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

Excited States and Luminescent Properties of Organic Systems

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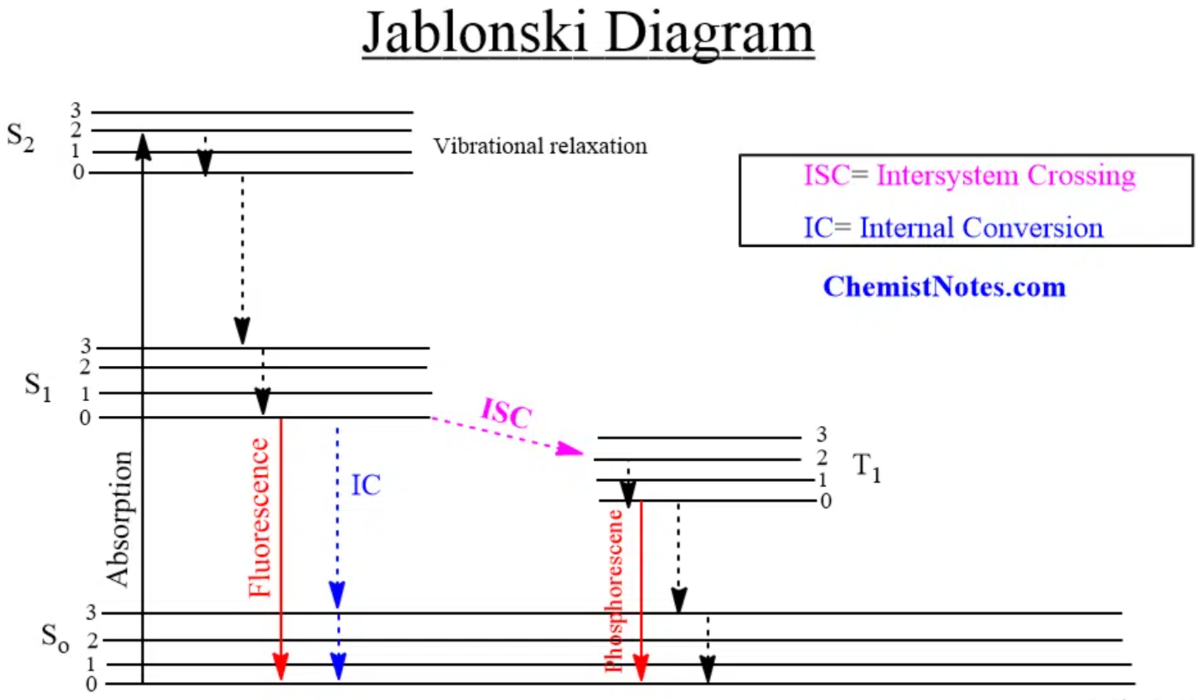
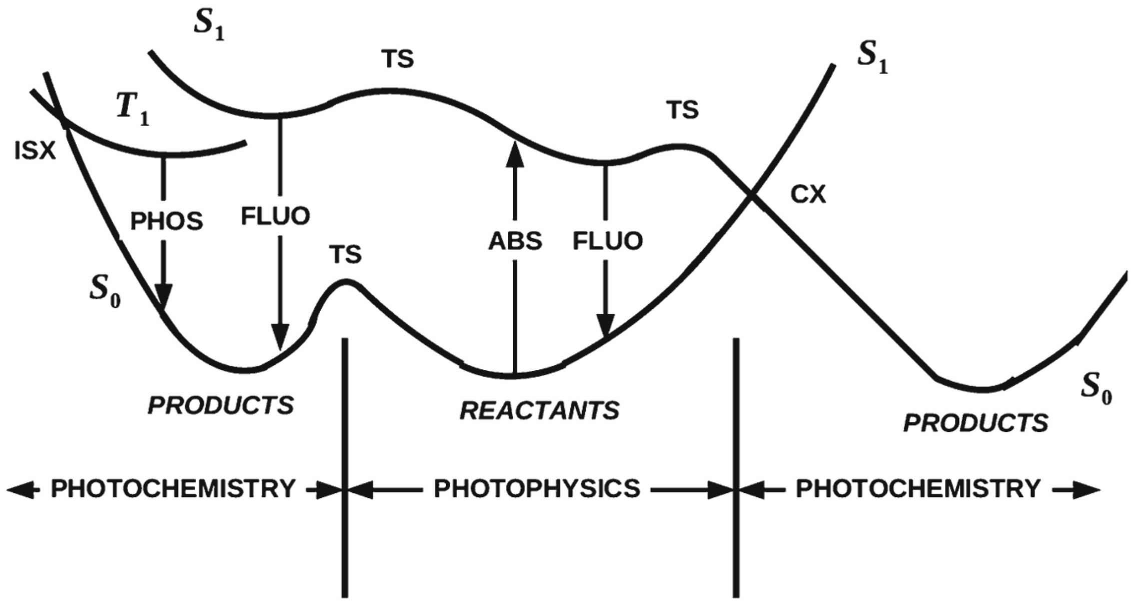
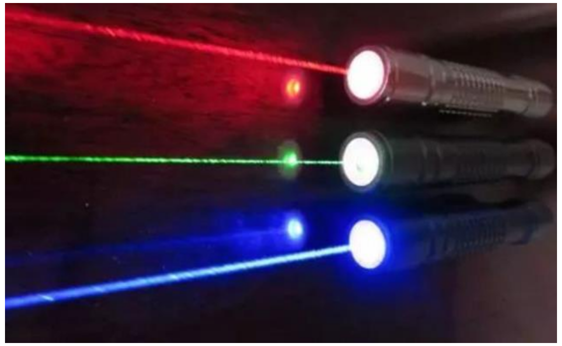
1. Organic Optoelectronic Materials



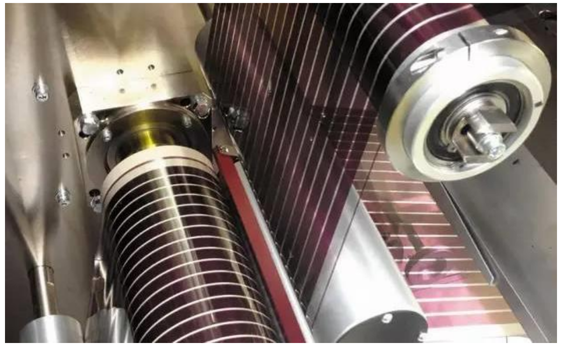


OLED screen

Lighting



Organic laser

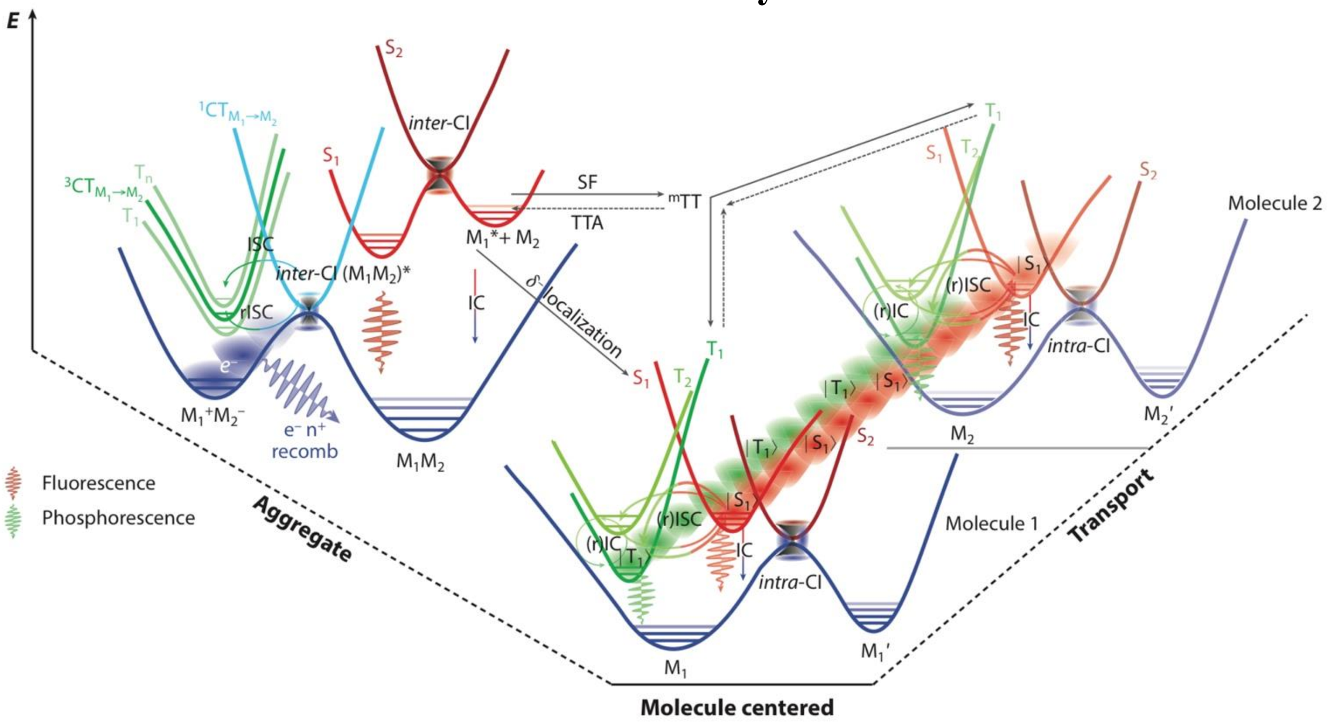


Flexible electronics

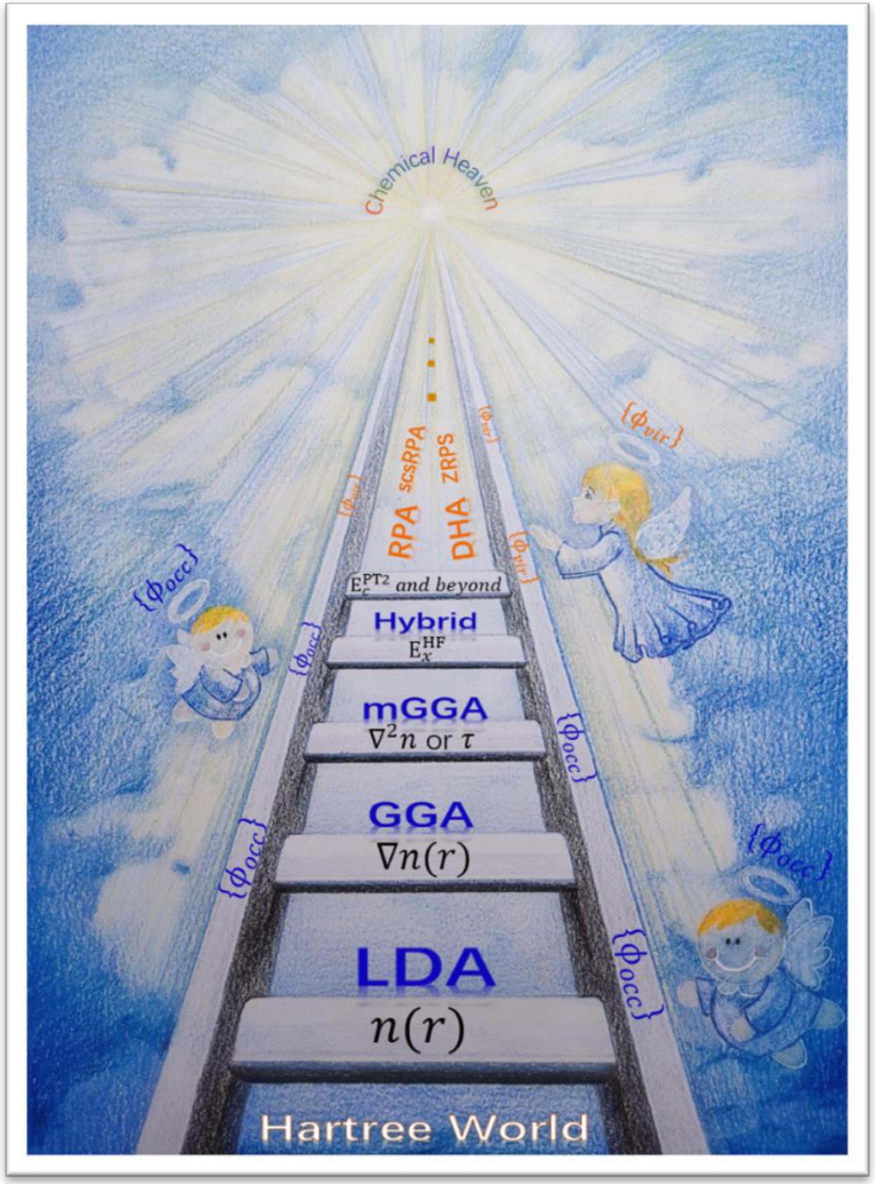
1. Organic Optoelectronic Materials– Electronic Structure Calculations

Method	Computational complexity	Features
Wave function theory e.g., configuration interaction (CI) method $\Psi = \sum_{I=1} C_I \lvert \phi_{I1}(x_1)\phi_{I2}(x_2)\cdots\phi_{IN_e}(x_{N_e}) \rvert$	$O(e^N)$	High accurary High cost
Density functional theory $E(\rho)$ $\rho(\mathbf{r}) = \sum_{i=1}^{N_e} f(\varepsilon_i)\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$	$O(N^3)$	Medium accuracy Low cost
Quantum Monte Carlo method $\langle E \rangle = \frac{\langle \Psi_\alpha \lvert \hat{H} \rvert \Psi_\alpha \rangle}{\langle \Psi_\alpha \vert \Psi_\alpha \rangle}$	$O(N^3\sim)$	High accuray High cost Easy to parallel
Many body Green's function method $G(t, \mathbf{r}, E)$	$O(N^3\sim)$	Medium accuray Excited states

Annu. Rev. Phys. Chem. 2023. 74:547–71



1.Density Functional Theory-Jacob Ladder



WIREs Comput Mol Sci. 2021; 11:e1490

Density Functional Theory Framework

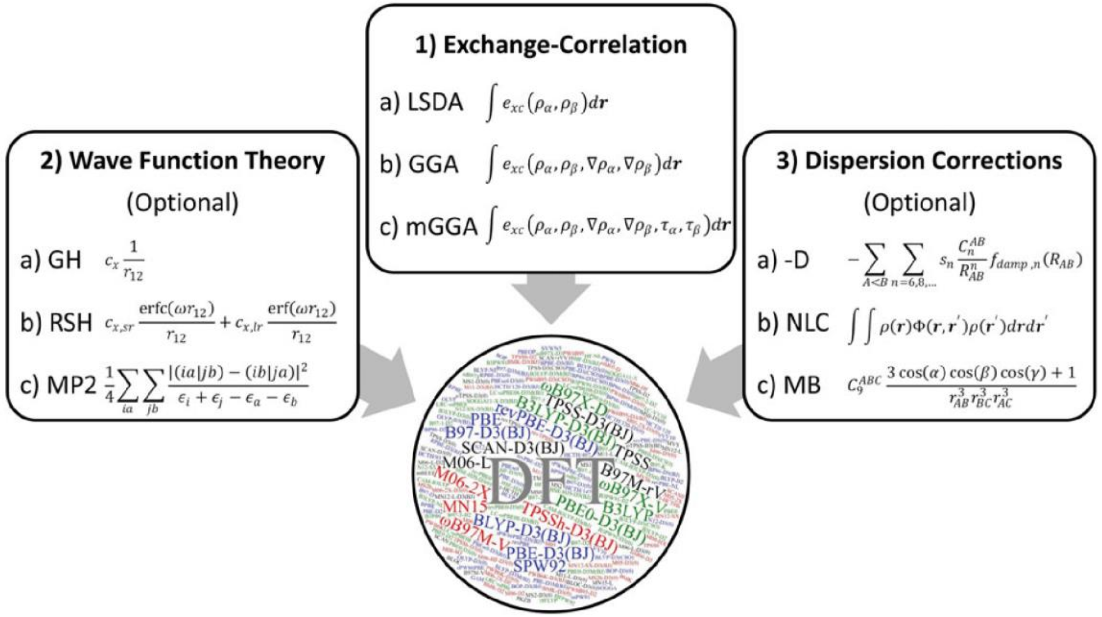
$$v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\}) \Leftrightarrow \rho(\boldsymbol{x}) \Leftrightarrow \{\psi_i(\boldsymbol{x})\}$$

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad \rho(\boldsymbol{x}) = \sum_i^N \psi_i^*(\boldsymbol{x})\psi_i(\boldsymbol{x})$$

$$\rho(\boldsymbol{x},\boldsymbol{x}') = \sum_i^N \psi_i^*(\boldsymbol{x})\psi_i(\boldsymbol{x}')$$

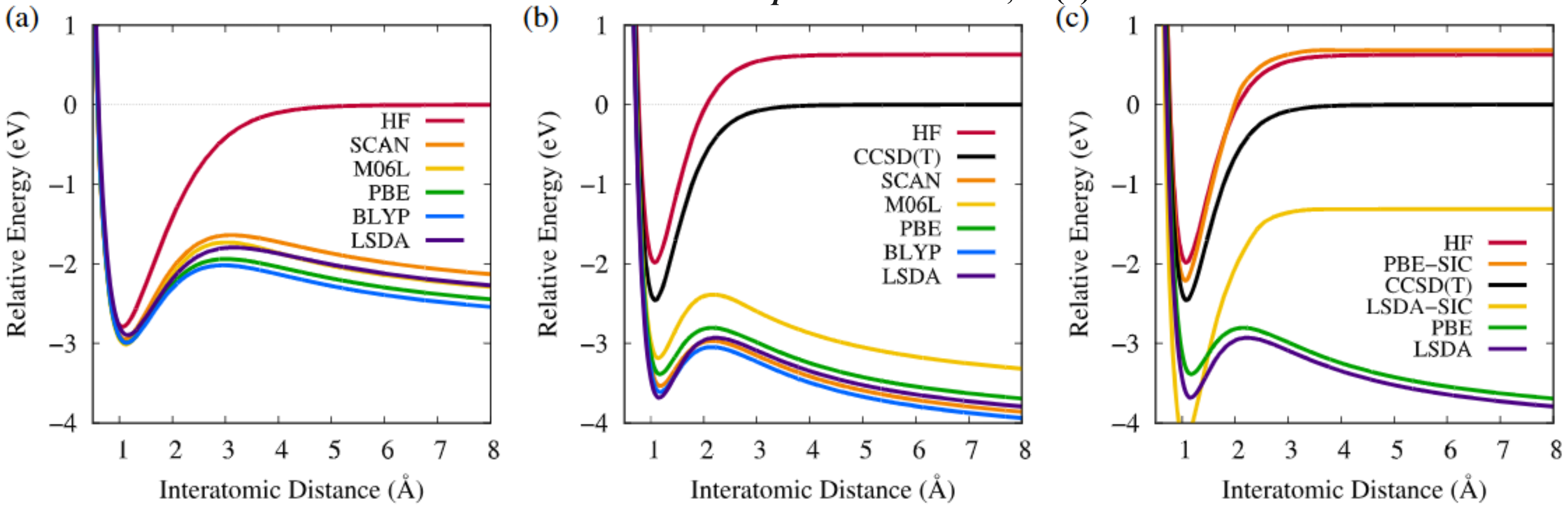
$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{x},\{\boldsymbol{R}\}) + v_H(\boldsymbol{x}) + v_{xc}(\boldsymbol{x})\right]\psi_i(\boldsymbol{x}) = \varepsilon_i\psi_i(\boldsymbol{x})$$

Phys. Rev. B 136, 864 (1964).



2.Self-Interaction Errors

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



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($|\boldsymbol{r}| \to \infty$)

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

2. Self-Interaction Errors-Adiabatic Connection

$$E_{xc} = \int_0^1 d\lambda\{\omega_\lambda - U_H[\rho(\boldsymbol{r})]\}, \omega_\lambda = \langle\phi_\lambda|v_{ee}|\phi_\lambda\rangle$$

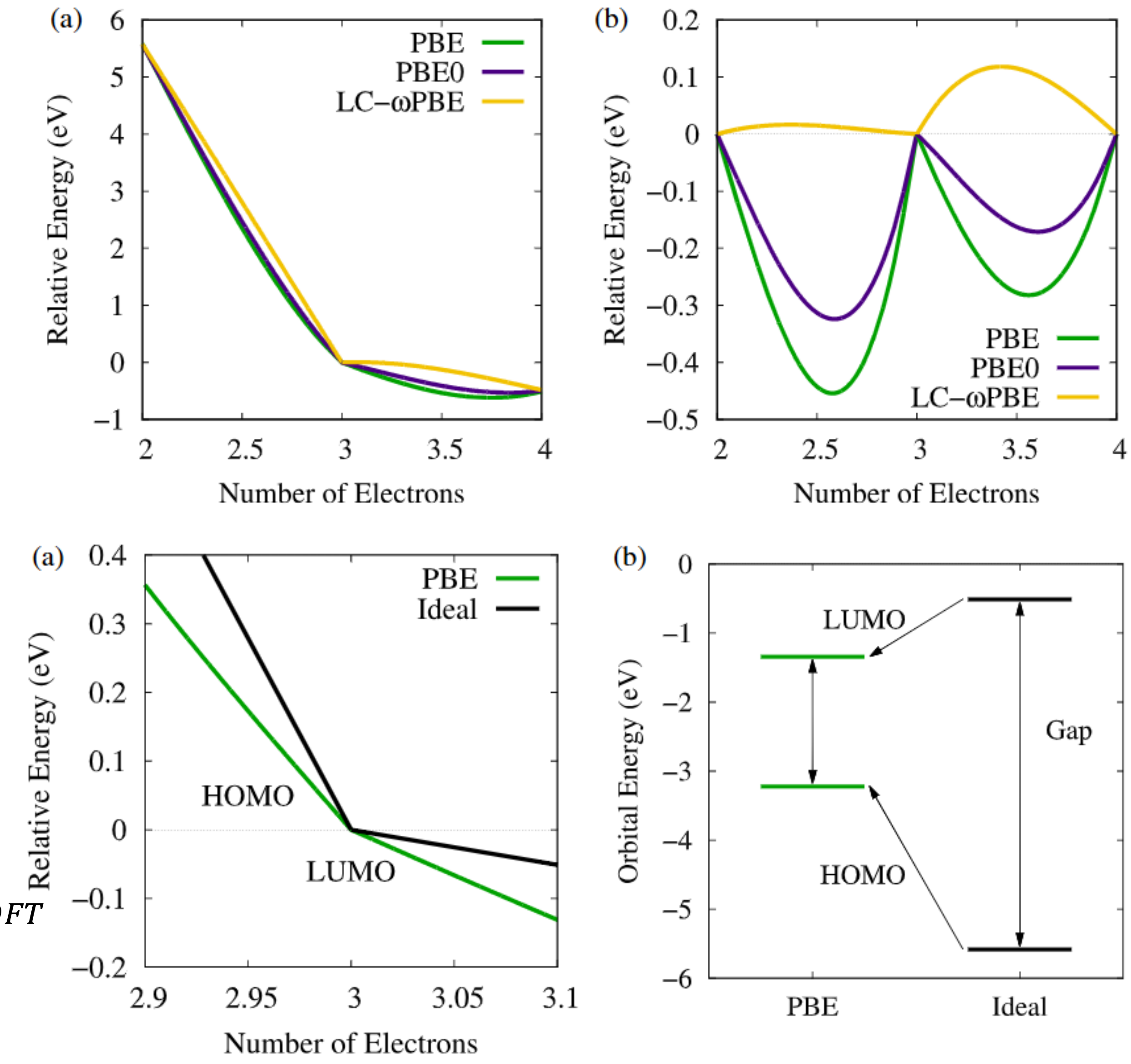
Adiabatic Connection

$$E_{xc} = (1-a)E_x^{DFT} + aE_x^{HF} + E_c$$

Global Hybrid Functionals

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

Range-Separated Hybrid Functionals

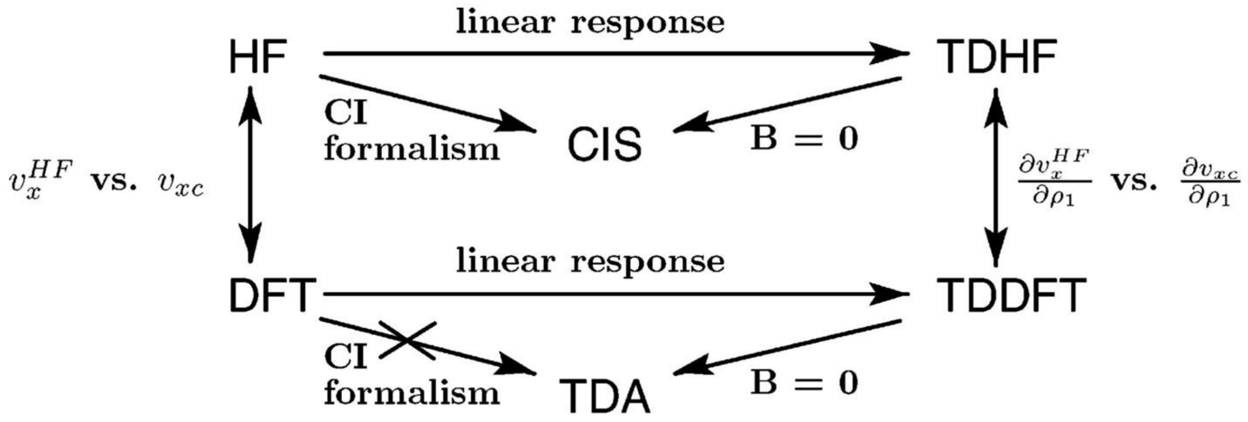


***WIREs Comput Mol Sci*. 2023; 13(2):e1631**

2. Charge-Transfer Excitation-RL-TDDFT

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

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



Runge-Gross Theorem

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

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

Linear-Response

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

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

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

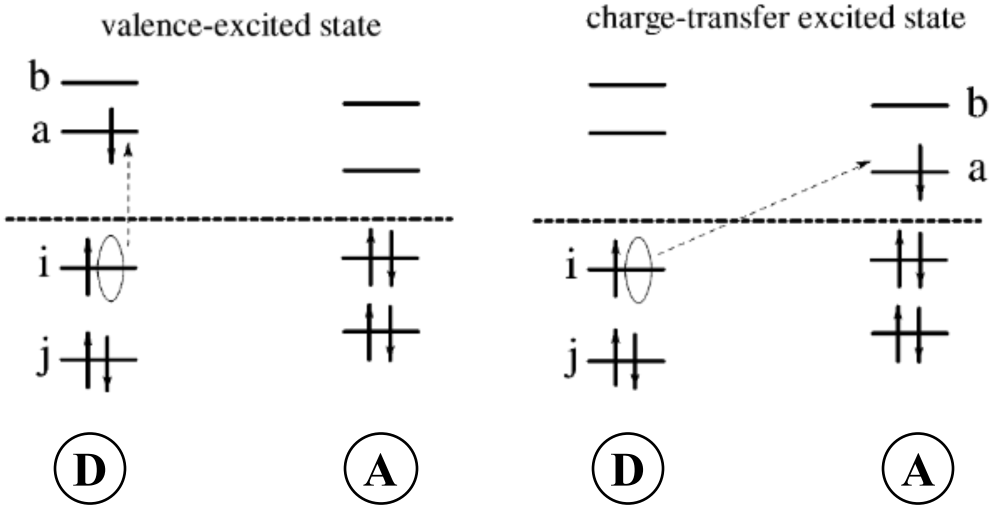
$$\psi_{ex} = \sum_{ai} x_{ai}\phi_{ai}$$

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

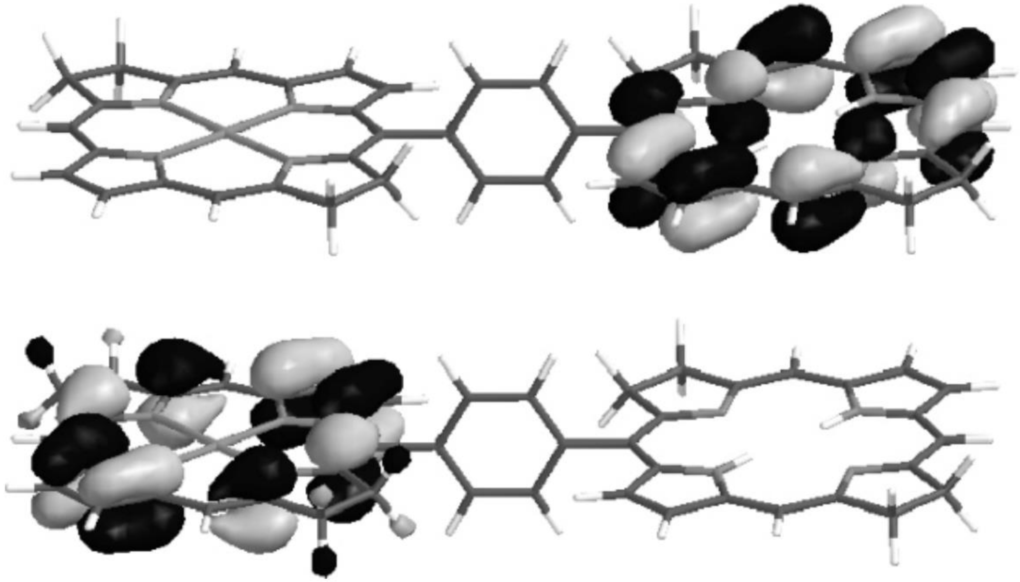
$$F_{aa}^{(0)} = \int d\boldsymbol{r}\psi_a^*(\boldsymbol{x},\boldsymbol{t})\left\{-\frac{1}{2}\nabla^2 + \nu_{ext}(\boldsymbol{x},\{\boldsymbol{R}\},\boldsymbol{t}) + \nu_H(\boldsymbol{x},\boldsymbol{t}) + \nu_{xc}(\boldsymbol{x},\boldsymbol{t})\right\}\psi_a(\boldsymbol{x},\boldsymbol{t})$$

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

2. Charge-Transfer Excitation



Chem. Rev. 2005, 105, 11, 4009–4037



J. Am. Chem. Soc. **2004, 126, 12, 4007–4016**

$$A = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ai|jb) - C_{HF}\,(ij|ab) + (1 - C_{HF})(ai|f_{xc}|jb)$$

$$B = (ai|jb) - C_{HF}(ai|jb) + (1 - C_{HF})(ai|f_{xc}|jb)$$

$$\int dr\, \psi_i^*(r_1)\psi_a\,(r_2) \sim 0$$

Long-Range Charge Transfer Excitation-Hybrid Functionals

$$A = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) - C_{HF}\,(ij|ab)$$

$$B = 0$$

DFT-Koopmans Theorem

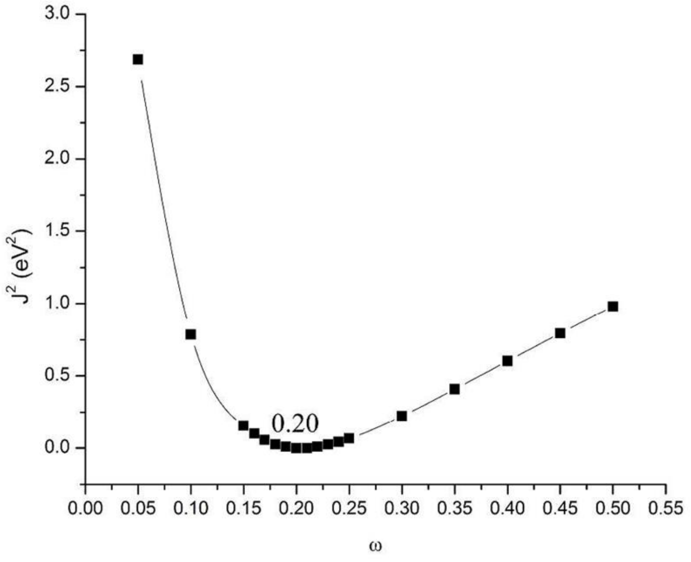
Long-Range Charge Transfer Excitation In TDHF and TDDFT

$$E_{CT}^{DFT} = IP - EA - \frac{C_{HF}}{R}$$

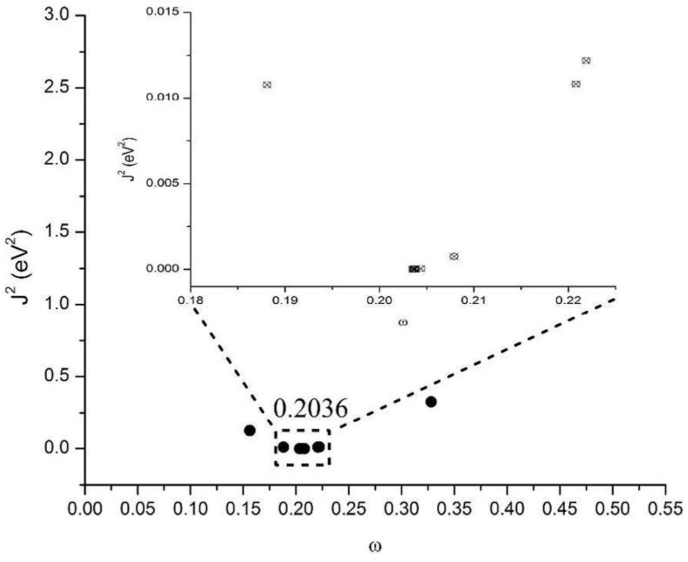
$$E_{CT}^{HF} = IP - EA - \frac{1}{R}$$

2. XC Functional Optimization

J. Chem. Theory Comput. 2015, 11, 8, 3851–3858



Fitting method



"Golden proportion" method
used in this work

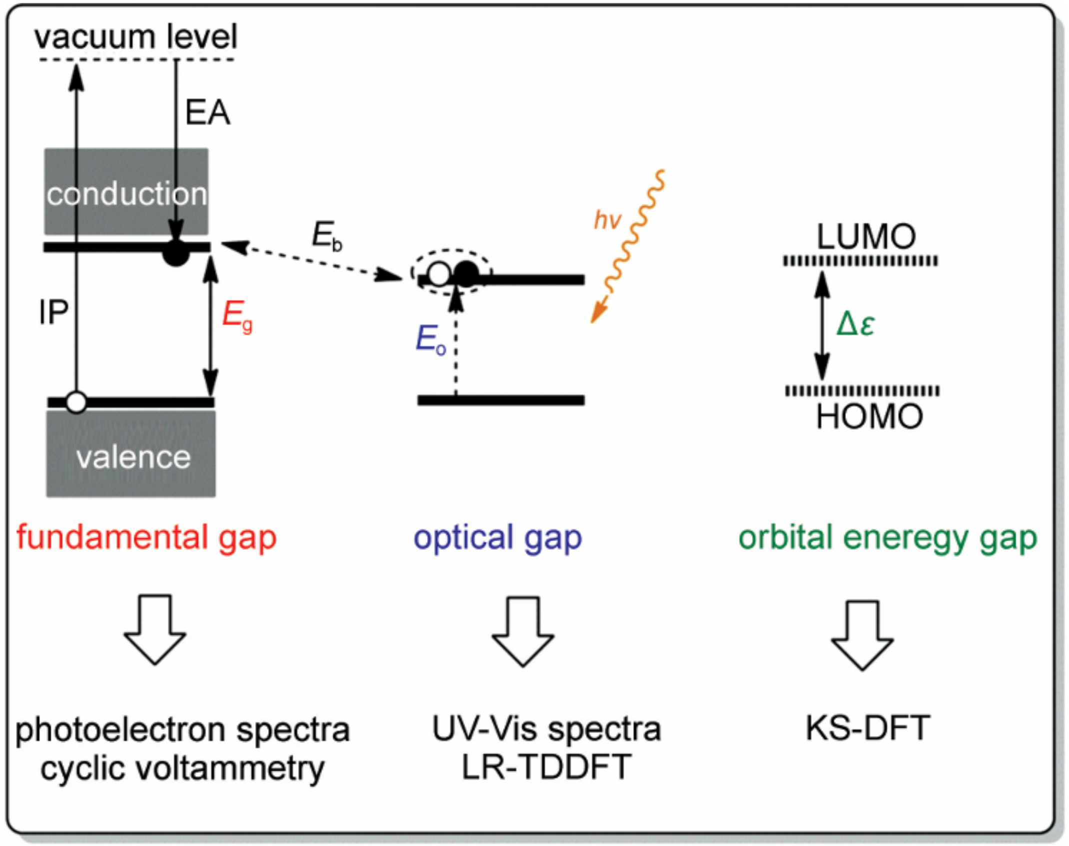
Fewer steps

More precision

Range-Separated Hybrid Functionals

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

$$\frac{1}{|r-r'|} \rightarrow \frac{1-[\alpha+\beta\mathrm{erf}(\omega|r-r'|)]}{|r-r'|} + \frac{\alpha+\beta\mathrm{erf}(\omega|r-r'|)}{|r-r'|}$$

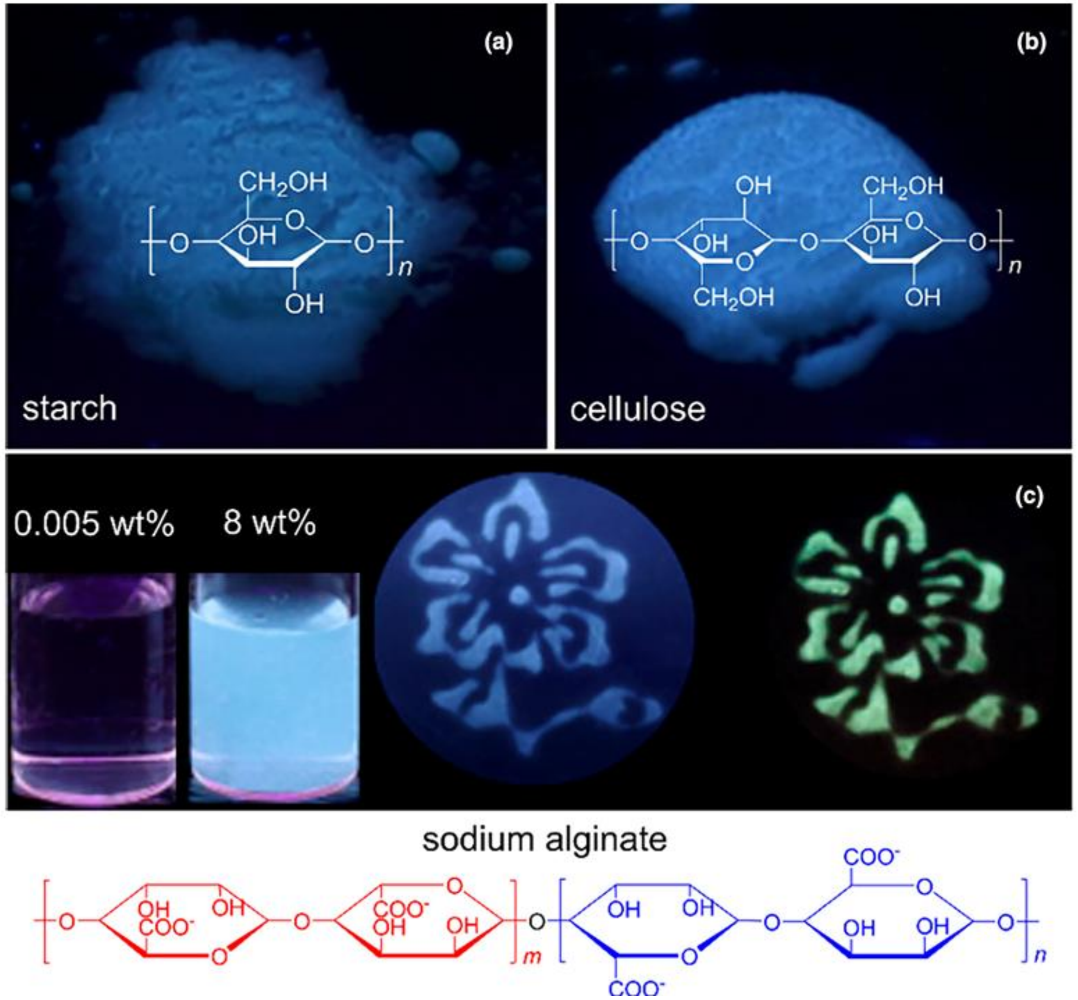


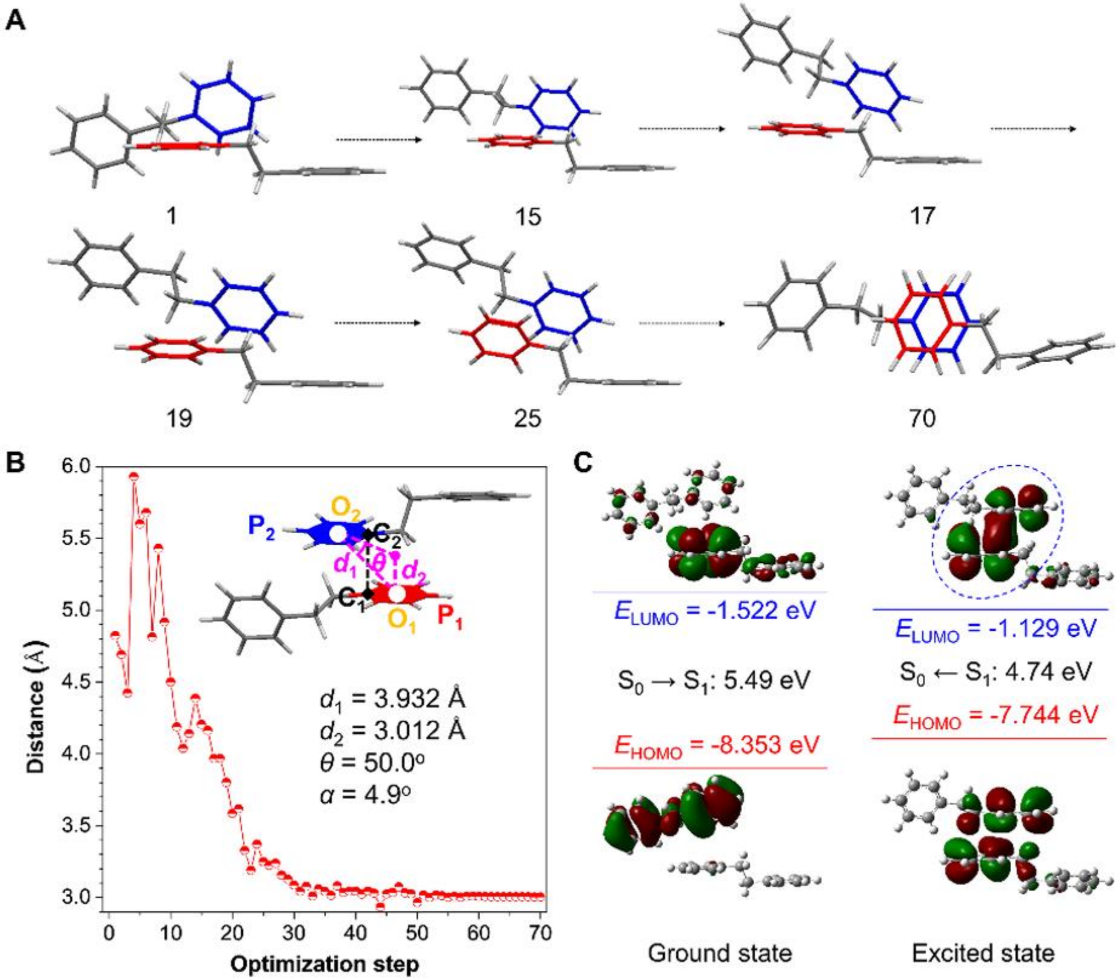
$$J(\omega) = J_N(\omega) + J_{N+1}(\omega) \rightarrow \mathrm{argmin}[J^2(\omega)]$$

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

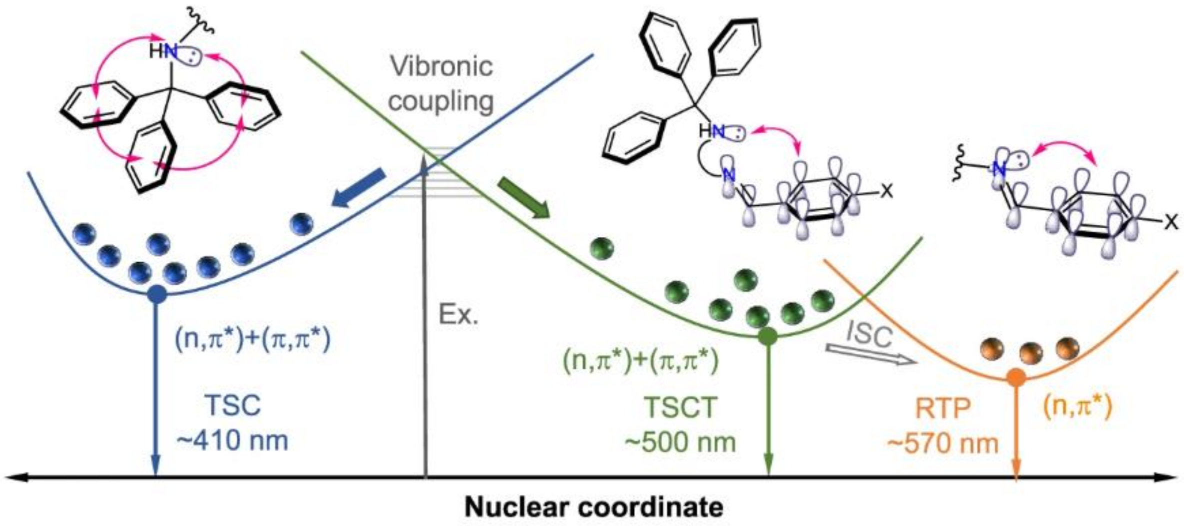
$$J_{N+1}(\omega) = |\varepsilon_{HOMO}^{\omega}(N+1) + IP(N+1)|$$

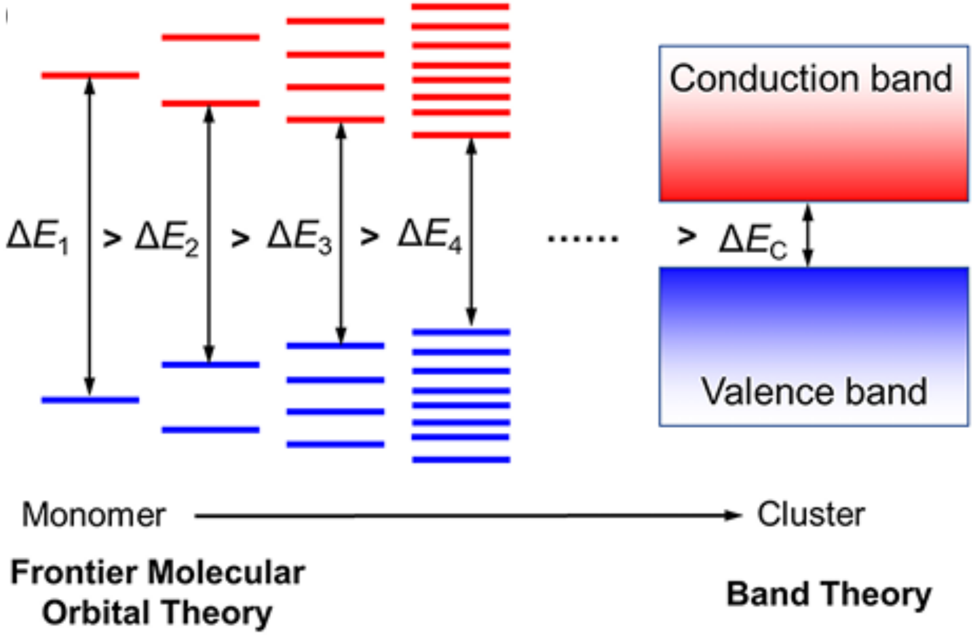
3. Complex Organic Systems

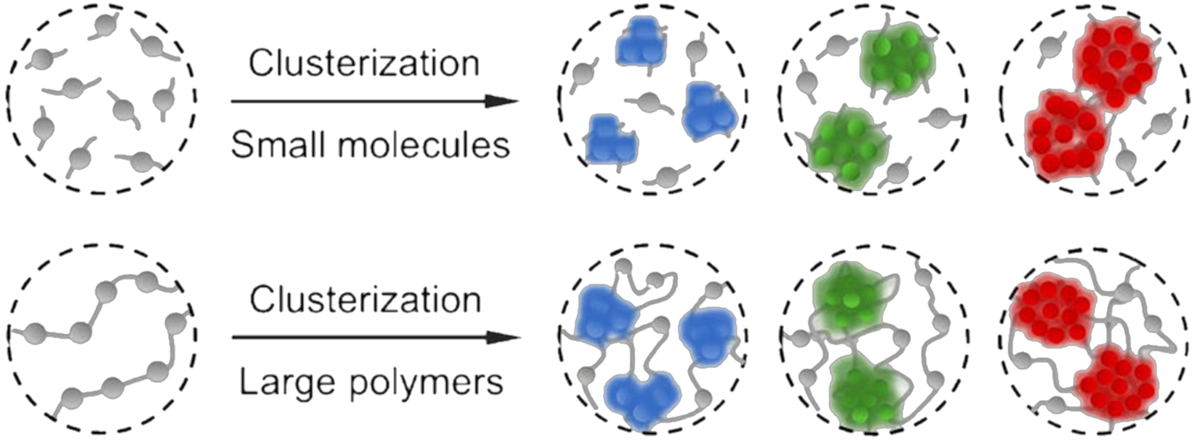


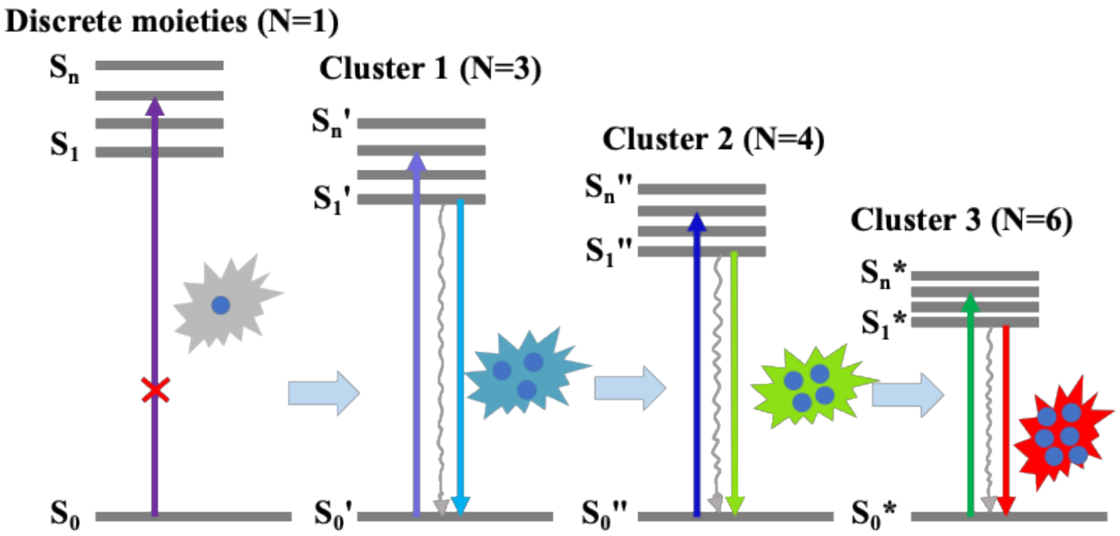


3. From Oligomer to Molecular Crystal

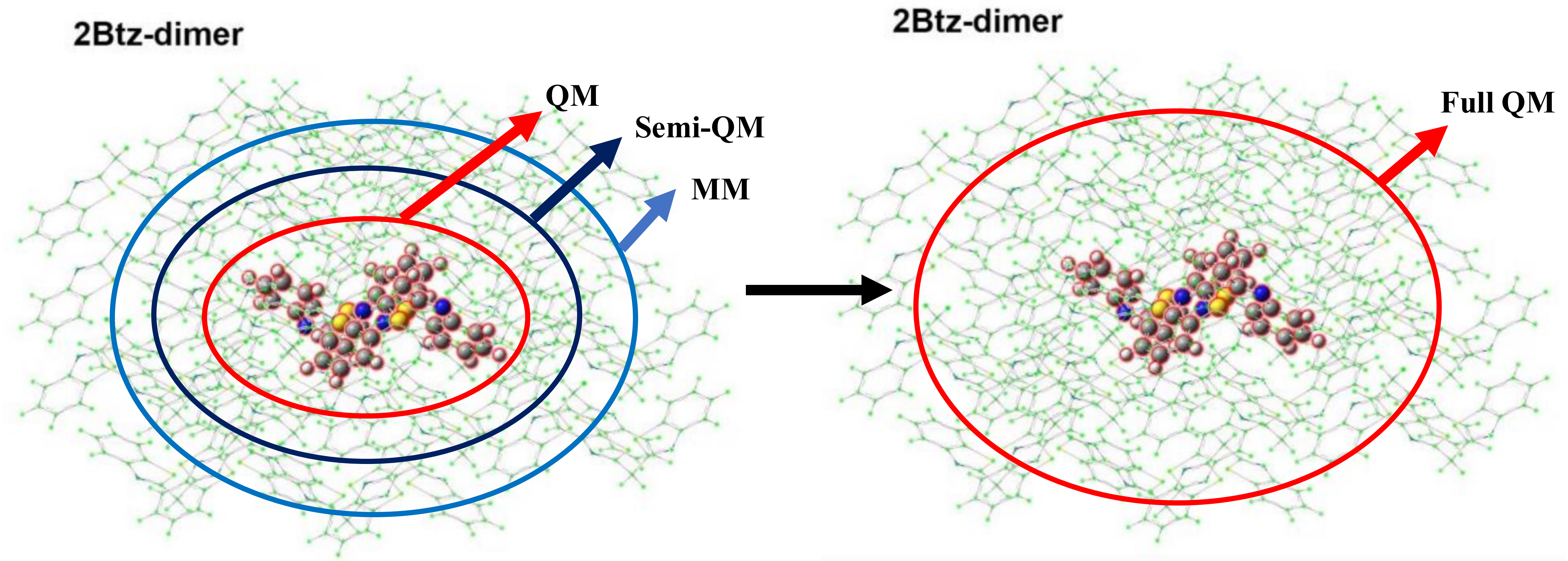






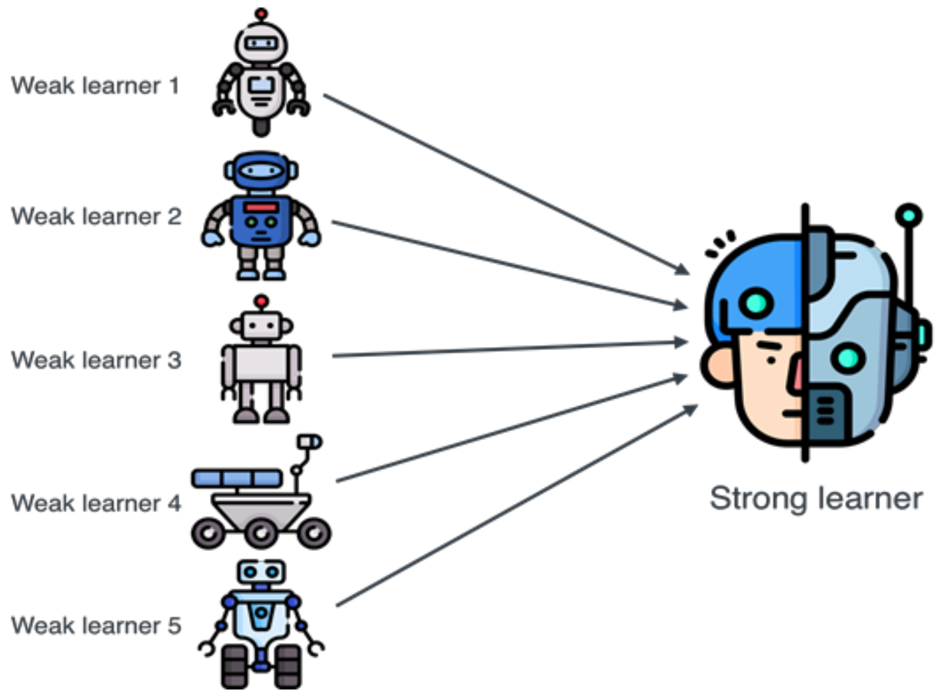


4. Motivation



- **Accurate excited states calculations for the systems with complex structure and serious SIE – Aggregate or Cluster Systems**

2. Super Learner



Regression Learning in Machine Learning

$$X_i = (Y_i, W_i), i = 1,2,3 \dots, n$$

$$\psi_0(W) = \arg\min_{\psi} E\left[L\left(X, \psi(W)\right)\right], L = L_2[\psi(w) - Y]$$

Stacked Generalized Learning-Super Learner

$$W_{V(\nu)} = \{W_i: X_i \in V(\nu)\}$$

$$m(z|\alpha) = \sum_{k}^{K} \alpha_k \psi_{k,T(\nu)}\left(W_{V(\nu)}\right), \alpha_k > 0\ \forall k, \sum_{k} \alpha_k = 1$$

$$\alpha = \arg\min_{\alpha} \sum_{i}^{n} \left(Y_i - m(z|\alpha)\right)^2$$

$$\psi_{SL}(W) = \sum_{k}^{K} \alpha_k \psi_k(W)$$

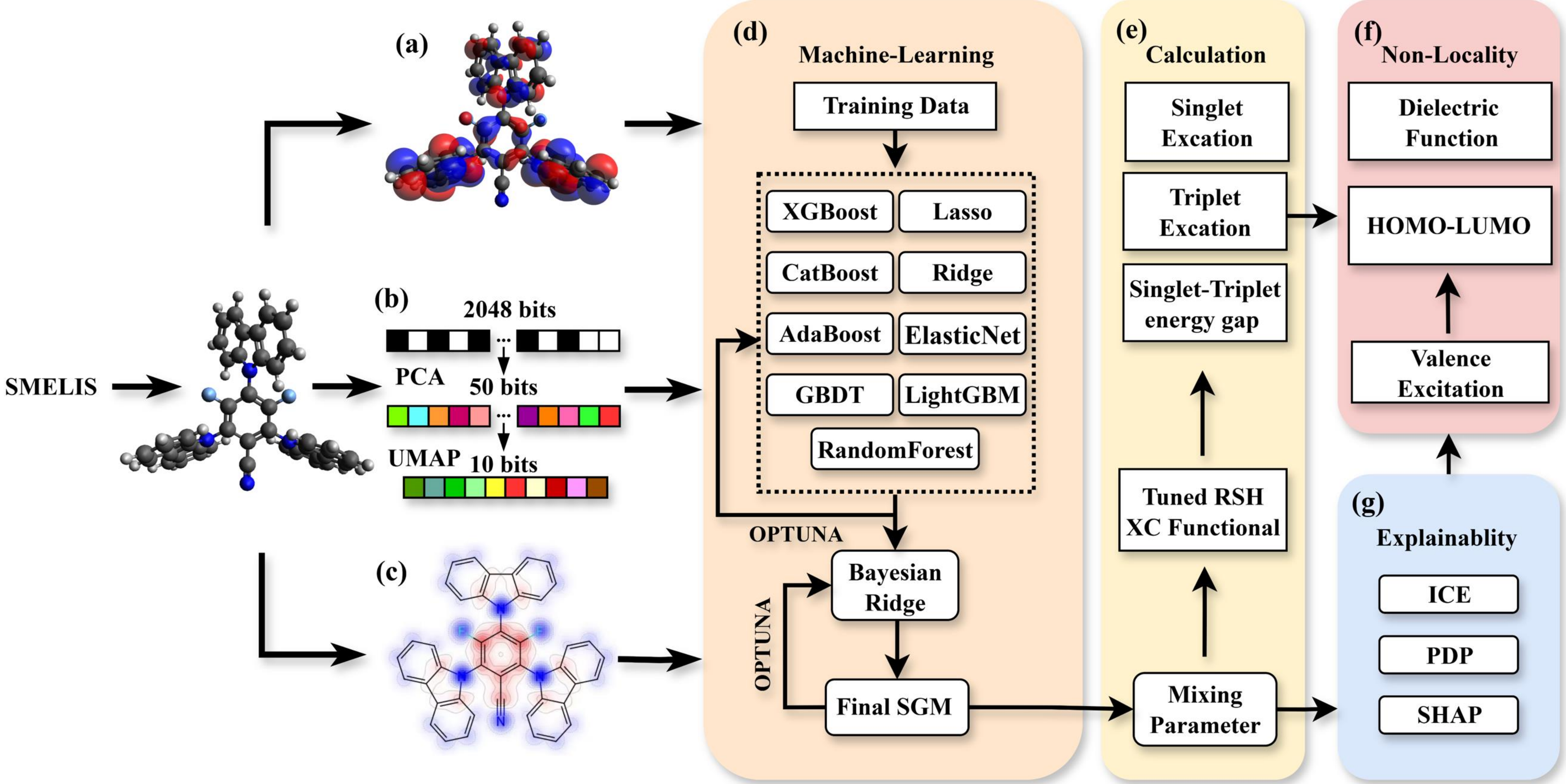
Loss Function

$$Loss_{\psi(W)} = \frac{1}{n} \sum_{i}^{n} \left(\omega_i^{base} - \omega_i^{ture}\right)^2 + L_n[\psi(W)]$$

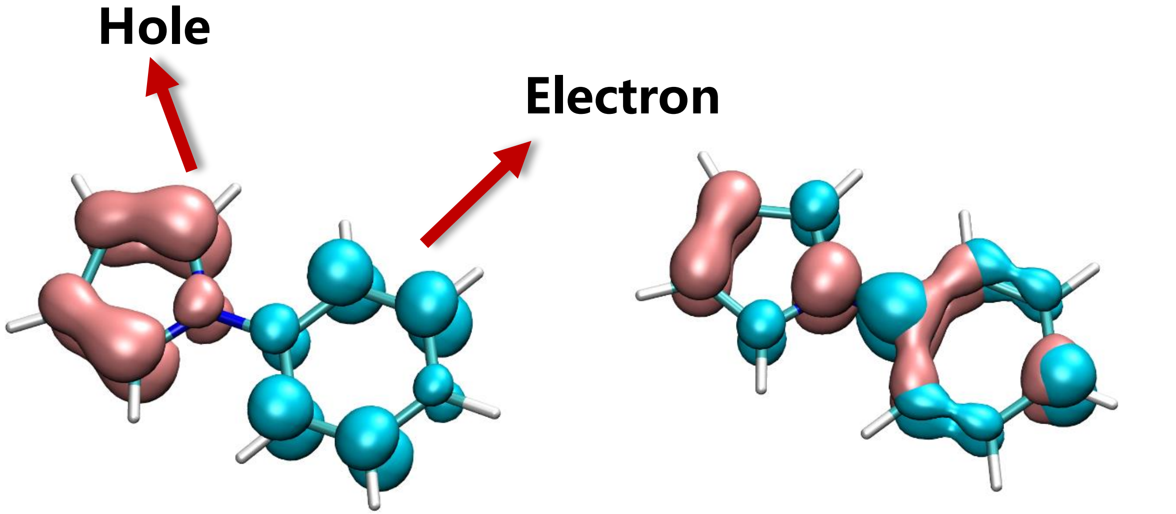
$$\omega_{\psi_{SGM}(W)}(W) = \sum_{m}^{M} \alpha_{\psi(W)} \omega_{\psi(W)}(W)$$

$$Loss_{\psi_{SGM}(W)} = \frac{1}{n} \sum_{i}^{n} \left(\omega_i^{SGM} - \omega_i^{ture}\right)^2 + L_n[\psi(W)]$$

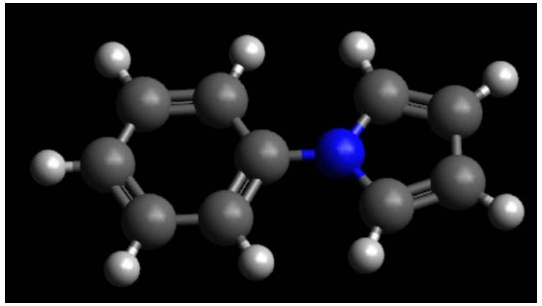
2. Super Learner



2. XC Functional Optimization-Machine Learning

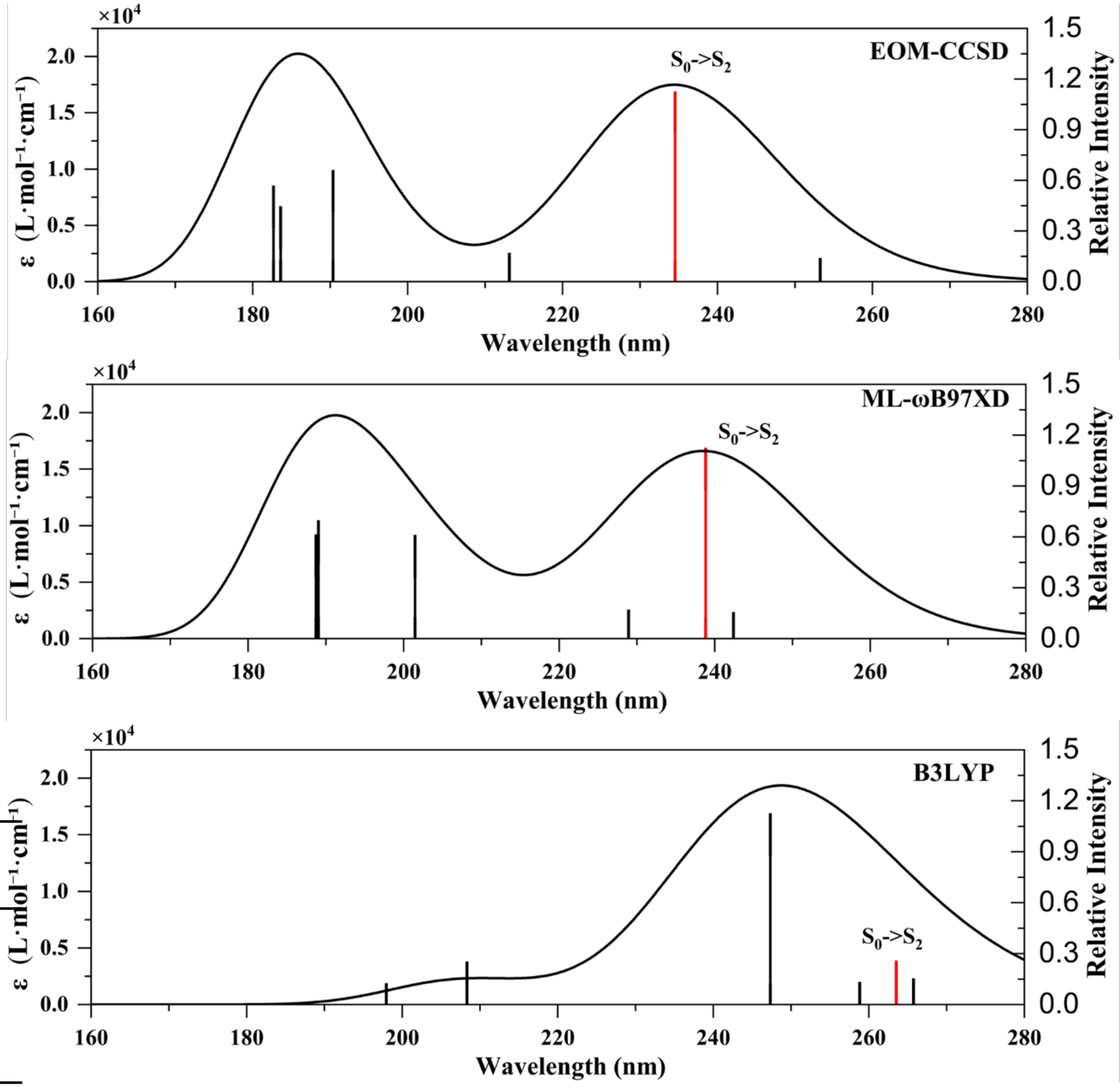


TDDFT@B3LYP/cc-pVTZ TDDFT@ωB97XD/cc-pVTZ

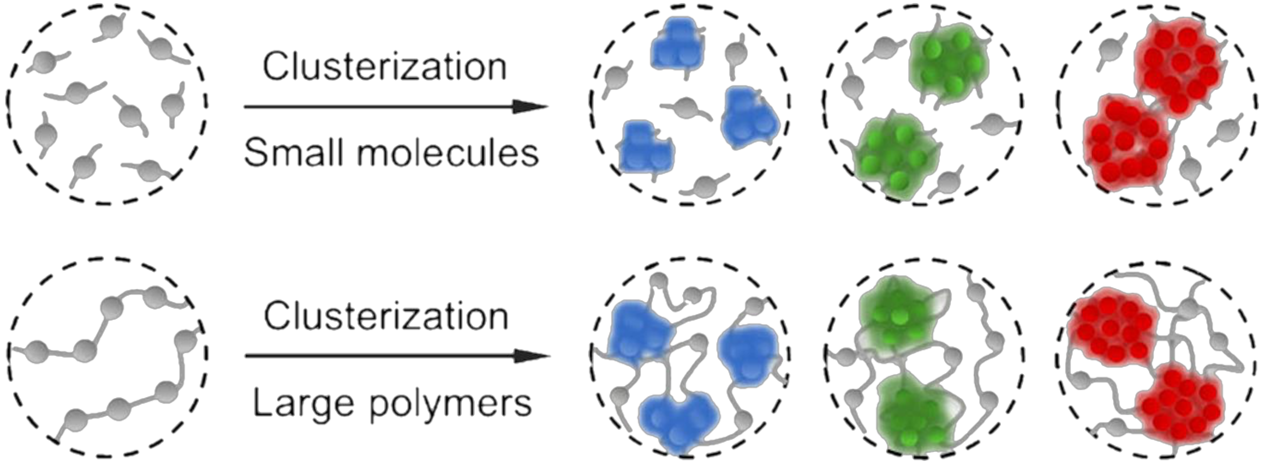


Intel(R) Xeon(R) Platinum 8160 CPU 2.10GH 96 CPU Cores

Method	CPU time/s	Elapsed time/s
EOM-CCSD/cc-pVTZ	5443200	57785.0
TD@ML-ωB97XD/cc-pVTZ	9794.8	154.7



3. Ground State-DeepH-From Monomer to Molecular Crystal



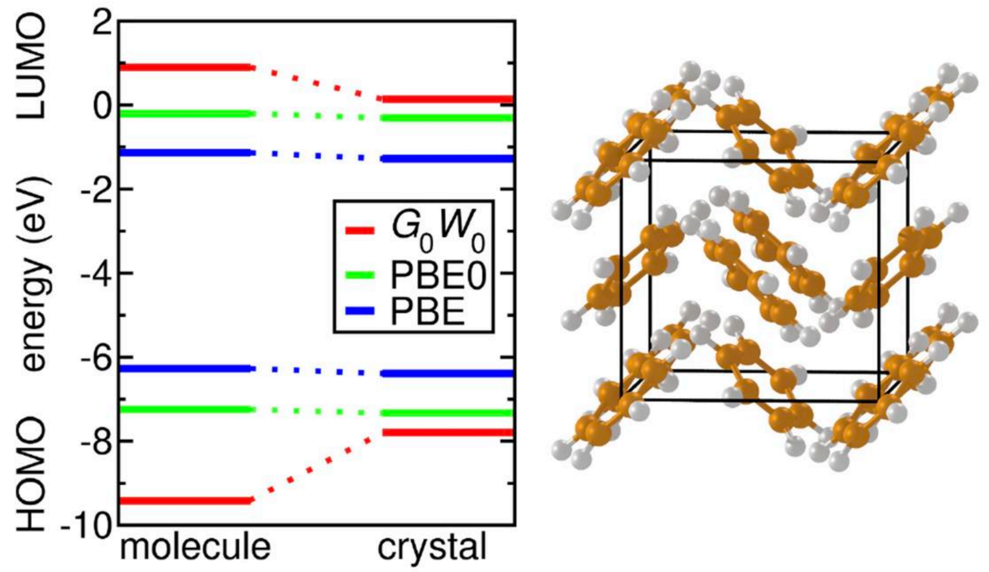


FIGURE 37 | Fundamental gaps of gas-phase benzene and band gap of the benzene crystal (space group Pbca). PBE was used as starting point for the G_0W_0 calculations. Data retrieved from Refaely-Abramson et al. (2013).

- **TD-B3LYP/cc-pVTZ** λ_{ex}: ~312, ~365nm^{exp} $\lambda_{em,FL}$: 360, 436, 500nm^{exp} $\lambda_{em,RTP}$: 456, 528nm^{exp}

B3LYP/6-31G*	1M	2M	3M	3M′	4M	4M′	6M	6M′	8M	8M′	9M	10M	12M	12M′	18M	18M′
$S_{1,ab}$	233.44	229.25	232.57	233.77	233.75	234.32	233.54	234.27	233.67	233.84	233.76	236.08	233.71	236.01	235.95	236.45
$T_{1,ab}$	257.8	248.9	257.31	258.95	259.19	259.5	258.88	259.7	258.7	258.4	259.37	262.02	259.32	261.92	261.97	262.4

3. Ground State-DeepH

Density Functional Theory Framework

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

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad \rho(\boldsymbol{x}) = \sum_i^N \psi_i^*(\boldsymbol{x})\psi_i(\boldsymbol{x})$$

$$\rho(\boldsymbol{x},\boldsymbol{x}') = \sum_i^N \psi_i^*(\boldsymbol{x})\psi_i(\boldsymbol{x}')$$

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

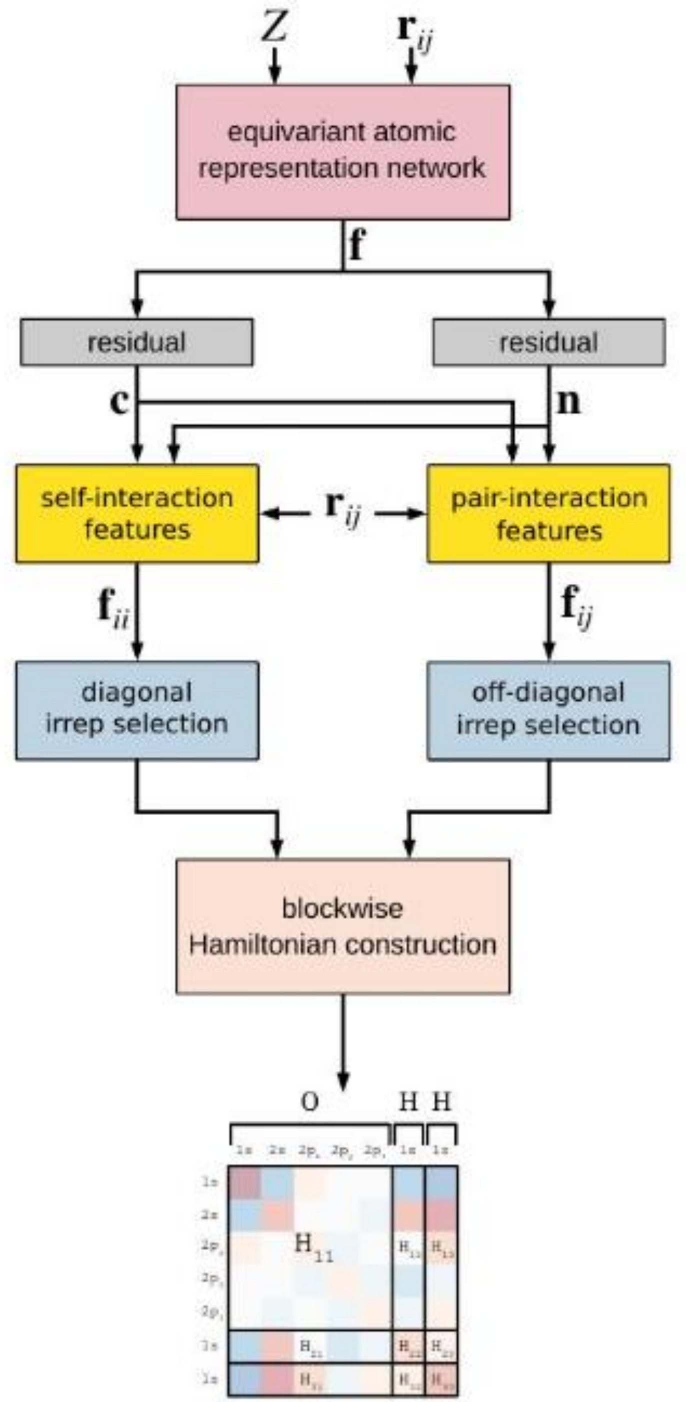
Phys. Rev. B 136, 864 (1964).

Atomic Basis Function

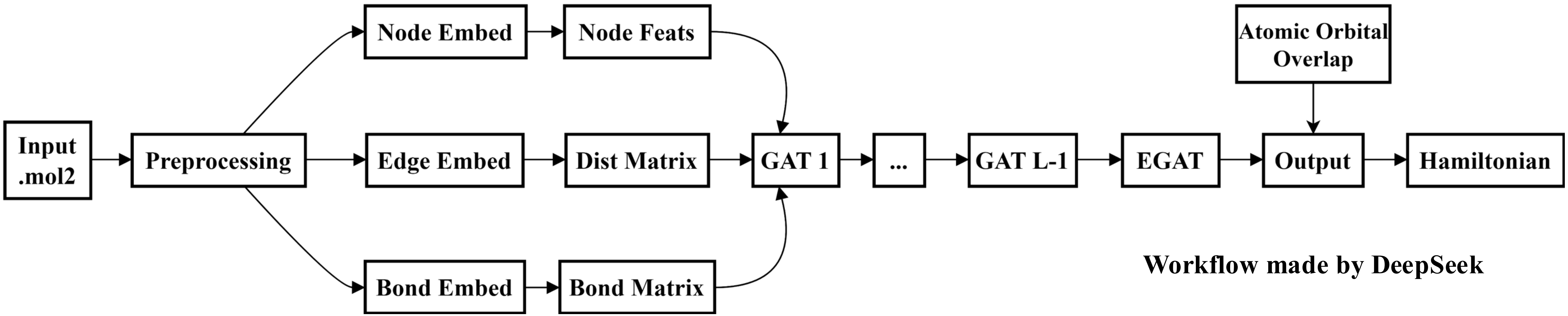
Hamiltonian Matrix in Atomic Basis Function

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

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



3. Ground State-DeepH



Workflow made by DeepSeek

Density Functional Theory Framework

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

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad \rho(\boldsymbol{x}) = \sum_i^N \psi_i^*(\boldsymbol{x})\psi_i(\boldsymbol{x})$$

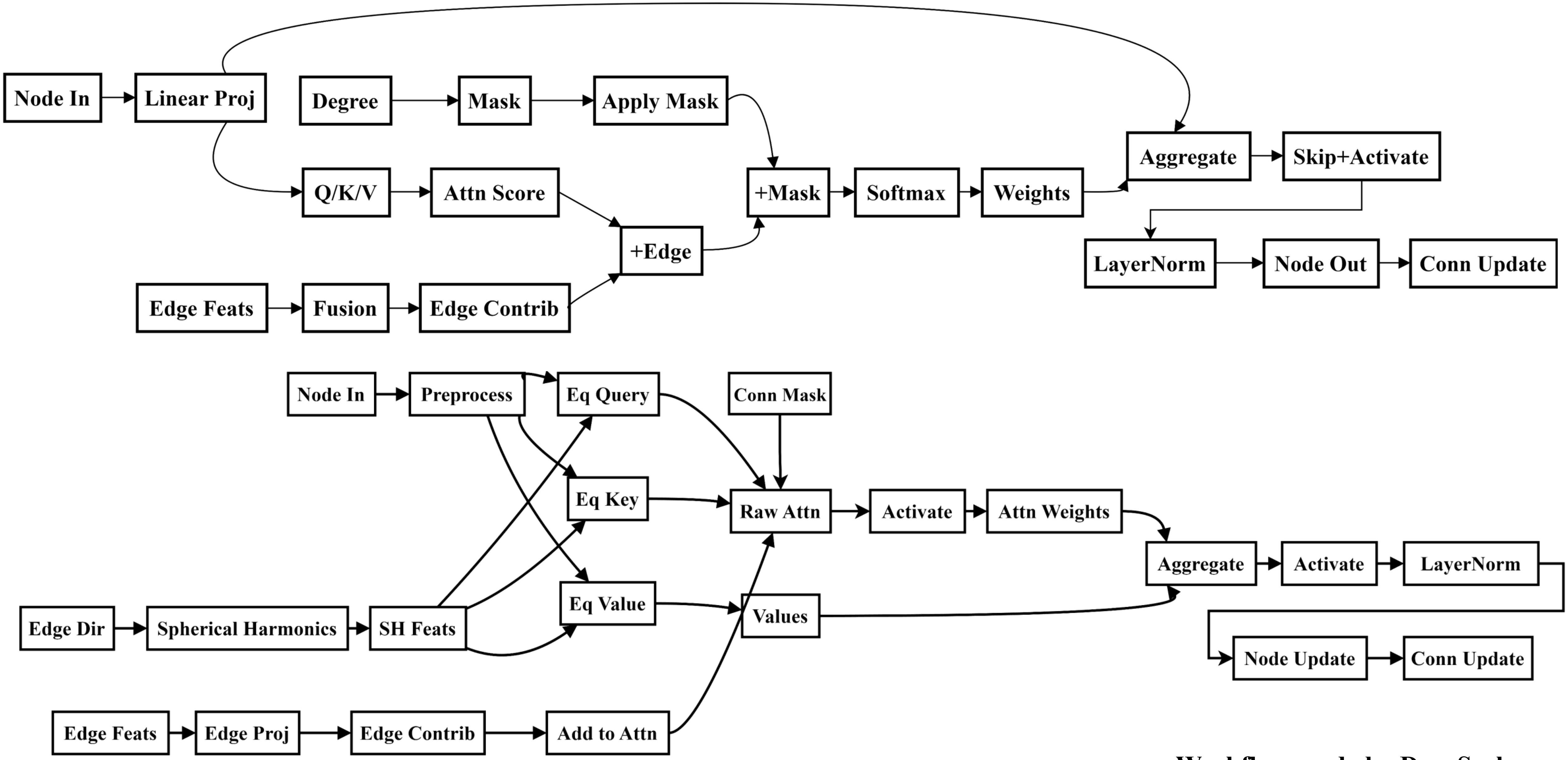
$$\rho(\boldsymbol{x}, \boldsymbol{x}') = \sum_i^N \psi_i^*(\boldsymbol{x})\psi_i(\boldsymbol{x}')$$

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

Phys. Rev. B 136, 864 (1964).

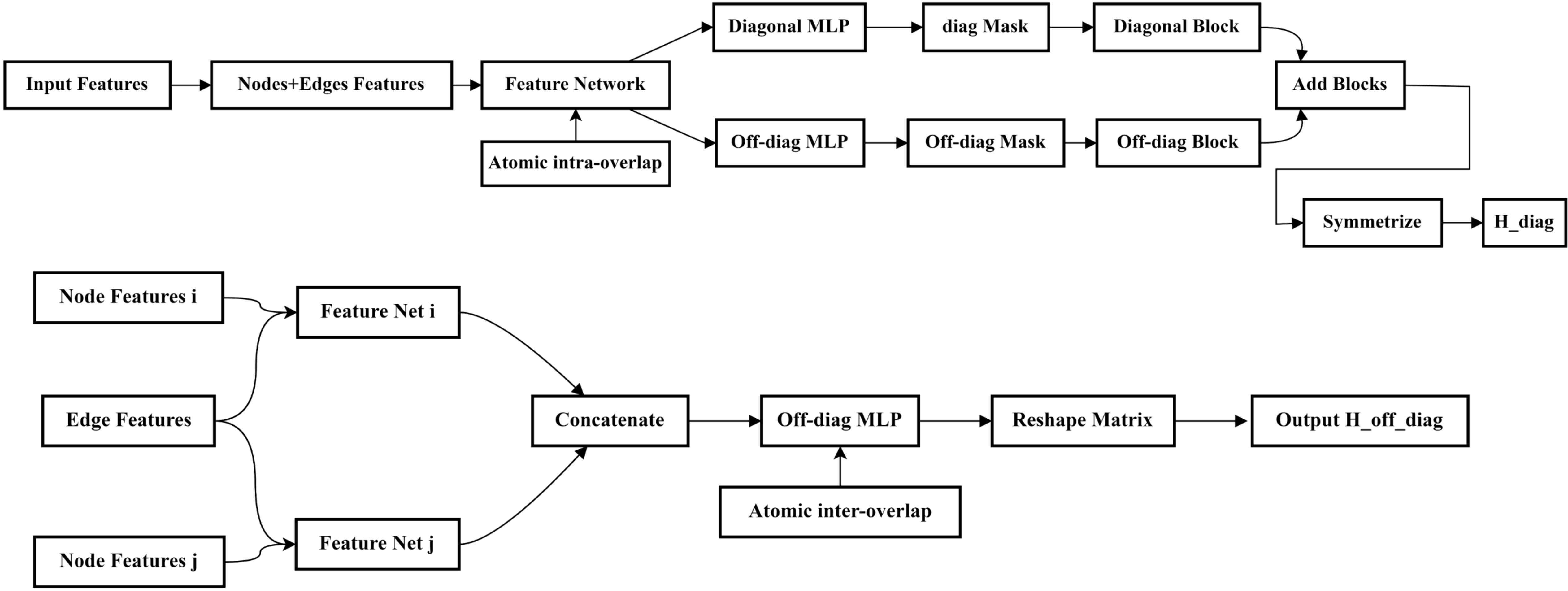
```
@<TRIPOS>MOLECULE
H2O
    3     2     1      0      0
SMALL
NO_CHARGES

@<TRIPOS>ATOM
      1 O1 0.0000     0.0000     0.0000    O.3 1  HOH  -0.0000
      2 H2 0.0000     0.0000     0.9600    H   1  HOH   0.0000
      3 H3 0.9280     0.0000    -0.2400    H   1  HOH   0.0000
@<TRIPOS>BOND
     1     1     2     1
     2     1     3     1
```

3. Ground State-DeepH-GAT/EGAT Layer



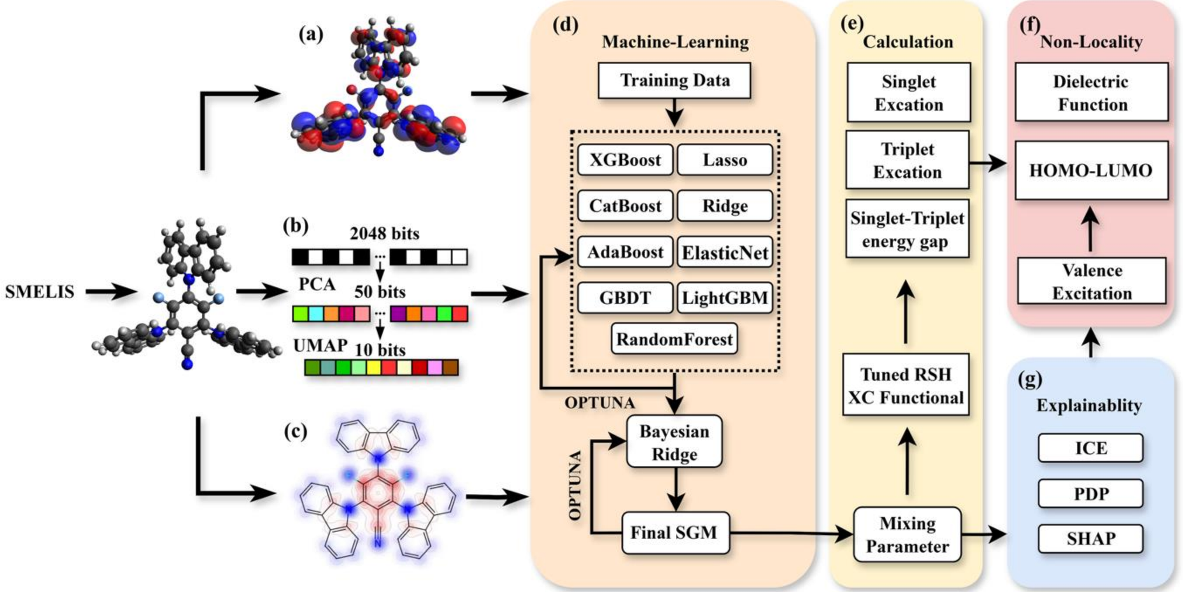
Workflow made by DeepSeek

3. Ground State-DeepH-Hamiltonian Block Layer



Workflow made by DeepSeek

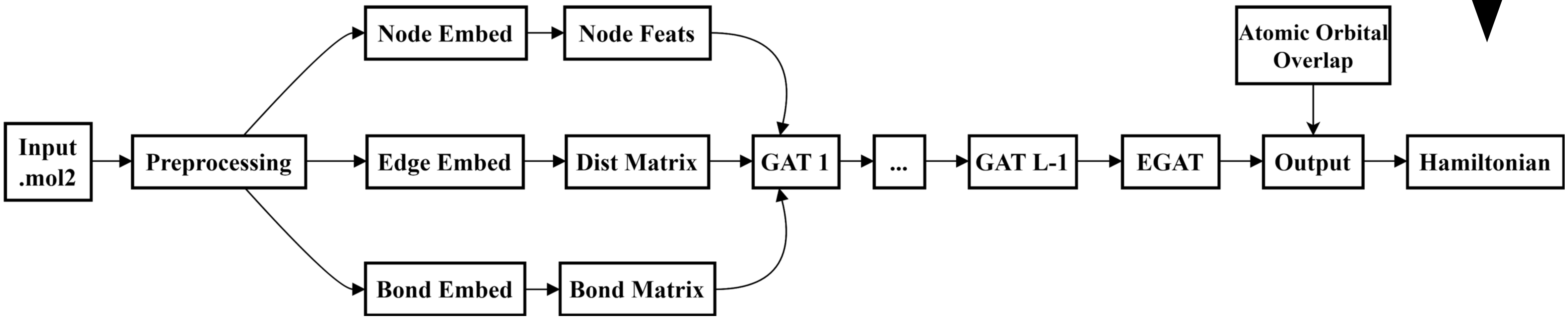
3. Ground State-DeepMolH-From Monomers to Oligomers



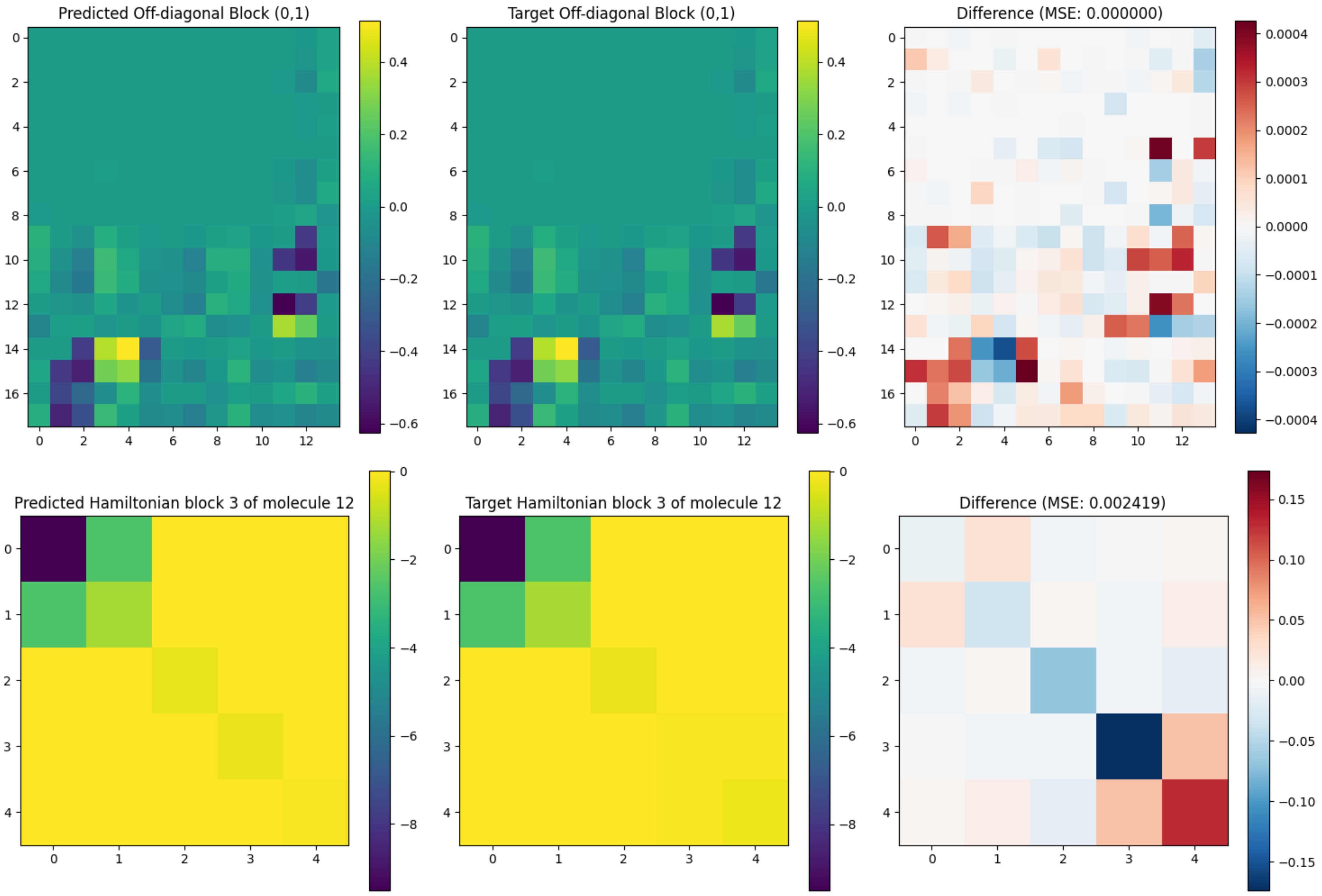
$$J(\omega) = J_N(\omega) + J_{N+1}(\omega) \rightarrow \text{argmin}[J^2(\omega)]$$

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

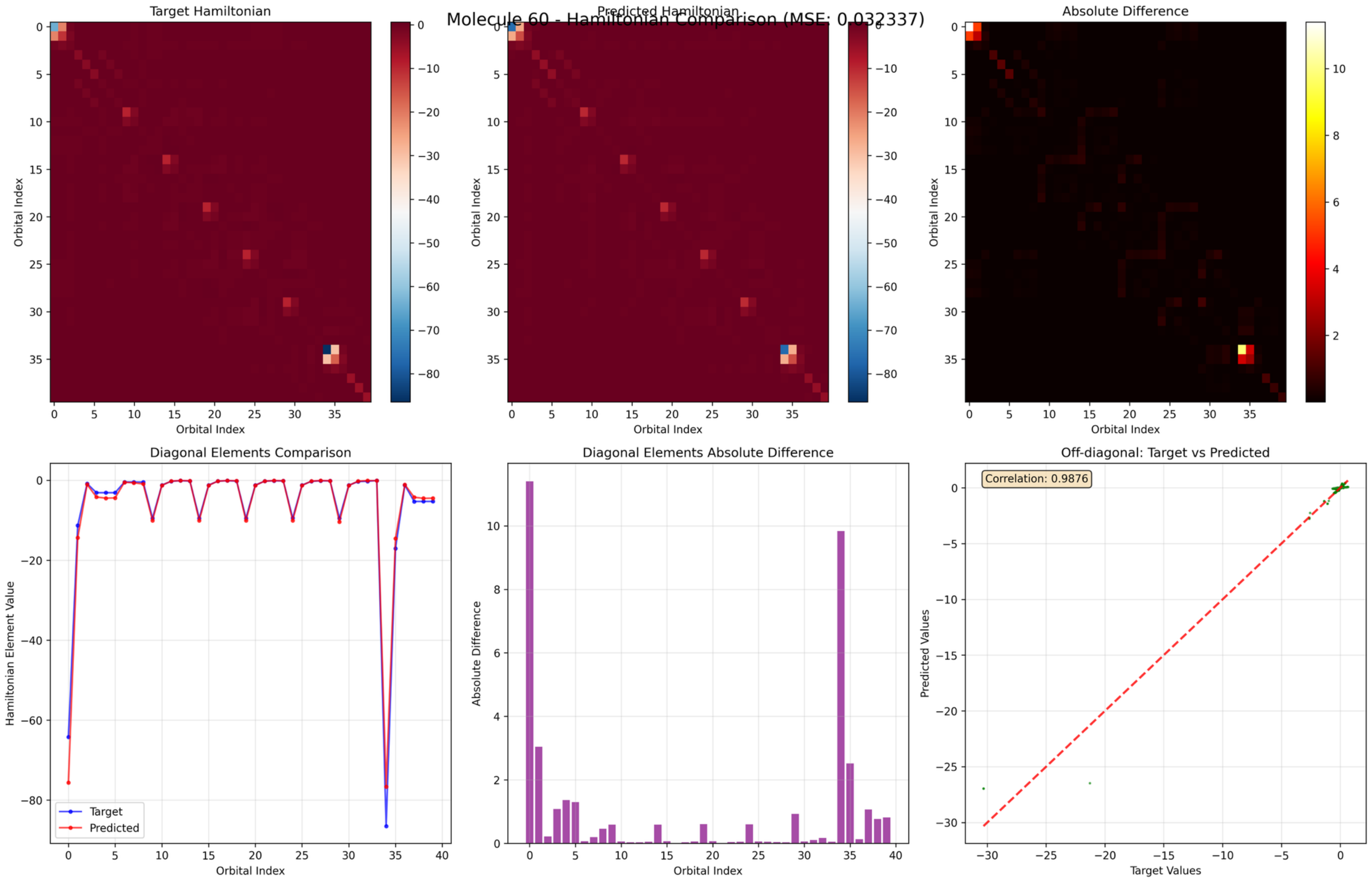
$$J_{N+1}(\omega) = |\varepsilon^{\omega}_{HOMO}(N+1) + IP(N+1)|$$

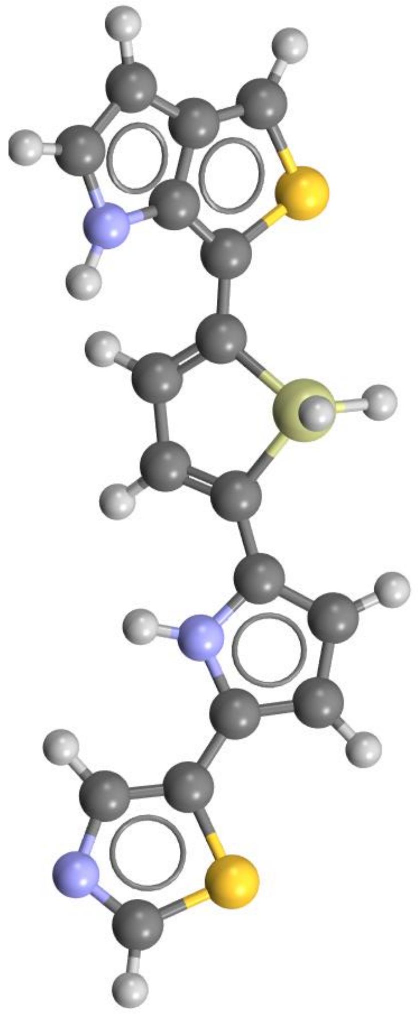


3. Ground State-DeepMolH-Testing on Single Atoms, Atom-Pairs



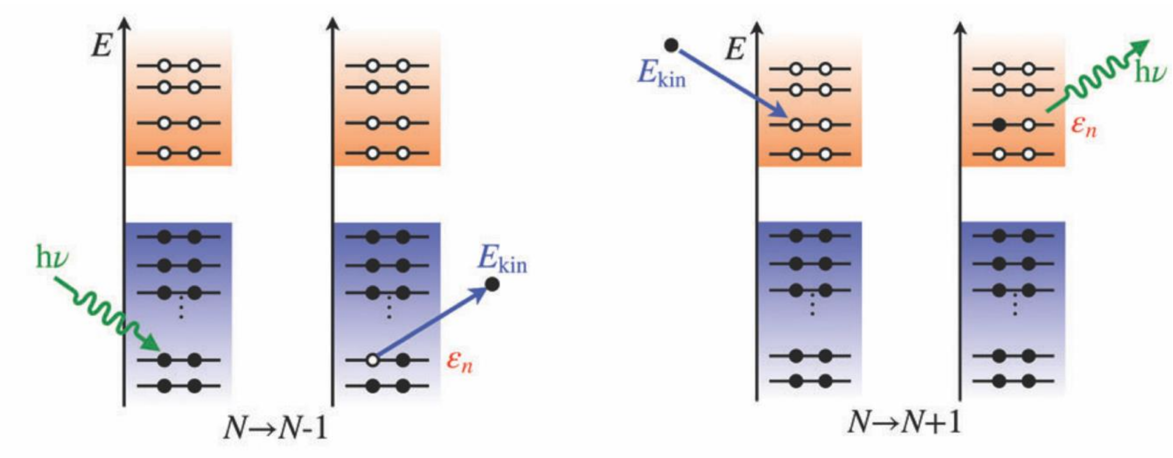
3. Ground State-Deep MolH-Testing on Molecules

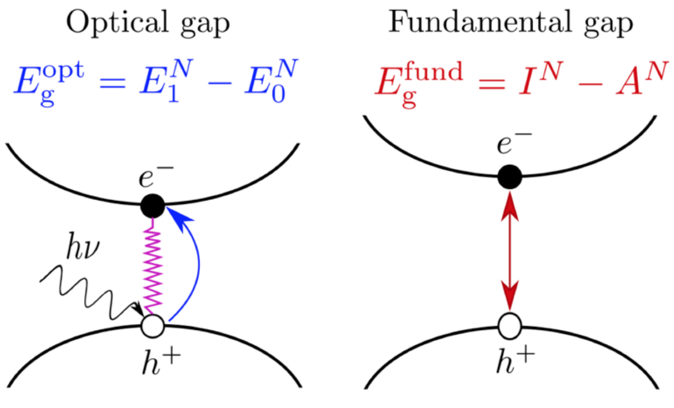


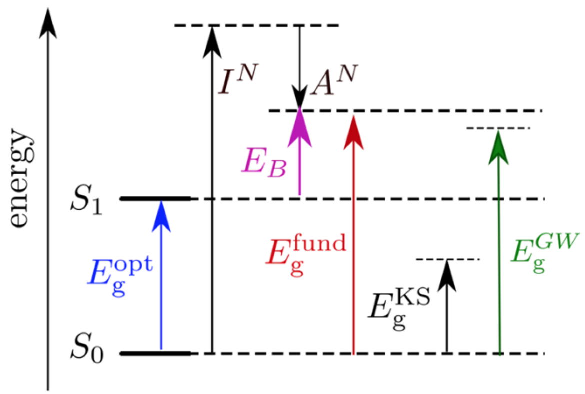


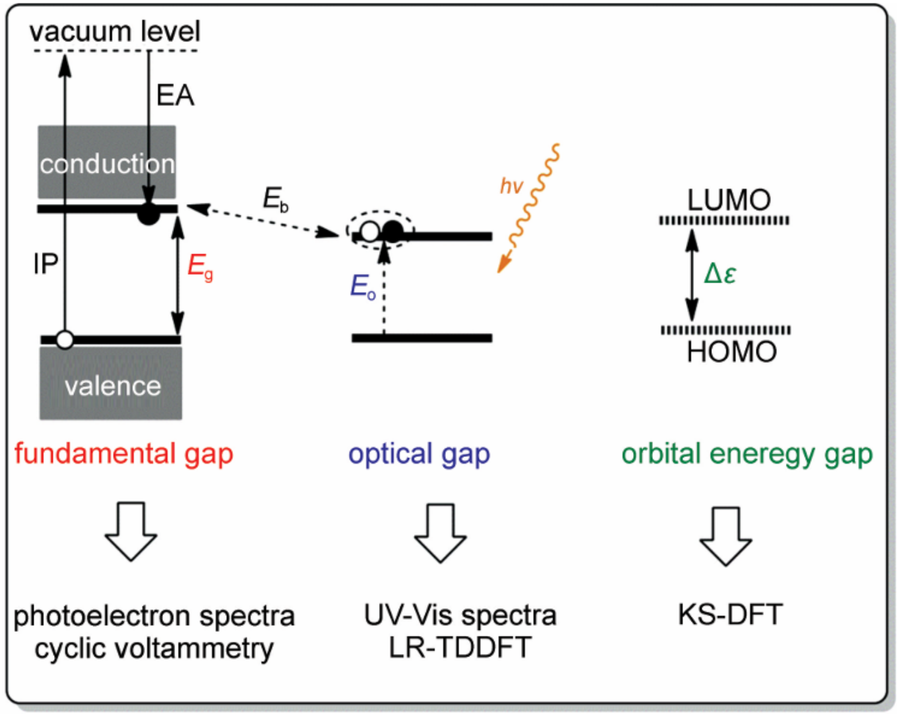
4. Excited State-Exciton Effect and Active Space

J. Phys. Chem. Lett. **2020, 11, 17, 7371–7382**










```
** Singlet excitation energies and oscillator strengths **
Excited State   1:      6.13166 eV    202.20 nm  f=0.0001
      17 -> 18        -0.62061
      17 -> 20         0.19622
      17 -> 24        -0.14537
```

$$\psi_{ex} = \sum_{ai} x_{ai}\phi_{ai} \qquad \psi_{di} = \sum_{ai} y_{ai}\phi_{ai}$$

$$\varepsilon_{ai} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) - C_{HF}\,(ij|ab)$$

4. Excited State-Exciton Effect and Active Space

TDDFT/GW+BSE(Bethe-Salpeter Equation)

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

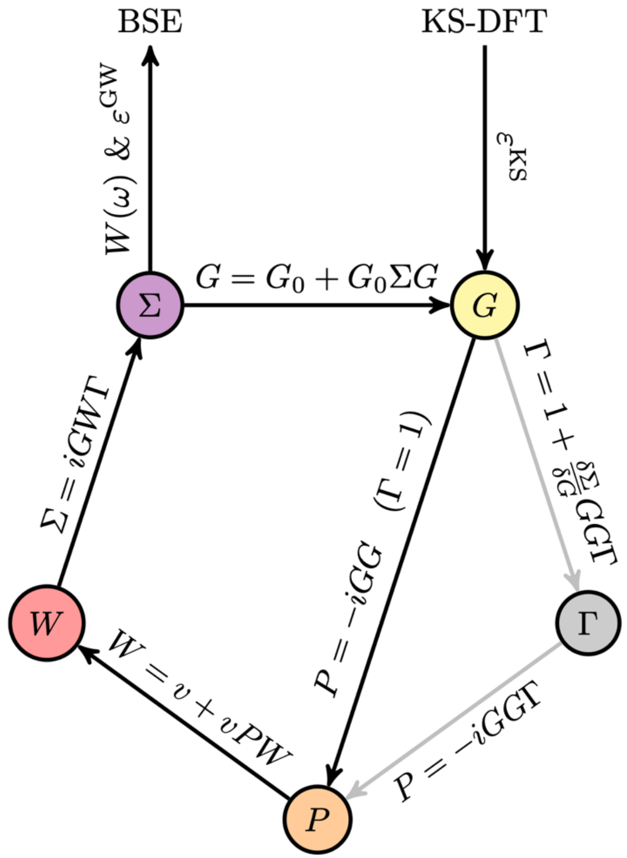
$$F_{aa}^{(0)}y_{ai} - y_{ai}F_{ii}^{(0)} - \sum_{bj}P_{ii}^{(0)}\left(\frac{\partial F_{ia}}{\partial P_{bj}}x_{bj} + \frac{\partial F_{ia}}{\partial P_{jb}}y_{bj}\right) = \omega x_{ia}$$

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

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

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

$$f_{xc} = \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \rightarrow \Sigma$$



4. Excited State-Exciton Effect and Active Space

TDDFT/GW+BSE

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

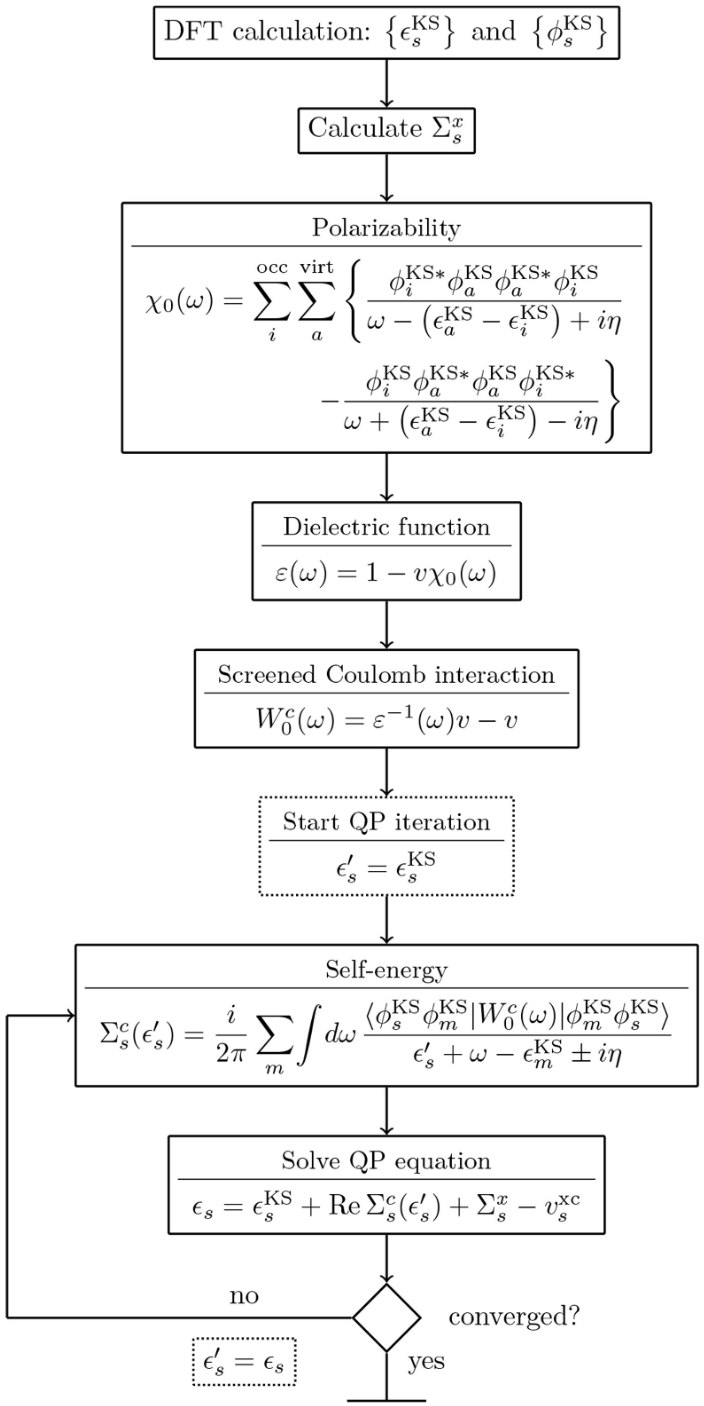
$$F^{(0)}_{aa} y_{ai} - y_{ai} F^{(0)}_{ii} - \sum_{bj} P^{(0)}_{ii} \left(\frac{\partial F_{ia}}{\partial P_{bj}} x_{bj} + \frac{\partial F_{ia}}{\partial P_{jb}} y_{bj} \right) = \omega x_{ia}$$

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

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

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

$$f_{xc} = \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \rightarrow \Sigma$$



5. Arrangement

Ground States:

- **Complete DeepH modules with attention mechanism✓**
- **Complete DeepH architecture and upgrade OPTXC with PySCF**
- **Expend monomer calculations to oligomer calculations**

Excited States:

- **Avoid to calculate x_{ai} or y_{ai} vai A matrix and B matrix with large active space**
- **Real-Time Time Dependent Density Functional Theory?**