民間企業でもやっている、第一原理計算手法の開発

時間に依存する外場下での電子・格子ダイナミクス

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謝辞

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第13回コンピュテーショナル・マテリアルズ・デザイン
CMD®ワークショップ　2008年9月10日

outline

1. Motivation
2. Time-Dependent Density Functional Theory
3. Energy conservation rule throughout the simulation
4. Some applications

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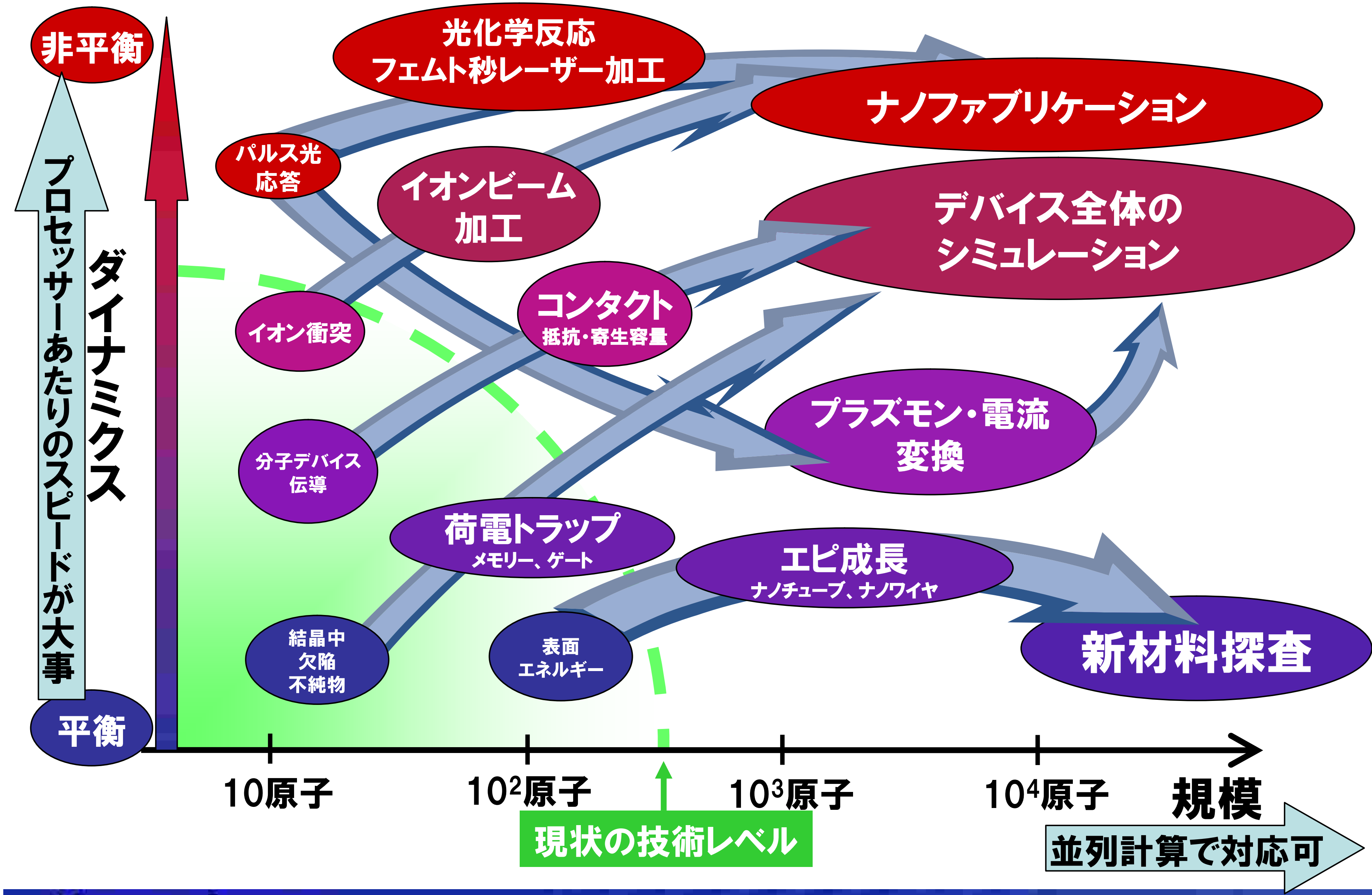
1. Motivation



1. Motivation
2. Time-Dependent Density Functional Theory
3. Energy conservation rule throughout the simulation
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2. Time-dependent version of the Density Functional Theory

E. Runge and E. K. U. Gross, PRL, 52, 997(1984).

Instead of total energy minimization, minimize an action given as,

$$A = \int_{t_0}^{t_1} dt \langle \Phi(t) | i\partial/\partial t - \hat{H}(t) | \Phi(t) \rangle$$

Within DFT $<\phi \mid H \mid \phi> = E_{tot}$ → $\delta A = 0$ gives

$$i\hbar \frac{d\psi_n(\vec{r},t)}{dt}$$

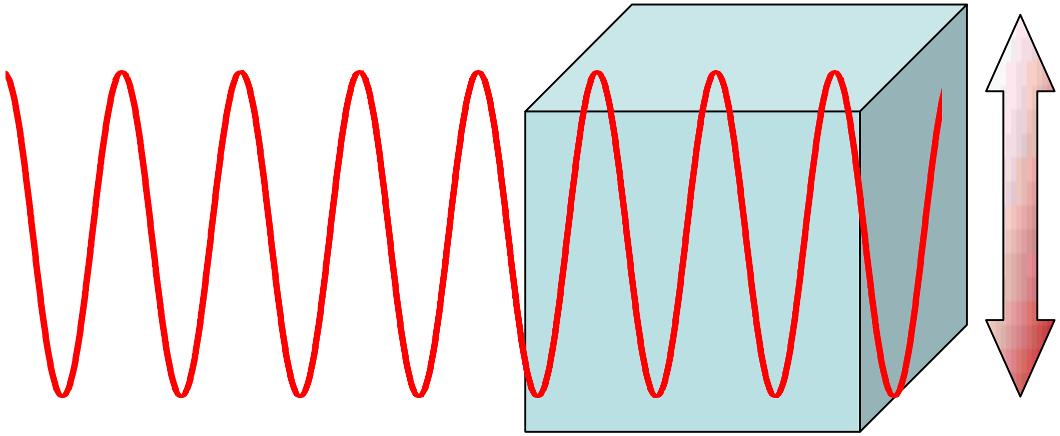
$$= \left(-\nabla^2 + \int \frac{\rho(\vec{r}',t)}{|\vec{r}-\vec{r}'|} d\vec{r}' + \mu_{XC}[\rho(\vec{r},t)] + \sum_I \tilde{v}(\vec{r}'-\vec{R}_I(t), \vec{r}-\vec{R}_I(t)) + \sum_I \frac{Z_I(\vec{R}_I)}{|\vec{r}-\vec{R}_I(t)|} \right) \psi_n(\vec{r},t)$$

⟶ one-to-one relation with $v(\vec{r},t)$ and $\rho(\vec{r},t)$ with proper initial condition

Time-dependent Kohn-Sham equation

Influence of optical perturbation!

Pioneering works: **筑波大学　矢花先生**

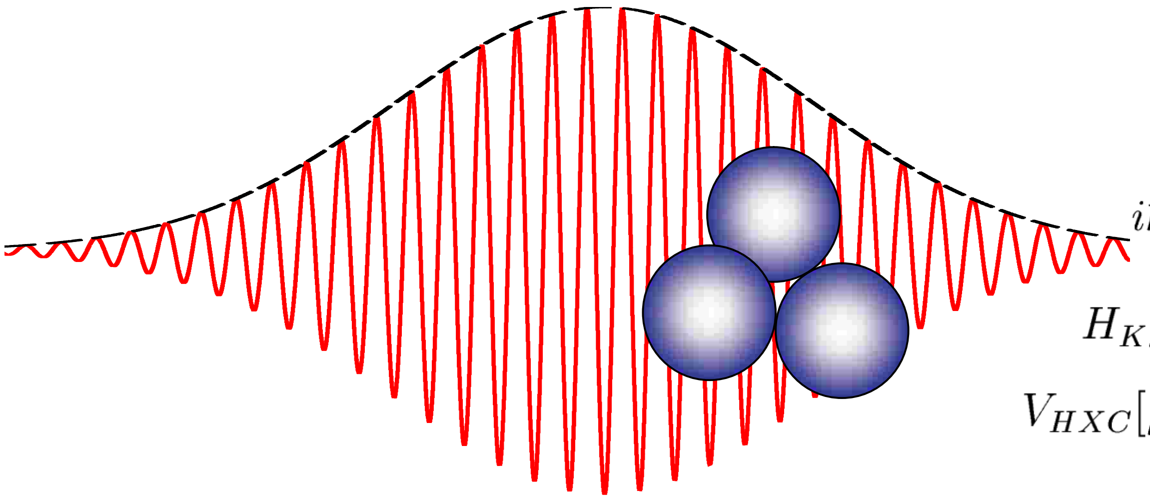


$$i\hbar\frac{d\psi_{n,k}(\mathbf{r},t)}{dt} = H_{KS}\left[\rho(\mathbf{r},t)\right]\psi_{n,k}(\mathbf{r},t)$$

$$H_{KS}\left[\rho(\mathbf{r},t)\right] \Rightarrow H_{KS}\left[\rho(\mathbf{r},t),\, \mathbf{A}(t)\right]$$

$$-\frac{\hbar^2}{2m}\left(\mathbf{P} - \frac{1}{c}\mathbf{A}(t)\right)^2$$

Bertsch, et al., PRB62 7998, (2000).



$$i\hbar\frac{d\psi_{n,k}(\mathbf{r},t)}{dt} = H_{KS}\left[\rho(\mathbf{r},t)\right]\psi_{n,k}(\mathbf{r},t)$$

$$H_{KS}\left[\rho(\mathbf{r},t)\right] \Rightarrow H_{KS}\left[\rho(\mathbf{r},t),\, V_{ext}(\mathbf{r},t)\right]$$

$$V_{HXC}[\rho(\mathbf{r},t)] \Rightarrow V_{HXC}[\rho(\mathbf{r},t)] + V_{ext}(\mathbf{r},t)$$

Castro et al., Eur. Phys. J. D 28, 211 (2004).

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How can we know that the simulation goes numerically correct?

Let's us re-visit the energy conservation rule.

In case of classical molecular dynamics (MD)

$$U(t) = \sum_I \frac{M_I}{2}\left(\frac{d\mathbf{R}_I}{dt}\right)^2 + V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right)$$

$$\frac{dU(t)}{dt} = \sum_I \left(\frac{d\mathbf{R}_I(t)}{dt} \cdot M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{d\mathbf{R}_I(t)}{dt} \cdot \frac{V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right)}{d\mathbf{R}_I(t)}\right) = 0$$

because $-\frac{V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right)}{d\mathbf{R}_I(t)} = M_I \frac{d^2\mathbf{R}_I(t)}{dt^2}$

In case of combination of MD and TDDFT

$$V\left(\mathbf{R}_1(t),\mathbf{R}_2(t),,,,\mathbf{R}_N(t)\right)\Rightarrow$$

$$\sum_i\left(\int\psi_i^*(\mathbf{r},t)\frac{-\hbar^2}{2m}\Delta\psi_i(\mathbf{r},t)d\mathbf{r}+\int\int\psi_i^*(\mathbf{r}',t)v_{nl}(\mathbf{r}',\mathbf{r})\psi_i(\mathbf{r},t)d\mathbf{r}'d\mathbf{r}\right)+\frac{1}{2}\int\int\frac{\rho(\mathbf{r}',t)\rho(\mathbf{r},t)}{|\,\mathbf{r}-\mathbf{r}'\,|}d\mathbf{r}'d\mathbf{r}$$

$$+\int E_{XC}[\rho(\mathbf{r},t)]d\mathbf{r}+\sum_I Z_I\left(\int\frac{\rho(\mathbf{r},t)}{|\,\mathbf{R}_I(t)-\mathbf{r}\,|}d\mathbf{r}+\sum_{J\neq I}\frac{Z_J}{|\,\mathbf{R}_I(t)-\mathbf{R}_J(t)\,|}\right)\equiv E_{tot}^{DFT}(\mathbf{r},t)$$

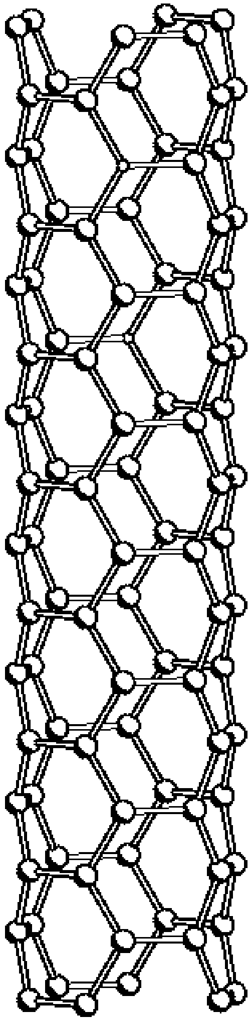
MD simulation must conserve

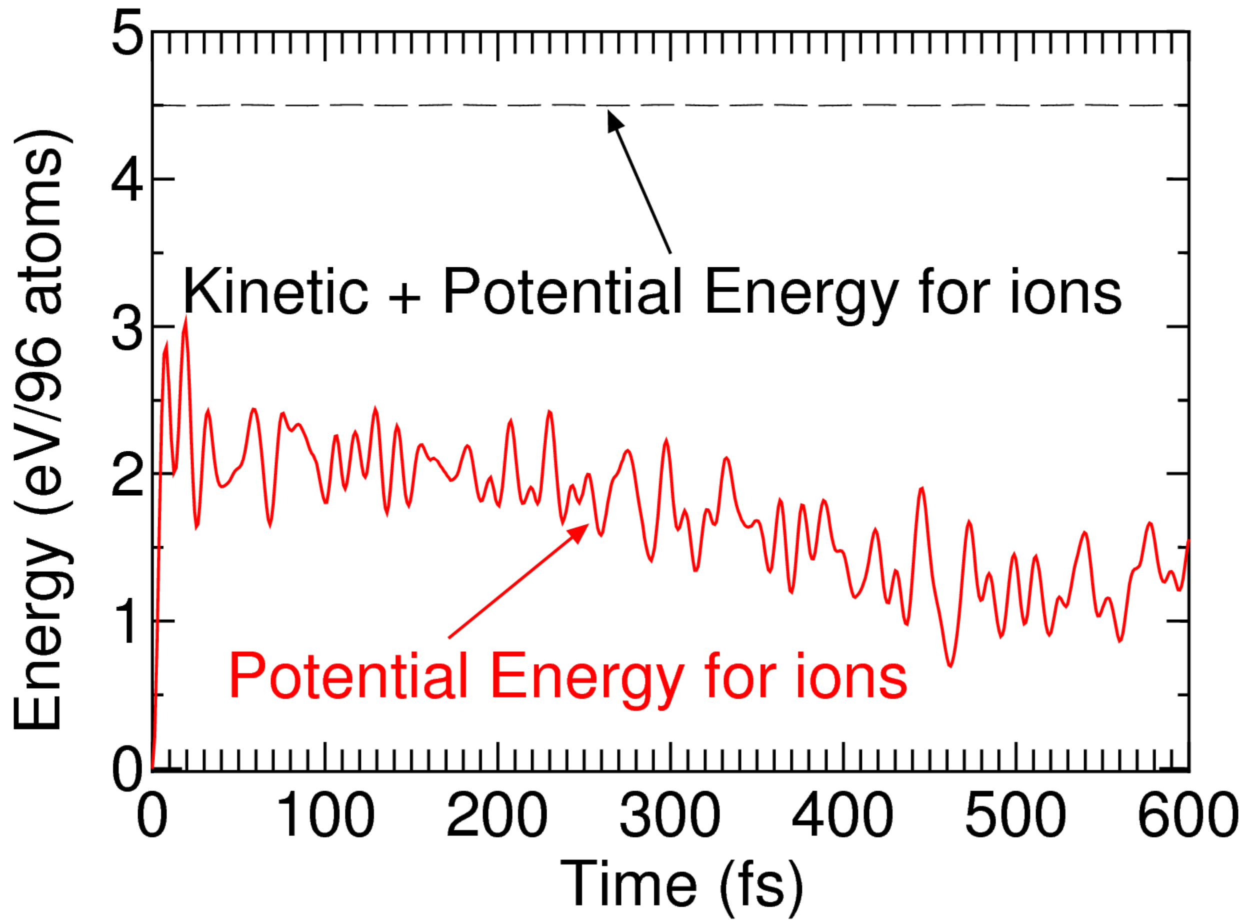
$$U(t)=\sum_I\frac{M_I}{2}\left(\frac{d\mathbf{R}_I}{dt}\right)^2+E_{tot}^{DFT}(\mathbf{r},t)$$

$$\frac{dU(t)}{dt}=\sum_I\frac{d\mathbf{R}_I(t)}{dt}\cdot\left(M_I\frac{d^2\mathbf{R}_I(t)}{dt^2}+\frac{dE_{tot}^{KS}(\mathbf{r},t)}{d\mathbf{R}_I(t)}\right)+\underbrace{\sum_i\left(\frac{d\psi_i^*(\mathbf{r},t)}{dt}\frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta\psi_i^*(\mathbf{r},t)}+C.C.\right)}_{\text{TDDFT term}}$$

$$\boxed{\begin{aligned}M_I\frac{d^2\mathbf{R}_I(t)}{dt^2}&=-\frac{dE_{tot}^{DFT}(\mathbf{r},t)}{d\mathbf{R}_I(t)}\\ \frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta\psi_i^*(\mathbf{r},t)}&=H_{KS}(\mathbf{r},t)\psi_i(\mathbf{r},t)=i\hbar\frac{d\psi_i(\mathbf{r},t)}{dt}\end{aligned}}\qquad =0$$

Example of TDDFT-MD 96 C atoms under R.T. and 173→231 excitation





Without time-varying external field

$$\sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \frac{1}{2} \int\int \frac{\rho(\mathbf{r}',t)\rho(\mathbf{r},t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$
$$+ \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r} + \sum_I Z_I \left(\int \frac{\rho(\mathbf{r},t)}{|\mathbf{R}_I(t)-\mathbf{r}|} d\mathbf{r} + \sum_{J \neq I} \frac{Z_J}{|\mathbf{R}_I(t)-\mathbf{R}_J(t)|} \right) \equiv E_{tot}^{DFT}(\mathbf{r},t)$$

With time-varying external field

$$V_{ext}(\mathbf{r},t) = \int \frac{\rho_{ext}(\mathbf{r}',t)}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}'$$

$$E_{tot}^{DFT}(\mathbf{r},t)$$
$$= \sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r}$$
$$+ \frac{1}{2} \int\int \frac{(\rho(\mathbf{r}',t)+\rho_{ext}(\mathbf{r}',t))(\rho(\mathbf{r},t)+\rho_{ext}(\mathbf{r},t))}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$
$$+ \sum_I Z_I \left(\int \frac{(\rho(\mathbf{r},t)+\rho_{ext}(\mathbf{r},t))}{|\mathbf{R}_I(t)-\mathbf{r}|} d\mathbf{r} + \sum_{J \neq I} \frac{Z_J}{|\mathbf{R}_I(t)-\mathbf{R}_J(t)|} \right)$$

$$
\begin{aligned}
E_{tot}^{DFT}(\mathbf{r},t) \\
&= \sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r} \\
&\quad + \frac{1}{2} \int\int \frac{(\rho(\mathbf{r}',t) + \rho_{ext}(\mathbf{r}',t))(\rho(\mathbf{r},t) + \rho_{ext}(\mathbf{r},t))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \\
&\quad + \sum_I Z_I \left(\int \frac{(\rho(\mathbf{r},t) + \rho_{ext}(\mathbf{r},t))}{|\mathbf{R}_I(t) - \mathbf{r}|} d\mathbf{r} + \sum_{J \neq I} \frac{Z_J}{|\mathbf{R}_I(t) - \mathbf{R}_J(t)|} \right)
\end{aligned}
$$

$$
U(t) = \sum_I \frac{M_I}{2} \left(\frac{d\mathbf{R}_I}{dt} \right)^2 + E_{tot}^{DFT}(\mathbf{r},t)
$$

Goes to zero!

$$
\begin{aligned}
\frac{dU(t)}{dt} &= \sum_I \frac{d\mathbf{R}_I(t)}{dt} \cdot \left(M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{dE_{tot}^{KS}(\mathbf{r},t)}{d\mathbf{R}_I(t)} \right) + \sum_i \left(\frac{d\psi_i^*(\mathbf{r},t)}{dt} \frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} + C.C. \right) \\
&\quad + \int \frac{d\rho_{ext}(\mathbf{r},t)}{dt} \left(\int \frac{(\rho(\mathbf{r}',t) + \rho_{ext}(\mathbf{r}',t))}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \sum_I Z_I \frac{1}{|\mathbf{R}_I(t) - \mathbf{r}|} \right) d\mathbf{r}
\end{aligned}
$$

Remains as non-zero!

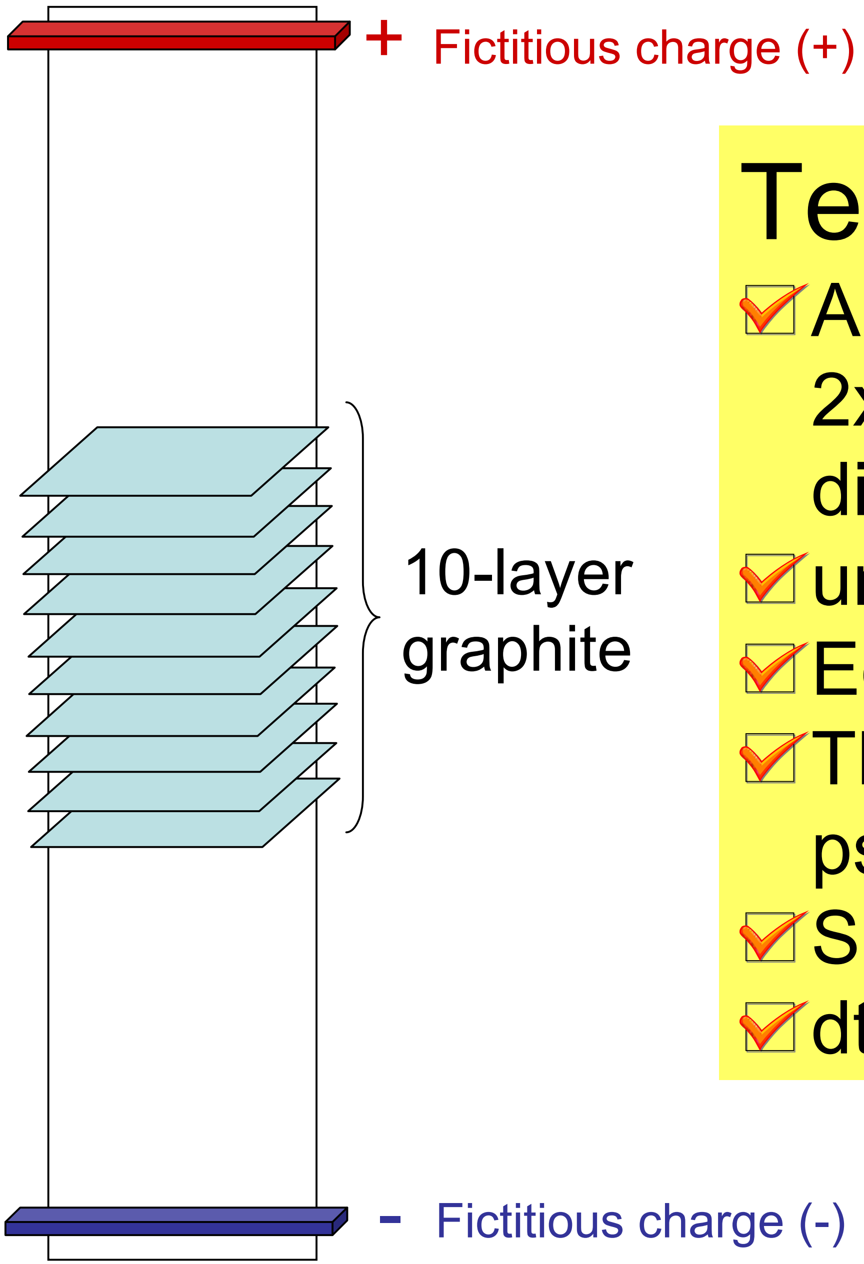
Work by external field is

$$W(t) = \int_{t_0}^{t} \frac{dU(t')}{dt'} dt' + W(t = t_0)$$

Thus a new conservation rule is

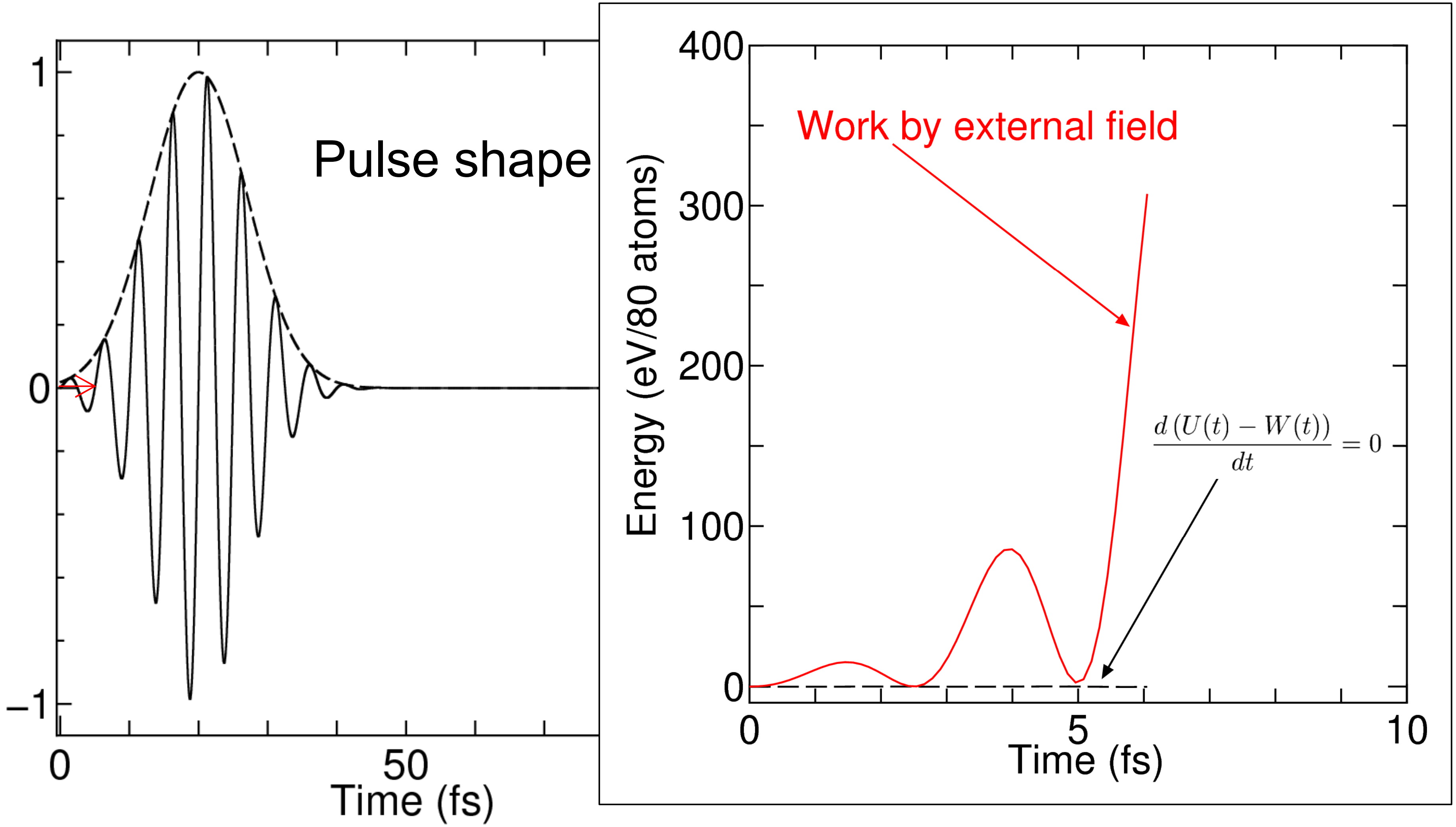
$$\frac{d\left(U(t) - W(t)\right)}{dt} = 0$$

Miyamoto, Zhang, Phys. Rev. B77, 165123 (2008)



Test calculation:

- AB-stacked graphite 2x2 cell in lateral directions
- under pulse E-field
- Ecut=60 Ry
- TM type pseudopotentials
- Single k-point
- dt=1.84 x 10^{-4} fs


1
0
−1
0
50
Time (fs)
Pulse shape
400
300
200
100
0
0
5
10
Time (fs)
Energy (eV/80 atoms)
Work by external field
$\frac{d\left(U(t)-W(t)\right)}{dt}=0$

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3. Energy conservation rule throughout the simulation
4. Some applications

The applications are still unpublished
so they will be shown in the lecture

sumarries

1. Time-dependent density functional approach as a practical tool for electron-ion dynamics under time-varying field
2. Energy conservation rule
3. Applications *(to be shown in the lecture day.)*