Advancement of RT-TDDFT from machine learning perspective

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Introduction to RT-TDFT

Project objectives

1. An efficient implementation of AES approach by integrating autoregressive Fourier neural operators to develop GKS-based RT-TDDFT dynamics.

2. An efficient accommodation of the Lindblad operators to encounter the electronic dephasing and plasmonic relaxation effects in conjunction with (1).

3. Development of a trajectory based nonadiabatic dynamics using the Ehrenfest approach in conjunction with (1) and (2).

RT-TDDFT within KS framework

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{KS}}(t)\ \phi_k(r,t)$$

Key Components :

- preparation of the initial density and orbitals
- selection of the density functional approximations (DFAs)
- formulation of the time-dependent KS potential
- choice of the time dependent propagation scheme

Time-dependent propagator

$$\mathbf{U}(t,0) = \mathscr{T}\exp\left\{ -i\int_0^t dt'\hat{h}_r^{\mathrm{KS}}[n](t')\right\}$$

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RT-TDDFT within KS framework

Time-dependent propagator

$$\mathbf{U}(t,0) = \mathcal{T}\exp\left\{-i\int_0^t dt'\hat{h}_r^{\mathrm{KS}}[n](t')\right\}$$

Short-time propagator

$$\mathbf{U}(t,0) = \prod_{i=0}^{N-1}\mathbf{U}(t_i + \Delta t, t_i)$$

Accuracy and efficiency of RT-TDFT

- Level of approximate time-dependent propagator (ATDP)
- Spectral characteristic of TD-KS Hamiltonian

RT-TDDFT within KS framework

Time-dependent propagator

$$\mathbf{U}(t,0) = \mathscr{T}\exp\left\{ -i\int_0^t dt'\hat{h}_r^{\mathrm{KS}}[n](t')\right\}$$

Short-time propagator

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Accuracy and efficiency of RT-TDFT

- Level of approximate time-dependent propagator (ATDP)
- Spectral characteristic of TD-KS Hamiltonian

This is limited to local or seminal density functional approximations (DFAs)

RT-TDDFT within GKS framework

Time-dependent GKS equation

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{GKS}}(t)\ \phi_k(r,t)$$

$$\hat{h}_r^{\mathrm{GKS}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(t)] + \hat{v}(r,t)$$

Time-dependent density matrix

$$\rho^{\mathrm{S}}(r,r',t) = \sum_{k=1}^{N} \phi_k(r,t)\phi_k^{\star}(r',t)$$

Time-dependent density

$$n^{\mathrm{S}}(r,t) = \rho^{\mathrm{S}}(r,r,t) = \sum_{k=1}^{N} |\phi_k(r,t)|^2$$

RT-TDDFT within GKS framework

Time-dependent GKS Hamiltonian

$$\hat{h}_r^{\mathrm{GKS}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(t)] + \hat{v}(r,t)$$

Exchange operator :

$$\hat{g}[\rho^{\mathrm{S}}(t)]\phi_k(r,t) = \int \frac{\rho^{\mathrm{S}}(r,r',t)}{|r-r'|}\mathrm{d}r'\phi_k(r',t)$$

Time-dependent one-body potential :

$$v(r,t) = v_{\mathrm{ext}}(t) + v_{\mathrm{R}}[n^{\mathrm{S}}(t)](r)$$

TD-GKS : generalised Runge-Gross theorem if $\mathrm{Im}[\hat{g}_r[\rho^{\mathrm{S}}(t)]\rho^{\mathrm{S}}(r,r',t)]_{r\equiv r'} = 0.$

RT-TDDFT within GKS framework

Time-dependent GKS Hamiltonian

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TD-GKS : generalised Runge-Gross theorem if $\mathrm{Im}[\hat{g}_r[\rho^{\mathrm{S}}(t)]\rho^{\mathrm{S}}(r,r',t)]_{r\equiv r'} = 0.$

In general Hybrid and Range-separated hybrid functionals satisfy this conditions.

Computational challenges

Classical propagation scheme

Time-dependent GKS equation

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{GKS}}(t)\ \phi_k(r,t)$$

$$\hat{h}_r^{\mathrm{GKS}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(t)] + \hat{v}(r,t)$$

Time-dependent propagation

$$n^{\mathrm{S}}(t) \rightarrow n^{\mathrm{S}}(t+\Delta t)$$

Computationally demanding step

$$\hat{g}[\rho^{\mathrm{S}}(t)]\phi_k(r)$$

Advantage of ML approach over classical propagation

Time-dependent GKS equation

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{GKS}}(t)\ \phi_k(r,t)$$

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ML based FNOs

Computationally demanding step

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$[\rho^{\mathrm{S}}(t)]$??

Advantage of ML approach over classical propagation

Time-dependent GKS equation

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{GKS}}(t)\ \phi_k(r,t)$$

$$\hat{h}_r^{\mathrm{GKS}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(t)] + \hat{v}(r,t)$$

ML based FNOs approach

$$\rho^{\mathrm{S}}(t) \rightarrow \rho^{\mathrm{S}}(t+\Delta t)$$

$$\frac{\partial}{\partial t}\rho(r,r',t) = i\left(\hat{h}_r^{\mathrm{GKS}}(t) - \hat{h}_{r'}^{\mathrm{GKS}}(t)\right)\rho(r,r',t)$$

Computationally Challenging

Advantage of ML approach over classical propagation

Time-dependent GKS equation

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{GKS}}(t)\ \phi_k(r,t)$$

$$\hat{h}_r^{\mathrm{GKS}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(t)] + \hat{v}(r,t)$$

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Alternative way ??

FNOs based ML approach in adiabatic Eigen subspace

TD-GKS framework in AES

Time-dependent GKS equation

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{GKS}}(t)\ \phi_k(r,t)$$

$$\hat{h}_r^{\mathrm{GKS}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(t)] + \hat{v}(r,t)$$

Adiabatic Eigen subspace

$$\phi_k(r,t) = \sum_l a_{kl}(t)\phi_l(r); \qquad a_{kl}(t) = \delta_{kl} \ \text{ at } t = 0$$

$$\hat{H}_r^{\mathrm{GKS}}(t) = \hat{H}_r^{\mathrm{GKS,st}}(t) + \hat{H}_r^{\mathrm{GKS,dy}}(t)$$

Stationary GKS Hamiltonian

$$\hat{H}_r^{\mathrm{GKS,st}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(0)] + v(r,0)$$

TD-GKS framework in AES

Time-dependent GKS equation

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Stationary GKS Hamiltonian

$$\hat{H}_r^{\mathrm{GKS,st}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(0)] + v(r,0)$$

Removes the high frequency oscillation $\exp(-i\frac{\epsilon}{2}\Delta t)$

TD-GKS framework in AES

Time-dependent GKS equation

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$$\hat{H}_r^{\mathrm{GKS}}(t) = \hat{H}_r^{\mathrm{GKS,st}}(t) + \hat{H}_r^{\mathrm{GKS,dy}}(t)$$

Dynamic GKS Hamiltonian

$$\hat{H}_r^{\mathrm{GKS,dy}}(t) = \left(\hat{g}[\rho^{\mathrm{S}}(t)] - \hat{g}[\rho^{\mathrm{S}}(0)]\right) + \left[v(r,t) - v(r,0)\right]$$

Time-dependent fluctuations which is very small compare to stationary part

TD-GKS framework in AES

Time-dependent GKS equation

$$i\dot{\phi}_k(r,t) = \hat{h}_r^{\mathrm{GKS}}(t)\ \phi_k(r,t)$$

$$\hat{h}_r^{\mathrm{GKS}}(t) = -\frac{\nabla^2}{2} + \hat{g}[\rho^{\mathrm{S}}(t)] + \hat{v}(r,t)$$

Adiabatic eigen subspace

$$\phi_k(r,t) = \sum_l a_{kl}(t)\phi_l(r); \qquad a_{kl}(t) = \delta_{kl} \ \text{ at } t = 0$$

$$\hat{H}_r^{\mathrm{GKS}}(t) = \hat{H}_r^{\mathrm{GKS,st}}(t) + \hat{H}_r^{\mathrm{GKS,dy}}(t)$$

Time-dependent GKS equation in AES

$$i\,\frac{\partial \mathrm{A}_k}{\partial t} = \left(\epsilon + \mathrm{H}^{\mathrm{GKS,dy}}\right)\mathrm{A}_k$$

It always follows slowest possible physical oscillations

The solution of the computationally demanding Problem

Mapping 1:1 $n^{\mathrm{S}}(r,t)$ and $\hat{H}_r^{\mathrm{GKS,dy}}(t)$

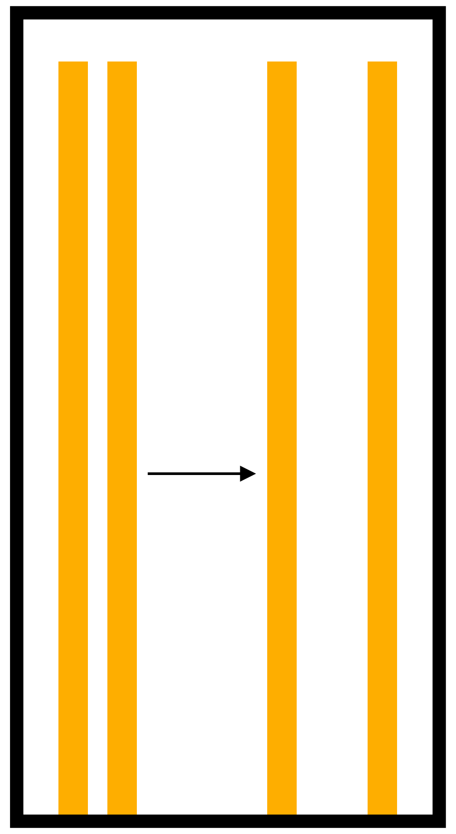
$$i\,\frac{\partial \mathrm{A}_k}{\partial t} = \left(\epsilon + \mathrm{H}^{\mathrm{GKS,dy}}\right)\mathrm{A}_k$$

$$\hat{H}_r^{\mathrm{GKS,dy}}(t) \rightarrow \hat{H}_r^{\mathrm{GKS,dy}}(t+\Delta t)$$

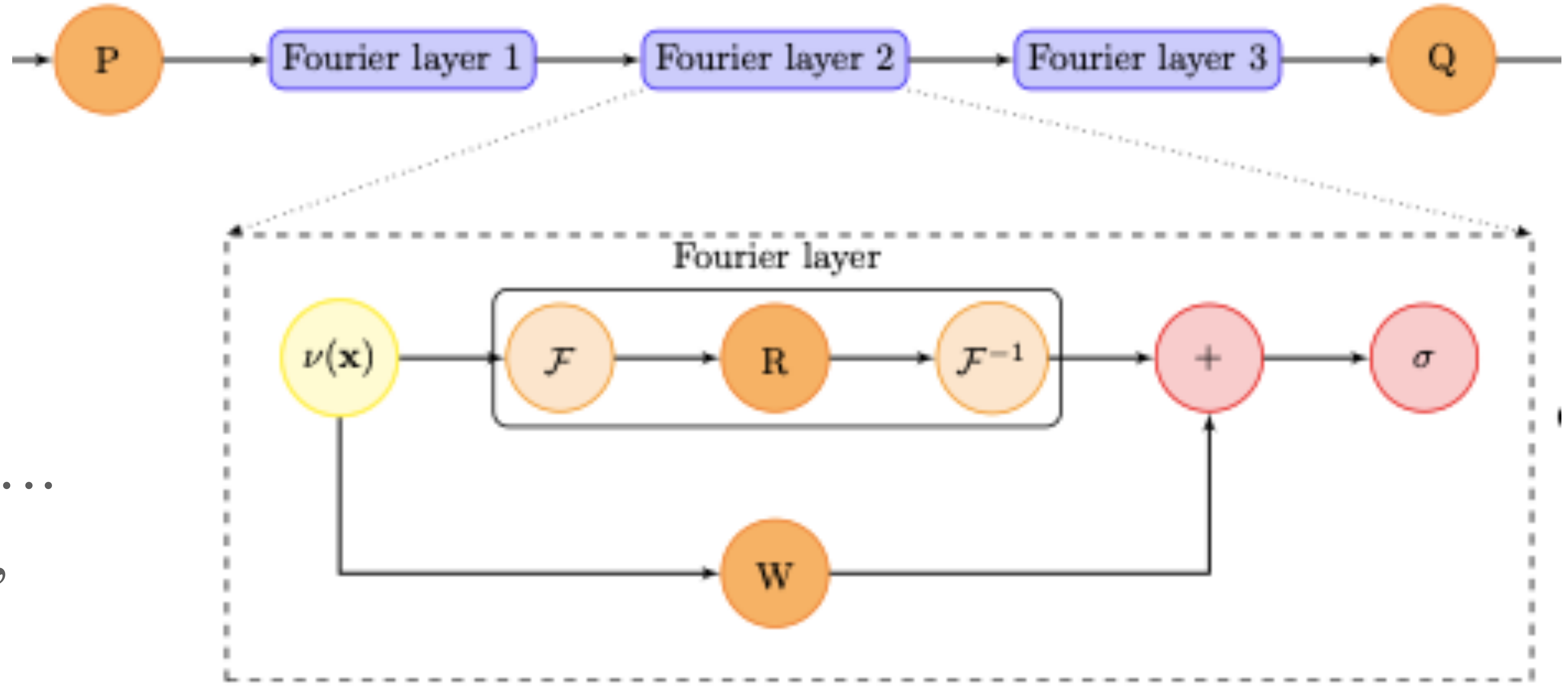
Extending the domain of FNOs in AES through dynamical GKS Hamiltonian

The solution of the computationally demanding Problem

$$\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) \,|\, \mathrm{H}_r^{\mathrm{GKS,dy}}(t) \,|\, \phi_j(r) \rangle$$



$\hat{H}_r^{\mathrm{GKS,dy}}(t-k)$, ….
$\hat{H}_r^{\mathrm{GKS,dy}}(t-1)$,
$\hat{H}_r^{\mathrm{GKS,dy}}(t)$



$\hat{H}_r^{\mathrm{GKS,dy}}(t+\Delta t)$

$[\rho^{S}(t)]$??

The solution of the computationally demanding Problem

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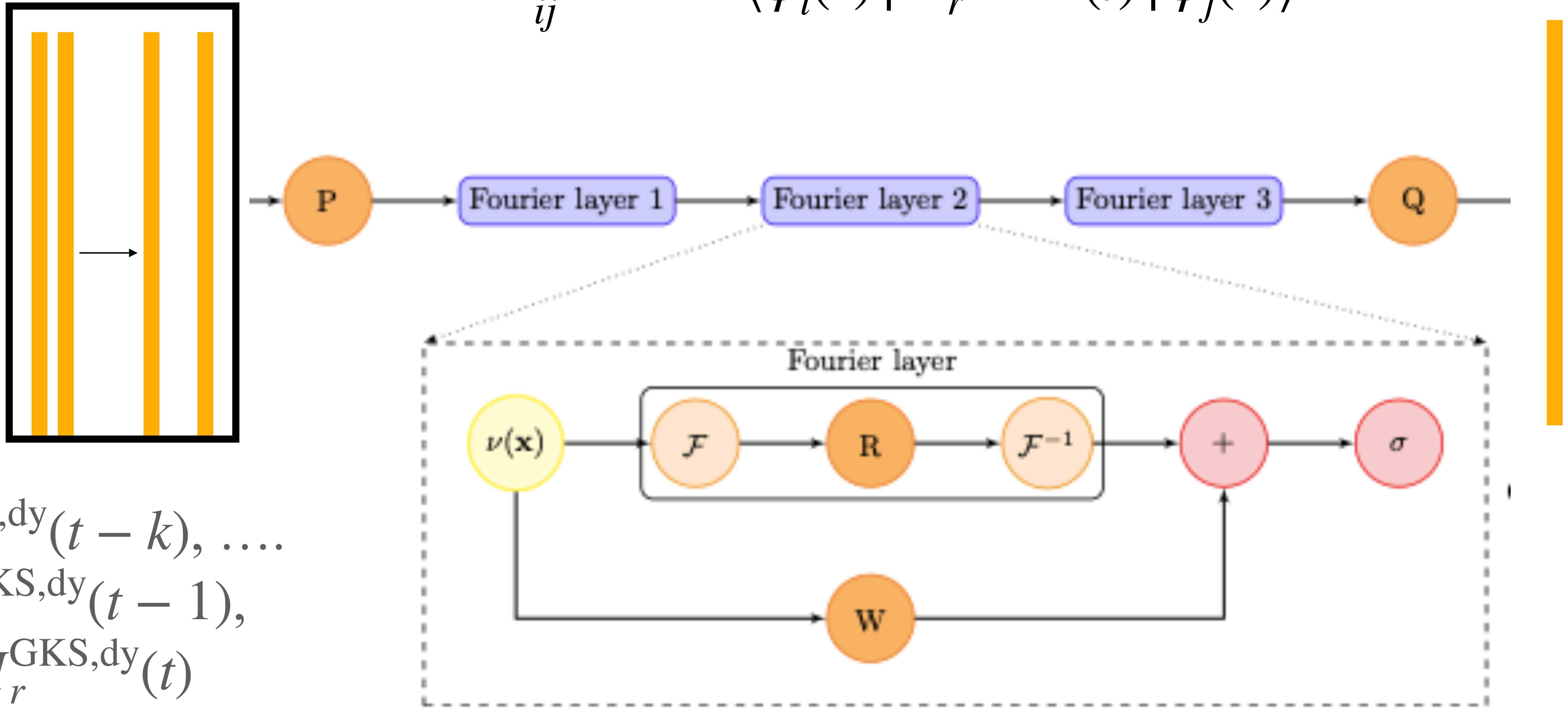


$\hat{H}_r^{\mathrm{GKS,dy}}(t+\Delta t)$

$\hat{H}_r^{\mathrm{GKS,dy}}(t-k)$, ….

$\hat{H}_r^{\mathrm{GKS,dy}}(t-1)$,

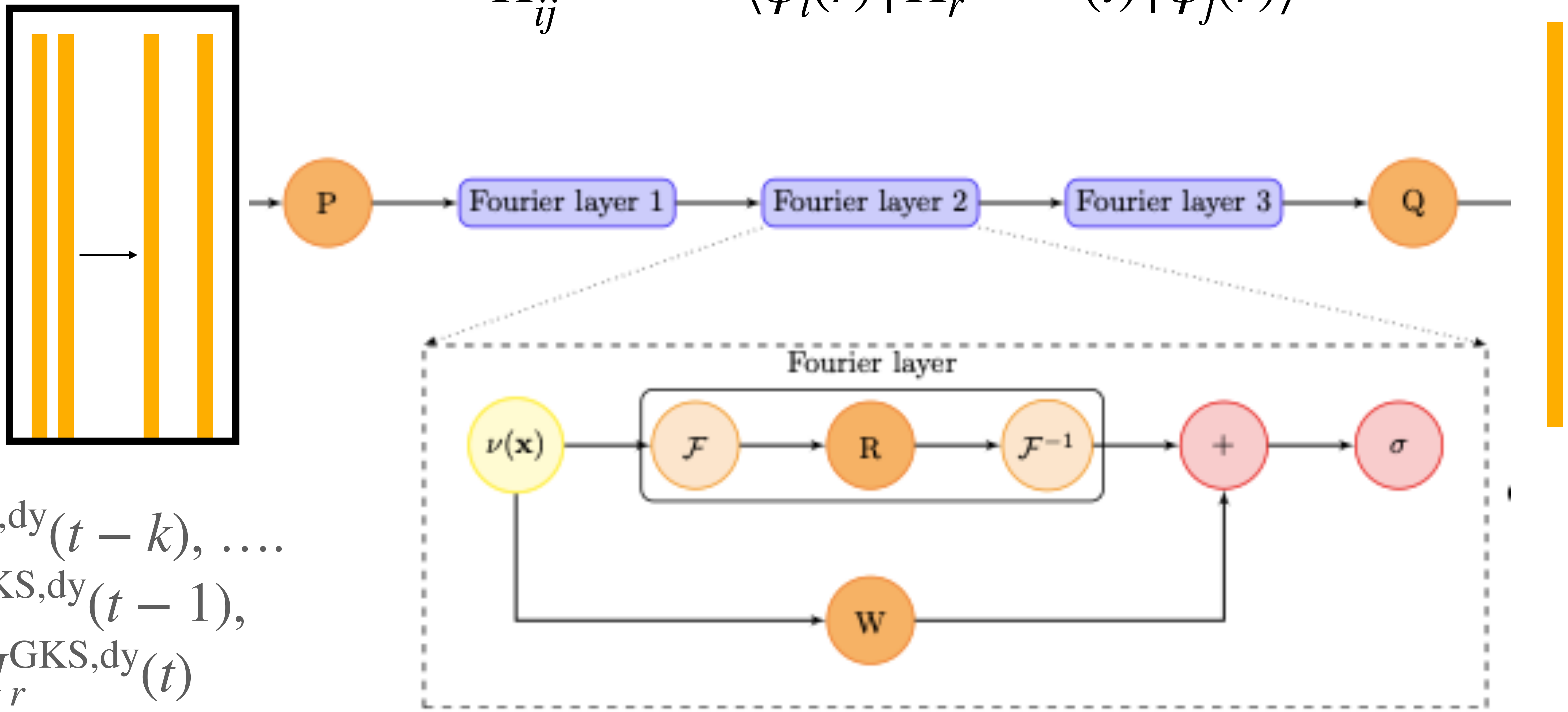
$\hat{H}_r^{\mathrm{GKS,dy}}(t)$

$[\rho^{\mathrm{S}}(t)]$:

$$\mathrm{A}_k(t+\Delta t) = \mathrm{U}(t+\Delta t)\mathrm{A}_k(t)$$

The solution of the computationally demanding Problem

$$\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) \,|\, \mathrm{H}_r^{\mathrm{GKS,dy}}(t) \,|\, \phi_j(r) \rangle$$



$\hat{H}_r^{\mathrm{GKS,dy}}(t+\Delta t)$

$\hat{H}_r^{\mathrm{GKS,dy}}(t-k)$, ….

$\hat{H}_r^{\mathrm{GKS,dy}}(t-1)$,

$\hat{H}_r^{\mathrm{GKS,dy}}(t)$

$[\rho^{\mathrm{S}}(t)]$:

$$\mathrm{A}_k(t+\Delta t) = \mathrm{U}(t+\Delta t)\mathrm{A}_k(t)$$

$$\mathrm{U}(t+\Delta t) = \left[\exp(-i\frac{\epsilon}{2}\Delta t)\exp(-i\mathrm{H}^{\mathrm{GKS,dy}}\Delta t)\exp(-i\frac{\epsilon}{2}\Delta t)\right]$$

Split-operator method in
the energy representation
Unconditionally stable

Construction of $\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) | \mathrm{H}_r^{\mathrm{GKS,dy}}(t) | \phi_j(r) \rangle$

$$\hat{H}_r^{\mathrm{GKS,dy}}(t) = \left(\hat{g}[\rho^{\mathrm{S}}(t)] - \hat{g}[\rho^{\mathrm{S}}(0)]\right) + \left[v(r,t) - v(r,0)\right]$$

Non-local part

local part

Non-local part

$$\hat{g}[\rho^{\mathrm{S}}(0)] | \phi_j(r) \rangle = \int \mathrm{d}r' \frac{\rho(r,r')}{|r-r'|} \phi_j(r')$$

$$\hat{g}[\rho^{\mathrm{S}}(t)] | \phi_j(r) \rangle = \int \mathrm{d}r' \frac{\rho(r,r',t)}{|r-r'|} \phi_j(r')$$

local part

$$\left[v(r,t) - v(r,0)\right] = v_h(r,t) + v_{xc}(r,t) - \left(v_h(r,0) + v_{xc}(r,0)\right) - z\,.\,E(t)$$

Explicit time-dependent Z-direction field Interaction within dipole approximation

Classical Coulomb interaction

$$v_h(r,t) = \int \mathrm{d}r' \frac{\rho(r',t)}{|r-r'|} \qquad v_h(r,0) = \int \mathrm{d}r' \frac{\rho(r',0)}{|r-r'|}$$

Construction of $\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) \,|\, \mathrm{H}_r^{\mathrm{GKS,dy}}(t) \,|\, \phi_j(r) \rangle$

$$\hat{H}_r^{\mathrm{GKS,dy}}(t) = \left(\hat{g}[\rho^{\mathrm{S}}(t)] - \hat{g}[\rho^{\mathrm{S}}(0)]\right) + \left[v(r,t) - v(r,0)\right]$$

Non-local part

local part

Non-local part

$$\hat{g}[\rho^{\mathrm{S}}(0)]\,|\,\phi_j(r)\rangle = \int \mathrm{d}r' \frac{\rho(r,r')}{|r-r'|}\phi_j(r')$$

$$\hat{g}[\rho^{\mathrm{S}}(t)]\,|\,\phi_j(r)\rangle = \int \mathrm{d}r' \frac{\rho(r,r',t)}{|r-r'|}\phi_j(r')$$

local part

$$\left[v(r,t) - v(r,0)\right] = v_h(r,t) + v_{xc}(r,t) - \left(v_h(r,0) + v_{xc}(r,0)\right) - z\,.\,E(t)$$

Explicit time-dependent
Z-direction field
Interaction within
dipole approximation

Adiabatic approximation

$$v_{xc}(r,t) = \frac{\partial E^{XC}[\rho(r,t)]}{\partial \rho(r,t)} \qquad v_{xc}(r,0) = \frac{\partial E^{XC}[\rho(r,0)]}{\partial \rho(r,0)}$$

Construction of non-local $\mathrm{H}_{ij}^{\mathrm{GKS,dy}}$

$$\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) \,|\, \mathrm{H}_r^{\mathrm{GKS,dy}}(t) \,|\, \phi_j(r) \rangle = \langle \phi_i(r) \,|\, \left(\hat{g}[\rho^{\mathrm{S}}(t)] - \hat{g}[\rho^{\mathrm{S}}(0)] \right) |\, \phi_j(r) \rangle$$

$$\langle \phi_i(r) \,|\, \hat{g}[\rho^{\mathrm{S}}(t)] \,|\, \phi_j(r) \rangle = \int \mathrm{d}r \int \mathrm{d}r' \phi_i(r) \frac{\rho(r, r', t)}{|r - r'|} \phi_j(r') = \sum_k \int \mathrm{d}r \int \mathrm{d}r' \phi_i(r) \frac{\phi_k(r, t)\phi_k(r', t)}{|r - r'|} \phi_j(r')$$

$$= \sum_k \int \mathrm{d}r \phi_{ik}(r, t) v_{kj}(r, t) = \sum_k \sum_{n_g} \phi_{ik}(n_g, t) v_{kj}(n_g, t) \mathrm{d}g$$

Cartesian coordinate grid (CCG)

$$n_g = n_x \, . \, n_y \, . \, n_z$$

$$\mathrm{d}g = \mathrm{d}x \, . \, \mathrm{d}y \, . \, \mathrm{d}z$$

$$v_{kj}(r, t) = \int \mathrm{d}r' \frac{\phi_k(r', t)\phi_j(r')}{|r - r'|} = \int \mathrm{d}r' \frac{\phi_{kj}(r', t)}{|r - r'|} = \mathscr{F}^{-1}[\phi_{kj}(K, t) \star v_{ck}(K)]$$

Fourier convolution theorem in momentum space (K)

Coulomb Kernel in real space

$$v_{ck}(r) = \frac{1}{r}$$

- It is straight forward to construct the time-independent part as I did in the code.

Construction of local $\mathrm{H}_{ij}^{\mathrm{GKS,dy}}$

$$\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) \,|\, \mathrm{H}_r^{\mathrm{GKS,dy}}(t) \,|\, \phi_j(r) \rangle = \langle \phi_i(r) \,|\, \big(v(r,t) - v(r,0)\big) \,|\, \phi_j(r) \rangle$$

Classical Coulomb interaction

$$\langle \phi_i(r) \,|\, v_h(r,t) \,|\, \phi_j(r) \rangle = \int \mathrm{d}r \int \mathrm{d}r' \phi_i(r) \frac{\rho(r',t)}{|r-r'|} \phi_j(r)$$

$$= \int \mathrm{d}r \phi_{ij}(r) v_h(r,t) = \sum_{n_g} \phi_{ij}(n_g) v_h(n_g,t) \mathrm{d}g$$

Cartesian coordinate grid (CCG)

$$n_g = n_x \,.\, n_y \,.\, n_z$$

$$\mathrm{d}g = \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z$$

$$v_h(r,t) = \int \mathrm{d}r' \frac{\rho(r',t)}{|r-r'|} = \mathscr{F}^{-1}[\rho(K,t) \star v_c(K)]$$

Fourier convolution theorem in momentum space (K)

Coulomb Kernel in real space

$$v_{ck}(r) = \frac{1}{r}$$

- It is straight forward to construct the time-independent part as I did in the code.

Construction of local $\mathrm{H}_{ij}^{\mathrm{GKS,dy}}$

$$\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) \,|\, \mathrm{H}_r^{\mathrm{GKS,dy}}(t) \,|\, \phi_j(r) \rangle = \langle \phi_i(r) \,|\, \big(v(r,t) - v(r,0) \big) \,|\, \phi_j(r) \rangle$$

Exchange-correlation

$$\langle \phi_i(r) \,|\, v_{xc}(r,t) \,|\, \phi_j(r) \rangle = \int \mathrm{d}r \phi_i(r) \frac{\partial E_{xc}[\rho(r,t)]}{\partial \rho(r,t)} \phi_j(r)$$

$$E^{XC} = \int \mathrm{d}r \; f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta})$$

$$\gamma_{\alpha,\alpha} = |\nabla \rho_\alpha|^2, \gamma_{\beta,\beta} = |\nabla \rho_\beta|^2, \gamma_{\alpha,\beta} = \nabla \rho_\alpha . \nabla \rho_\beta$$

LDA :

$$\langle \phi_i(r) \,|\, v_{xc}^{\alpha}(r,t) \,|\, \phi_j(r) \rangle = \int \mathrm{d}r \phi_i(r) \frac{\partial f[\rho_\alpha(r,t)]}{\partial \rho_\alpha(r,t)} \phi_j(r)$$

$$= \int \mathrm{d}r \phi_{ij}(r) \frac{\partial f[\rho_\alpha(r,t)]}{\partial \rho_\alpha(r,t)} = \sum_{n_g} \phi_{ij}(n_g) \frac{\partial f[\rho_\alpha(n_g,t)]}{\partial \rho_\alpha(n_g,t)} \mathrm{d}g$$

Cartesian coordinate grid (CCG)

$n_g = n_x . n_y . n_z$

$\mathrm{d}g = \mathrm{d}x . \mathrm{d}y . \mathrm{d}z$

- It is straight forward to construct β component which is independent to each other.
- It is straight forward to construct the time-independent part as I did in the code.

Construction of local $\mathrm{H}_{ij}^{\mathrm{GKS,dy}}$

$$\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) | \mathrm{H}_r^{\mathrm{GKS,dy}}(t) | \phi_j(r) \rangle = \langle \phi_i(r) | \big(v(r,t) - v(r,0) \big) | \phi_j(r) \rangle$$

Exchange-correlation

$$\langle \phi_i(r) | v_{xc}(r,t) | \phi_j(r) \rangle = \int \mathrm{d}r \phi_i(r) \frac{\partial E_{xc}[\rho(r,t)]}{\partial \rho(r,t)} \phi_j(r)$$

$$E^{XC} = \int \mathrm{d}r\, f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta})$$

$$\gamma_{\alpha,\alpha} = |\nabla \rho_\alpha|^2, \gamma_{\beta,\beta} = |\nabla \rho_\beta|^2, \gamma_{\alpha,\beta} = \nabla \rho_\alpha . \nabla \rho_\beta$$

GGA :

$$\langle \phi_i(r) | v_{xc}^{\alpha}(r,t) | \phi_j(r) \rangle = \int \mathrm{d}r \left[\left(2 \frac{\partial f[\rho(r,t)]}{\partial \gamma_{\alpha\alpha}(r,t)} \nabla \rho_\alpha(r,t) + \frac{\partial f[\rho(r,t)]}{\partial \gamma_{\alpha\beta}(r,t)} \nabla \rho_\beta(r,t) \right) . \nabla \big(\phi_i(r) \phi_j(r) \big) \right]$$

$$= \sum_{n_g} \left[\left(2 \frac{\partial f[\rho(n_g,t)]}{\partial \gamma_{\alpha\alpha}(n_g,t)} \nabla \rho_\alpha(n_g,t) + \frac{\partial f[\rho(n_g,t)]}{\partial \gamma_{\alpha\beta}(n_g,t)} \nabla \rho_\beta(n_g,t) \right) . \nabla \big(\phi_i(n_g) \phi_j(n_g) \big) \right]$$

- It is straight forward to construct β component, however it is dependent on α spin.
- It is straight forward to construct the time-independent part but it is opt out in the code for the time-being.

Cartesian coordinate grid (CCG)

$n_g = n_x . n_y . n_z$, $\mathrm{dg} = \mathrm{d}x . \mathrm{d}y . \mathrm{d}z$

Construction of local $\mathrm{H}_{ij}^{\mathrm{GKS,dy}}$

$$\mathrm{H}_{ij}^{\mathrm{GKS,dy}} = \langle \phi_i(r) \,|\, \mathrm{H}_r^{\mathrm{GKS,dy}}(t) \,|\, \phi_j(r) \rangle = \langle \phi_i(r) \,|\, \big(v(r,t) - v(r,0) \big) \,|\, \phi_j(r) \rangle$$

Z-component of dipole integral

$$\langle \phi_i(r) \,|\, zE(t) \,|\, \phi_j(r) \rangle = E(t) \int \mathrm{d}r \phi_i(r) \; z \; \phi_j(r)$$

Analytical : $\langle \phi_i(r) \,|\, zE(t) \,|\, \phi_j(r) \rangle = E(t) \sum_{rs} \sum_{ab} C_i^r C_j^s P_r^a P_s^b \int \mathrm{d}r \chi_i^{ra}(r) \; z \; \chi_j^{sb}(r)$

Four-index integral over primitive Gaussian functions

- Analytical one consist of six nested loop and it will be costly for larger basis set. Here also we do need OpenMP for parallelisation.

Numerical : $\langle \phi_i(r) \,|\, zE(t) \,|\, \phi_j(r) \rangle = E(t) \int \mathrm{d}r \phi_i(r) \; z \; \phi_j(r) = E(t) \sum_{n_g} \phi_i(n_g) z(n_g) \phi_j(n_g) \mathrm{dg}$

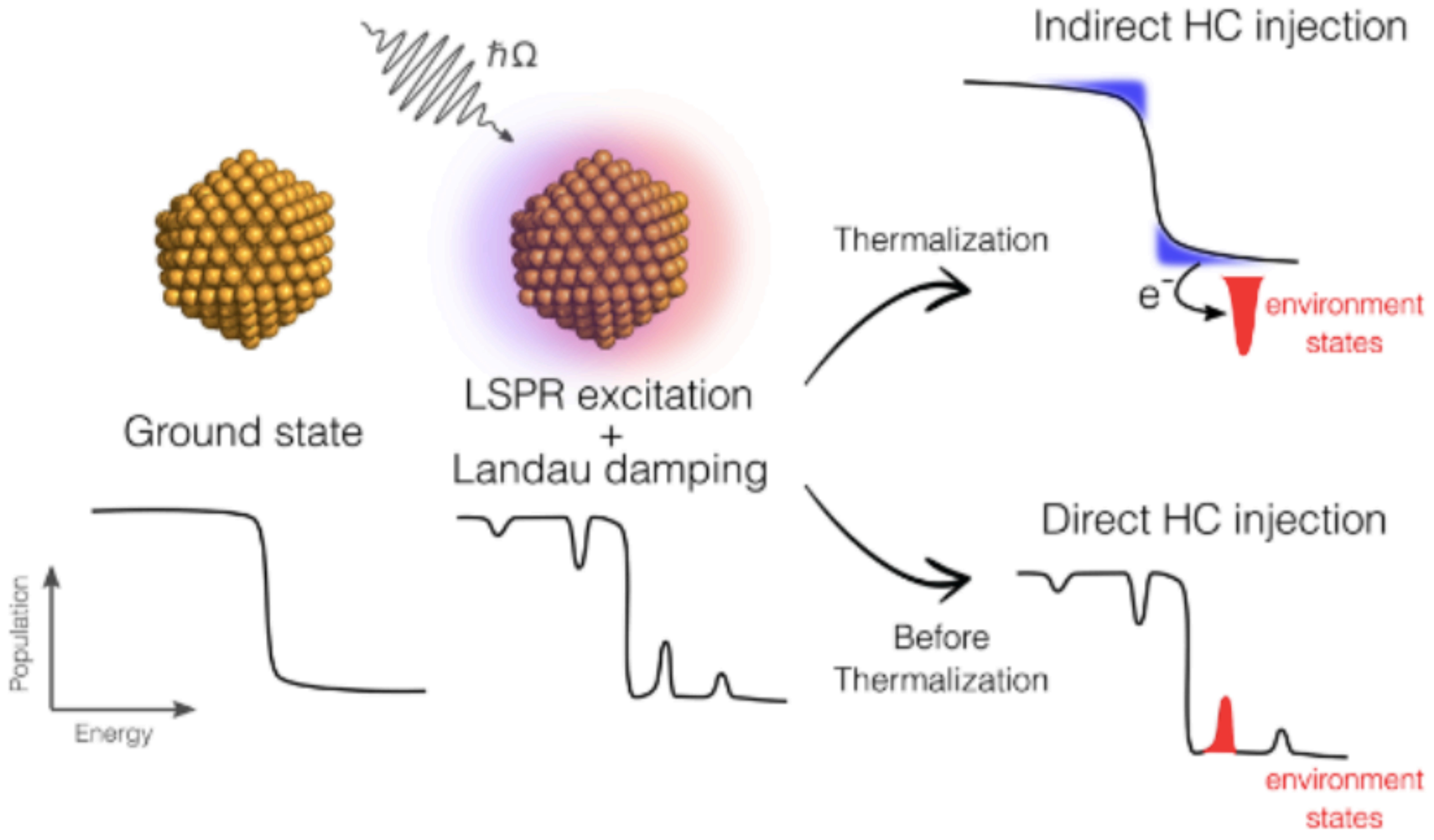
- It is straight forward to include numerical one in our code and it becomes faster if we use OpenMP.

Cartesian coordinate grid (CCG)

$$n_g = n_x \,.\, n_y \,.\, n_z \,,\; \mathrm{dg} = \mathrm{d}x \,.\, \mathrm{dy} \,.\, \mathrm{dz}$$

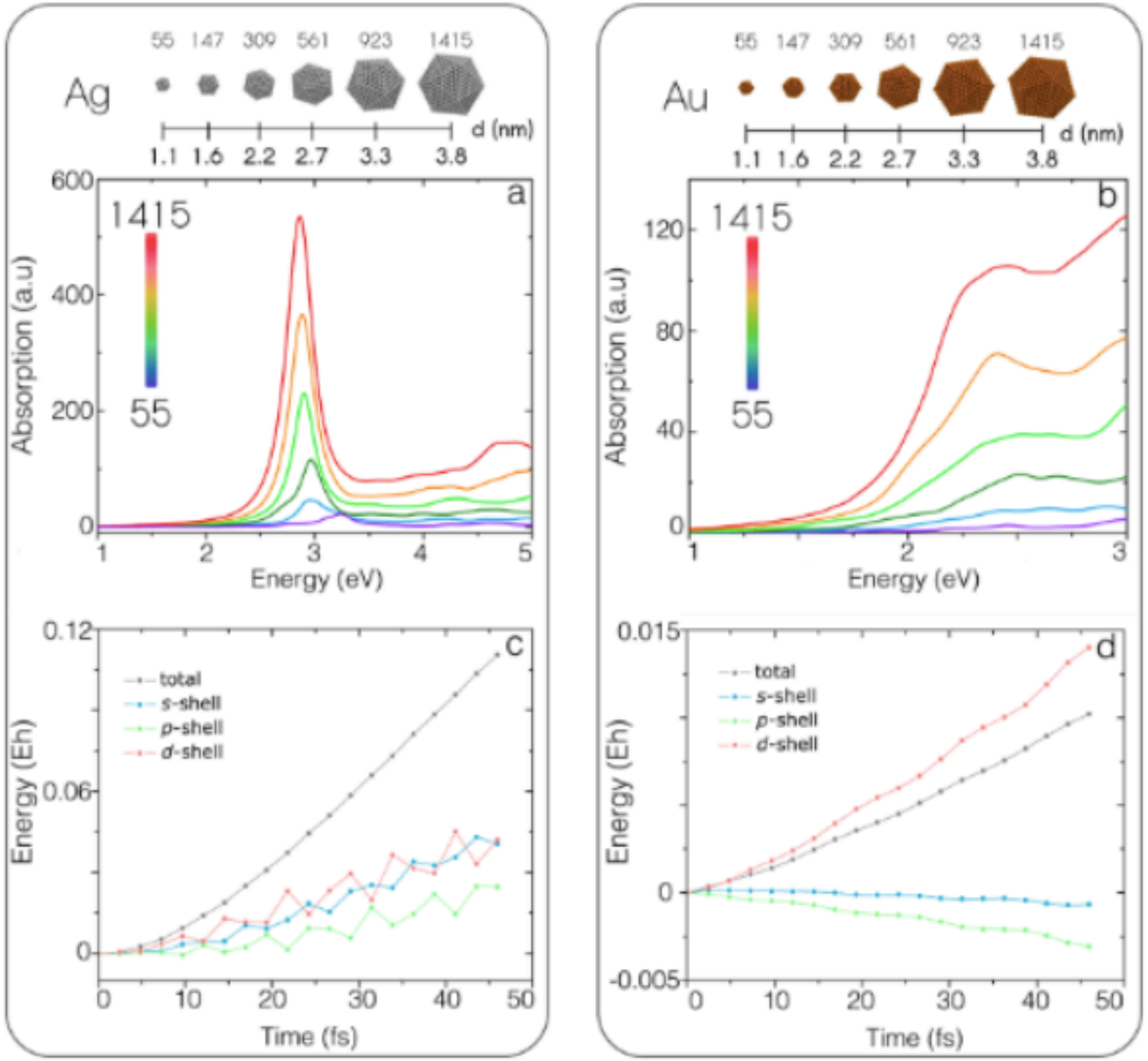
Application towards plasmonic photocatalysis

The schematic presentation of HC generation for plasmonic photocatalysis



J Pays. Chem. C, 2022

The absorption spectrum of Ag and Au nanoparticles



Nanoscale, 2019

The current scenario for the first phase of Ob. (1)

1. Ensuring size extensivity or data transferability, enabling models trained on small systems to generalise effectively to larger systems.

2. Training on short-time data and predicting longer time-scale developments.

3. Optimising the pulse properties for photocatalysis using a Gaussian process-based Bayesian optimisation technique.

THANK YOU