Molecular Excited States, Time-Dependent Density Functional Theory and Vibe-Coding with Agent

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Outline

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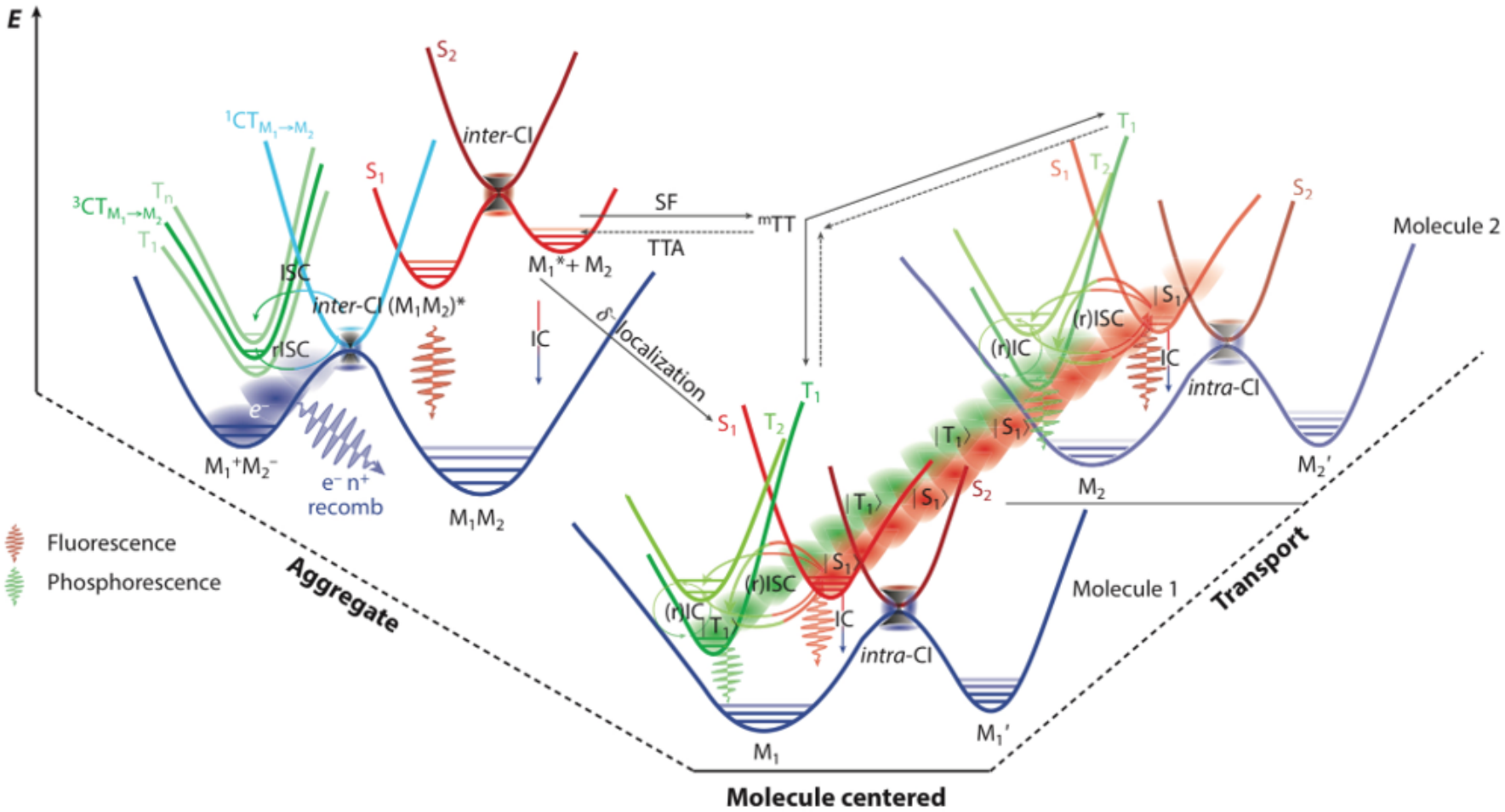
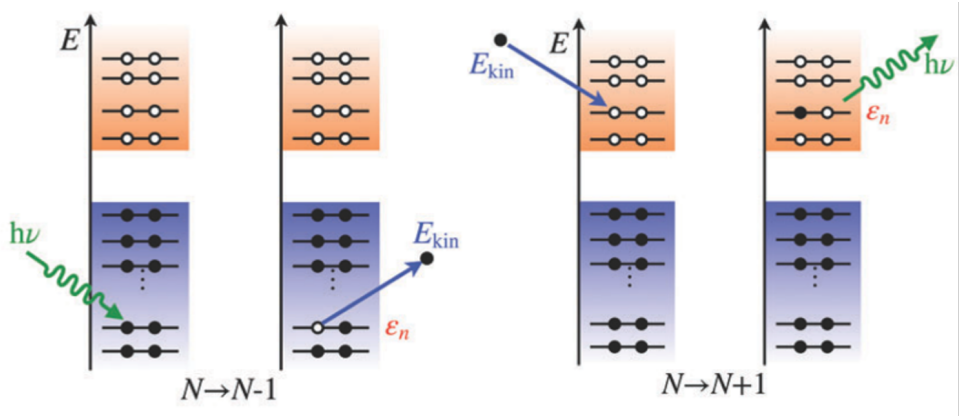
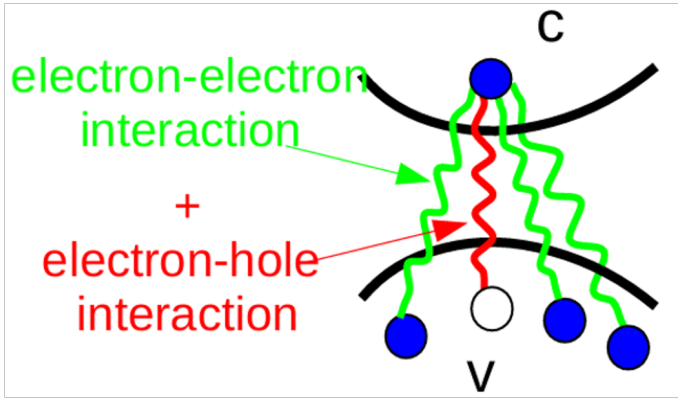
Molecular Excited States

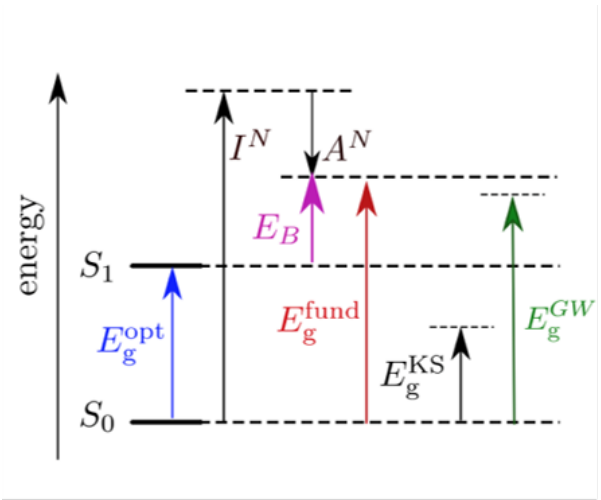


Absorption, Emission and Photoemission Process





- **Absorption**: Ground state to excited state
- **Emission**: Excited state to ground state
- **Photoemission**: Ground state to ionized state



Line spectra has two basic properties:

- **Location**: The location of the absorption peak-excitation ω_i
- **Intensity**: The height of the absorption peak-oscillator strength f_I

If we have the excited state wavefunction Ψ_I, the oscillator strength is defined as:

$$f_I = \frac{2}{3}\omega_I \sum_{n=x,y,z} |\langle \Psi_0 | \hat{r}_n | \Psi_I \rangle|^2$$

Where the Ψ_0 is the ground state wavefunction, and Ψ_I is the excited state wavefunction. We could also get the absorption spectra from the dynaimic polarizability $\alpha_{ij}(\omega)$:

$$\sigma(\omega) = -\frac{4\pi\omega}{3c}\Im(\alpha_{ii}(\omega))$$

Outline

Hohenberg-Kohn Theorem:

- HK I: The ground state or electron's density is only depended on external potential.
- HK II: For a given external potential, the energy functional is the global minimum value varying every density. And this density could be considered as the ground state electron's density.

Based on HK I ansatz, the many-electron Schrödinger equation is written in ν-representation as:

$$(\hat{T} + \hat{V}_{ee} + \hat{\nu})\Psi_0[\nu] = E_0[\nu]\Psi_0[\nu]$$

Based on HK II ansatz, the many-electron Schrödinger equation could be considered as a minimum problem of energy functional.

$$E_0[\nu] = \min_{\rho(\mathbf{r})\to N}\{F[\rho(\mathbf{r})] + \int d\mathbf{r}\nu(\mathbf{r})\rho(\mathbf{r})\}$$

The Runge-Gross theorem establishes the foundation of time-dependent density functional theory (TDDFT) by proving a one-to-one correspondence between the time-dependent electron density $\rho(\mathbf{r}, t)$ and the external potential $v_{ext}(\mathbf{r}, t)$, for a given initial state.

- **Core statement**: $\rho(\mathbf{r}, t) \leftrightarrow v_{ext}(\mathbf{r}, t)$
- **Condition**: Initial state must be non-degenerate
- **Significance**: Time-dependent generalization of the Hohenberg-Kohn theorem

$$\rho(\mathbf{r}, t) \leftrightarrow \Psi(\mathbf{r}, t) \leftrightarrow v_{ext}(\mathbf{r}, t)$$

For a many-electron system, the time-dependent Schrödinger equation can be written as:

$$i\partial_t \Psi(\mathbf{r}, t) = \hat{H}\Psi(\mathbf{r}, t)$$

The details of Hamiltonian of Schrödinger equation is:

$$\hat{H} = \hat{T}(\mathbf{r}) + \hat{V}_{e-e}(\mathbf{r}) + \hat{V}_{n-e}(\mathbf{r}) + \hat{V}_{ext}(\mathbf{r}, t)$$

The action integral is defined as:

$$A = \int_{t_0}^{t_1} dt \, \langle \Psi | \, i\partial_t - \hat{H}(r, t) \, | \Psi \rangle$$

Just like ground state Kohn-Sham equation, the action integral of Kohn-Sham system is:

$$A_S[\rho] = B_S[\rho] - \int_{t_0}^{t_1} dt \int d^3 r \rho_S(\mathbf{r}, t) v_S(\mathbf{r}, t)$$

The action integral B could be rewritten as:

$$B_s[\rho] = \int_{t_0}^{t_1} dt \sum_i \langle \phi_i[\rho] | \, i\partial_t - \hat{T}(\mathbf{r}) \, | \phi_i[\rho] \rangle + \int_{t_0}^{t_1} dt \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|r - r'|}$$

The stationary condition of action integral gives:

$$\frac{\delta A_S[\rho]}{\delta \rho} = \frac{\delta B_S[\rho]}{\delta \rho} - v_S(\mathbf{r}, t) = 0$$

So, the action integral could be rewritten as:

$$A[\rho] = B_S[\rho] - \int_{t_0}^{t_1} dt \int d^3\mathbf{r}\rho(\mathbf{r},t)v_{ext}(\mathbf{r},t)$$

$$- \int_{t_0}^{t_1} dt \int d^3\mathbf{r}d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|r-r'|} - A_{xc}[\rho]$$

and the action integral of exchange-correlation is defined as:

$$A_{xc}[\rho] = B_S[\rho] - B[\rho]$$

$$B[\rho] = \int_{t_0}^{t_1} dt \left\langle \Psi[\rho] \right| i\partial_t - \hat{T}(\mathbf{r}) - \hat{V}_{e-e}(\mathbf{r}) \left| \Psi[\rho] \right\rangle$$

with adiabatic approximation of exchange-correlation functional:

$$E_{xc}[\rho] = \frac{\delta A_{xc}[\rho]}{\delta \rho}|_{\rho(t)=\rho(0)}$$

the effective potential is defined as:

$$v_s(\mathbf{r}, t) = v_{ext} + \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho]$$

Time-dependent Kohn-Sham equation:

$$i\partial_t \phi_i = [-\frac{1}{2}\nabla^2 + v_{ext} + \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho]]\phi_i$$

Outline

In most of the TDDFT calculations of molecular systems, we have some basic assumptions:

- **Adiabatic approximation**: The exchange-correlation potential at any time depends only on the instantaneous electron density, neglecting memory effects.
- **Spin-restriction**: The spin-up and spin-down electron densities are assumed to be equal, simplifying the treatment of spin effects.
- **No fractional occupation**: Electrons are assumed to occupy orbitals in integer numbers, avoiding complications from partial occupancies.
- **Non-periodic systems**: The systems under study are considered to be non-periodic, which simplifies the boundary conditions and computational methods used.

The time-dependent Kohn-Sham equation is:

$$i\partial_t \phi_k(\mathbf{r},t) = \hat{H}_{KS}(\mathbf{r},t)\phi_k(\mathbf{r},t)$$

with a simple external potential:

$$v_{ext}(\mathbf{r},t) = -e\mathbf{r}\cdot\mathbf{E}_0\delta(t) = -e\mathbf{r}\cdot\mathbf{E}_0\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\omega t}d\omega$$

So, the ground state orbitals can be simply replaced by a time-evolution operator:

$$\phi_k(\mathbf{r},t=0^+) = exp(ie\mathbf{r}\cdot\mathbf{E}_0)\phi_k(\mathbf{r},t=0^-)$$

and the time-dependent dipole moment is defined as:

$$\mu(t) = -e\int \rho(\mathbf{r},t)\mathbf{r}d^3\mathbf{r}$$

The we could calculate the dynamic polarizability with Fourier transform of time-dependent dipole moment:

$$\alpha_{ij}(\omega) = \frac{1}{E_{0j}} \int_0^\infty exp(-i\omega t)[\mu_i(t) - \mu_i(0)]dt$$

Finally, the absorption spectrum comes from the diagonal elements of dynamic polarizability:

$$Absorption \;\; Spectrum \rightarrow \alpha_{ii}(\omega)$$

Expand time-dependent Kohn-Sham orbitals with perturbation parameter λ:

$$\phi_i(\mathbf{r},t) = \phi_i^{(0)}(\mathbf{r},t) + \lambda\phi_i^{(1)}(\mathbf{r},t) + \lambda^2\phi_i^{(2)}(\mathbf{r},t) + O(\lambda^3)$$

External perturbation potential:

$$\hat{H}_{KS}(\mathbf{r},t) = \hat{H}_{KS}^{(0)}(\mathbf{r}) + \lambda v_{ext}^{(1)}(\mathbf{r},t) + \lambda\hat{H}_{KS}^{(1)}(\mathbf{r},t)$$

Density expansion:

$$\rho(\mathbf{r},t) = \sum_i f_i|\phi_i|^2 = \rho^{(0)}(\mathbf{r},t) + \lambda\rho^{(1)}(\mathbf{r},t) + \lambda^2\rho^{(2)}(\mathbf{r},t) + O(\lambda^3)$$

in detail:

$$\rho^{(0)}(\mathbf{r},t) = \sum_i n_i |\phi_i^{(1)}|^2$$

$$\rho^{(1)}(\mathbf{r},t) = \sum_i n_i |[\phi_i^{(0)}]^*[\phi_i^{(1)}] + [\phi_i^{(1)}]^*[\phi_i^{(0)}]|$$

The first-order response Hamiltonian is defined as:

$$\hat{H}_{KS}^{(1)}(\mathbf{r},t) = \int d^3\mathbf{r}' \frac{\rho^{(1)}(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + \int d^3\mathbf{r}' f_{xc}^{(0)}(\mathbf{r},t;\mathbf{r}',t')\rho^{(1)}(\mathbf{r}',t')$$

and the TDKS equation is:

$$i\partial_t \phi_i^{(1)}(\mathbf{r},t) = \hat{H}_{KS}^{(0)}(\mathbf{r})\phi_i^{(1)}(\mathbf{r},t) + [v_{ext}^{(1)}(\mathbf{r},t) + \hat{H}_{KS}^{(1)}(\mathbf{r},t)]\phi_i^{(0)}(\mathbf{r},t)$$

Consider a periodic perturbation with single frequency ω for most of the cases:

$$v_{ext}^{(1)}(\mathbf{r},t) = v_{ext}^{+\omega}(\mathbf{r})e^{i\omega t} + h.c.$$

So, the general solution of first-order TDKS equation is:

$$\phi_i(\mathbf{r},t) = e^{-i\varepsilon_i^{(0)}t - \lambda i \Delta\varepsilon_i^{(1)}t}$$

$$\times\{\phi_i^{(0)}(\mathbf{r}) + \lambda[\phi_i^{(1),+\omega}(\mathbf{r})e^{i\omega t} + \phi_i^{(1),-\omega}(\mathbf{r})e^{-i\omega t}]\} + O(\lambda^2)$$

Where the $\phi_i^{(1),+\omega}(\mathbf{r})$ and $\phi_i^{(1),-\omega}(\mathbf{r})$ are the first-order response orbitals with frequency of $+\omega$ and $-\omega$. And the $\Delta\varepsilon_i^{(1)}$ is the level shift of first-order response Hamiltonian.

$$\Delta\varepsilon_i^{(1)} = \int dt \,\langle\phi_i^{(0)}|\,[v_{ext}^{(1)} + \hat{H}_{KS}^{(1)}]\,|\phi_i^{(0)}\rangle$$

So, the first-order density is:

$$\rho^{(1)}(\mathbf{r},t) = \sum_i n_i \{[\phi_i^{(0)}]^* \phi_i^{+\omega,(1)} + [\phi_i^{-\omega,(1)}]^* \phi_i^{(0)}\} e^{-i\omega t} + c.c.$$

After some algebra, we could get the Sternheimer equation:

$$i\partial_t e^{-i\varepsilon_i^{(0)}t - \lambda i \Delta\varepsilon_i^{(1)}t} \{\phi_i^{(0)}(\mathbf{r}) + \lambda[\phi_i^{(1),+\omega}(\mathbf{r}) e^{i\omega t} + \phi_i^{(1),-\omega}(\mathbf{r}) e^{-i\omega t}]\}$$

$$= \hat{H}_{KS}^{(0)}(\mathbf{r}) e^{-i\varepsilon_i^{(0)}t - \lambda i \Delta\varepsilon_i^{(1)}t} \{\phi_i^{(0)}(\mathbf{r}) + \lambda[\phi_i^{(1),+\omega}(\mathbf{r}) e^{i\omega t} + \phi_i^{(1),-\omega}(\mathbf{r}) e^{-i\omega t}]\}$$

$$+\lambda\{[\int d^3 f_{Hxc} \rho^{(1)}(\mathbf{r}'.t) + v_{ext}^{(1)}(\mathbf{r},t)]\phi_i^{(0)}(\mathbf{r})\} e^{-i\varepsilon_i^{(0)}t - \lambda i \Delta\varepsilon_i^{(1)}t}$$

Now we divide the equation into two parts with frequency of $+\omega$ and $-\omega$ for resonant and anti-resonant solution. So we could rewrite the Sternheimer equation in a compact form:

For resonant solution $(+\omega)$:

$$[\hat{H}_{KS}^{(0)} - \varepsilon_i^{(0)} + \omega + i\eta]\phi_i^{(1),+\omega}(\mathbf{r}) = -Q_i^{+\omega}(\mathbf{r})\phi_i^{(0)}(\mathbf{r})$$

where $Q_i^{+\omega}(\mathbf{r}) = \int d^3\mathbf{r}' f_{Hxc}\rho^{+\omega,(1)}(\mathbf{r}', t) + \nu_{ext}^{+\omega}(\mathbf{r})$

For anti-resonant solution $(-\omega)$:

$$[\hat{H}_{KS}^{(0)} - \varepsilon_i^{(0)} - \omega + i\eta]\phi_i^{(1),-\omega}(\mathbf{r}) = -Q_i^{-\omega}(\mathbf{r})\phi_i^{(0)}(\mathbf{r})$$

where $Q_i^{-\omega}(\mathbf{r}) = \int d^3\mathbf{r}' f_{Hxc}\rho^{-\omega,(1)}(\mathbf{r}', t) + \nu_{ext}^{-\omega}(\mathbf{r})$

with a decay factor η of external perturbation in $e^{-\eta t}$.

The electron-hole basis is defined as:

$$\phi_i^{(1)} = \sum_a c_{ai} \phi_a^{(0)}(\mathbf{r})$$

Then, rewrite the first-order Sternheimer equation in electron-hole basis:

$$\sum_{aj} (-\omega + \varepsilon_j^{(0)}) \delta_{ab} \delta_{ij} c_{aj}^{+\omega} + \sum_{aj} (\omega + \varepsilon_i^{(0)}) \delta_{ab} \delta_{ij} c_{aj}^{-\omega}$$

$$= \sum_{aj} \varepsilon_a^{(0)} \delta_{ab} \delta_{ij} c_{aj}^{+\omega} + \sum_{aj} \varepsilon_a^{(0)} \delta_{ab} \delta_{ij} c_{aj}^{-\omega}$$

$$+ \langle \phi_b^{(0)} | f_{Hxc}[\rho^{(0)}] \rho^{(1)} + v_{ext}^{(1)} | \phi_i^{(0)} \rangle$$

The Hartree-exchange-correlation kernel:

$$f_{Hxc}(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r},\mathbf{r}')$$

Coupling matrices in electron-hole basis:

$$K_{bi,aj} = \int d^3\mathbf{r} \int d^3\mathbf{r}' \phi_a^{*(0)}(\mathbf{r}')\phi_j^{(0)}(\mathbf{r}') \times f_{Hxc}(\mathbf{r},\mathbf{r}')\phi_b^{*(0)}(\mathbf{r})\phi_i^{(0)}(\mathbf{r})$$

Compact form:

$$\langle \phi_b^{(0)} | f_{Hxc}[\rho^{(0)}]\rho^{(1)} | \phi_i^{(0)} \rangle = \sum_{aj} n_j \{K_{bi,aj}(c_{aj}^{+\omega} e^{-i\omega t} + c_{aj}^{-\omega} e^{i\omega t}) + K_{bi,ja}(c_{aj}^{+\omega} e^{i\omega t} + c_{aj}^{-\omega} e^{-i\omega t})\}$$

with the coupling matrix $K_{bi,aj}$ as defined previously.
The Casida equation in matrix form:

$$\begin{bmatrix} -\Delta E - \mathbf{K} & -\mathbf{K}' \\ \mathbf{K}' & \Delta E + \mathbf{K} \end{bmatrix} \begin{bmatrix} Re[B^{+\omega}] \\ Re[B^{-\omega}] \end{bmatrix} = \omega \begin{bmatrix} Re[B^{+\omega}] \\ Re[B^{-\omega}] \end{bmatrix}$$

where $\Delta E_{bi,aj} = (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij}$

We rewrite the Casida equation in a more familiar form:

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

with the matrix elements:

A-matrix:

$$A_{bi,aj} = \delta_{ij}\delta_{ab}(\epsilon_j - \epsilon_b) + \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r})\phi_b(\mathbf{r})$$

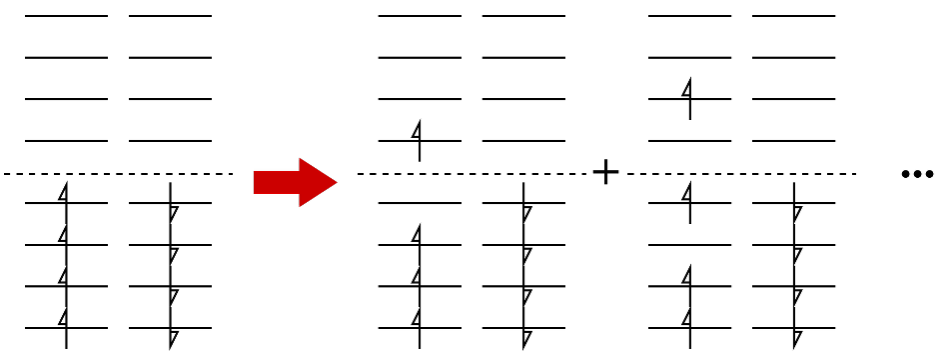
$$\times \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right] \phi_a^*(\mathbf{r}')\phi_j(\mathbf{r}')$$

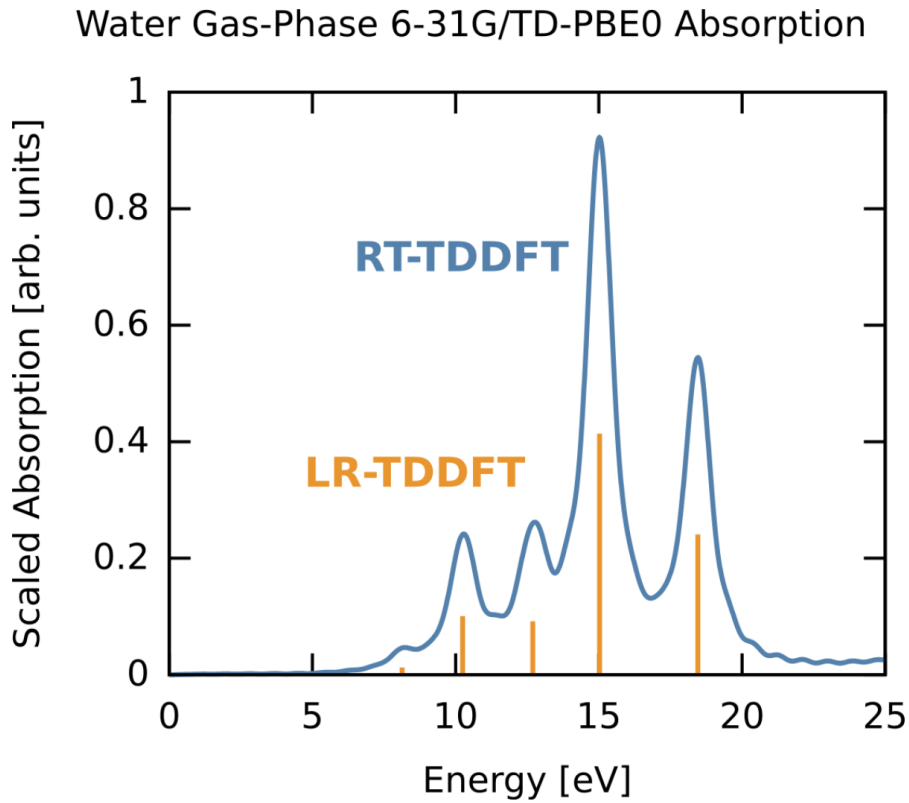
B-matrix:

$$B_{bi,aj} = \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r})\phi_b(\mathbf{r})$$

$$\times \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right] \phi_j^*(\mathbf{r}')\phi_a(\mathbf{r}')$$

- Time-Propagation Approach
- Sternheimer Approach
- Casida Approach





Appendix-Matrix Size of Hamiltonian in DFT and TDDFT

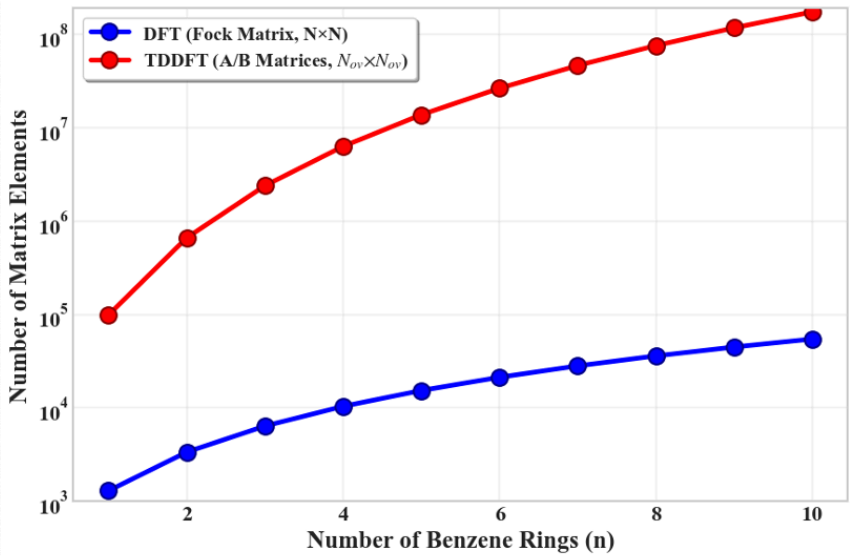
Casida Equation

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

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

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

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



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

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

Excited State AB Matrix: $\sim O(N_e^5)$ for calculation $\sim O(N_e^4)$ 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**

Outline

Given the Casida matrix:

$$\mathcal{L} = \begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix}$$

and we want to solve

$$\mathcal{L}\Psi_k = \omega_k \Psi_k$$

where Ψ_k stacks (X_k, Y_k).
Assume we have a set of orthonormal subspace trial vectors:

$$\{\Psi_j\}_{j=1}^{m}, \quad \Psi_j = \begin{pmatrix} X_j \\ Y_j \end{pmatrix}$$

Construct matrix $W \in \mathbb{C}^{2N\times m}$, with columns Ψ_j.

Project $\mathcal{L}$ into this subspace:

$$H_{\text{eff}} = W^{\dagger} \mathcal{L} W \in \mathbb{C}^{m \times m}$$

Solve the projected problem:

$$H_{\text{eff}} \mathbf{y}_i = \omega_i \mathbf{y}_i$$

Ritz vectors:

$$\Psi_i^{(\text{Ritz})} = W \mathbf{y}_i$$

Residuals:

$$\mathbf{r}_i = \mathcal{L} \Psi_i^{(\text{Ritz})} - \omega_i \Psi_i^{(\text{Ritz})}$$

If all $\|\mathbf{r}_i\|$ are below tolerance, the solution is found. Otherwise, use preconditioned residuals to further expand subspace W and repeat.

If the residual is too large, expand the subspace as follows:

1. Compute the residual:

$$\mathbf{r}_i = \mathcal{L}\Psi_i^{(\text{Ritz})} - \omega_i \Psi_i^{(\text{Ritz})}$$

2. Apply a preconditioner:

$$t_i \approx \frac{\mathbf{r}_i}{\text{diag}(H_{\text{eff}}) - \omega_i}$$

3. Orthonormalize t_i against existing subspace vectors.
4. If t_i is not linearly dependent ($\|t_i\|$ big enough), add it to the subspace.
5. Repeat the Rayleigh-Ritz projection with the enlarged subspace.

Outline

Vibe Coding represents a new paradigm where developers interact with AI coding assistants through natural language conversations to build software solutions.

Key characteristics:

- Natural language interface for coding
- Iterative refinement through conversation
- AI handles implementation details
- Human focuses on high-level design
- Rapid prototyping and exploration

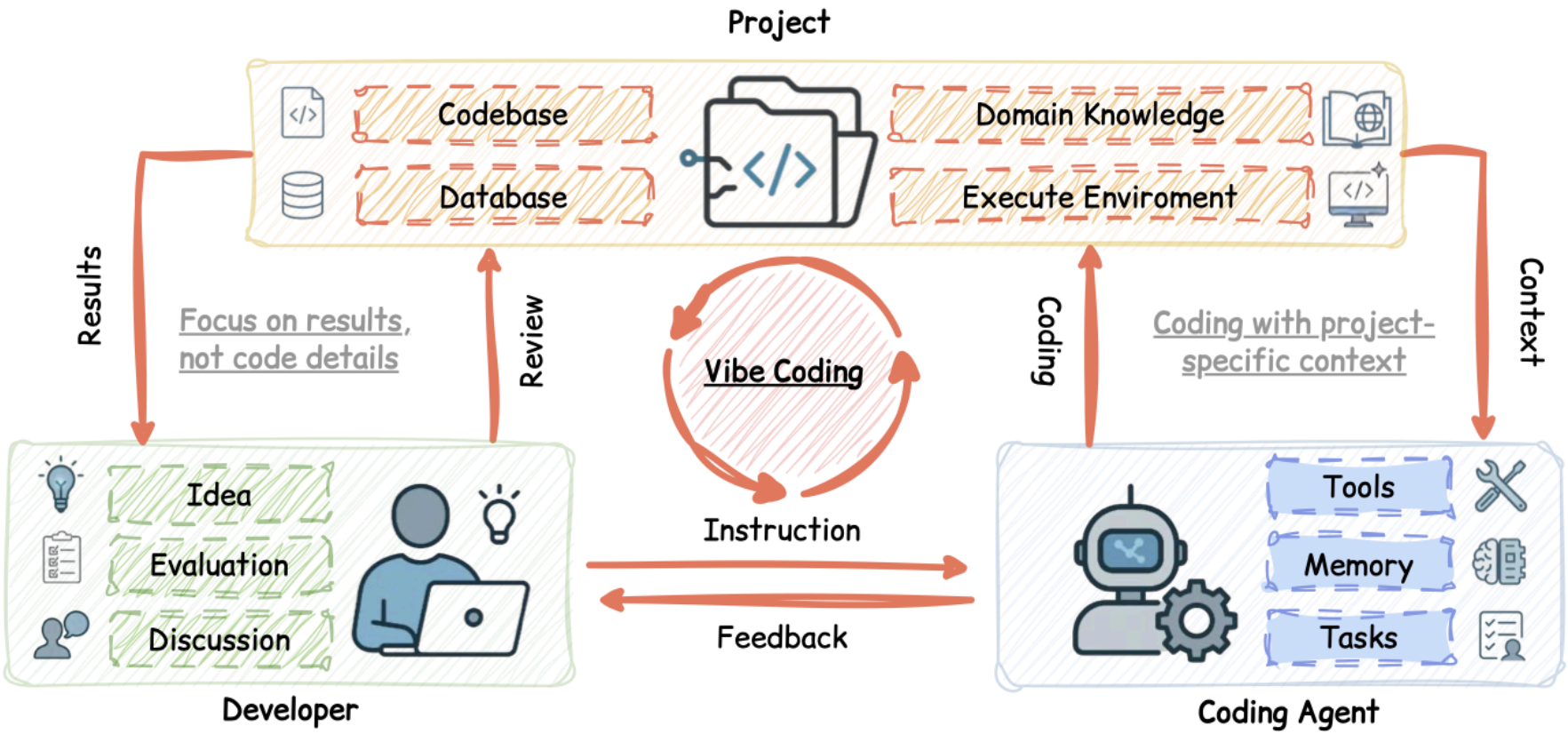


Figure 1: AI-Assisted Development Environment

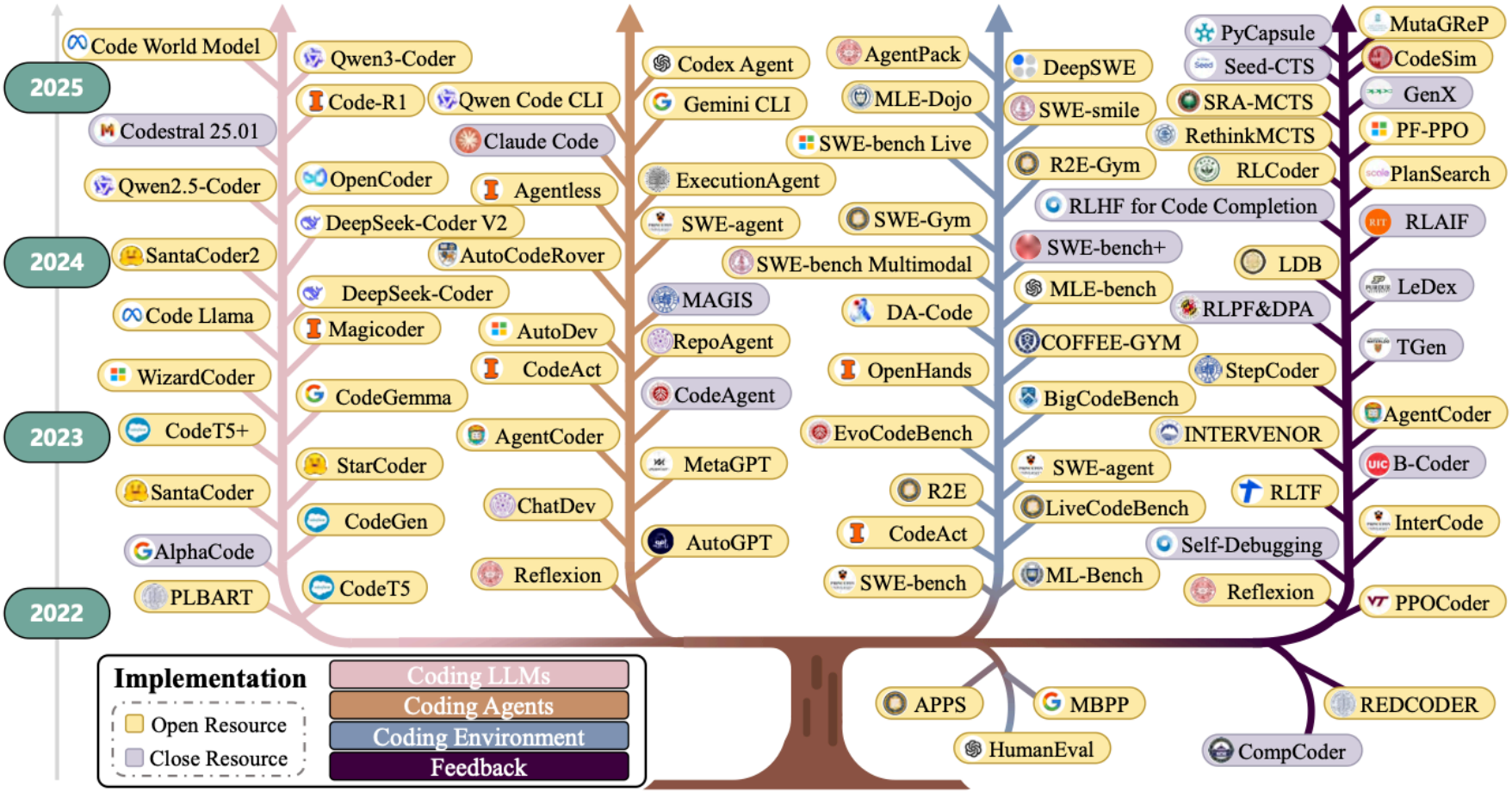


Figure 2: Interactive Code Generation

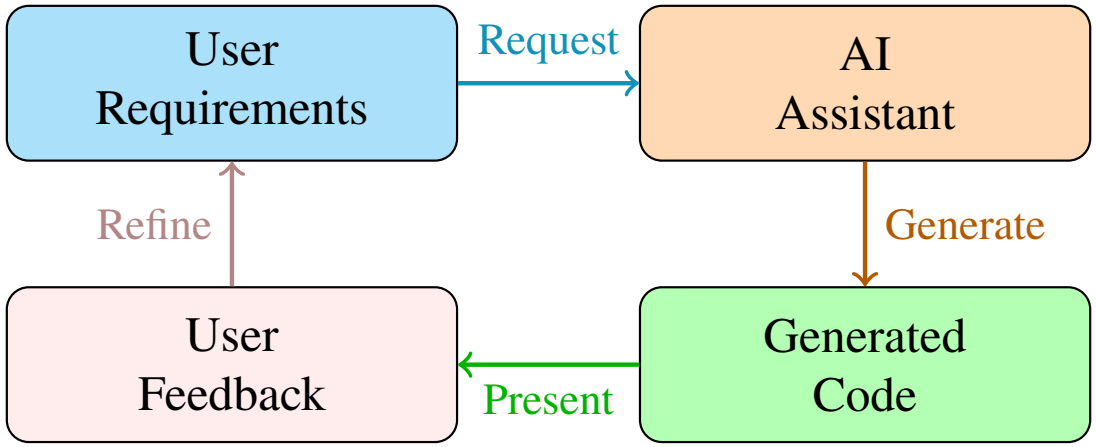


Figure 3: Vibe Coding Iterative Workflow

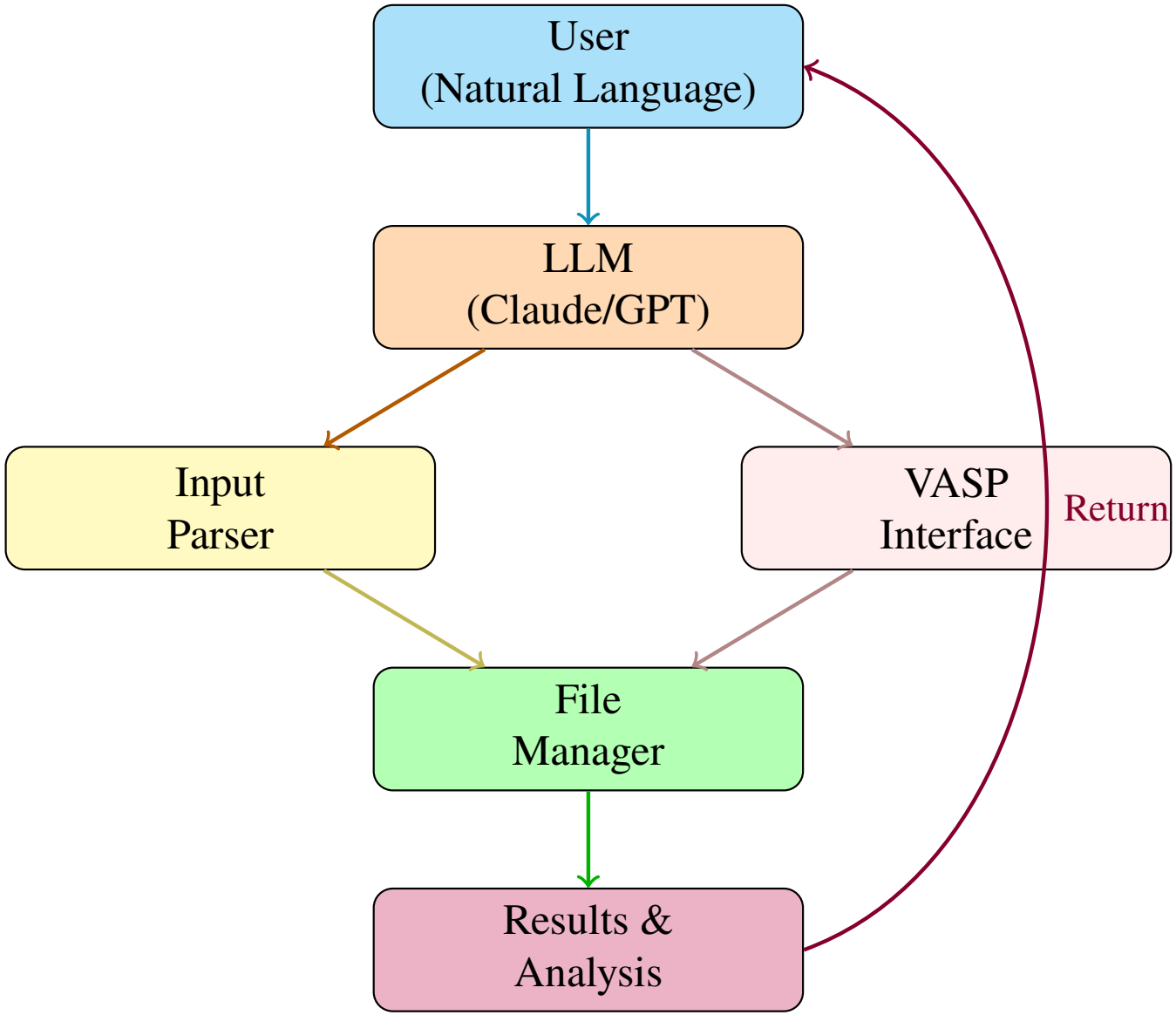


Figure 4: VASPilot Architecture [1]

Core Capabilities:

- Natural language input for VASP calculations
- Automatic INCAR, KPOINTS, POSCAR generation
- Job submission and monitoring
- Result extraction and analysis
- Integration with popular quantum chemistry packages

User Request:
"Calculate the band structure of silicon with PBE functional"

Process

VASPilot Response:
- Generates INCAR with PBE functional
- Creates KPOINTS file
- Sets up POSCAR structure
- Submits calculation to queue
- Returns band structure results

Figure 5: Example VASPilot Interaction

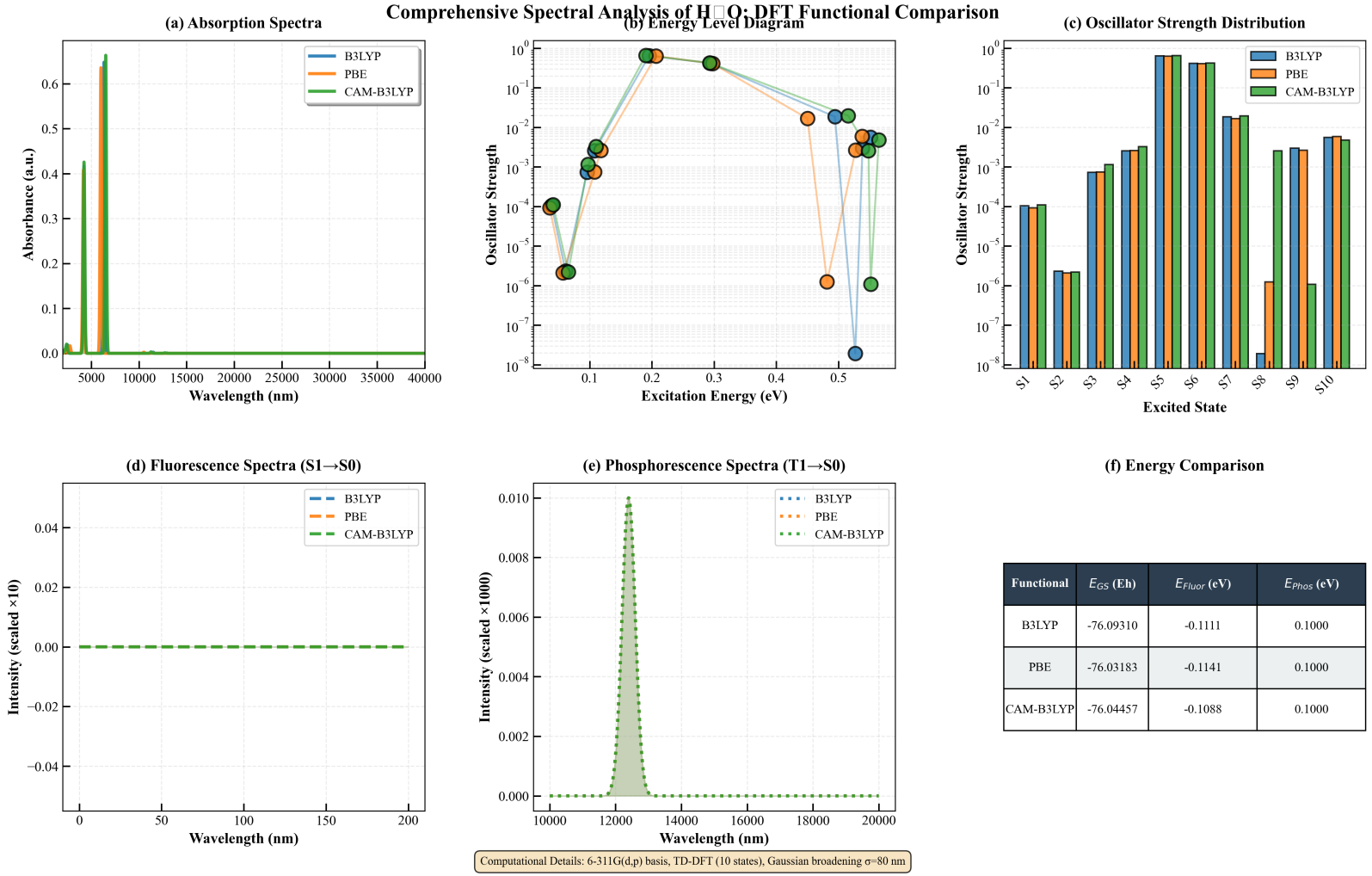
Computational Setup:

- **Molecule:** H_2O (water molecule)
- **Method:** TDDFT with various functionals
- **Basis Set:** 6-31G(d) and 6-31+G(d,p)
- **Functionals Tested:**
  - PBE (GGA functional)
  - B3LYP (Hybrid functional)
  - CAM-B3LYP (Long-range corrected hybrid)

Vibe Coding Approach:

- Used natural language to describe requirements
- AI assistant generated Python code for TDDFT calculations
- Automated spectrum plotting and analysis
- Interactive refinement of visualization

Water Molecule Absorption Spectrum



Functional	E_{GS} (Eh)	E_{Fluor} (eV)	E_{Phos} (eV)
B3LYP	-76.09310	-0.1111	0.1000
PBE	-76.03183	-0.1141	0.1000
CAM-B3LYP	-76.04457	-0.1088	0.1000

Figure 6: Absorption spectrum of water molecule calculated with TDDFT using different functionals

Key Observations:

- PBE underestimates excitation energies
- B3LYP provides better agreement with experiment
- CAM-B3LYP improves for charge-transfer states
- Basis set effects are significant

Functional	Peak (eV)	Intensity
PBE	7.2	0.85
B3LYP	7.8	0.92
CAM-B3LYP	8.1	0.88
Exp.	7.9	-

Table 1: Comparison of excitation energies

Workflow:

1. **Natural Language Request:**
   - ”Calculate absorption spectrum of water molecule using TDDFT with B3LYP functional and 6-31G(d) basis set”
2. **AI Code Generation:**
   - Python script using PySCF
   - Automatic geometry optimization
   - TDDFT calculation
   - Spectrum extraction and plotting
3. **Interactive Refinement:**
   - Adjust plotting style
   - Add Gaussian broadening
   - Compare multiple functionals
   - Annotate peaks

Advantages:

- **Accessibility:** Lower barrier to entry
- **Efficiency:** Rapid prototyping
- **Flexibility:** Easy modification and exploration
- **Learning:** Natural learning curve
- **Documentation:** Self-documenting conversations

Applications:

- Method development
- Rapid screening
- Educational tools
- Automated workflows

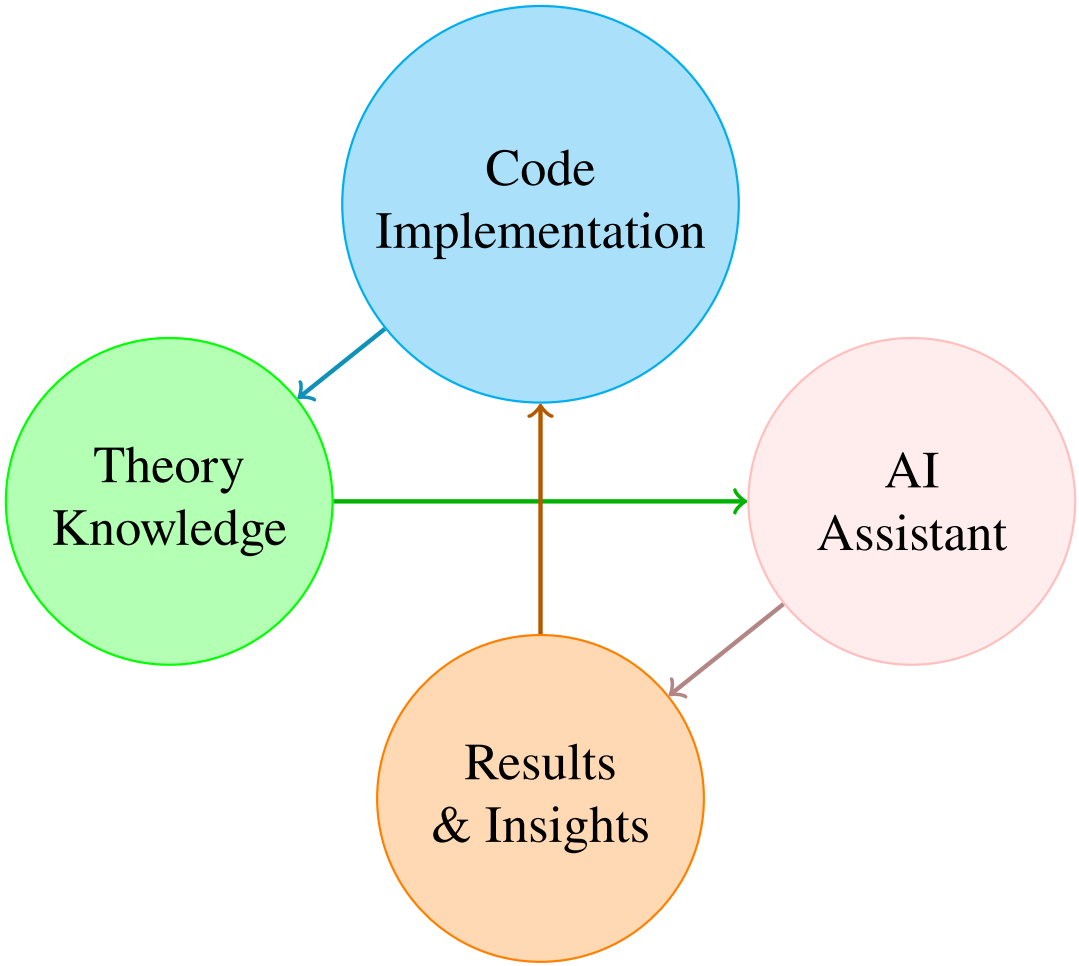


Figure 7: Vibe Coding Iterative Development Cycle

Problem Statement:

- Rapid growth of scientific literature in electronic structure theory and AI
- Time-consuming to manually track relevant papers
- Need for automated, personalized paper collection
- Integration of theoretical chemistry with AI tools

Objectives:

- Automated daily paper fetching from arXiv
- Keyword-based filtering (electronic structure + AI)
- LaTeX PDF report generation
- Cross-platform compatibility
- Scheduled execution with notifications

Interactive Development with AI:

1. **Initial Request:** ”Create a Python program to collect arXiv papers on electronic structure and AI, generate PDF reports”
2. **AI Iterations:**
   - Architecture design
   - Code implementation (6 core modules)
   - Bug fixing (datetime, Jinja2, LaTeX)
   - Portability improvements
3. **User Feedback Loop:**
   - Testing and validation
   - Feature requests (notifications, scheduling)
   - Documentation improvements
4. **Final Deployment:** GitHub repository with automatic scheduling

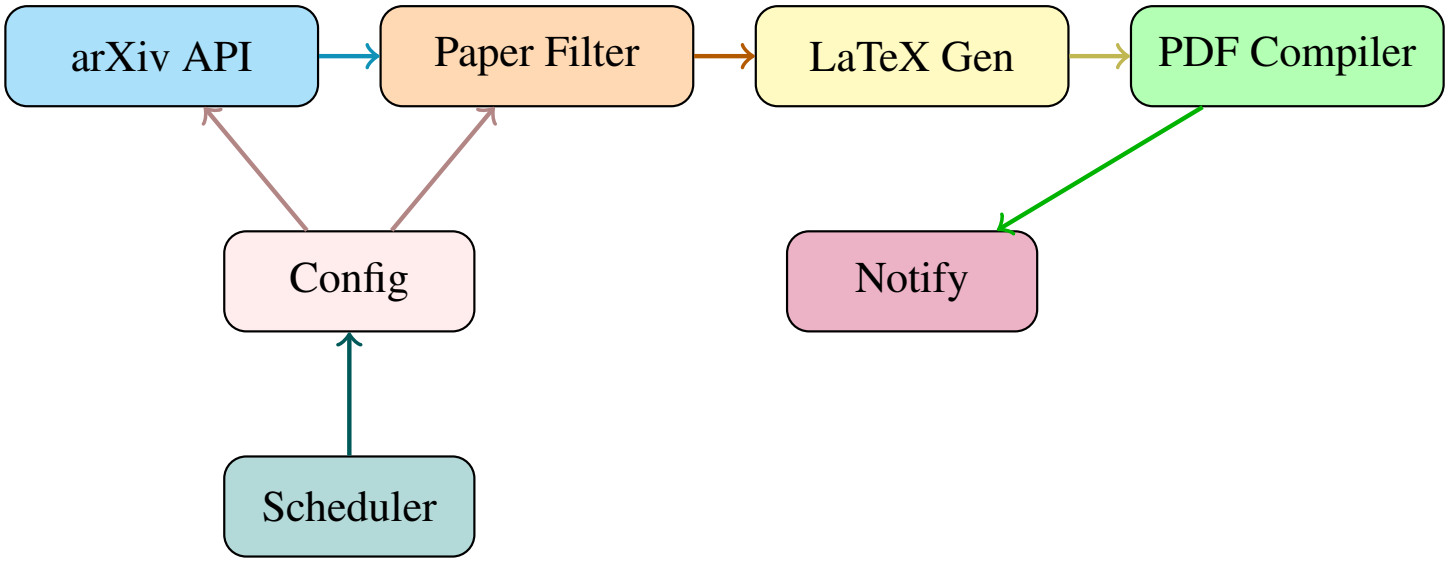


Figure 8: ArXiv Paper Collector Architecture

Six Core Modules:

1. **arxiv_fetcher.py**
   arXiv API integration
2. **paper_filter.py**
   Keyword-based filtering
3. **latex_generator.py**
   LaTeX document generation
4. **pdf_compiler.py**
   PDF compilation (pdflatex/xelatex)
5. **scheduler.py**
   Task scheduling
6. **notifications.py**
   System & email notifications

Key Features

- ✓ 1000+ lines of Python code
- ✓ Cross-platform support
- ✓ YAML configuration
- ✓ Automatic installation
- ✓ Scheduled execution
- ✓ Notification system

Sample Output:

- **Date:** 2026-01-12
- **Papers Collected:** 394 papers (7 days)
- **Groups:**
  - Electronic Structure: 327 papers
  - Artificial Intelligence: 317 papers
  - Uncategorized: 14 papers
- **PDF Size:** 170 KB

Report Contents:

- Paper title and authors
- arXiv ID and PDF download link
- Publication date and categories
- Formatted abstract (truncated)
- Hyperlinked references

Cron Job Configuration:

- Automatic daily execution at 10:00 AM
- Log file: `output/cron.log`
- Error handling and retries

Notification System:

- Desktop notifications (macOS/Linux/Windows)
- Email notifications via SMTP
- Success/failure status updates

Sample Notification

"Successfully collected 394 papers
PDF: output/papers/arxiv_papers_2026-01-12.pdf"

Repository:

- `https://github.com/STOKES-DOT/arxiv-paper-collector`
- Open source (MIT License)
- Complete documentation
- Installation scripts for all platforms

Portability Features:

- Cross-platform (Windows/macOS/Linux)
- Virtual environment support
- User configuration directory (`~/.config/arxiv-collector`)
- Path auto-expansion
- One-command setup: `./install.sh`

Vibe Coding Benefits Demonstrated

Development Time: ~2 hours (from concept to deployment)

Key Advantages Shown:

- **Rapid Prototyping:** Working code after initial prompt
- **Iterative Refinement:** Bug fixes and features through conversation
- **Cross-Disciplinary:** Combined TDDFT knowledge with software engineering
- **Best Practices:** Clean code, documentation, version control
- **Deployment:** GitHub integration, CI/CD ready

Impact:

- Automated daily literature review
- Saved hours of manual work
- Customizable for any research field
- Shareable with research community

TDDFT:

- Powerful method for excited states
- Three main approaches (Time-Propagation, Sternheimer, Casida)
- Balance between accuracy and computational cost

Vibe Coding:

- Natural language interface
- AI-assisted development
- Democratizing computational chemistry

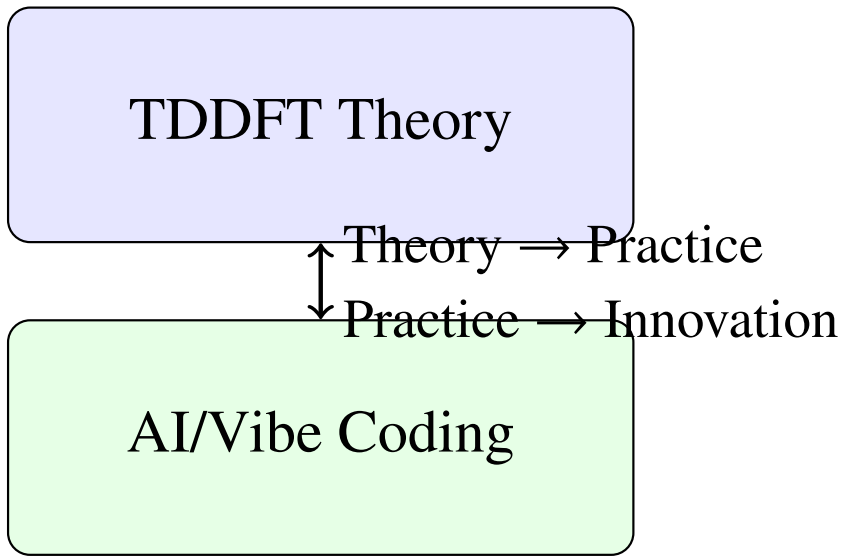


Figure 9: Synergy of Theory and AI