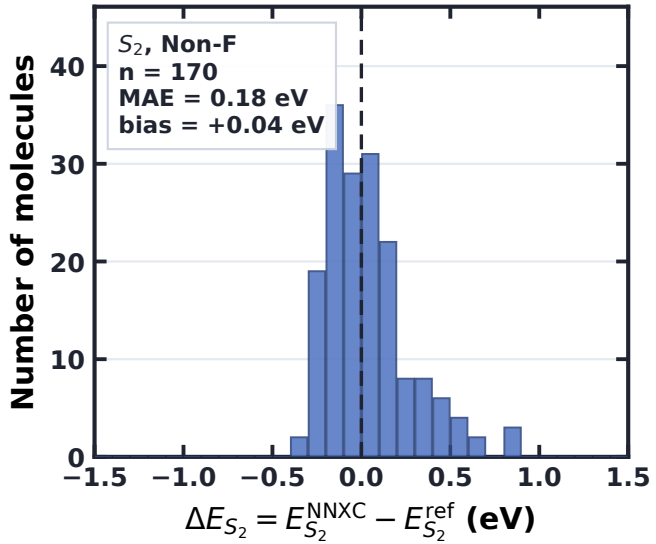
- Implicit SCF/Davidson Solver for QH9 Excited State S_1 with def2-SVP, grid level = 1

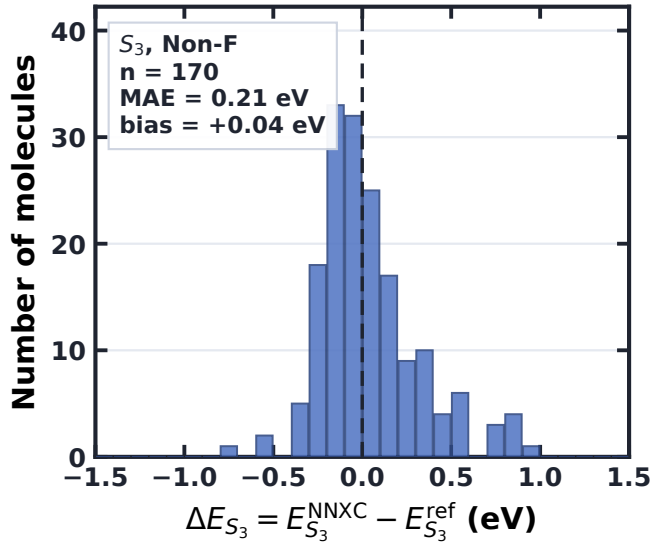






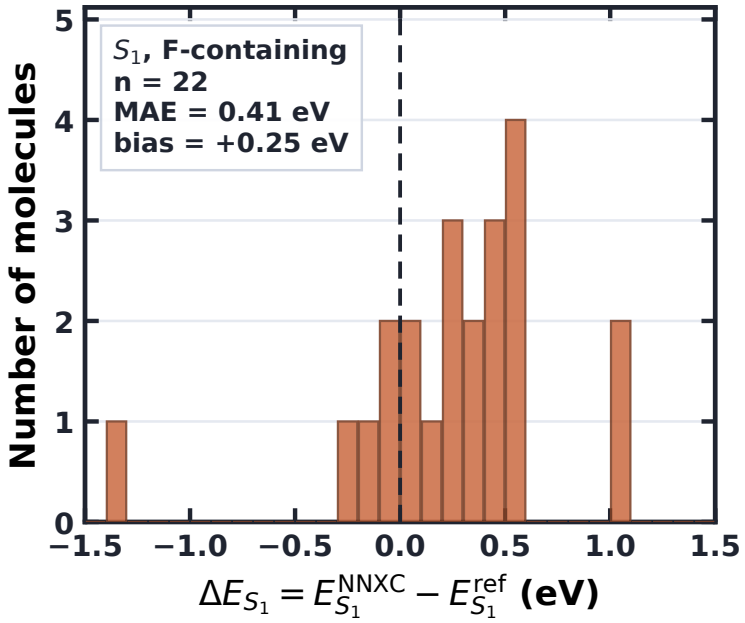


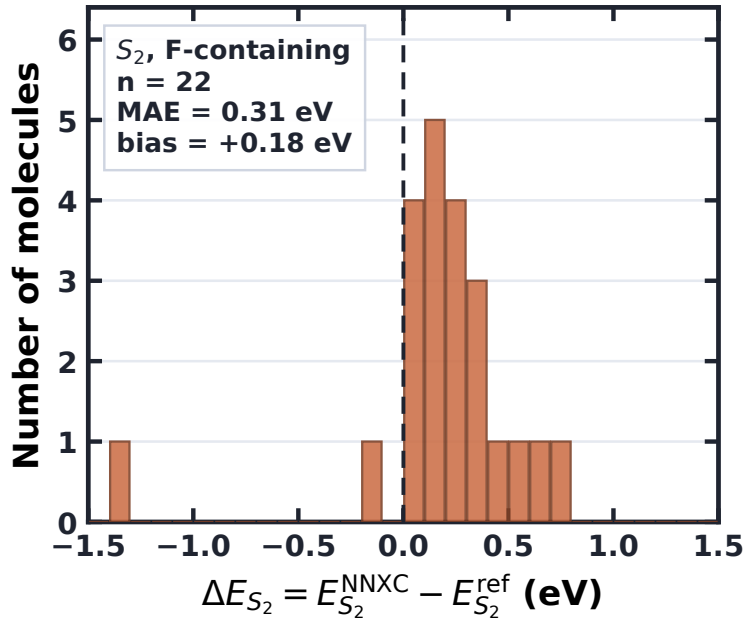


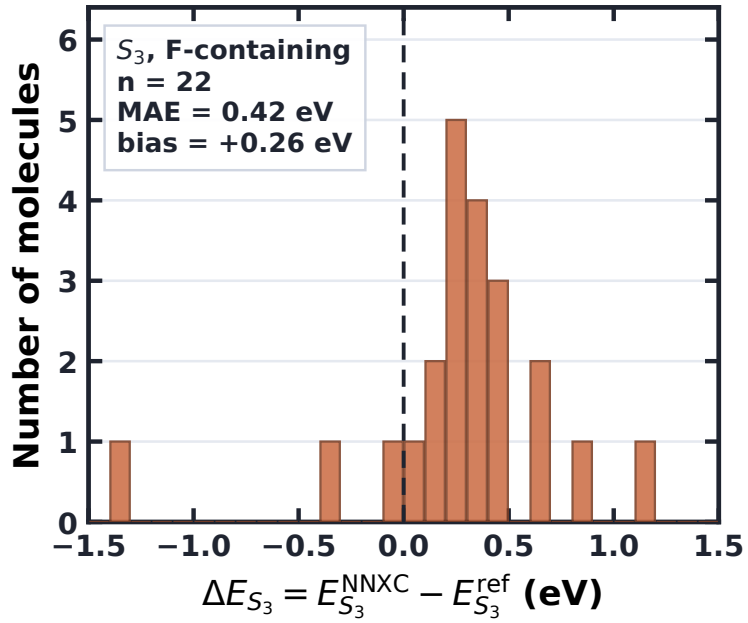


■ GradTDDFT – Training Modes in Neural Network XC Functional

- Implicit SCF/Davidson Solver for QH9 Excited State S_1 with def2-SVP, grid level = 1

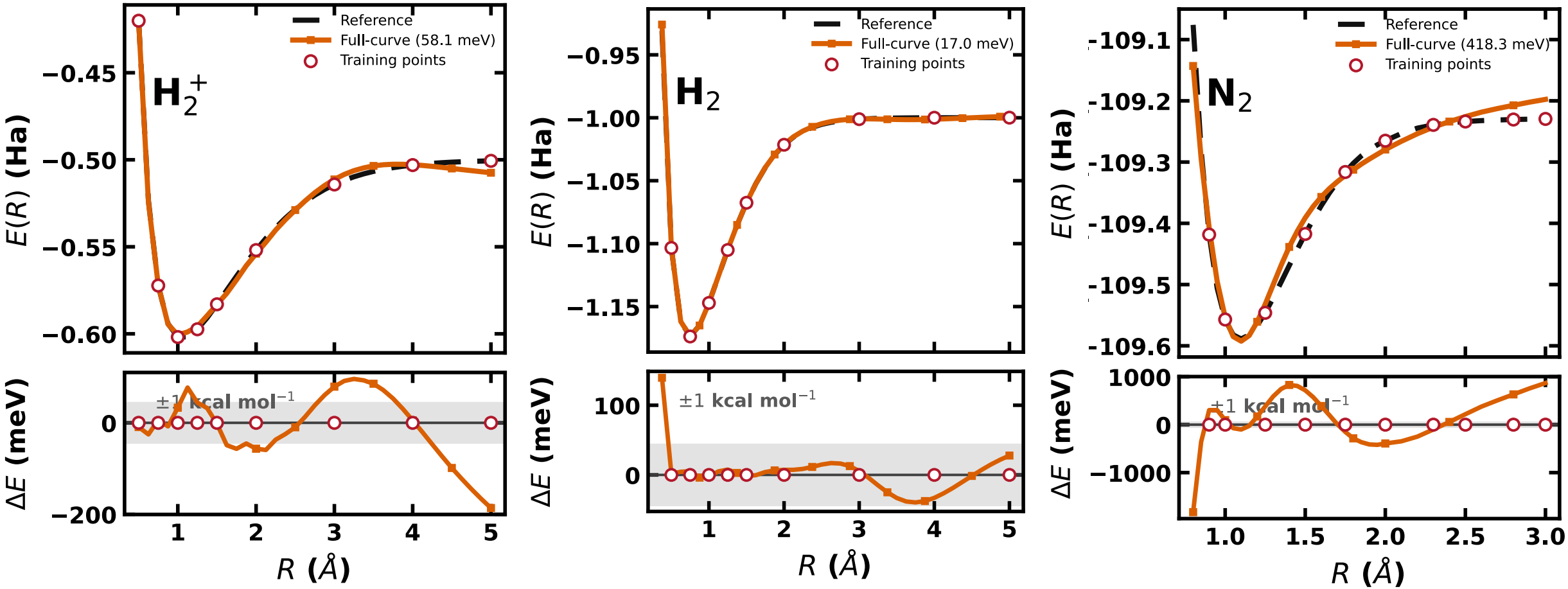




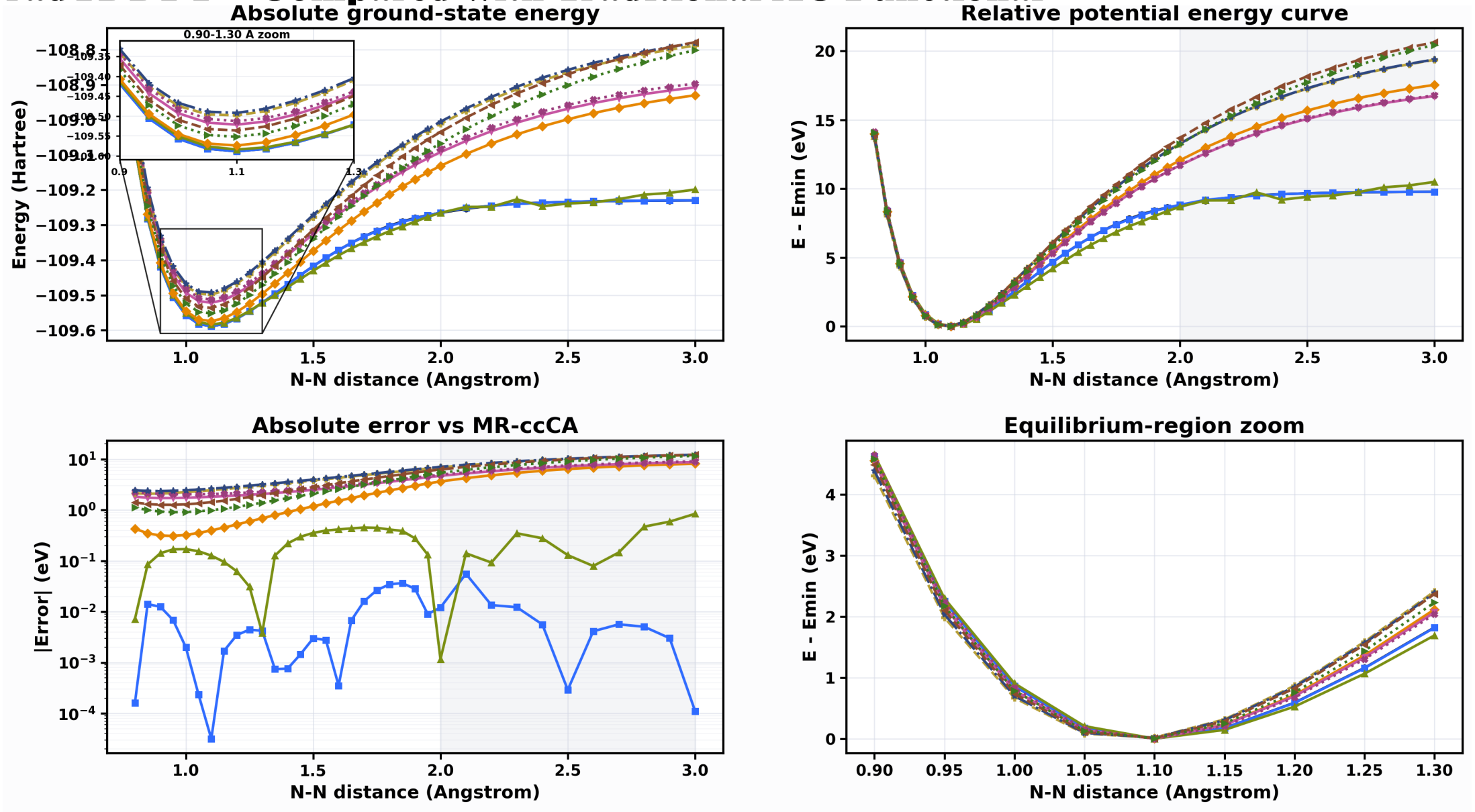


■ GradTDDFT – Compared with GradDFT

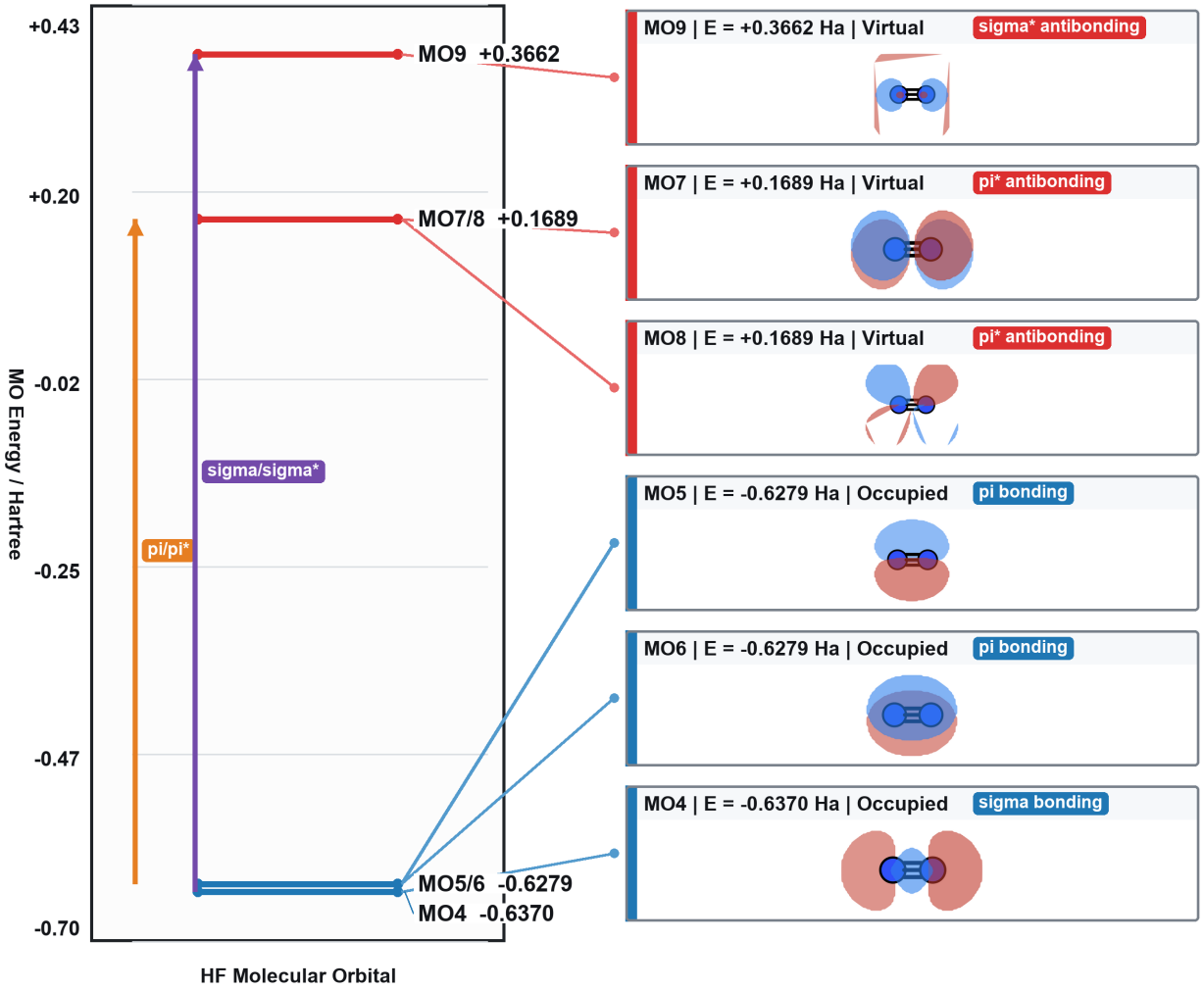
- GradDFT

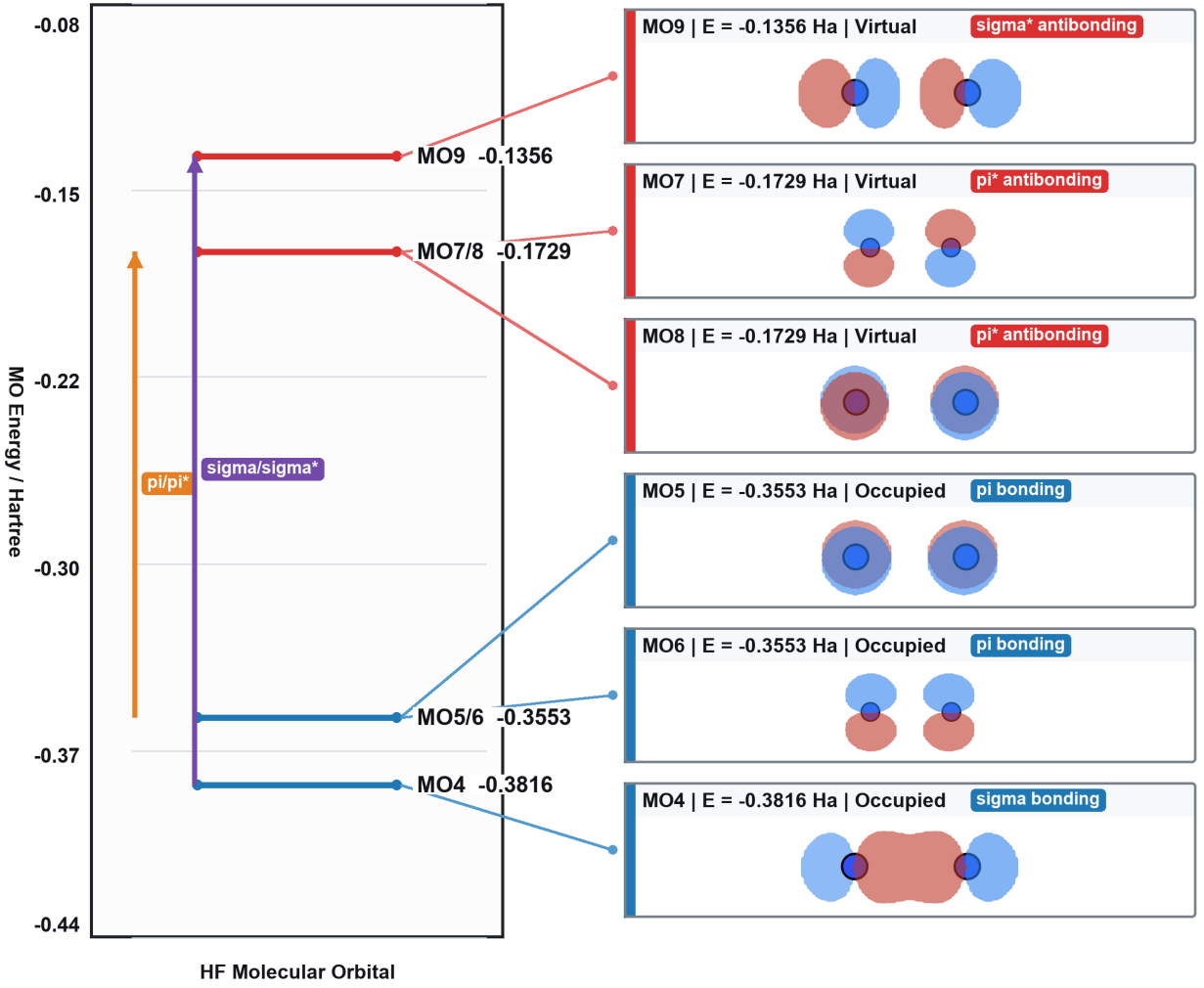


GradTDDFT – Compared with Traditional XC Functional



■ MCSCF – Limitation of GradTDDFT?





■ MCSCF – Limitation of GradTDDFT?

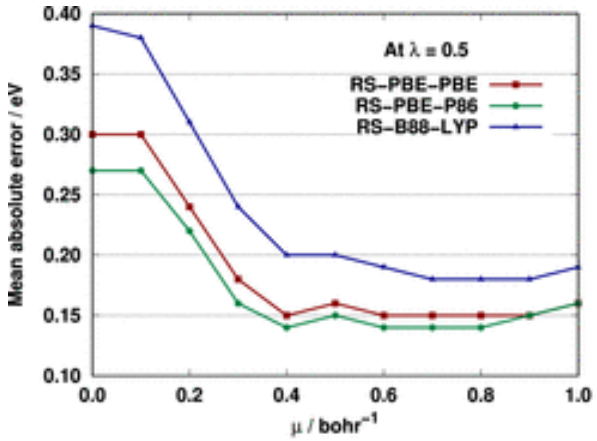
- **TDDFT is not a rigorous theorem for excited state wave function**

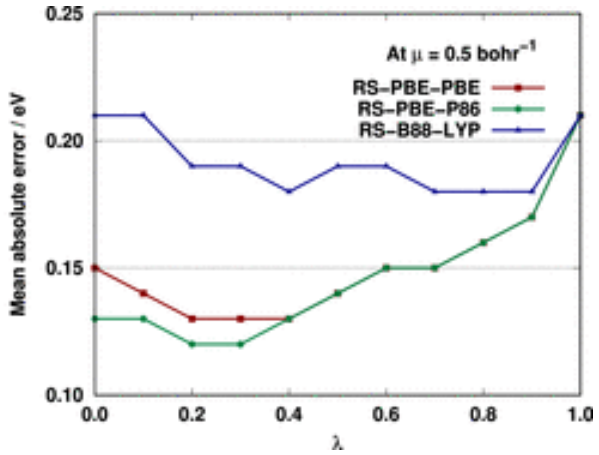
$$\psi_{ex}^{CIS} = \phi_0 + \sum_{ai} x_{ai}\phi_a^i$$

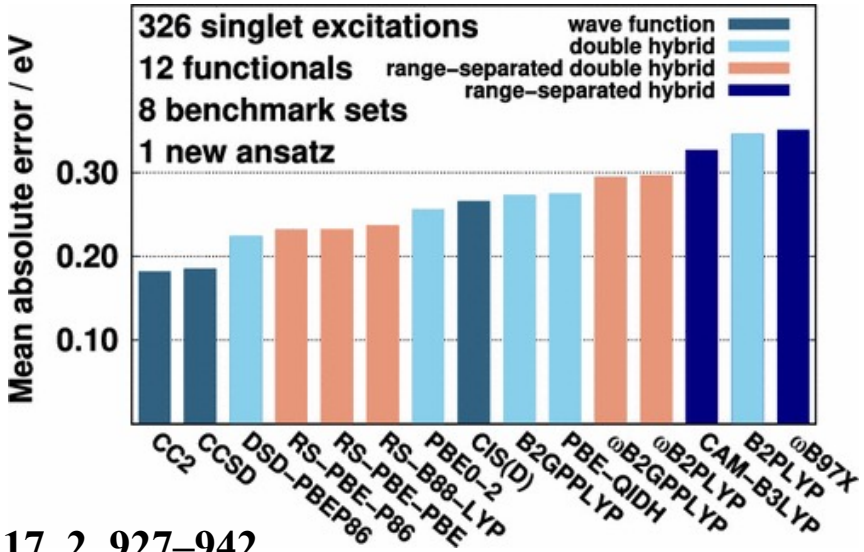
$$\psi_{ex}^{FCI} = \phi_0 + \sum_{ai} c_{ai}\phi_a^i + \sum_{aibj} c_{aibj}\phi_{ab}^{ij} + \sum_{aibjck} c_{aibjck}\phi_{abc}^{ijk} + \cdots$$

- **No Ground Truth has a good performance both on ground state and excited state for complex electron configuration**

But !







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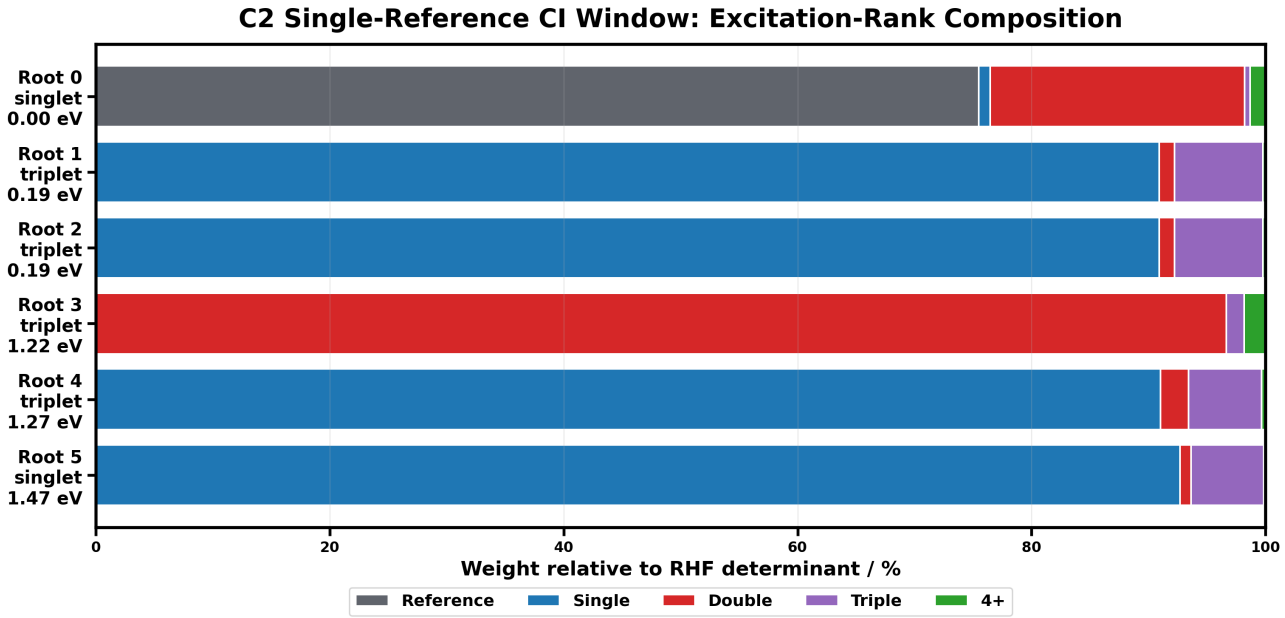
■ MCSCF – Electron Correlation in HF

- **Dynamic Correlation Error**

$$\psi_{CIS} = \phi_0 + \sum_{ai} x_{ai}\phi_a^i$$

$$\psi_{CISD} = \phi_0 + \sum_{ai} c_{ai}\phi_a^i + \sum_{aibj} c_{aibj}\phi_{ab}^{ij}$$

$$\psi_{CISDT} = \phi_0 + \sum_{ai} c_{ai}\phi_a^i + \sum_{aibj} c_{aibj}\phi_{ab}^{ij} + \sum_{aibjck} c_{aibjck}\phi_{abc}^{ijk}$$



- **Static Correlation Error**

  σ_g^2 **Binding Orbital**

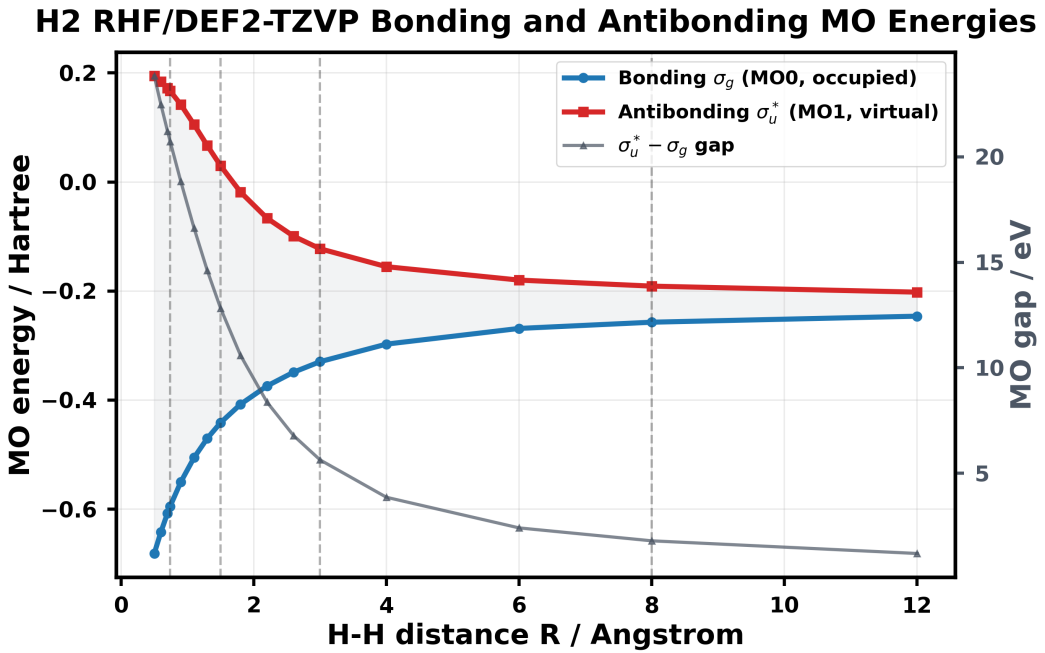
  σ_u^2 **Antibinding Orbital**

  - **MCSCF**

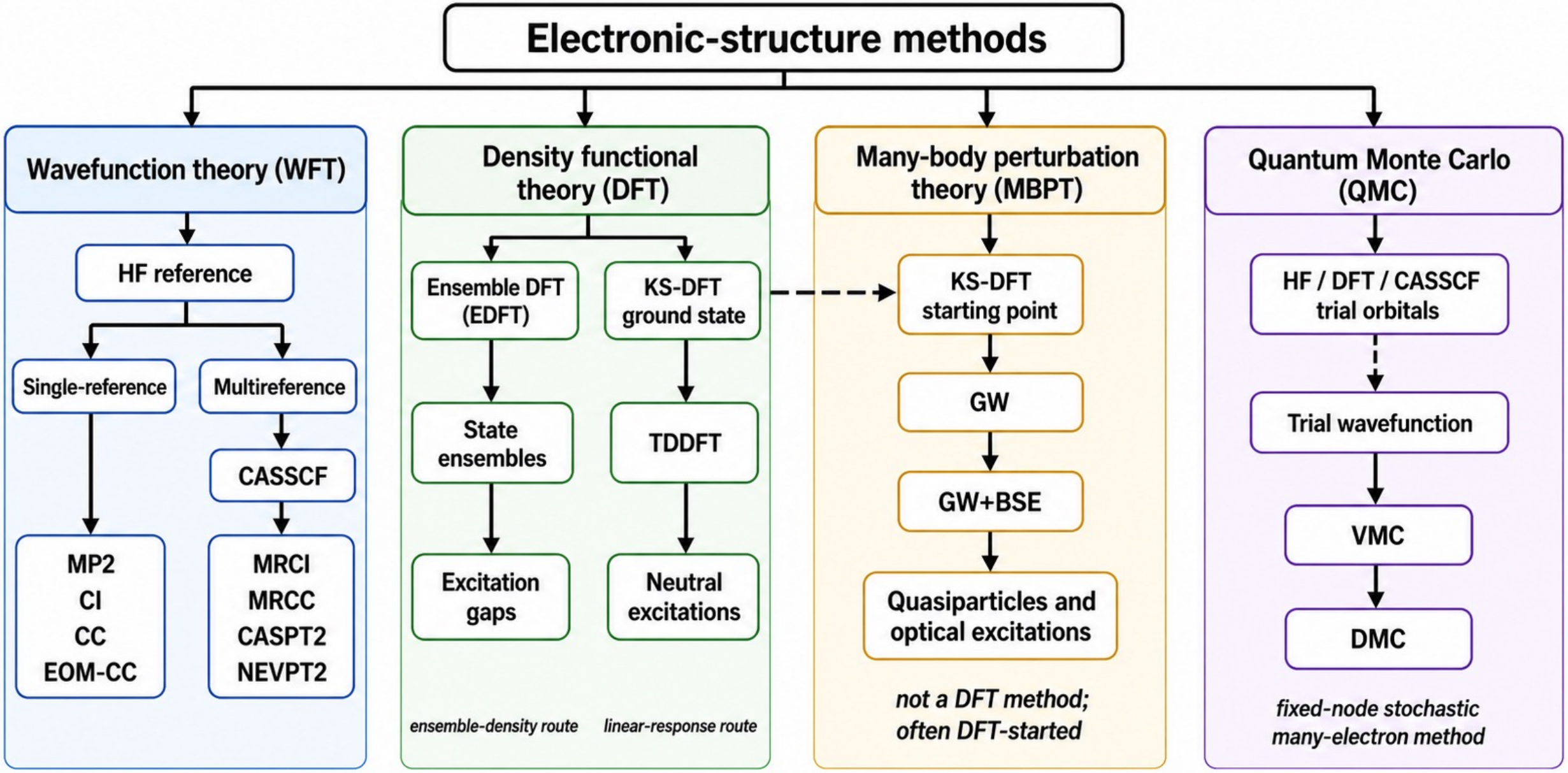
$$\psi = c_u\phi(\sigma_g^2) + c_u\phi(\sigma_u^2)$$

  - **Hartree-Fock**

$$\psi_1 = \phi(\sigma_g^2) \quad \psi_2 = \phi(\sigma_u^2)$$



■ MCSCF – Multi-Configuration Self-Consistent Field



■ MCSCF – Multi-Configuration Self-Consistent Field

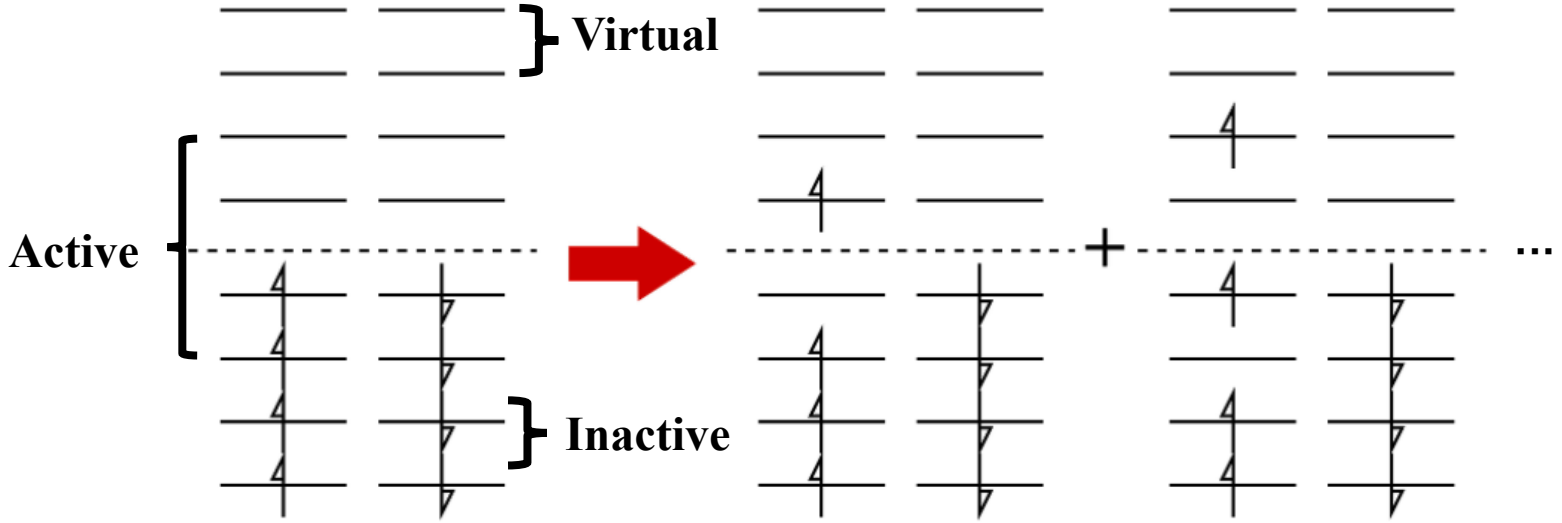
- **Basic Theory of MCSCF**

$$|\psi\rangle = \sum_I c_I |\Phi_I\{\phi_\nu\}\rangle \qquad |\Phi_I\{\phi_\nu\}\rangle = |\phi_1, \phi_2 \dots \phi_j|$$

$$\phi_\nu = \sum_k c_{\nu k}\chi_k \qquad \begin{cases} Fixed\ c_I \\ Fixed\ c_{\nu i} \end{cases}$$

$$E = \min_{c_I, c_{\nu k}} \frac{\langle \Psi(c_I, c_{\nu k}) | \hat{H} | \Psi(c_I, c_{\nu k}) \rangle}{\langle \Psi(c_I, c_{\nu k}) | \Psi(c_I, c_{\nu k}) \rangle}$$

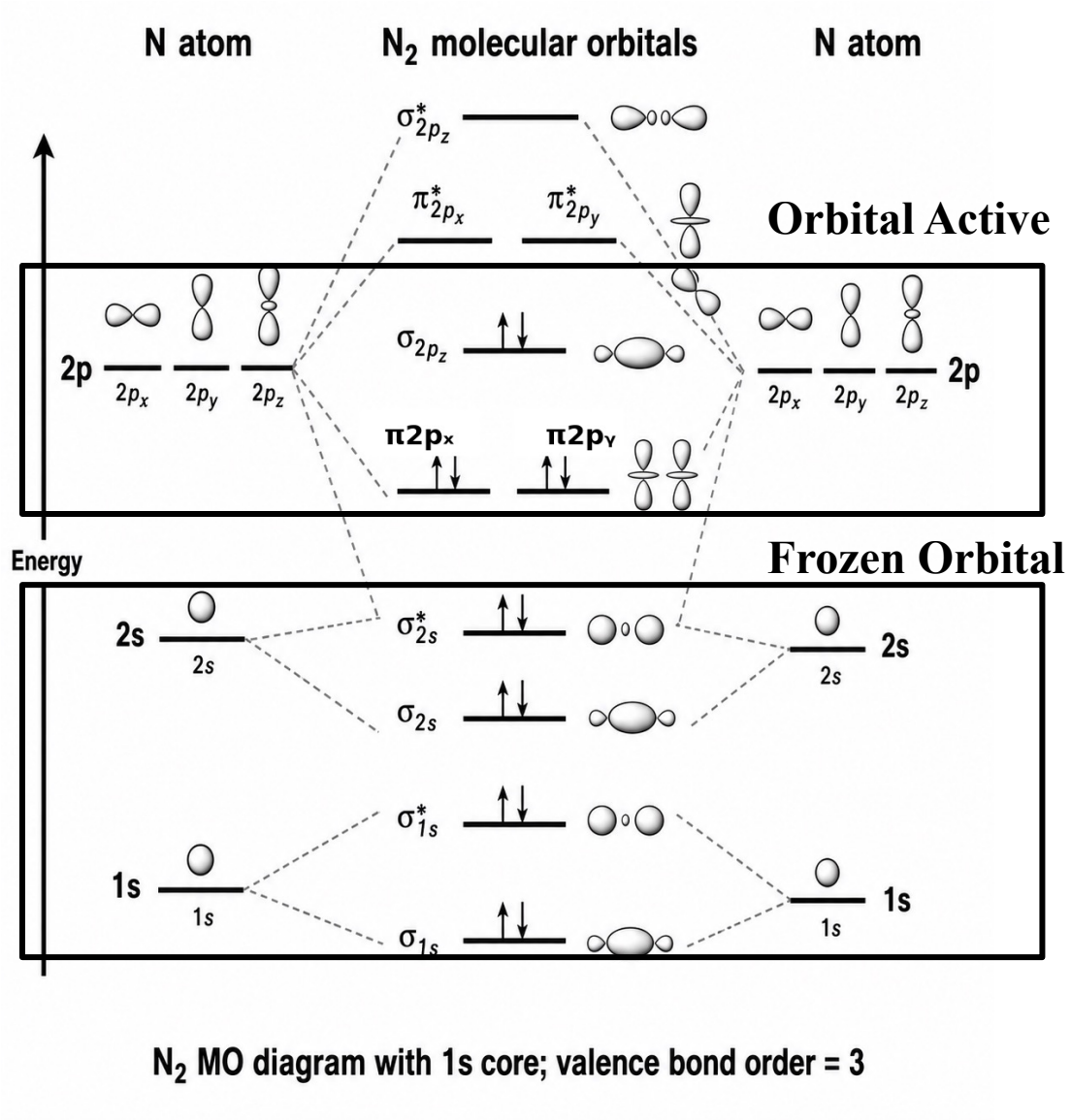
$$F_i(\{c_I\}\{c_{\nu k}\})c_i = \varepsilon_i S c_i + \sum_{j \neq i} \varepsilon_{ij} S c_j$$



- **FCI in Active Space-CASSCF**

$$\psi = \sum_I c_I \Phi_I \longrightarrow \begin{cases} Inactive\ space \\ active\ space \\ virtual\ space \end{cases} \longrightarrow \begin{array}{l} |\psi_{CAS}\rangle = |\psi_{\text{core}}\rangle \wedge |\psi_{\text{active}}\rangle \\ |\psi_{\text{active}}\rangle \rightarrow FCI\ in\ active \\ |\psi_{core}\rangle = \prod a_{i\alpha}^{+} a_{i\beta}^{+} |0\rangle \end{array} \longrightarrow E = \min_{c_I, c_{\nu k}} \frac{\langle \Psi(c_I, c_{\nu k}) | \hat{H} | \Psi(c_I, c_{\nu k}) \rangle}{\langle \Psi(c_I, c_{\nu k}) | \Psi(c_I c_{\nu k}) \rangle}$$

■ MCSCF – Multi-Configuration Self-Consistent Field



N_2 MO diagram with 1s core; valence bond order = 3

$2p_x, 2p_y, 2p_z$ $\quad (3\sigma\ \ )^2(1\pi_x)^2(1\pi_y)^2$

Stable Configuration

$$|\psi\rangle = |(3\sigma\ \ )^2(1\pi_x)^2(1\pi_y)^2\rangle$$

HF/DFT→Single Slater Determinant is enough!

Stretched Configuration

$$E(1\pi_x)\sim E(1\pi_x^*)\ E(1\pi_y)\sim E(1\pi_y^*)\ E(3\sigma\ \ )\sim E(3\sigma^*)$$

$$|\psi\rangle = |(3\sigma\ \ )^2(1\pi_x)^2(1\pi_y)^2\rangle$$

CAS(6,6)←Single Slater Determinant is not enough!

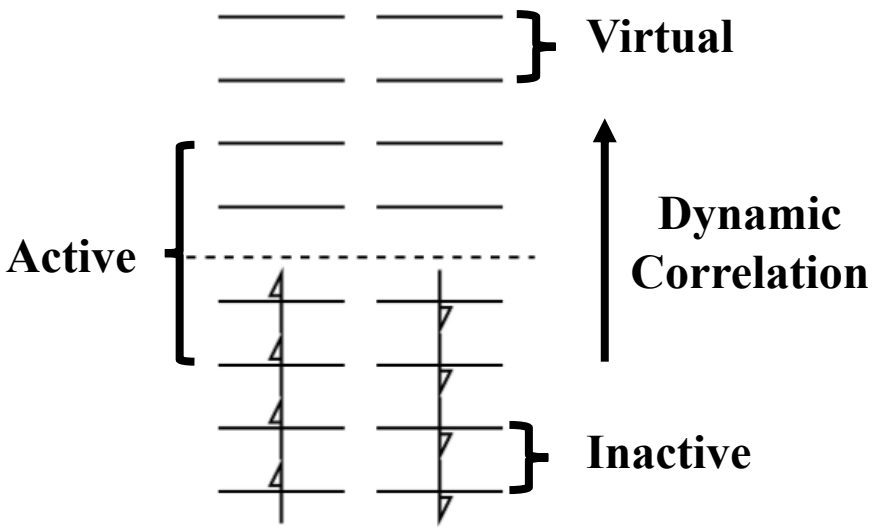
$$|\psi_{CASSCF}\rangle = C_1\,|(3\sigma)^2(1\pi_x)^2(1\pi_y)^2\rangle + C_2\,|(3\sigma)^1(3\sigma^*)^1(1\pi_x)^2(1\pi_y)^2\rangle + \cdots + C_{400}\,|(3\sigma^*)^2(1\pi_x^*)^2(1\pi_y^*)^2\rangle$$

■ MCSCF – CASPT2

- **Dynamic Correlation of CASSCF**

$$|\psi_{CASSCF}\rangle = |\Psi_0\rangle = \sum_{I \in CAS} c_I |\Phi_I\{\phi_v\}\rangle$$

$$P = \sum_{I \in CAS} |\Phi_I\{\phi_v\}\rangle\langle|\Phi_I\{\phi_v\}| \quad Q = \mathbb{I} - P$$



- **Reference Hamiltonian of CASSCF**

$$f_{pq} = h_{pq} + \sum_{rs} D_{rs} \left[(pq|rs) - \frac{1}{2}(pr|sq) \right]$$

$$\hat{f} = \sum_{pq} f_{pq}\, \hat{\mathrm{E}}_{\mathrm{pq}} \qquad \hat{\mathrm{E}}_{\mathrm{pq}} = \sum_{\sigma} a^{+}_{p\sigma} a_{q\sigma} \quad \langle \Psi_0 | \hat{f} | \Psi_0 \rangle \neq E_{CAS}$$

$$\hat{F} = \hat{f} + E_{CAS} - \langle \Psi_0 | \hat{f} | \Psi_0 \rangle$$

$$\hat{H}_0 = P\hat{F}P + Q\hat{F}Q \quad P\hat{H}_0 Q = Q\hat{H}_0 P = 0 \quad \hat{H}_0 |\Psi_0\rangle = E_{CAS} |\Psi_0\rangle \quad \hat{H}_0 |\Omega_\mu\rangle = E_\mu^{(0)} |\Omega_\mu\rangle$$

$$\hat{H} = E_{nuc} + \sum_{pq} h_{pq}\, a_p^{+} a_q + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle\, a_p^{+} a_q^{+} a_s a_r \qquad \hat{H} = \hat{H}_0 + \hat{\mathrm{V}}$$

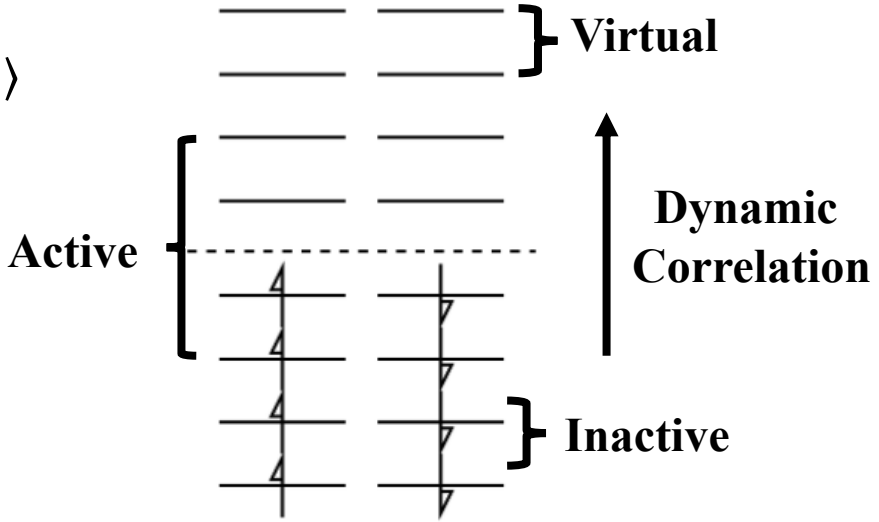
$$\langle \psi_{CASPT2} | \hat{H} | \psi_{CASPT2} \rangle = \begin{pmatrix} \langle \Psi_0 | \hat{H} | \Psi_0 \rangle & \langle \Psi_0 | \hat{H} | \Omega_\nu \rangle \\ \langle \Omega_\mu | \hat{H} | \Psi_0 \rangle & \langle \Omega_\mu | \hat{H} | \Omega_\nu \rangle \end{pmatrix} \qquad \langle \psi_{CASPT2} | \hat{H}_0 | \psi_{CASPT2} \rangle = \begin{pmatrix} E_{CAS} & 0 \\ 0 & \langle \Omega_\mu | \hat{F} | \Omega_\nu \rangle \end{pmatrix}$$

■ MCSCF – CASPT2

- **Single and Double Excitation of CASSCF Wave Function**

$$|\psi_{CASPT2}\rangle = \sum_{I\in CAS} c_I|\Phi_I\{\phi_\nu\}\rangle + \sum_\mu T_\mu|\Omega_\mu\rangle = |\Psi_0\rangle + |\Psi_1\rangle$$

$$|\Omega_\mu\rangle = QE_\mu|\psi_{CASSCF}\rangle$$



- **Single and Double Excitation of CASSCF Wave Function**

$$\left(\hat{H}_0 - E^{(0)}\right)\left|\Psi^{(1)}\right\rangle = -\left(\hat{V} - E^{(1)}\right)\left|\Psi^{(0)}\right\rangle$$

$$P|\Psi_1\rangle = 0, \qquad |\Psi_1\rangle = Q|\Psi_1\rangle, \qquad Q|\Psi_0\rangle = 0$$

$$\text{left} = Q\left(\hat{H}_0 - E_{CAS}\right)Q|\Psi_1\rangle$$

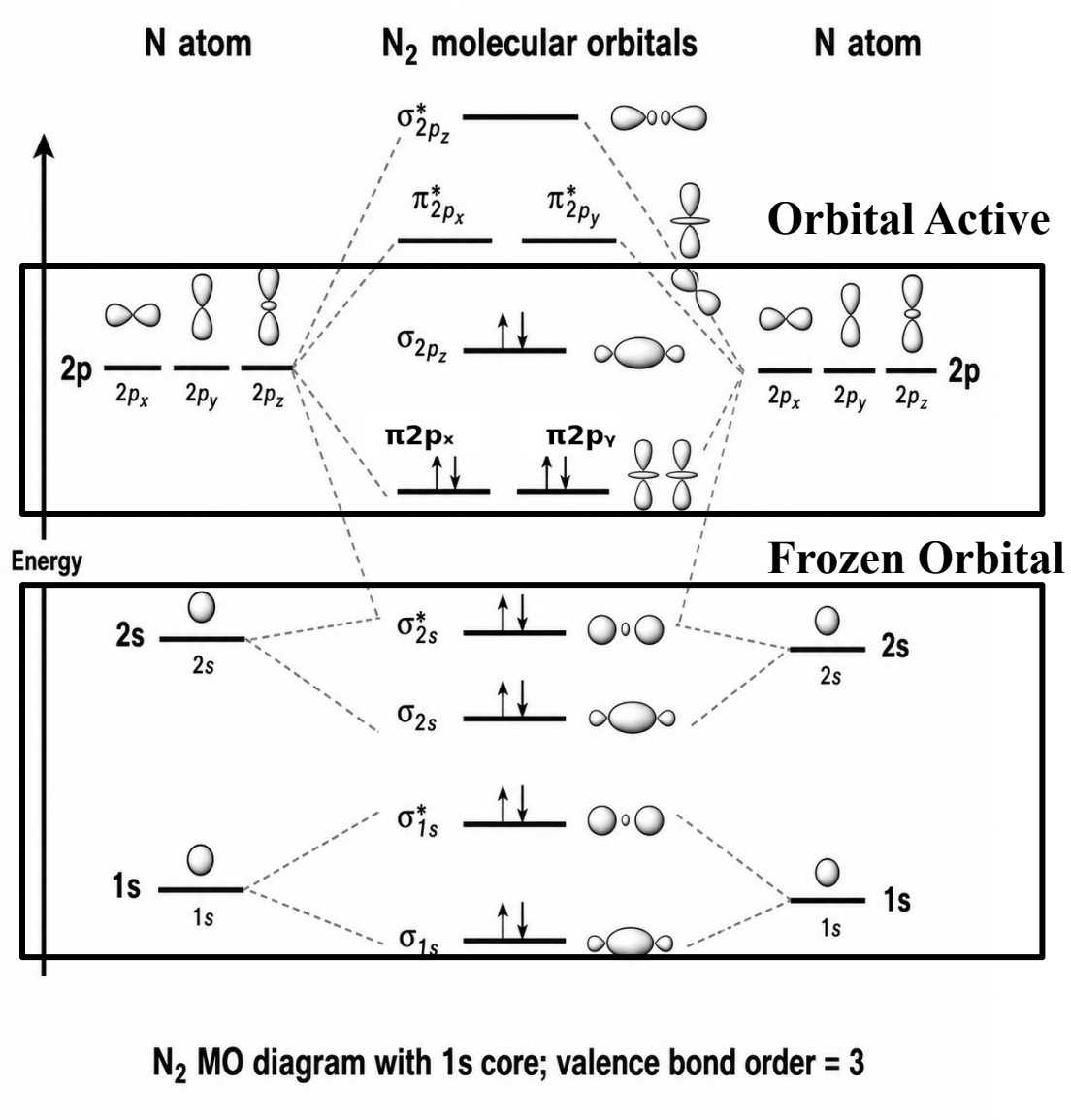
$$\begin{aligned} right &= -Q\left(\hat{V} - E^{(1)}\right)\left|\Psi^{(0)}\right\rangle \\ &= -Q\hat{V}|\Psi_0\rangle \\ &= -Q\left(\hat{H} - \hat{H}_0\right)|\Psi_0\rangle \\ &= -Q\hat{H}|\Psi_0\rangle \end{aligned}$$

$$Q\left(\hat{H}_0 - E_{\text{CAS}}\right)\left|\Psi_1\right\rangle = -Q\hat{H}|\Psi_0\rangle$$

$$\sum_\nu \left\langle\Omega_\mu\left|\hat{H}_0 - E_{CAS}\right|\Omega_\nu\right\rangle T_\nu = -\left\langle\Omega_\mu\left|\hat{H}\right|\Psi_0\right\rangle$$

$$E^{(1)} = 0 \qquad E^{(2)} \approx \sum_\mu \frac{\left|\left\langle\Omega_\mu\left|\hat{H}\right|\Psi_0\right\rangle\right|^2}{E_{CAS} - E_\mu^{(0)}}$$

■ MCSCF – CASPT2



N2 MO diagram with 1s core; valence bond order = 3

Stretched Configuration

$$E(\pi_x)\sim E(\pi_x^*) \quad E(\pi_y)\sim E(\pi_y^*) \quad E(\sigma)\sim E(\sigma^*)$$

CAS(6,6)→Dynamic Correlation Correction

$$|\psi_{CASSCF}\rangle = C_1\,|(3\sigma)^2(1\pi_x)^2(1\pi_y)^2\rangle + C_2\,|(3\sigma)^1(3\sigma^*)^1(1\pi_x)^2(1\pi_y)^2\rangle + \cdots + C_{400}\,|(3\sigma^*)^2(1\pi_x^*)^2(1\pi_y^*)^2\rangle$$

CASPT2→Double Excitation!

$$E_\mu|\psi_{inactive}\rangle = E_\mu|(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2\rangle$$

$$E_\mu|\psi_{inactive}\rangle = E_\mu|(3\sigma^*)^2(1\pi_x^*)^2(1\pi_y^*)^2\rangle$$

$$\downarrow$$

$$E_\mu|\psi_{inactive}\rangle = |(1\sigma)^1(1\sigma^*)^1(2\sigma)^2(2\sigma^*)^2a^1b^1\rangle\cdots$$

$$E_\mu|\psi_{inactive}\rangle = |(3\sigma^*)^2(1\pi_x^*)^1(1\pi_y^*)^1a^1b^1\rangle \ldots$$

■ MCSCF – MC-PDFT

- **DFT –like Dynamic Correlation Correction**

$$E_{CASSCF} = V_{nn} + \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} (pq|rs) D_{pq} D_{rs}$$

$$E_{MC-PDFT} = V_{nn} + \langle \psi_{CASSCF} | T + V_{en} | \psi_{CASSCF} \rangle + U_H + E_{ot}[\rho, \Pi]$$

- **From XC Functional to On-Top Functional**

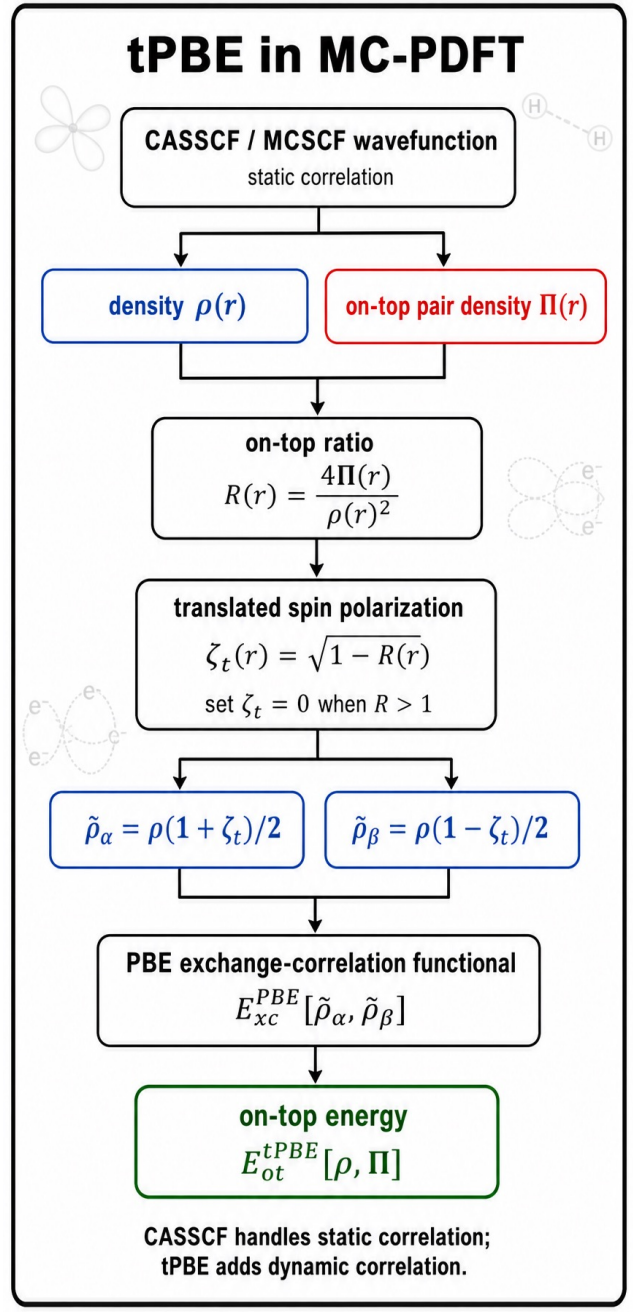
$$E_{ot}[\rho, \Pi] = \langle \psi_{FCI} | T + V_{en} | \psi_{FCI} \rangle - U_H - \langle \psi_{CASSCF} | T | \psi_{CASSCF} \rangle$$

$$R(\mathbf{r}) = \frac{4\Pi(\mathbf{r})}{\rho(\mathbf{r})^2} \qquad \Pi(\mathbf{r}) \approx \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r})$$

$$\zeta_t(\mathbf{r}) = \sqrt{1 - R(\mathbf{r})}$$

$$\widetilde{\rho_\beta} = \frac{\rho}{2}(1 - \zeta_t) \qquad \widetilde{\rho_\alpha} = \frac{\rho}{2}(1 + \zeta_t)$$

$$E_{ot}[\rho, \Pi] \approx E_{xc}^{DFT}[\widetilde{\rho_\alpha}, \widetilde{\rho_\beta}]$$



■ MCSCF – MC-PDFT

Table 3. Singlet-to-Singlet Atomic and Vertical Electronic Excitation Energies (eV)

system	Excitation Energy (eV)									
	AS[a]	CASSCF	CASPT2	tBLYP	tPBE	tGVWN3	BLYP	PBE	GVWN3	Exp
Be $^1S \rightarrow {}^1P$ ($s \rightarrow p$)	2, 4	6.2	5.7	4.2	4.4	4.3	5.0	5.0	5.0	5.28[b]
N_2 $^1\Sigma_g^+ \rightarrow {}^1\Pi_g$ ($\sigma_g \rightarrow \pi_g$)	6, 6	11.9	9.4	8.6	8.6	8.6	9.1	9.1	9.1	9.31[c]
N_2 $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^-$ ($\pi_u \rightarrow \pi_g$)	6, 6	10.9	9.8	9.5	9.6	9.6	9.6	9.7	9.7	9.92[c]
s-trans-1,3-butadiene ^1A_g to ^1B_u ($\pi \rightarrow \pi^*$)	4, 4	7.6	6.8	5.6	5.7	5.9	5.3	5.5	5.5	5.92[d]
pyrazine ^1A_g to $^1B_{3u}$ ($n \rightarrow \pi^*$)	10, 10	5.3	4.1	3.9	3.9	3.8	3.6	3.6	3.5	4.20[e]
cyclopentadiene $^1A_1$ to $^1B_2$ ($\pi \rightarrow \pi^*$)	4, 4	7.3	5.5	4.1	4.1	4.1	4.9	5.0	5.0	5.26[f,g]
formaldehyde $^1A_1$ to $^1A_2$ ($I \rightarrow \pi^*$)	8, 6	4.4	4.0	4.0	4.0	4.0	4.0	3.9	3.8	4.00[h]
mean absolute error, MAE[i]		1.4	0.3	0.6	0.5	0.5	0.3	0.3	0.3	

[a]For Be and N_2, the active space (AS) in each case is the full valence active space. For *s-trans*-1,3-butadiene, cyclopentadiene, and pyrazine, the AS includes the π electrons, π bonding and antibonding orbitals, and additional nitrogen lone pairs/orbitals for pyrazine. For formaldehyde, the AS includes all the electrons, lone pair orbitals, and bonding and antibonding orbitals of the carbonyl. [b]Data taken from ref 129. [c]Data taken from ref 130. [d]Data taken from ref 131. [e]Data taken from ref 132. [f]Data taken from ref 133. [g]Data taken from ref 134. [h]Data taken from ref 135. For N_2, an equilibrium geometry of 1.098 Å was used.[4] All other geometries were optimized according to specifications in Table S5 in the SI with M06-L.[3] [i]Mean unsigned deviation from the experimental value.

Truhlar & Gagliardi et al., JCTC 2014, 10, 3669–3680.

■ GradTDDFT – Functional and Outlook

- **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!(Mesh-Free NNXC)**
- **Automatic Differentiation for Geometry Optimization and Response Properties of molecules**

☐ **Short-Term(pre-release):**

- **Accurate Excitation Energy and Ground State Energy Reference on QH9(aug-cc-pVTZ)**
- **New Reference of all kinds of heavy atoms and Benchmark of popular XC functionals**