Light–Matter interaction

Multiscale, Multicalculator Modelling with Atomic Simulation Environment

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Advertisement: Solving the Poisson Equation in GPAW the Fast Way

- Let there be N_d grid points in dimension d. We obtain $N_d \times N_d$ circulant/Toeplitz matrix finite difference representation of ∇^2.
- The 3D laplace operator is now constructed with Kroenecker products $T^{3\mathrm{D}} = T^x \otimes I^y \otimes I^z + I^x \otimes T^y \otimes I^z + I^x \otimes I^y \otimes T^z$
- Depending on boundary conditions (charge mirroring metallic, or periodic), the operator is diagonalizable with Fast Sin Transform/Fast Fourier Transform.

$$\phi = F_x^{-1}[F_y^{-1}[F_z^{-1}[\epsilon_{G_x G_y G_z} F_x[F_y[F_z[n]]]]]], \quad (1)$$

  where the eigenvalues $\epsilon_{G_x G_y G_z}$ are an expression depending on stencil coefficients.
- The FAST Poisson solver is implemented to GPAW, resulting $\times$ 200 improvement of elongated systems. General improvement about $\times$ 10.

$$\vec{\nabla}^2 \phi(\vec{r}t) = -\frac{1}{\epsilon_0} \psi^*(\vec{r}t)\psi(\vec{r}t) \quad (2)$$

Review of Classical Mechanics

- We define the Poisson bracket using symplectic 2-form Ω_{ij}. $\{f(\vec{z}), g(\vec{z})\} = \sum_{ij} \Omega^{ij} \frac{\partial f}{\partial z^i} \frac{\partial g}{\partial z^j}$. Thus, $\{z_i, z_j\} = \Omega^{ij}$.
- The equations of motion for classical system, with Hamiltonian function H, is given by the Poisson bracket (in analogy to Liouville-von-Neumann equation of quantum mechanics) $\dot{\vec{z}}_k = \{z_k, H\} = \sum_{ij} \Omega^{ij} \underbrace{\frac{\partial z_k}{\partial z^i}}_{\delta_{ik}} \frac{\partial H}{\partial z_j}$, or in linear algebra form,

  $\vec{z} = \Omega \vec{\nabla}_z H$.

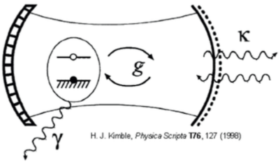
Example: Verlet Propagation

- Exact solution to $\dot{\vec{z}} = \{\vec{z}, H(\vec{p}, \vec{q})\}$ is given as $\vec{z}(t) = \hat{T}\exp\left(\{\cdot, H(\vec{p}, \vec{q})\}t\right)\vec{z}(0)$.
- If H can be split as $H(\vec{p}, \vec{q}) = H(\vec{q}) + H(\vec{p})$. Since, $\{H(p), \{H(p), \cdot\}\} = 0$, we have $\exp(\{\cdot, H(\vec{p})\}t)\vec{z} = z(0) + \{H, z\}t$ exactly.
- Thus

$$e^{\{\cdot,H\}dt} \cong e^{\{\cdot,T\}dt/2} e^{\{\cdot,V\}dt} e^{\{\cdot,T\}dt/2} \tag{3}$$

is exactly symplectic Verlet propagation method.

Cavity QED



H. J. Kimble, *Physica Scripta* **T76**, 127 (1998)

- $\gamma \rightarrow$ Decay rate of the atom into free-space
- $\kappa \rightarrow$ Decay rate of the cavity field
- $g \rightarrow$ Rate of coherent atom-cavity field coupling

Advanced example: Cavity ED

- The phase space of the quantum system $\boldsymbol{n}$ with Hamiltonian $\boldsymbol{H_n}$ is given as $(\vec{\boldsymbol{q}}_n, \vec{\boldsymbol{p}}_n)$, where this vector vector has potentially extremely many elements.

$$H = \frac{1}{2}\sum_c p_c^2 + \frac{1}{2}\left(\omega_c q_c + \sum_n \vec{\lambda}_{cn} \cdot \vec{d}_n(\vec{q}_n, \vec{p}_n)\right)^2 \quad (4)$$

$$+ \sum_n H_n(\vec{q}_n, \vec{p}_n) \quad (5)$$

- Combine all degrees of freedoms to a single vector $\boldsymbol{z} = (\boldsymbol{q}, \boldsymbol{p})$.

Cavity ED Equations of Motion

$$\underbrace{\begin{bmatrix} \dot{\vec{q}}_c \\ \dot{\vec{p}}_c \\ \dot{\vec{q}}_1 \\ \dot{\vec{p}}_1 \\ \vdots \\ \dot{\vec{q}}_N \\ \dot{\vec{p}}_N \end{bmatrix}}_{\vec{z}} = \underbrace{\begin{bmatrix} 0 & -I_c & 0 & 0 & \dots & 0 & 0 \\ I_c & 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & 0 & 0 & -I_1 & \dots & 0 & 0 \\ 0 & 0 & I_1 & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \\ 0 & 0 & 0 & 0 & \dots & 0 & -I_N \\ 0 & 0 & 0 & 0 & \dots & I_N & 0 \end{bmatrix}}_{\Omega} \underbrace{\begin{bmatrix} \frac{\partial H}{\partial \vec{q}_c} \\ \frac{\partial H}{\partial \vec{p}_c} \\ \frac{\partial H}{\partial \vec{q}_1} \\ \frac{\partial H}{\partial \vec{p}_1} \\ \vdots \\ \frac{\partial H}{\partial \vec{q}_N} \\ \frac{\partial H}{\partial \vec{p}_N} \end{bmatrix}}_{\vec{\nabla}_z H} \tag{6}$$

Cavity ED Hamiltonian and Equations of Motion

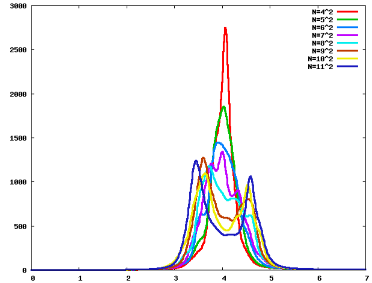
$$H = \frac{1}{2}\sum_c p_c^2 + \frac{1}{2}\sum_c \left(\omega_c q_c - \sum_n \vec{\lambda}_{cn} \cdot \vec{d}_n(\vec{q}_n, \vec{p}_n)\right)^2 \quad (7)$$

$$+ \sum_n H_n(\vec{q}_n, \vec{p}_n) \quad (8)$$

$$\begin{bmatrix} \dot{q}_c \\ \dot{p}_c \\ \vdots \\ \dot{q}_{n\mu} \\ \dot{p}_{n\mu} \\ \vdots \end{bmatrix} = \Omega \begin{bmatrix} \left(\omega_c q_c - \sum_n \vec{\lambda}_{cn} \cdot \vec{d}_n(\vec{q}_n, \vec{p}_n)\right)\omega_c \\ p_c \\ \vdots \\ \frac{\partial H_n}{\partial q_{n\mu}} - \sum_c \left(\omega_c q_c - \sum_{n'} \vec{\lambda}_{cn'} \cdot \vec{d}_{n'}(\vec{q}_{n'}, \vec{p}_{n'})\right)\lambda_{cn}\frac{\partial d_n}{\partial q_{n\mu}} \\ \frac{\partial H_n}{\partial p_{n\mu}} - \sum_c \left(\omega_c q_c - \sum_{n'} \vec{\lambda}_{cn'} \cdot \vec{d}_{n'}(\vec{q}_{n'}, \vec{p}_{n'})\right)\lambda_{cn}\frac{\partial d_n}{\partial p_{n\mu}} \end{bmatrix} \quad (9)$$

Cavity QED implementation on ASE


```
from ase.qed import CavityQED, LorentzResonance
qed = CavityQED(omega = [ 2.2 ], eta=[0.1])
for i in range(100):
    qed.add_calculator(LorentzResonance(2.2+0.1*np.random.randn(), eta=0.2,
    coupling = [ 0.01 ])
qed.propagate(0.01, 1000, trajectory='out.txt')
```



Quantization of Models

- One degree of freedom quantizes easily

$$\rho(P, Q) = \sum_i C_i \phi(Q), \texttt{given}[\hat{P}, \hat{Q}] = 1 \tag{10}$$

- Things get out of hand quickly, as Hilbert spaces need to be Kroenecker multiplied.
- The Hilbert space for the system of M isolated molecules and a single cavity mode is given as

$$\mathcal{H}_s = \left(\mathcal{H}_{\mathrm{el}} \otimes \mathcal{H}_{\mathrm{ph}}\right)^{\otimes M} \otimes \mathcal{H}_{\mathrm{c}}, \tag{11}$$

  where $\mathcal{H}_{el}$ is the Hilbert space for the 2-state Fermionic system $\mathcal{H}_{ph}$ is the countably infinite dimensional phonon Hilbert space, and $\mathcal{H}_{\mathrm{c}}$ is the Hilbert space for the single cavity mode.

Symplectic Propagator For LCAO

$$\underbrace{\begin{bmatrix} \dot{\vec{q}}_c \\ \dot{\vec{p}}_c \\ \dot{\vec{q}}_1 \\ \dot{\vec{p}}_1 \\ \vdots \\ \dot{\vec{q}}_N \\ \dot{\vec{p}}_N \end{bmatrix}}_{\vec{z}} = \underbrace{\begin{bmatrix} 0 & -I_c & 0 & 0 & \dots & 0 & 0 \\ I_c & 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & 0 & 0 & -S_1^{-1} & \dots & 0 & 0 \\ 0 & 0 & S_1^{-1} & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \\ 0 & 0 & 0 & 0 & \dots & 0 & -S_N^{-1} \\ 0 & 0 & 0 & 0 & \dots & S_N^{-1} & 0 \end{bmatrix}}_{\Omega} \underbrace{\begin{bmatrix} \frac{\partial H}{\partial \vec{q}_c} \\ \frac{\partial H}{\partial \vec{p}_c} \\ \frac{\partial H}{\partial \vec{q}_1} \\ \frac{\partial H}{\partial \vec{p}_1} \\ \vdots \\ \frac{\partial H}{\partial \vec{q}_N} \\ \frac{\partial H}{\partial \vec{p}_N} \end{bmatrix}}_{\vec{\nabla}_z H} \tag{12}$$

Lagrangian for Symplectic LCAO

$$L = \frac{1}{2} i C^* S_{\mu\nu} \dot{C}' - \frac{1}{2} i C \dot{C}'^* + \underbrace{\frac{1}{2} C^*_{n\mu} H_{\mu\nu} C_{n\nu}}_{H_1} + \underbrace{\frac{1}{2} C'^*_{n\mu} H_{\mu\nu} C_{n\nu}}_{H_2} \tag{13}$$

$$(I + \{\cdot, H_1\} dt)(I + \{\cdot H_2\} dt) \begin{bmatrix} C \\ C' \end{bmatrix} = \begin{bmatrix} I & -iS_N^{-1} H_N dt \\ 0 & I \end{bmatrix} \begin{bmatrix} I & 0 \\ -iS_N^{-1} H_N dt & I \end{bmatrix} \begin{bmatrix} C \\ C' \end{bmatrix} \tag{14}$$

Results in symplectic matrices. Symplectic matrix is what preserves the symplectic 2-form.

Polarization in Solids

- Macroscopic electomagnetic field affects Schrödinger equations via minimal coupling $\frac{1}{2}\left(-i\vec{\nabla}+\vec{A}\right)^2$.
- The wave functions $\psi_k(\mathbf{r})$ at different k-points are not unitary transformable into each other (different symmetry). However, the Bloch gauge transformed $u_{\vec{k}n}(\mathbf{r}) = e^{-i\vec{k}r}\psi_k(\mathbf{r})$ wave are.

$$i\dot{u}_{\vec{k}n}(\vec{r})\frac{1}{2}\left(-i\vec{\nabla}+\vec{k}+\vec{A}\right)^2 u_{\vec{k}n}(\vec{r}) \tag{15}$$

If we expand the wave functions at each $\vec{k}+\vec{A}$ point, this means that the basis changes in time

$$\psi_k(\vec{r}) = \sum_n C_n u_{k+An}(\mathbf{r}) \tag{16}$$

If $\vec{A}(\vec{r}t)$ undergoes an adiabatic, or diabatic trajectory (path), it can be represented via unitary operator $C_n^{k_3} = U_{nn'}^{k_2\to k_1} U_{nn'}^{k_3\to k_2} U_{nn}^{k_3\to k_2} C_n^{k_3}$

LCAO-TDDFT: Polarization in Solids

$$\mathcal{L} = \sum_{\mu\nu\vec{k}} iC^*_{n\nu} \int \mathrm{d}\vec{r}\phi_{\vec{k}\nu}(\vec{r}t)\frac{\mathrm{d}}{\mathrm{d}t}\phi_{\vec{k}\mu}(\vec{r}t)C_{n\nu} - \frac{1}{2}\sum_{\vec{k}\mu\nu} iC^*_{n\nu} \int \mathrm{d}\vec{r}\phi_{\vec{k}\nu}(\vec{r}t)\left(-i\nabla + \vec{A}(t)\right)^2 \phi_{\vec{k}\mu}(\vec{r}t)C_{n\mu} \quad (17)$$

Gauge transform the Bloch orbitals a la Zak

$$\phi_{\vec{k}\vec{A}(t)\mu}(\vec{r}t) = \frac{1}{\sqrt{|R|}}\sum_{\vec{R}} \phi_\mu(\vec{r}-\vec{R})e^{i(\vec{k}+\vec{A})\cdot\vec{R}}e^{-i\vec{A}\cdot r}, \quad (18)$$

Results into equation of motion

$$-i\mathbf{S}_{\vec{k}+\vec{A}}(t)\dot{\mathbf{C}}(t) + \mathbf{H}_{\vec{k}+\vec{A}}\mathbf{C}(t) + \dot{\vec{A}}(t)\cdot\vec{X}_{\vec{k}+\vec{A}}(t)\mathbf{C}(t) = 0, \quad (19)$$

where

$$X_{\vec{k}+\vec{A}\mu\nu} = \sum_{\Delta\vec{R}} e^{i(\vec{k}+\vec{A})\cdot\Delta\vec{R}} \int \mathrm{d}\vec{r}\phi^*_\mu(\vec{r}-\Delta\vec{R})(-\vec{r})\phi_\nu(\vec{r}), \quad (20)$$

So what is the Polarization Operator

- For electric field $\vec{E}(t) = \vec{E}_0\delta(t)$, one has $\vec{A}(t) = \vec{E}_0\Theta(t)$. But this shifts the k-points from $\vec{k}$ to $\vec{k} + A$, and hence the operation is not Hermitian.
- We can directly integrate the kick

$$C_{\vec{k}+\vec{A}}(0+) = \underbrace{T\exp\left(\int_0^{0+} d\tau S^{-1}_{\vec{k}+\vec{A}} \vec{X}_{\vec{k}+\vec{A}} \cdot \vec{E}_0\delta(t)\right)}_{V} C_{\vec{k}}(0) \tag{21}$$

and obtain the mapping for the polarization $P = \frac{1}{iE_0} S_{\vec{k}} \log V$, but this needs to be evaluated as $P(t) = C^{\dagger}_{\vec{k}+\vec{A}} P C_{\vec{k}}$.

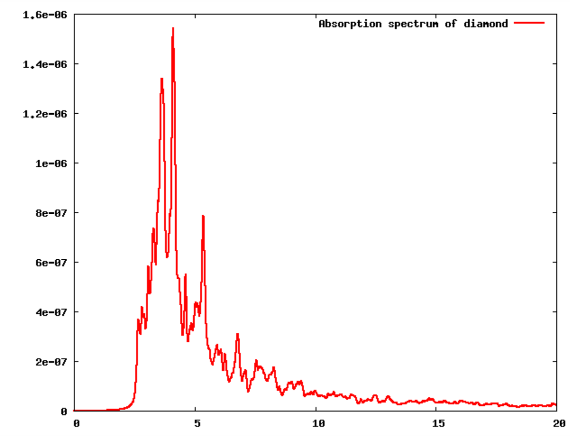
So what is the Polarization Operator

- We use electric field $\vec{E}(t) = \vec{E}_0\delta(t)$, but now one has $\vec{A}(t) = -\vec{E}_0\Theta(-t)e^{-\eta|t|}$. The vector potential starts at zero, adiabatically increases to $-E_0$ and suddenly switches off to produce the electric field pulse $\delta(t)\vec{E}_0$.
- We can directly integrate the kick

$$\mathbf{C}_{\vec{k}}(\mathbf{0}+) = V^{\dagger}_{\text{adia}}(\vec{k} \rightarrow \vec{k} + \vec{A})V_{\text{dia}}(\vec{k} \rightarrow \vec{k} + \vec{A})C_{\vec{k}}(\mathbf{0}) \quad (22)$$

and obtain the mapping for the polarization $P = \frac{1}{iE_0}S_{\vec{k}}\log V^{\dagger}_{\text{adia}}V_{\text{dia}}$, and this can be evaluated as $P(t) = C^{\dagger}_{\vec{k}}PC_{\vec{k}}$.

Absorption spectrum of Diamond



Orbital Free TDDFT Field Lagrangian

We begin with simpler problem without the vector potential, i.e. non-retarded electrodynamics

$$\mathcal{L}^{\text{el}}(\psi, \psi^*, \dot{\psi}, \dot{\psi}^*, \vec{\nabla}\psi, \vec{\nabla}\psi^*, \phi, \vec{\nabla}\phi) \tag{23}$$

$$= -i\dot{\psi}^*\psi - \frac{\mu}{2}\vec{\nabla}\psi^* \cdot \vec{\nabla}\psi \tag{24}$$

$$-\frac{1}{2}\epsilon_0 \left(\vec{\nabla}\phi\right)^2 - \mathcal{L}_{\text{txc}}[n] - \psi^*\psi\phi, \tag{25}$$

The equations of motion are given by Euler–Lagrange equations,

$$\frac{\delta S}{\delta\psi^*(\vec{r}t)} = 0, \frac{\delta S}{\delta\phi(\vec{r}t)} = 0, \tag{26}$$

Euler-Lagrange Equations

$$\frac{\partial \mathcal{L}}{\partial \psi^*} - \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{\psi}^*}\right) - \vec{\nabla} \cdot \left(\frac{\partial \mathcal{L}}{\partial \vec{\nabla}\psi^*}\right) = 0, \quad (27)$$

$$\frac{\partial \mathcal{L}}{\partial \phi} - \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{\phi}}\right) - \vec{\nabla}\left(\cdot\frac{\partial \mathcal{L}}{\partial \vec{\nabla}\phi}\right) = 0, \quad (28)$$

$$(29)$$

Which yields TDDFT equations

$$i\dot{\psi}(\vec{r}t) = -\frac{\mu}{2}\vec{\nabla}^2\psi(\vec{r}t) + \phi(\vec{r}t)\psi(\vec{r}t) + \frac{\delta \mathcal{L}_{\text{txc}}}{\delta n}\psi(\mathbf{r}) \quad (30)$$

$$\vec{\nabla}^2\phi(\vec{r}t) = -\frac{1}{\epsilon_0}\psi^*(\vec{r}t)\psi(\vec{r}t) \quad (31)$$

Symplectic Propagator

- Let's look at the kinetic part of the classical field $\mathcal{L}^{\text{kin}} = -i\dot{\psi}^*\psi$ and add a total time derivative $\frac{d}{dt}\left(\frac{i}{2}\psi^*\psi\right)$:

$$\mathcal{L}'^{\text{kin}} = -\frac{i}{2}\left(\dot{\psi}^*\psi - \psi^*\dot{\psi}\right) \tag{32}$$

- Substitute for $\Psi_R = \frac{1}{\sqrt{2}}\left(\Psi + \Psi^*\right)$ and $= \frac{1}{\sqrt{2}}\frac{\Psi - \Psi^*}{i}$

$$\mathcal{L}''^{\text{kin}} = -\dot{\Psi}_R\Psi_I + \Psi_R\dot{\Psi}_I \tag{33}$$

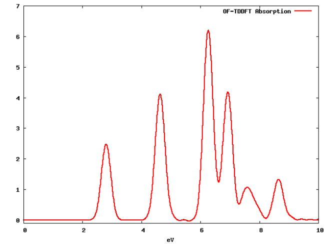
- Legendre transform into Hamiltonian

$$H = \frac{\partial \mathcal{L}}{\partial \dot{\Psi}_R}\dot{\Psi}_R + \frac{\partial \mathcal{L}}{\partial \dot{\Psi}_I}\dot{\Psi}_I - \mathcal{L}'' \tag{34}$$

$$H(\Psi_R, \Psi_I) = \frac{1}{2}\begin{bmatrix}\Psi_R & \Psi_I\end{bmatrix}\begin{bmatrix}-\frac{\mu}{2}\nabla^2 + \phi & 0 \\ 0 & -\frac{\mu}{2}\nabla^2 + \phi\end{bmatrix}\begin{bmatrix}\Psi_R \\ \Psi_I\end{bmatrix} \tag{35}$$

Example


```
gd = GridDescriptor([80,80,80], cell_cv=np.diag([80,80,80]))
n = 2.0 / ((4.29/Bohr)**3)
of = OrbitalFree(0, NanoParticle([40,40,40], 32, n))
of.initialize(gd)
of.relax()
of.kick(ConstantField([0.00001,0,0]), 'out.dm')
of.propagate(10000, 0.1)
```



Fully Interacting Lagrangian

The Lagrangian density for the free photon field coupled to light matter field is given as

$$\mathcal{L} = \frac{1}{2}\epsilon\vec{E}^2(\vec{r}t) - \frac{1}{2\mu_0}\vec{B}^2(\vec{r}t) - i\dot{\psi}^*\psi - \frac{\mu}{2}\psi^*(-i\vec{\nabla} + \vec{A}(\vec{r}t))^2\psi - \mathcal{L}_{\text{txc}}[n] - \psi^*\psi\phi \quad (36)$$

$$\frac{1}{2}\epsilon_0\left(\dot{\mathbf{A}}(\mathbf{r}) + \nabla\phi(\mathbf{r})\right)^2 - \frac{1}{2\mu_0}\left(\nabla\times\mathbf{A}(\vec{r})\right)^2 - i\dot{\psi}^*\psi - \frac{\mu}{2}\psi^*(-i\vec{\nabla} + \vec{A}(\vec{r}t))^2\psi \quad (37)$$

$$-\mathcal{L}_{\text{txc}}[n] - \psi^*\psi\phi \quad (38)$$

Euler-Lagrange equations of Classical Electromagnetism

The Euler-Lagrange equations become

$$\frac{\partial \mathcal{L}}{\partial \vec{A}(\vec{r}t)} - \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\vec{A}}(\vec{r}t)} - \vec{\nabla}\cdot\frac{\partial \mathcal{L}}{\partial \vec{\nabla}\vec{A}(\vec{r}t)} = 0, \quad (39)$$

$$\frac{\partial \mathcal{L}}{\partial \vec{A}(\vec{r}t)} - \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \partial_t \vec{A}(\vec{r}t)} - \frac{d}{dx}\frac{\partial \mathcal{L}}{\partial \partial_x \vec{A}(\vec{r}t)} - \frac{d}{dy}\frac{\partial \mathcal{L}}{\partial \partial_y \vec{A}(\vec{r}t)} - \frac{d}{dz}\frac{\partial \mathcal{L}}{\partial \partial_z \vec{A}(\vec{r}t)} = 0 \quad (40)$$

yield following equations of motion

$$-\epsilon_0\mu_0\ddot{\vec{A}}(\vec{r}t) - \epsilon_0\mu_0\vec{\nabla}\dot{\phi}(\vec{r}t) + \nabla^2\vec{A}(\vec{r}t) - \vec{\nabla}(\vec{\nabla}\cdot\vec{A}(\vec{r}t)) = \vec{J}(\vec{r}t), \quad (41)$$

$$-\epsilon_0\vec{\nabla}^2\phi(\vec{r}t) - \epsilon_0\frac{d}{dt}(\vec{\nabla}\cdot\vec{A}(\vec{r}t)) = -\psi^*\psi,$$

$$\vec{J}(\vec{r}t) = \frac{1}{2i}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) + \frac{1}{2}\vec{A}\psi^*\psi \quad (42)$$

Coulomb Gauge

Let $\vec{\nabla} \cdot \vec{A} = 0$.

$$-\epsilon_0 \ddot{\vec{A}} - \frac{1}{\mu_0} \vec{\nabla}^2 \vec{A}(\mathbf{r}) + J_T = 0$$
$$n - \epsilon_0 \nabla^2 \phi = 0,$$
$$i\dot{\psi} = -\frac{\mu}{2} \left(-i\nabla + \vec{A} \right)^2 \psi + v_{txc} \psi + \phi\psi \quad (43)$$

Where we have defined the transverse current

$$J_T = J_{\text{para}} + J_{\text{dia}} - \epsilon_0 \nabla \dot{\phi} \quad (44)$$

Parallel Transport of Finite Difference Operators

- For constant vector potential, the minimal coupling ($\boldsymbol{p_x} \to \boldsymbol{p_x} + \boldsymbol{A_x}$) may be written as for individual direction:

$$\hat{\boldsymbol{p}}_{\boldsymbol{x}} \to \boldsymbol{e}^{-\boldsymbol{i}\boldsymbol{A}_{\boldsymbol{x}}\boldsymbol{x}}\hat{\boldsymbol{p}}_{\boldsymbol{x}}\boldsymbol{e}^{\boldsymbol{i}\boldsymbol{A}_{\boldsymbol{x}}\boldsymbol{x}} = \boldsymbol{e}^{-\boldsymbol{i}\boldsymbol{A}_{\boldsymbol{x}}\boldsymbol{x}}(-\boldsymbol{i}\boldsymbol{\nabla}_{\boldsymbol{x}})\boldsymbol{e}^{\boldsymbol{i}\boldsymbol{A}_{\boldsymbol{x}}\boldsymbol{x}} = -\boldsymbol{i}\boldsymbol{\nabla}_{\boldsymbol{x}} + \hat{\boldsymbol{A}}_{\boldsymbol{x}} \tag{45}$$

- For non constant vector potential, we have

$$\hat{\boldsymbol{p}}_{\boldsymbol{x}} \to \boldsymbol{e}^{-\boldsymbol{i}\int_0^{\boldsymbol{x}} \mathrm{d}\boldsymbol{x}'\boldsymbol{A}_{\boldsymbol{x}}(\boldsymbol{x}',\boldsymbol{y},\boldsymbol{z})}\hat{\boldsymbol{p}}_{\boldsymbol{x}}\boldsymbol{e}^{\boldsymbol{i}\int_0^{\boldsymbol{x}} \mathrm{d}\boldsymbol{x}'\boldsymbol{A}_{\boldsymbol{x}}(\boldsymbol{x}',\boldsymbol{y},\boldsymbol{z})} = \boldsymbol{p}_{\boldsymbol{x}} + \boldsymbol{A}_{\boldsymbol{x}}(\boldsymbol{x},\boldsymbol{y},\boldsymbol{z}) \tag{46}$$

Lagrangian

- Consider one dimensional Lagrangian for simplicity

$$\begin{aligned} L = \frac{\epsilon_0}{2}\int dx(\dot{A}_x(x) + \nabla\phi)^2 \\ + \int \mathrm{d}x i\psi^*(x)\partial_t\psi(x) - \frac{1}{2\mu_0}\int dx A_x(x)\nabla_x^2 A_x(x) \\ - \int dx\psi^*(x)(-i\nabla_x + A_x(x))^2\psi(x) - \int dx\psi^*(x)\psi(x)\phi(x) \end{aligned} \tag{47}$$

- The conjugate field variables are given as

$$\pi_A(x) = \frac{\partial L}{\partial \dot{A}(x)} = \epsilon_0\dot{A}_x(x) + \epsilon_0\nabla\phi \tag{48}$$

$$\pi_\phi(x) = 0, \pi_{\psi^*}(x) = 0 \tag{49}$$

$$\pi_\psi(x) = \frac{\partial L}{\partial\dot{\psi}} = i\psi^* \tag{50}$$

Hamiltonian

- We obtain the Hamiltonian to be

$$\begin{aligned} H &= \int dx \pi_A(x) \dot{A}(x) + \int dx \pi_\psi(x) \dot{\psi}(x) - L \\ &= \frac{\epsilon_0}{2} \int dx \dot{A}_x^2(x) \\ &+ \frac{\epsilon_0}{2} \int dx (\nabla \phi(x))^2 + \frac{1}{2\mu_0} \int dx A_x(x) \nabla_x^2 A_x(x) \\ &+ \int dx \psi^*(x)(-i\nabla_x + A_x(x))^2 \psi(x) + \int dx \psi^*(x)\psi(x)\phi(x) \end{aligned} \tag{51}$$

Hamiltonian in more Familiar Form

$$H = \int dx \underbrace{\frac{1}{2\epsilon_0} (\pi_A - \epsilon_0 \nabla \phi)^2}_{\frac{\epsilon_0}{2} E_\perp^2} + \underbrace{\frac{\epsilon_0}{2} \int dx (\nabla \phi)^2}_{\frac{1}{2} E_\|^2}$$

$$+ \underbrace{\frac{1}{2\mu_0} \int dx A_x(x) \nabla^2 A_x(x)}_{\frac{1}{2\mu_0}(\nabla \times A)^2, given \; \nabla \cdot A = 0}$$

$$+ \int dx \psi^*(x) (-i\nabla_x + A_x(x))^2 \psi(x) + \int dx \psi^*(x) \psi(x) \phi(x) \quad (52)$$

Hamiltonian Equations of Motion

$$\dot{\boldsymbol{A}} = \{\boldsymbol{A}, \boldsymbol{H}\} = \frac{\partial \boldsymbol{H}}{\partial \pi_{\boldsymbol{A}}}, \dot{\pi}_{\boldsymbol{A}} = \{\pi_{\boldsymbol{A}}, \boldsymbol{H}\} = -\frac{\partial \boldsymbol{H}}{\partial \boldsymbol{A}} \tag{53}$$

$$\dot{\psi} = \{\psi, \boldsymbol{H}\} = \boldsymbol{i}\frac{\partial \boldsymbol{H}}{\partial \psi^*} \tag{54}$$

$$\tag{55}$$

The equations of motion are

$$\dot{\boldsymbol{A}}(\boldsymbol{x}) = \frac{1}{\epsilon_0}(\pi_{\boldsymbol{A}}(\boldsymbol{x}) - \epsilon_0 \nabla \phi(\boldsymbol{x})) \tag{56}$$

$$\dot{\pi}_{\boldsymbol{A}}(\boldsymbol{x}) = -\frac{1}{\mu_0}\nabla^2 \boldsymbol{A}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{J} \tag{57}$$

$$\boldsymbol{i}\dot{\psi}(\boldsymbol{x}) = -\frac{1}{2}(-\boldsymbol{i}\nabla + \boldsymbol{A})^2\psi(\boldsymbol{x}) + \phi(\boldsymbol{x})\psi(\boldsymbol{x}) \tag{58}$$

- The equations can be put into more familiar form, by substituting back for π_A
- The equations of motion are now

$$\dot{A}(x) = \frac{1}{\epsilon_0}(\epsilon_0 \dot{A}_x(x) + \epsilon_0 \nabla\phi - \epsilon_0 \nabla\phi(x)) \tag{59}$$

$$(\epsilon_0 \ddot{A}_x(x) + \epsilon_0 \nabla\dot{\phi}) = -\frac{1}{\mu_0}\nabla^2 A_x(x) + J \tag{60}$$

$$\tag{61}$$

$$i\dot{\psi}(x) = -\frac{1}{2}(-i\nabla + A)^2\psi(x) + \phi(x)\psi(x) \tag{62}$$

- Which are simplified to

$$\dot{A}(x) = Y_x(x) \tag{63}$$

$$\epsilon_0 \dot{Y}_x(x) = -\frac{1}{\mu_0}\nabla^2 A_x(x) + \underbrace{J - \epsilon_0 \nabla\dot{\phi}}_{J_T} \tag{64}$$

$$i\dot{\psi}(x) = -\frac{1}{2}(-i\nabla + A)^2\psi(x) + \phi(x)\psi(x) \tag{65}$$

Parallel Transport of Finite Difference Operators

- We proceed into finite difference sparse matrix representation of Hamitonian

$$\frac{1}{dV}H = \sum_{c=x,y,z} \frac{1}{2\epsilon_0}\left(P_g^c - \epsilon_0 \nabla_{gg}^c \phi_g\right)^2 - \frac{\epsilon_0}{2}\phi_g \nabla_{gg}^2 \phi_g \qquad (66)$$

$$+ \sum_{c=x,y,z} \frac{1}{2\mu_0} A_g^c \nabla_{gg}^2 A_g^c$$

$$+ \sum_{c=x,y,z} \psi_g exp(-iS_{gg}^c A_g^c)(-\frac{1}{2}{\nabla_{gg}^c}^2) exp(iS_{gg}^c A_g^c)\psi_g + \psi_g^* \psi_g \phi_g \qquad (67)$$

- Implemented based on GPAW grid descriptor operators and a custom gauge including laplacian operator.

Full Nuclear Dynamics

$$L[\psi_n(\mathbf{r}), \dot{\psi}_n(\mathbf{r}), \psi_n^*(\mathbf{r}), \dot{\psi}_n^*(\mathbf{r}), \mathbf{A}(\mathbf{r}), \dot{\mathbf{A}}(\mathbf{r}), V(\mathbf{r}), \dot{V}(\mathbf{R}), \mathbf{R}, \dot{\mathbf{R}}]$$
$$= \underbrace{i \int d\dot{\psi}_n^*(\mathbf{r}) f_n \psi_n(\mathbf{r})}_{\texttt{electron kinetics}} + \underbrace{\int d\mathbf{r} \frac{\epsilon_0}{2} \dot{\mathbf{A}}^2(\mathbf{r})}_{\texttt{photon kinetics}} + \underbrace{\sum_\alpha \frac{1}{2M_\alpha} \dot{\mathbf{R}}_\alpha^2}_{\texttt{nuclear kinetics}} - E \tag{68}$$

$$E = \underbrace{\frac{1}{2}\epsilon_0 \int d\mathbf{r} |\nabla V(\mathbf{r})|^2}_{\texttt{Coulomb energy}} + \underbrace{E_{xc}[n] + \int d\mathbf{r} V_{ext}[\mathbf{R}_\alpha](\mathbf{r}) n(\mathbf{r})}_{\texttt{electron potential energy terms}}$$
$$+ \underbrace{\sum_n f_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \left[\frac{1}{2}(\mathbf{p} + \mathbf{A}(\mathbf{r}))^2 + V(\mathbf{r})\right] \psi_n(\mathbf{r})}_{\texttt{electron kinetic energy and light-matter coupling}} + \underbrace{\frac{1}{2\mu_0}(\nabla \times \mathbf{A}(\mathbf{r}))^2}_{\texttt{photon potential}} \tag{69}$$

From Schrödinger equation to Casida

- The Schrödinger Lagrangian is singular due to gauge invariance of degenerate occupation subspace rotations.
- Hence, instead of $\boldsymbol{U}(\boldsymbol{N})$, one operates in quotient space $\mathcal{U}(\boldsymbol{N})/\bigotimes_{i=0}^{|m|}\mathcal{U}(\boldsymbol{m_i})$ or on zero Kelvin, on Grassman manifold $\mathcal{U}(\boldsymbol{N_e}+\boldsymbol{N_h})/\mathcal{U}(\boldsymbol{N_e})\otimes\mathcal{U}(\boldsymbol{N_h})$.
- Projecting the degrees of freedom into this manifold, yields into TDDFT Casida equation.
- To second order, the density matrix is written utilizing only the electron-hole part

$$\rho[\rho_{eh}^{(1)}] = \begin{bmatrix} I - \rho_{he}^{(1)*}\rho_{eh}^{(1)} & \rho_{he}^{(1)} \\ \rho_{eh}^{(1)*} & \rho_{eh}^{(1)*}\rho_{he}^{(1)}, \end{bmatrix} \tag{70}$$

Coupled Fluctuations around Equilibrium

$$\begin{bmatrix} \dot{A}_{G\zeta} \\ \dot{Y}_{G\zeta} \\ \dot{R}_\alpha \\ \dot{P}_\alpha \\ \dot{P}_{ia} \\ \dot{Q}_{ia} \end{bmatrix} = J \begin{bmatrix} -\frac{1}{\epsilon_0} G^2 \delta_{GG'}\delta_{\zeta\zeta'} & & & & & \frac{d^2E}{dA_{G\zeta}\, dP_{i'a'}} \\ & \frac{1}{\mu_0}\delta_{GG'}\delta_{\zeta\zeta'} & & & & \\ & & M_\alpha^{-1}\delta_{\alpha\alpha'} & & \frac{d^2E}{dR_{\alpha'}\, dP_{ia}} & \frac{d^2E}{dR_{\alpha'}\, dP_{ia}} \\ \vdots & & & \frac{dE}{dR_\alpha\, dR'_\alpha} & & \\ h.c. & \ddots & & & \frac{d^2E}{dP_{ia}\, dP_{i'a'}} & \frac{d^2E}{dP_{ia}\, dQ_{i'a'}} \\ & & \dots & & \frac{d^2E}{dQ_{ia}\, dP_{i'a'}} & \frac{d^2E}{dQ_{ia}\, dQ_{i'a'}} \end{bmatrix} \begin{bmatrix} A_{G\zeta} \\ Y_{G\zeta} \\ R_\alpha \\ P_\alpha \\ P_{ia} \\ Q_{ia} \end{bmatrix} \tag{71}$$

where J is a symplectic matrix

$$J = \mathrm{diag}\left(\begin{bmatrix} 0 & \delta_{GG'}\delta_{\zeta\zeta'} \\ -\delta_{GG'}\delta_{\zeta\zeta'} & 0 \end{bmatrix}, \begin{bmatrix} 0 & \delta_{\alpha\alpha'} \\ -\delta_{\alpha\alpha'} & 0 \end{bmatrix}, \begin{bmatrix} 0 & \delta_{ii'}\delta_{aa'} \\ -\delta_{ii'}\delta_{aa'} & 0 \end{bmatrix} \right).$$

Conclusions

- Extremely important to carefully realize the degrees of freedom of the system: gauge freedoms, photon freedoms, electronic freedoms. After that, all classical propagations are trivial.
- Towards quantum description of light-matter.