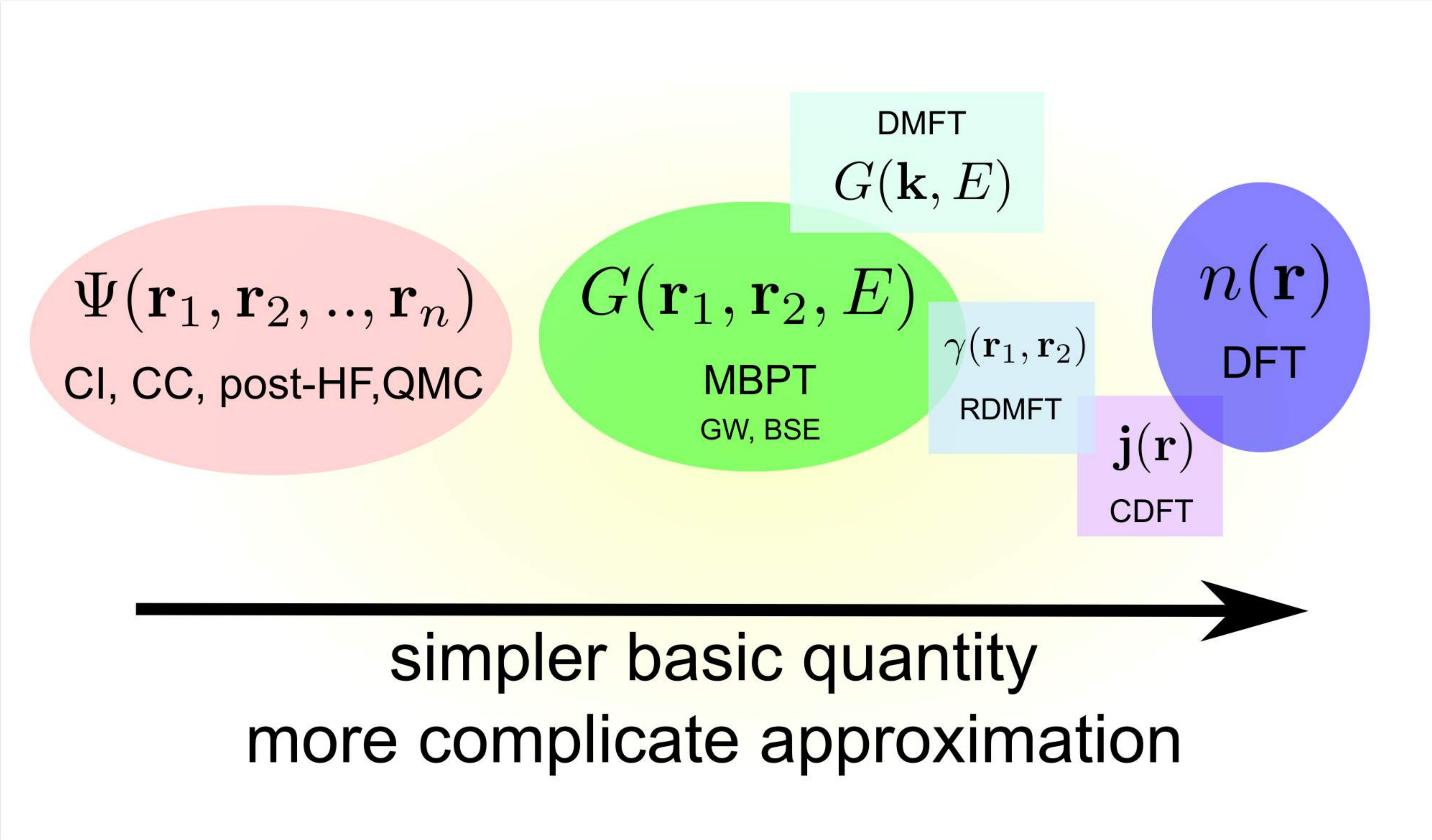
Time Dependent Density Functional Theory

Francesco Sottile

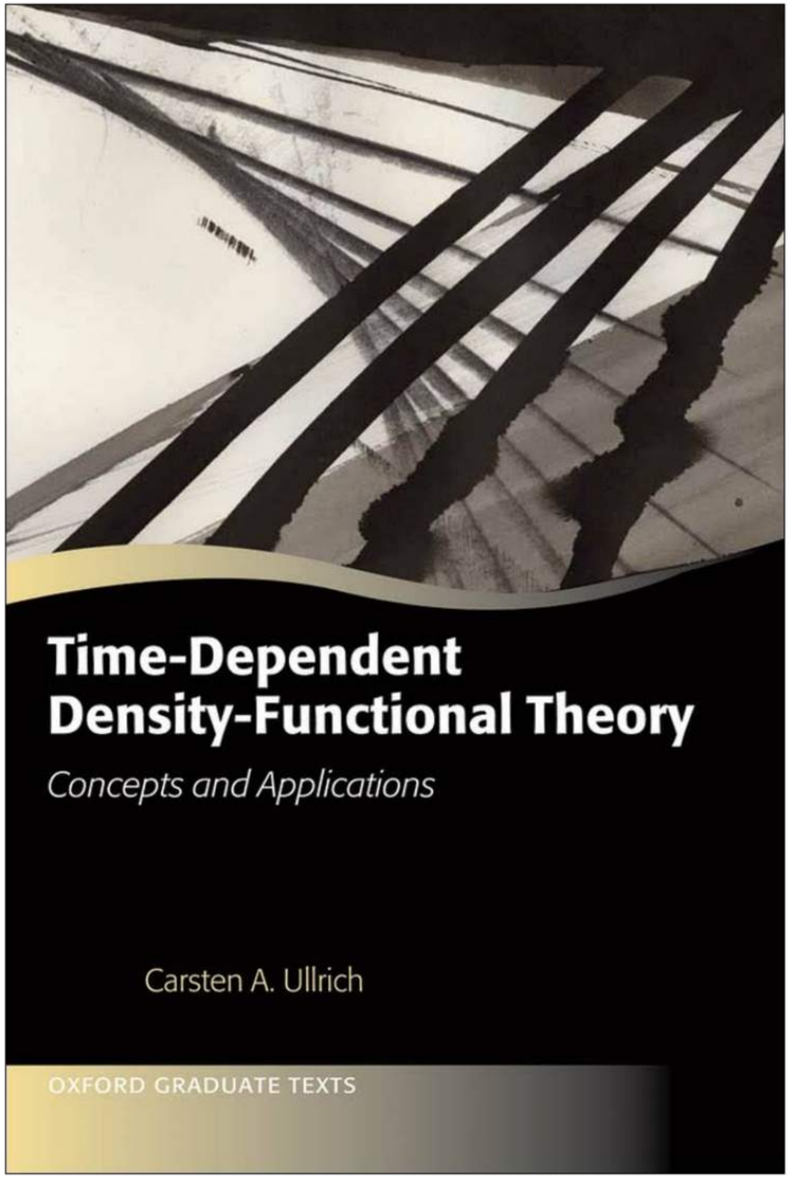
International summer School in electronic structure Theory: electron correlation in Physics and Chemistry (ISTPC)

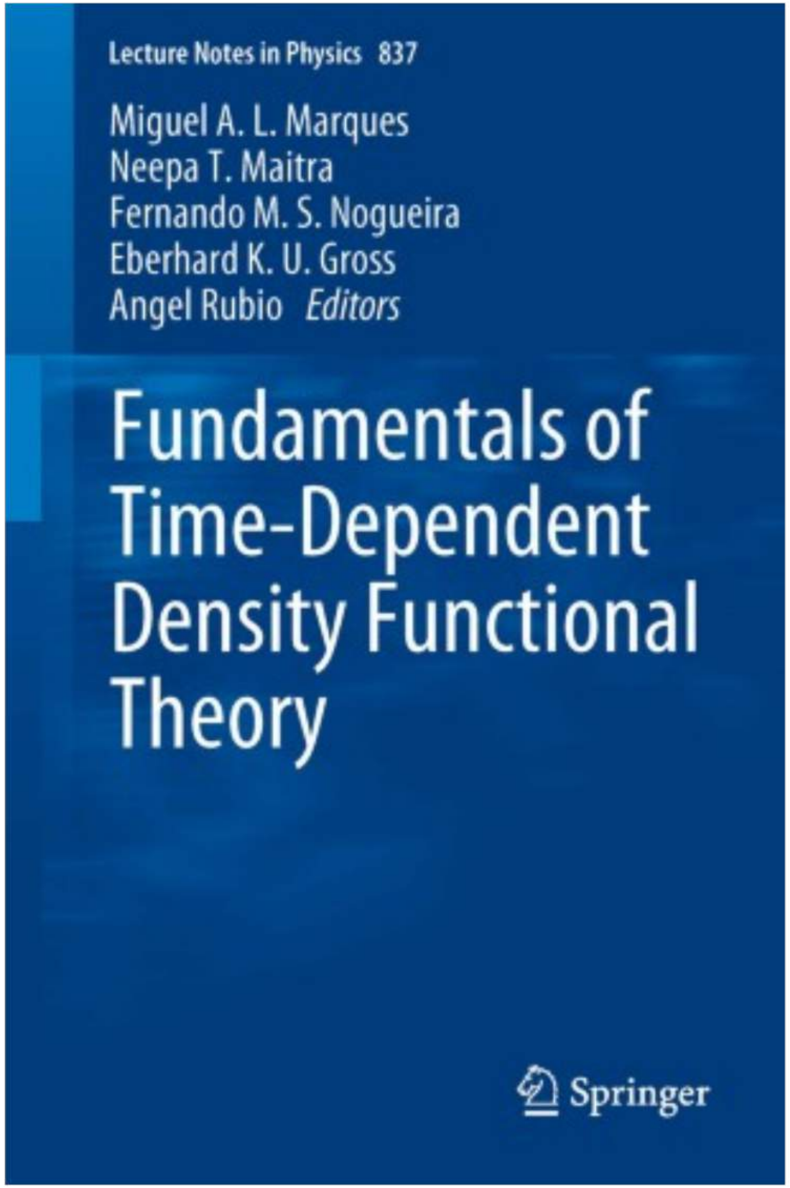
27 June

ISTPC 2022

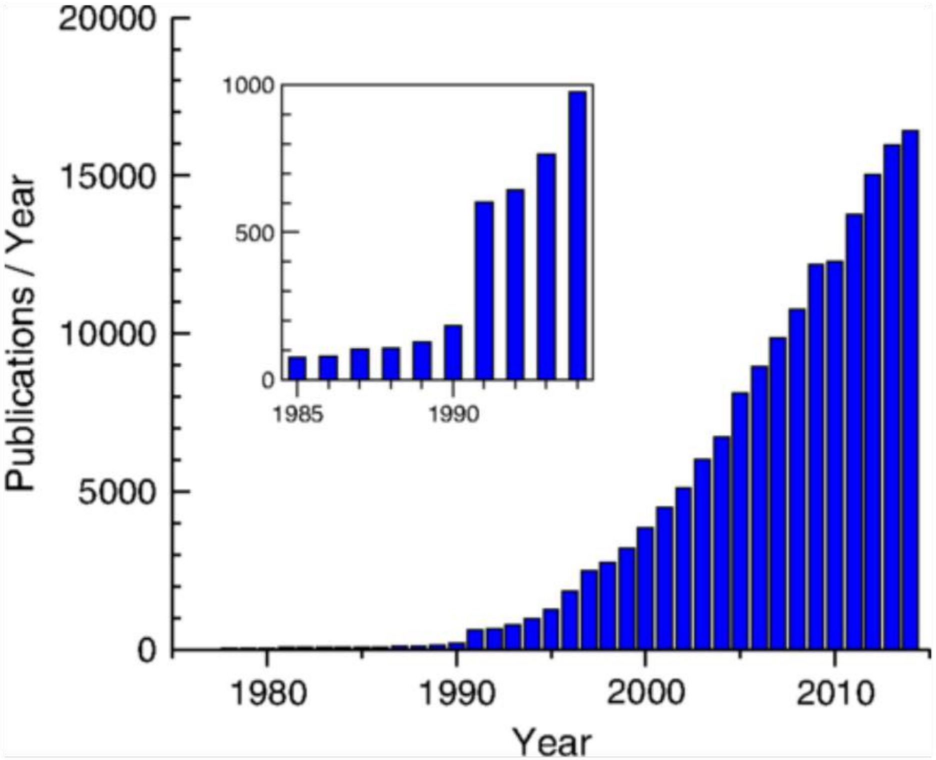


DMFT
$G(\mathbf{k}, E)$
$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n)$
CI, CC, post-HF,QMC
$G(\mathbf{r}_1, \mathbf{r}_2, E)$
MBPT
GW, BSE
$\gamma(\mathbf{r}_1, \mathbf{r}_2)$
RDMFT
$\mathbf{j}(\mathbf{r})$
CDFT
$n(\mathbf{r})$
DFT
simpler basic quantity
more complicate approximation


Time-Dependent
Density-Functional Theory
Concepts and Applications
Carsten A. Ullrich
OXFORD GRADUATE TEXTS


Lecture Notes in Physics 837
Miguel A. L. Marques
Neepa T. Maitra
Fernando M. S. Nogueira
Eberhard K. U. Gross
Angel Rubio Editors
Fundamentals of
Time-Dependent
Density Functional
Theory
Springer

Success of DFT

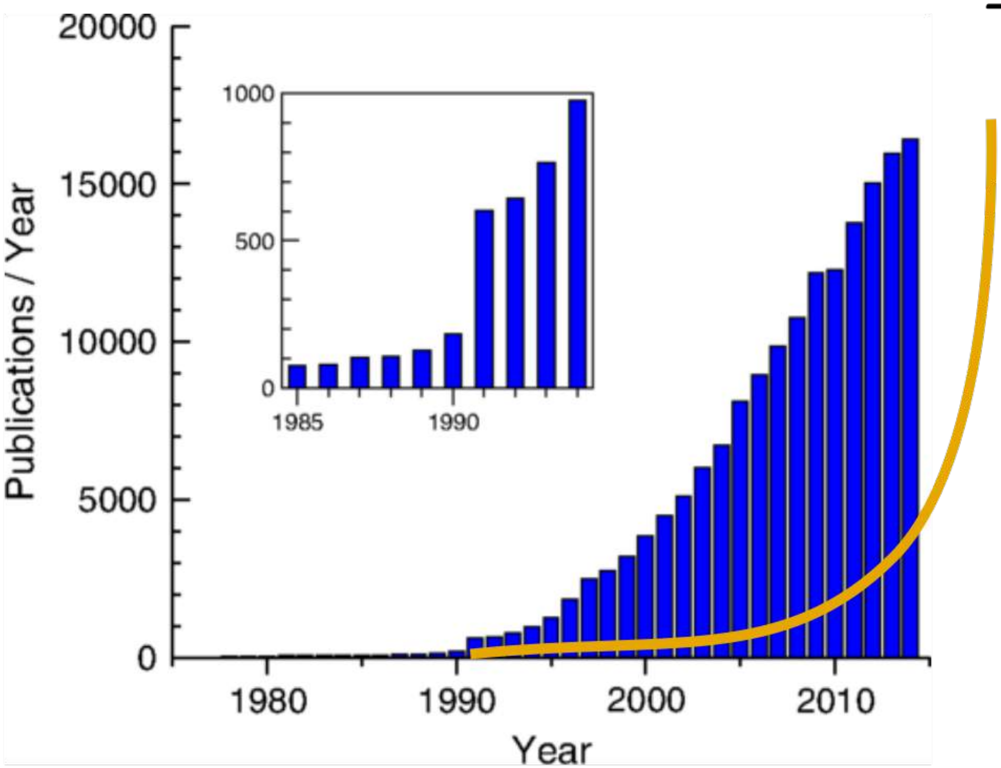


R. O. Jones Rev. Mod. Phys. 87, 897 (2015)

Success of DFT

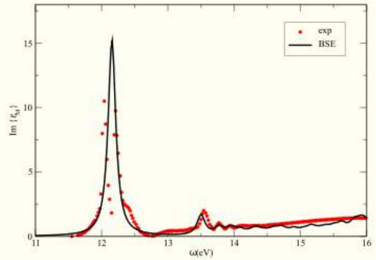
+ Machine Learning

J. Phys. Mater. **2** 032001 (2019)



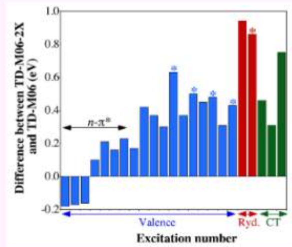
R. O. Jones Rev. Mod. Phys. 87, 897 (2015)

Optical Spectra



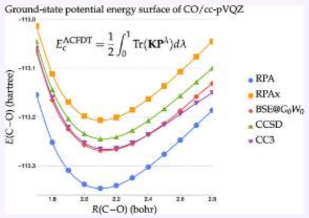
Phys. Rev. B **76**, 161103 (2007)

Excitation energies



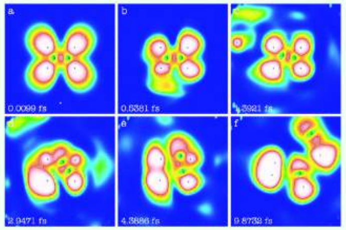
J.Phys.Chem.Lett. **8**, 1524 (2017)

Ground-state total energy



Phys. Rev. Lett. **98**, 157404 (2007)

Electrons in intense laser fields

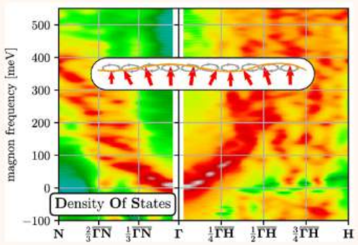


Phys. Rev. A **71**, 010501 (2004)

Electron-ion dynamics

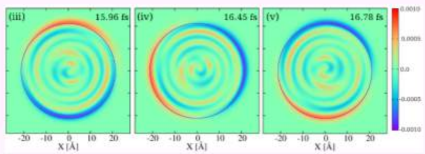
A. Castro - https://youtu.be/VixOLFubxBw

Magnetic excitations



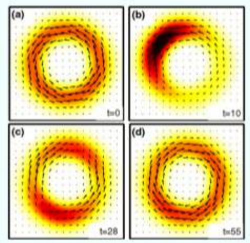
J. Chem. Theory Comput. **16**, 1007 (2020)

Quantum plasmonics



ACS photonics, **7**, 2429 (2020)

Optimal control theory



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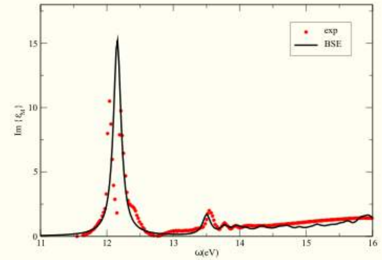

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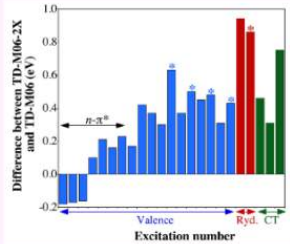

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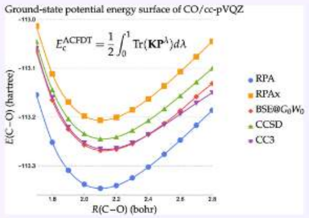

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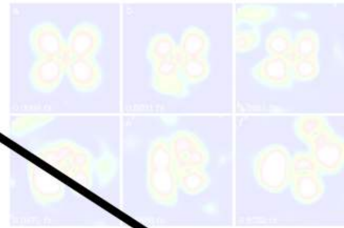
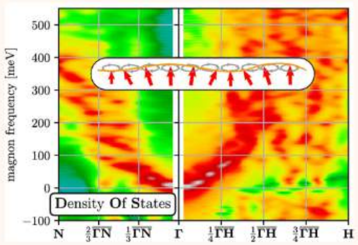


Electron-ion dynamics

Perturbative approaches

Magnetic excitations



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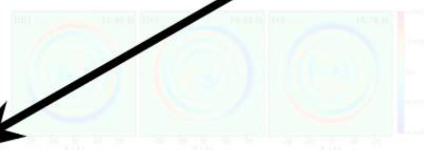


ACS photonics. **7**, 2429 (2020)

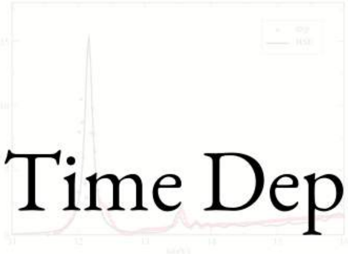
Optimal control theory

Phys. Rev. Lett. **98**, 157404 (2007)

Time Dependent phenomena

$$V_{\text{ext}}(t)$$

Optical Spectra



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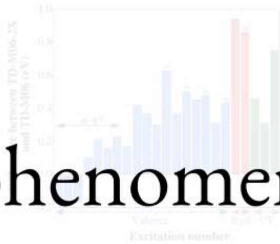

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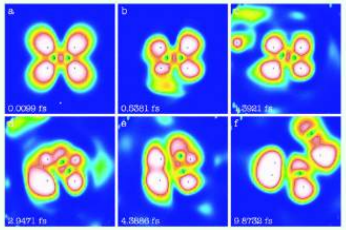

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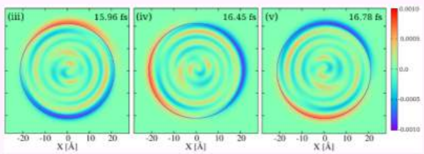

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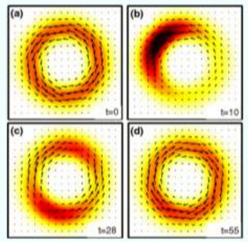
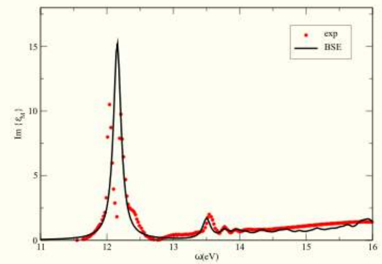


Phys. Rev. Lett. **98**, 157404 (2007)

Serious applications

Optical Spectra



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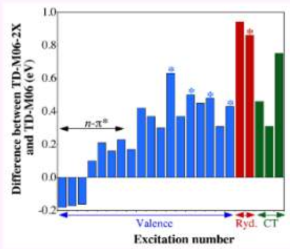

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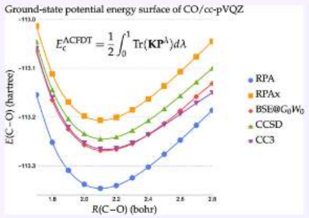

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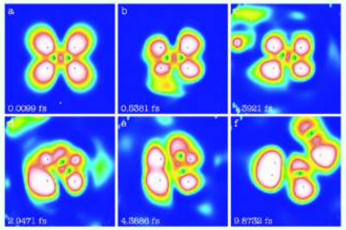

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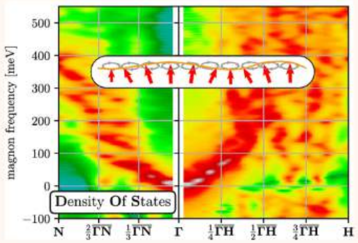

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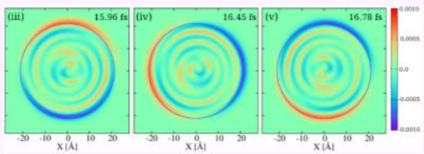

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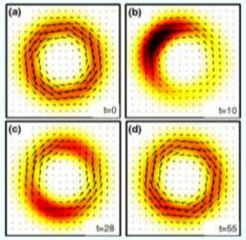

Phys. Rev. Lett. **98**, 157404 (2007)

Name of the game

$$[T + V_{e-e} + V_N + V_{\text{ext}}(t)]\,\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t) = i\hbar\frac{\partial\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t)}{\partial t}$$

given $\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, 0)$

Name of the game

$$[T + V_{e-e} + V_N + V_{\text{ext}}(t)]\,\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t) = i\hbar \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t)}{\partial t}$$

given $\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, 0)$

→ DFT world

Name of the game

DFT

Hohenberg-Kohn theorem

$$V_{\text{ext}} \longleftrightarrow n$$

$$\left\langle \Psi^0 \middle| O \middle| \Psi^0 \right\rangle = O[n]$$

TDDFT

Runge-Gross theorem

$$V_{\text{ext}}(t) \longleftrightarrow n(t)$$

$$\langle \Psi(t) | O(t) | \Psi(t) \rangle = O[n, \Psi^0](t)$$

Hohenberg and Kohn, Phys. Rev. **136**, B864 (1964)

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

Name of the game

TDDFT

Runge-Gross theorem

$$V_{\mathrm{ext}}(t) \quad \longleftrightarrow \quad n(t)$$

$$\langle \Psi(t) | O(t) | \Psi(t) \rangle = O[n, \Psi^0](t)$$

→ is it true?

→ but in practice?

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

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is it true?

Demonstration

but in practice?

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

Name of the game

TDDFT

Runge-Gross theorem

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$$\langle \Psi(t)|O(t)|\Psi(t)\rangle = O[n, \Psi^0](t)$$

is it true?

Demonstration

but in practice?

KS equations

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

Name of the game

Demonstration

Runge-Gross theorem

$$V_{\rm ext}(t) \quad \longleftrightarrow \quad n(t)$$

Demonstration

Runge-Gross theorem

$$V_{\text{ext}}(t) \quad \longleftrightarrow \quad n(t)$$

Demonstration

1) $$V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$$

2) $$\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$$

Demonstration of the Runge Gross theorem

1) $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

Taylor expandable (in t)

Demonstration of the Runge Gross theorem

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$$i\frac{\partial \mathbf{j}(\mathbf{r},t)}{\partial t} = \langle \Psi(t)|[\mathbf{j}(\mathbf{r}), H(t)]|\Psi(t)\rangle$$

Taylor expandable (in t)

Demonstration of the Runge Gross theorem

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$$i\frac{\partial}{\partial t}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\bigg|_{t=0} = \langle \Psi_0|[\mathbf{j}(\mathbf{r}), H(0) - H'(0)]|\Psi_0\rangle$$

Taylor expandable (in t)

Demonstration of the Runge Gross theorem

1) $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

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$$= -i\, n_0(\mathbf{r}) \nabla \left[V_{\text{ext}}(\mathbf{r},0) - V'_{\text{ext}}(\mathbf{r},0)\right]$$

Taylor expandable (in t)

Demonstration of the Runge Gross theorem

1) $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

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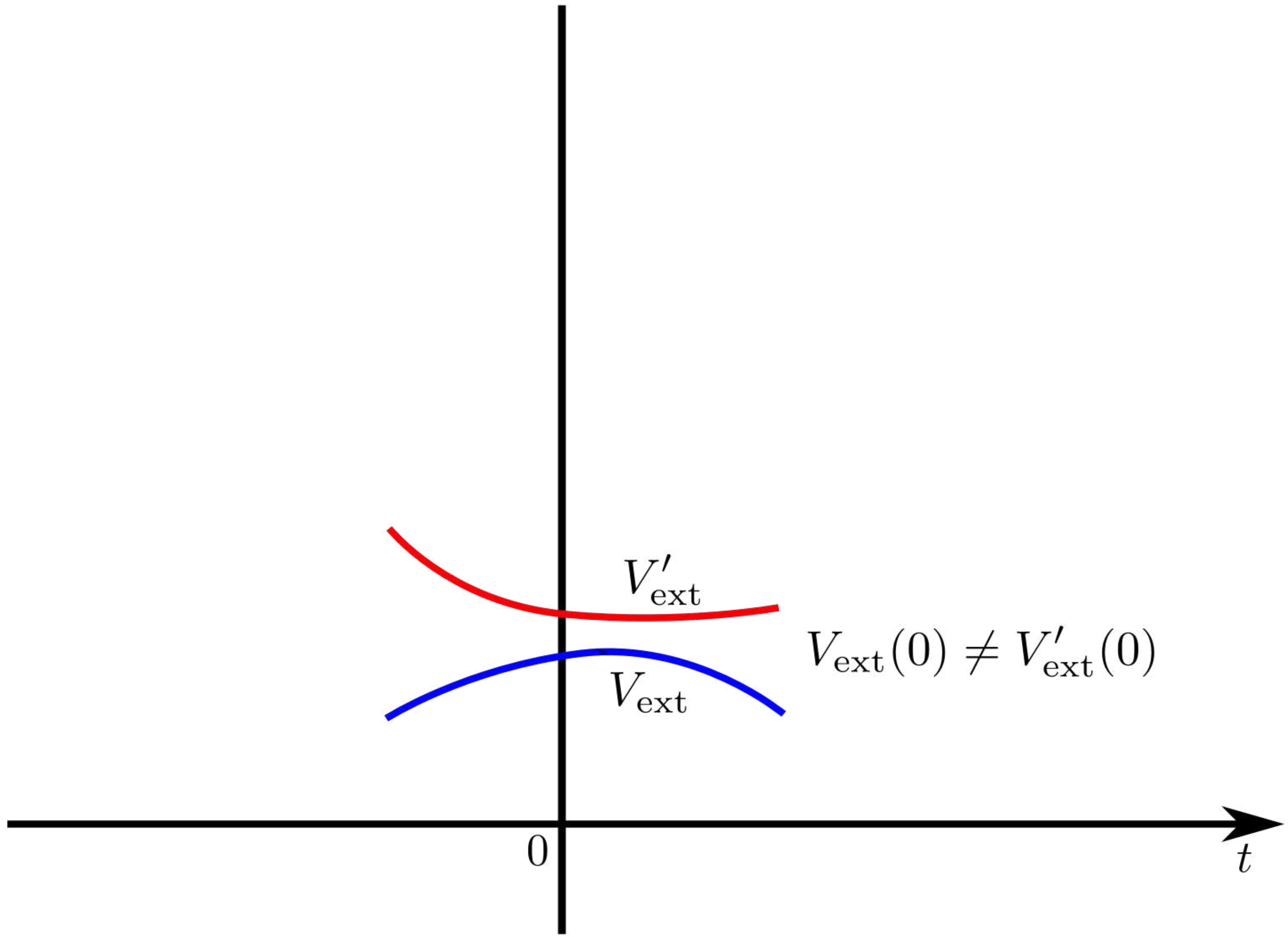
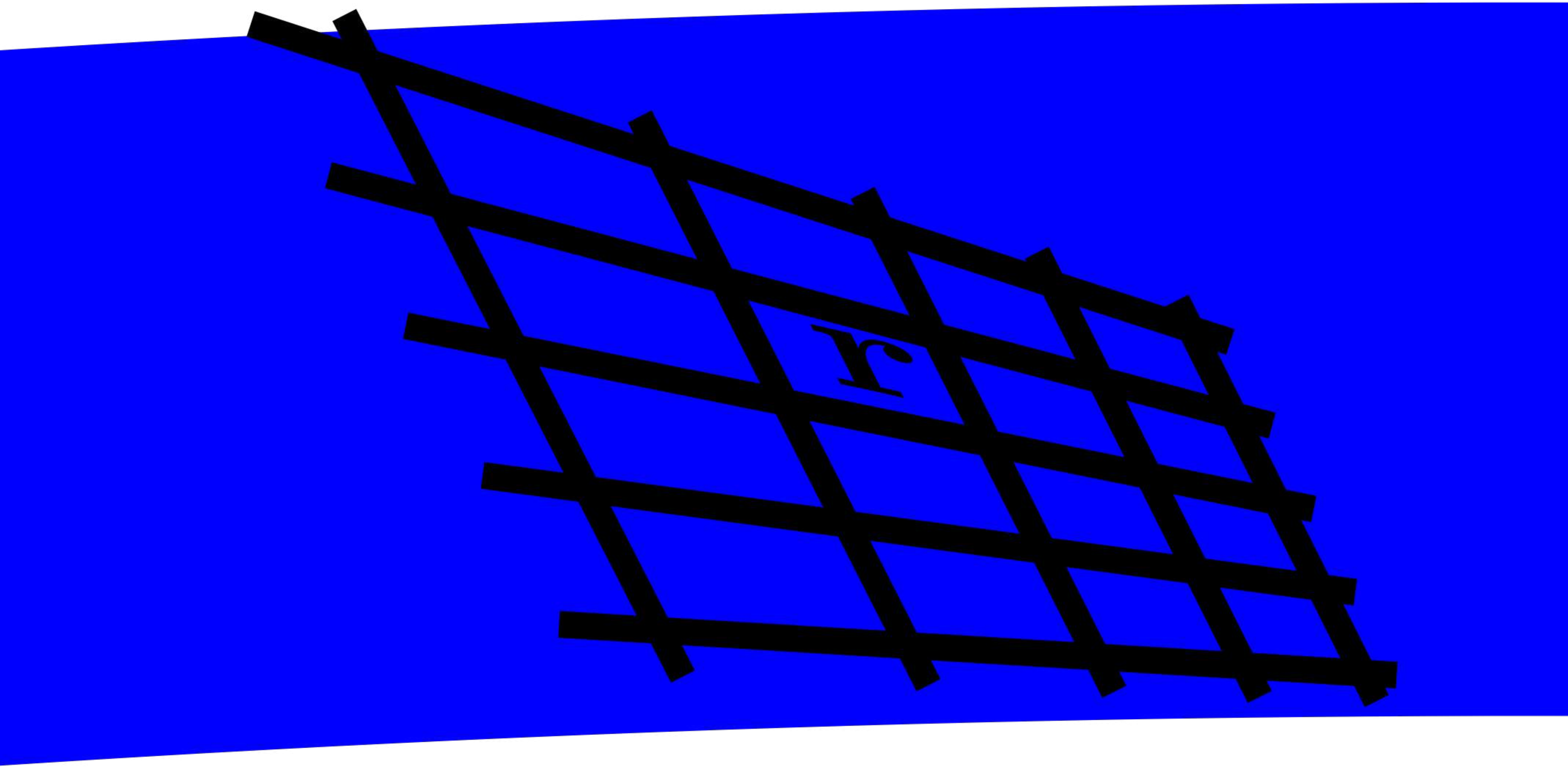
$$= -i\, n_0(\mathbf{r}) \nabla \left[V_{\text{ext}}(\mathbf{r},0) - V'_{\text{ext}}(\mathbf{r},0)\right]$$

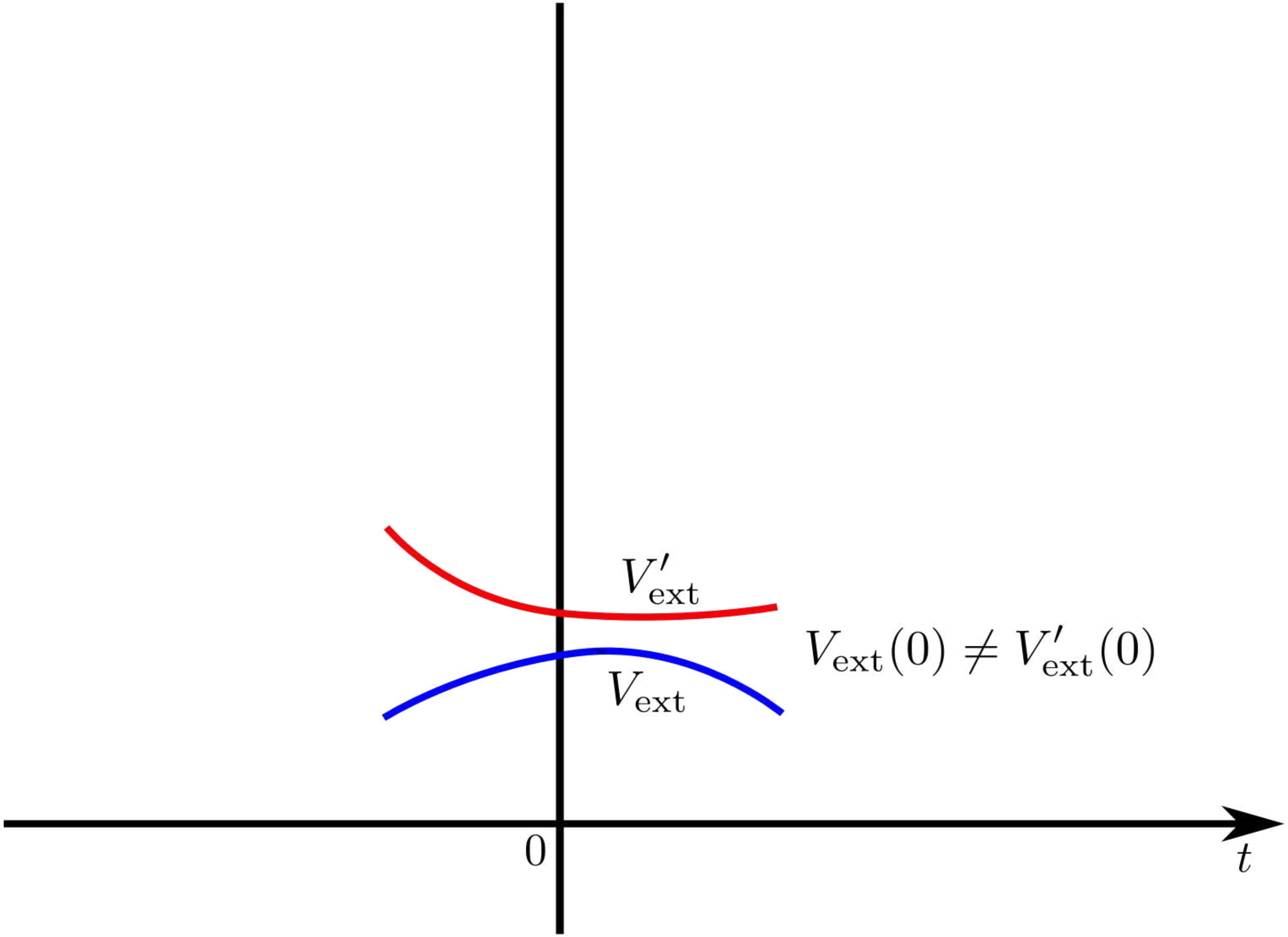
if two potentials differ by more than a constant at t=0, they will generate two different current densities

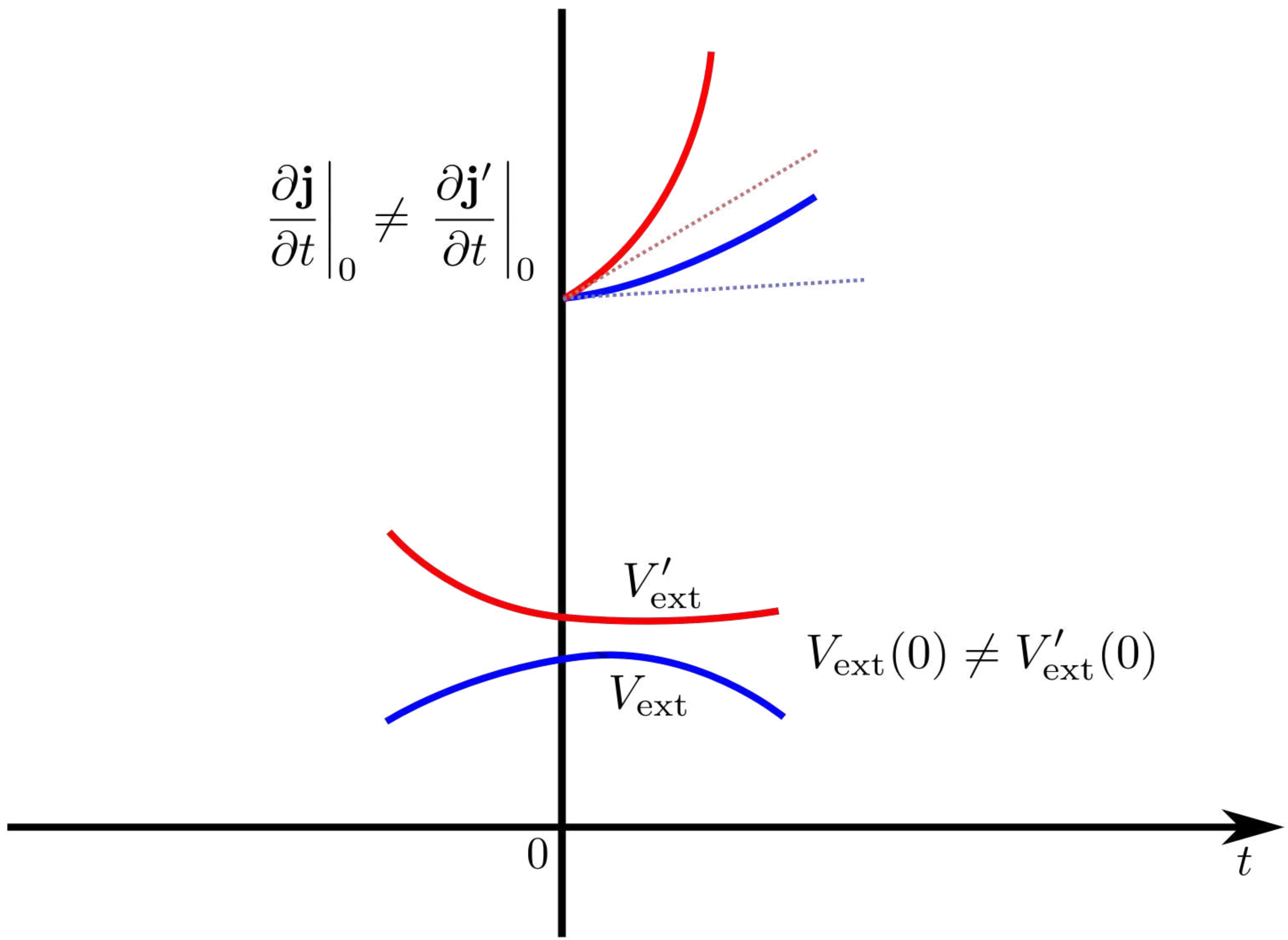
Taylor expandable (in t)



V'_{ext}
$V_{\text{ext}}(0) \neq V'_{\text{ext}}(0)$
V_{ext}
0
t


r


V'_{ext}
$V_{\text{ext}}(0) \neq V'_{\text{ext}}(0)$
V_{ext}
0
t


$\left.\frac{\partial \mathbf{j}}{\partial t}\right|_0 \neq \left.\frac{\partial \mathbf{j}'}{\partial t}\right|_0$
V'_{ext}
$V_{\mathrm{ext}}(0) \neq V'_{\mathrm{ext}}(0)$
V_{ext}
0
t

Demonstration of the Runge Gross theorem

1) $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

$$i\frac{\partial \mathbf{j}(\mathbf{r},t)}{\partial t} = \langle \Psi(t)|[\mathbf{j}(\mathbf{r}), H(t)]|\Psi(t)\rangle$$

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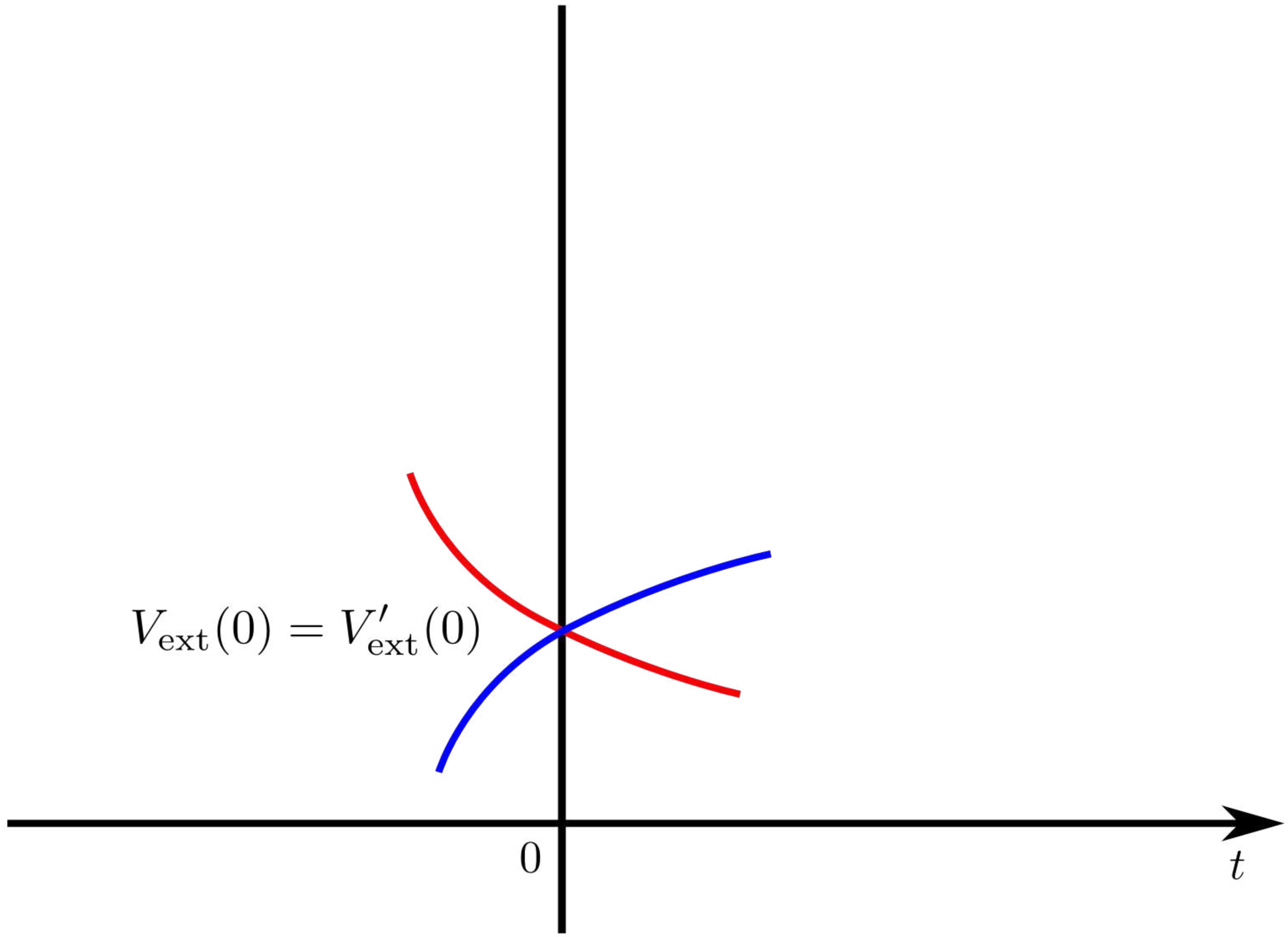
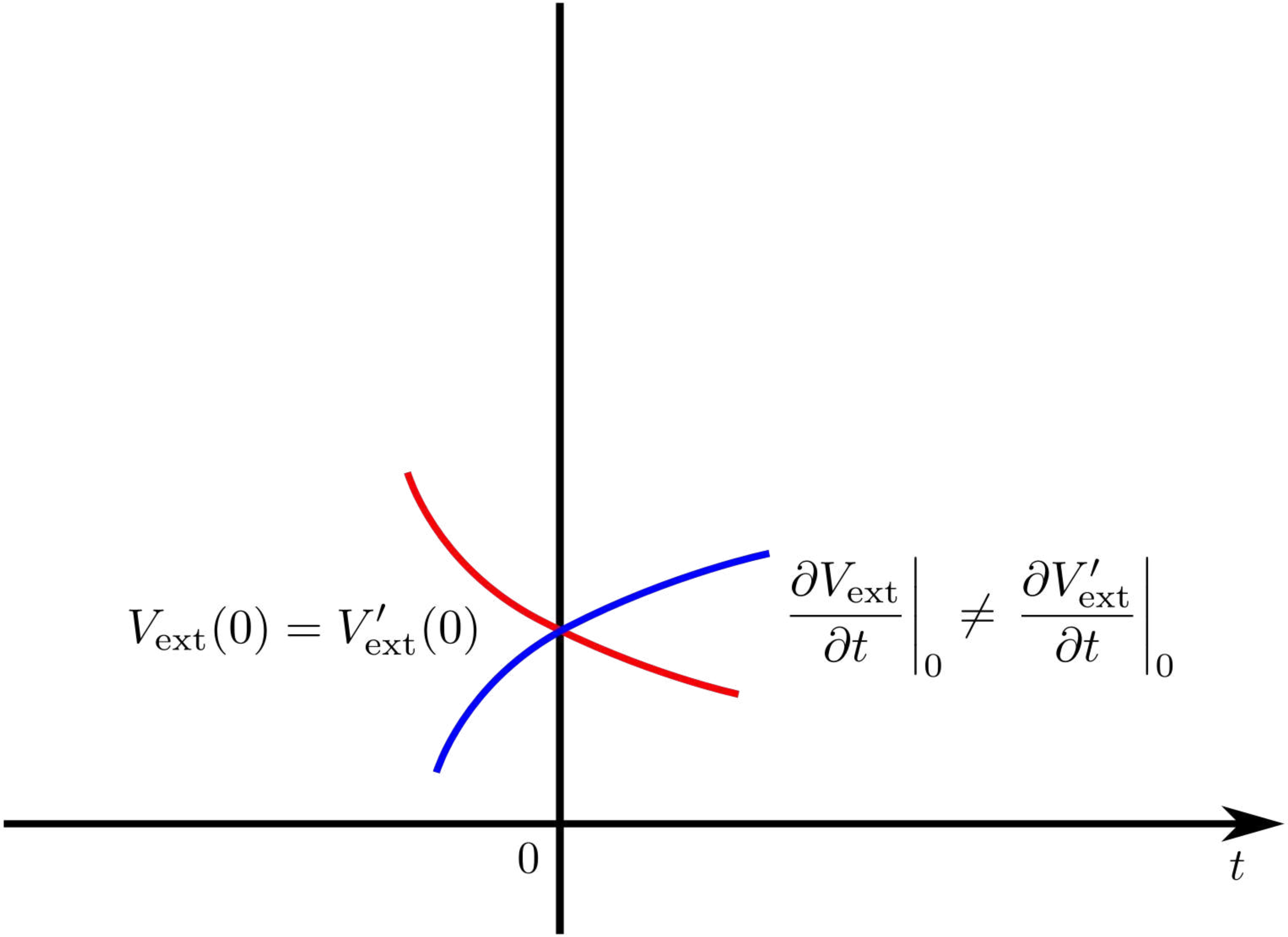
$$= -i\, n_0(\mathbf{r})\nabla\left[V_{\text{ext}}(\mathbf{r},0) - V'_{\text{ext}}(\mathbf{r},0)\right]$$

if two potentials differ by more than a constant at t=0, they will generate two different current densities

Taylor expandable (in t)



$V_{\text{ext}}(0) = V'_{\text{ext}}(0)$
0
t



$V_{\rm ext}(0) = V'_{\rm ext}(0)$
$\left.\frac{\partial V_{\rm ext}}{\partial t}\right|_0 \neq \left.\frac{\partial V'_{\rm ext}}{\partial t}\right|_0$
0
t

$$i\frac{\partial \left\langle \left|\left[\mathbf{j}(\mathbf{r}), H(t)\right]\right|\right\rangle}{\partial t} = \left\langle \Psi(t) \right| \left[\left[\mathbf{j}(\mathbf{r}), H(t)\right], H \right] \left| \Psi(t) \right\rangle$$

$$i\frac{\partial \langle|[\mathbf{j}(\mathbf{r}), H(t)]|\rangle}{\partial t} = \langle\Psi(t)|\Big[\,[\mathbf{j}(\mathbf{r}), H(t)]\,, H\Big]|\Psi(t)\rangle$$

$$i\frac{\partial \langle|[\mathbf{j}'(\mathbf{r}), H'(t)]|\rangle}{\partial t} = \langle\Psi(t)|\Big[\,[\mathbf{j}'(\mathbf{r}), H'(t)]\,, H'(t)\Big]|\Psi(t)\rangle$$

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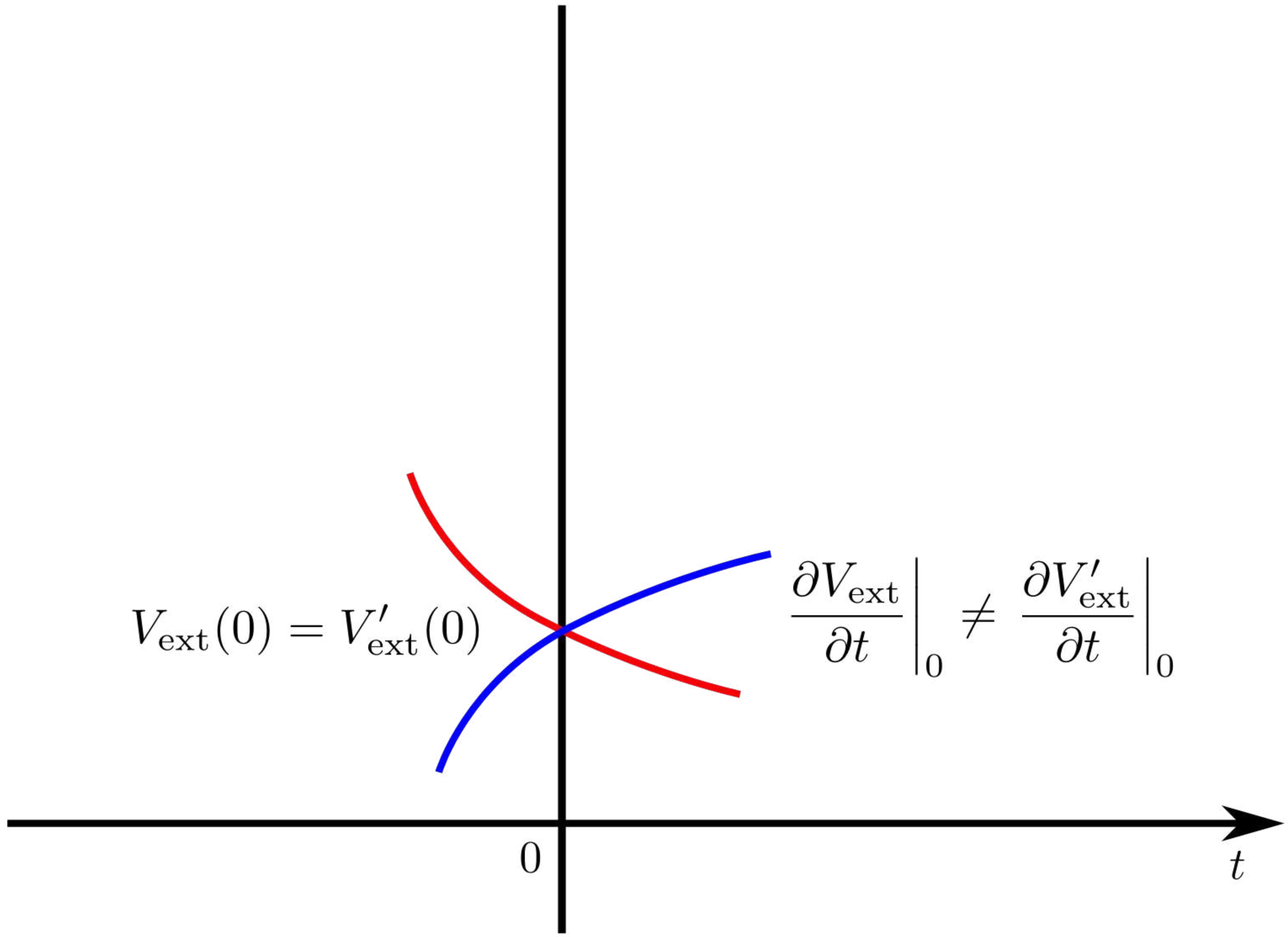
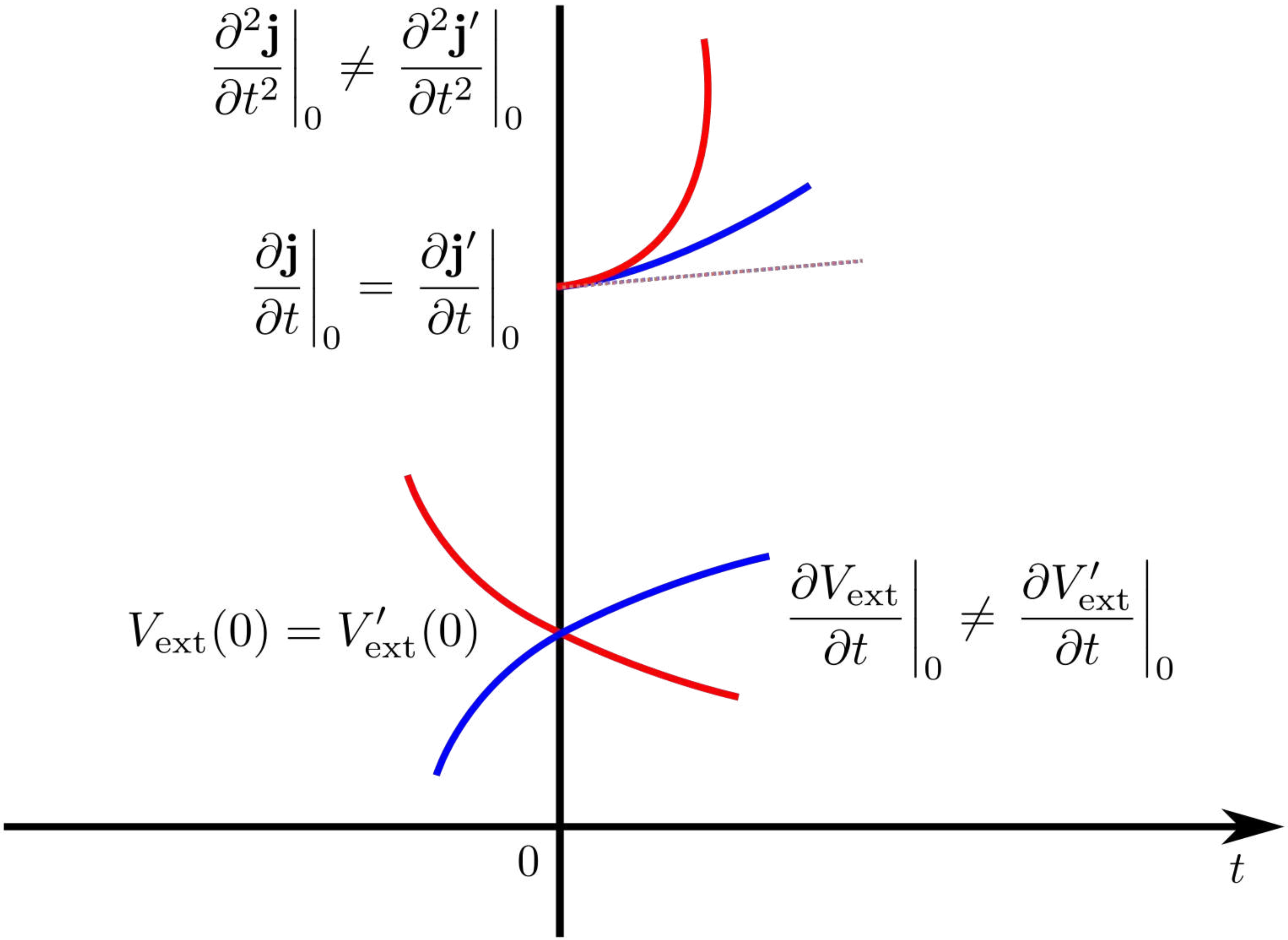


$V_{\text{ext}}(0) = V'_{\text{ext}}(0)$
$\left.\frac{\partial V_{\text{ext}}}{\partial t}\right|_0 \neq \left.\frac{\partial V'_{\text{ext}}}{\partial t}\right|_0$
0
t



$\left.\frac{\partial^2 \mathbf{j}}{\partial t^2}\right|_0 \neq \left.\frac{\partial^2 \mathbf{j}'}{\partial t^2}\right|_0$
$\left.\frac{\partial \mathbf{j}}{\partial t}\right|_0 = \left.\frac{\partial \mathbf{j}'}{\partial t}\right|_0$
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t

$$i\frac{\partial\left\langle\left|[\mathbf{j}(\mathbf{r}),H(t)]\right|\right\rangle}{\partial t} = \langle\Psi(t)|\Big[\,[\mathbf{j}(\mathbf{r}),H(t)]\,,H\Big]|\Psi(t)\rangle$$

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$$\vdots$$

$$\frac{\partial^{k+1}}{\partial t^{k+1}}\left[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=t_0} = -n_0(\mathbf{r})\nabla\,\frac{\partial^k}{\partial t^k}\left[V_{\mathrm{ext}}(\mathbf{r},t)-V'_{\mathrm{ext}}(\mathbf{r},t)\right]\Big|_{t=0}$$

two different potentials will generate two different current densities

$$i\frac{\partial \langle|[\mathbf{j}(\mathbf{r}), H(t)]|\rangle}{\partial t} = \langle\Psi(t)|\big[\,[\mathbf{j}(\mathbf{r}), H(t)]\,, H\big]|\Psi(t)\rangle$$

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v_{ext}

Taylor expandable

$$\frac{\partial^2}{\partial t^2}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=t_0} = -n_0(\mathbf{r})\nabla\,\frac{\partial}{\partial t}\left[V_{\text{ext}}(\mathbf{r},t) - V'_{\text{ext}}(\mathbf{r},t)\right]\Big|_{t=0}$$

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two different potentials will generate two different current densities

Runge-Gross theorem

$$V_{\text{ext}}(t) \longleftrightarrow n(t)$$

Demonstration

✓ $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \longleftrightarrow \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \longleftrightarrow n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

Demonstration of the Runge Gross theorem

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

Demonstration of the Runge Gross theorem

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$$\frac{\partial n(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r},t)$$

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$$i\frac{\partial}{\partial t}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=0} = \langle \Psi_0 | [\mathbf{j}(\mathbf{r}), H(0) - H'(0)] | \Psi_0 \rangle$$

$$= n_0(\mathbf{r}) \nabla \left[v_{\text{ext}}(\mathbf{r},0) - v'_{\text{ext}}(\mathbf{r},0)\right]$$

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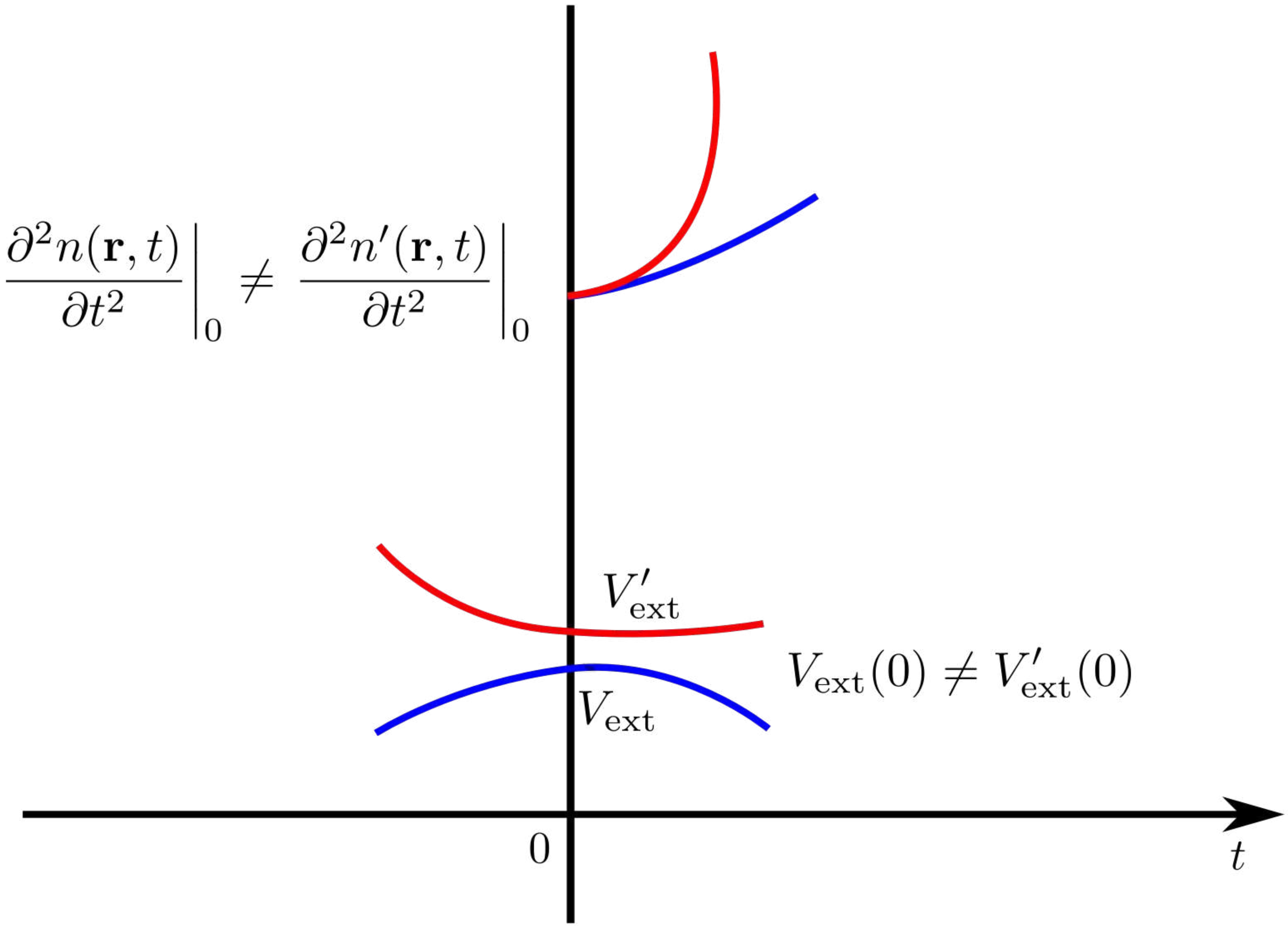
$$= \nabla \cdot \Big[n_0(\mathbf{r}) \nabla \left[v_{\rm ext}(\mathbf{r},0) - v'_{\rm ext}(\mathbf{r},0)\right] \Big]$$


$\left.\frac{\partial^2 n(\mathbf{r},t)}{\partial t^2}\right|_0 \neq \left.\frac{\partial^2 n'(\mathbf{r},t)}{\partial t^2}\right|_0$
V'_{ext}
$V_{\text{ext}}(0) \neq V'_{\text{ext}}(0)$
V_{ext}
0
t

Demonstration of the Runge Gross theorem

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$i\frac{\partial^{k+2}}{\partial t^{k+2}}\left[n(\mathbf{r},t) - n'(\mathbf{r},t)\right]\Big|_{t=0} = \nabla \cdot \left[n_0(\mathbf{r})\nabla\, \frac{\partial^k}{\partial t^k}\left[V_{\text{ext}}(\mathbf{r},t) - V_{\text{ext}}(\mathbf{r},t)\right]\Big|_{t=0}\right.$$

two different potentials will generate two different densities

Demonstration of the Runge Gross theorem

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two different potentials will generate two different densities

provided that the divergence does not vanish

Runge-Gross Theorem

$$V_{\text{ext}}(t) \quad \longleftrightarrow \quad n(t)$$

$$\langle \Psi(t) | O(t) | \Psi(t) \rangle = O[n, \Psi^0](t)$$

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

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- Functional of the TD density $n(\mathbf{r}, t)$ **and** of the initial state Ψ^0

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- Functional of the TD density $n(\mathbf{r},t)$ **and** of the initial state Ψ^0
- V_{ext} Taylor expandable
- $\nabla \cdot \left[n_0(\mathbf{r})\nabla V_k\right] \neq 0$ non-vanishing divergence

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

Name of the game

TDDFT

Runge-Gross theorem

$$V_{\rm ext}(t) \quad \longleftrightarrow \quad n(t)$$

$$\langle\Psi(t)|O(t)|\Psi(t)\rangle = O[n,\Psi^0](t)$$

is it true?

✓ Demonstration

but in practice?

KS equations

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

$$V_{\mathrm{ext}}(\mathbf{r}, t) \quad \longleftrightarrow \quad n(\mathbf{r}, t) \qquad \text{given} \;\; \Psi^0(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t = 0)$$

$$V_{\mathrm{ext}}(\mathbf{r}, t) \quad \longleftrightarrow \quad n(\mathbf{r}, t) \qquad \text{given} \;\; \Psi^0(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t = 0)$$

$$V_{ee} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$V_{\text{ext}}(\mathbf{r}, t) \quad \longleftrightarrow \quad n(\mathbf{r}, t) \qquad \text{given} \;\; \Psi^0(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t = 0)$$

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$$V_{\text{KS}}([n,\Phi^0],\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \;\; \text{given} \;\; \Phi^0(\{\mathbf{r}_i\},t=0) = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & .. & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & .. & \psi_2(\mathbf{r}_N) \\ .. & .. & .. & .. \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & .. & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

$$n(\mathbf{r},t) = \sum_{\text{occ}} |\psi_i(\mathbf{r},t)|^2$$

$$V_{\rm ext}(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \qquad \text{given} \;\; \Psi^0(\mathbf{r}_1,\mathbf{r}_2,..,\mathbf{r}_N,t=0)$$

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$$V_{\rm KS}[n,\Phi^0](\mathbf{r},t) = V_{\rm ext}[n,\Psi^0](\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\rm xc}[n,\Psi^0,\Phi^0](\mathbf{r},t)$$

Kohn-Sham potential

$$V_{\text{ext}}(\mathbf{r},t) \longleftrightarrow n(\mathbf{r},t) \qquad \text{given} \;\; \Psi^0(\mathbf{r}_1,\mathbf{r}_2,..,\mathbf{r}_N,t=0)$$

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Kohn-Sham potential

$$\left[-\frac{\nabla^2}{2}+V_{\text{KS}}[n,\Phi^0](\mathbf{r},t)\right]\psi_i(\mathbf{r},t)=i\frac{\partial\psi_i(\mathbf{r},t)}{\partial t}$$

Kohn-Sham equations

Kohn-Sham Equations

$$\left[-\frac{\nabla^2}{2} + v_{\rm KS}[n;\Phi^0](\mathbf{r},t)\right]\psi_i(\mathbf{r},t) = i\frac{\partial\psi_i(\mathbf{r},t)}{\partial t}$$

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- No self-consistency
- No variational principle

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$$n(\mathbf{r},t) = \sum_{\mathrm{occ}} |\psi_i(\mathbf{r},t)|^2$$

- No self-consistency
- No variational principle
- $V_{\mathrm{xc}}[n,\Psi^0,\Phi^0](\mathbf{r},t)$

(local in space and time) functionally non-local

non-interacting v-representability

non-interacting v-representability

van Leeuwen theorem

conditions for the existence of $V_{\mathrm{xc}}[n, \Psi^0, \Phi^0](\mathbf{r}, t)$

R.van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999)

Name of the game

TDDFT

Runge-Gross theorem

$$V_{\rm ext}(t) \quad \longleftrightarrow \quad n(t)$$

$$\langle\Psi(t)|O(t)|\Psi(t)\rangle = O[n,\Psi^0](t)$$

is it true?

✓ Demonstration

but in practice?

✓ KS equations

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

1 approximate $V_{\mathrm{xc}}[n, \Psi^0, \Phi^0](\mathbf{r}, t)$

2 solve the TD Kohn-Sham equations

C look at some observables

Approximations

$$V_{\mathrm{xc}}[n(\mathbf{r}', t' < t), \Psi^0, \Phi^0](\mathbf{r}, t)$$

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Approximations

$$V_{\rm xc}[n(\mathbf{r}', t' < t), \Psi^0, \Phi^0](\mathbf{r}, t)$$

Live in the present
or *no grudge*
approximation

Approximations

- Adiabatic $V_{\mathrm{xc}}^{A}[n(\mathbf{r}',t)](\mathbf{r},t)$

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- Adiabatic $V_{\text{xc}}^{A}[n(\mathbf{r}',t)](\mathbf{r},t)$
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  - AGGA
  - Orbital dependent
- non-adiabatic (few examples like Vignale Kohn)

✓ approximate $V_{\mathrm{xc}}[n, \Psi^0, \Phi^0](\mathbf{r}, t)$

2 solve the TD Kohn-Sham equations

C look at some observables

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}[n](\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad \Rightarrow \quad n(\mathbf{r})$$

KS equations

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TD KS equations

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KS equations

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TD KS equations

Time evolution operator

$$i\frac{\partial\psi(t)}{\partial t} = H(t)\psi(t) \quad \longrightarrow \quad \psi(t) = U(t, t_0)\psi(t_0)$$

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Time evolution operator

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$$i\frac{d\,U(t,t_0)}{dt} = H(t)U(t,t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1)U(\tau_1,t_0)$$

Time evolution operator

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Time evolution operator

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$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + (-i)^2\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_1)H(\tau_2) +$$

$$(-i)^3\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \int_{t_0}^{\tau_2} d\tau_3 H(\tau_1)H(\tau_2)H(\tau_3) + \cdots$$

Time evolution operator

$$i\frac{\partial\psi(t)}{\partial t} = H(t)\psi(t) \longrightarrow \psi(t) = U(t,t_0)\psi(t_0)$$

$$i\frac{dU(t,t_0)}{dt} = H(t)U(t,t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1)U(\tau_1,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + (-i)^2\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_2)U(\tau_2,t_0)$$

$$U(t,t_0) = 1 + \sum_{n=1}^{\infty}(-i)^n \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \cdot\cdot \int_{t_0}^{\tau_{n-1}} d\tau_n H(\tau_1)H(\tau_2)\cdot\cdot H(\tau_n)$$

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$$U(t,t_0) = 1 + \sum_{n=1}^{\infty}\frac{(-i)^n}{n!}\int_{t_0}^{t} d\tau_1 \int_{t_0}^{t} d\tau_2 \cdot\cdot \int_{t_0}^{t} d\tau_n \mathcal{T}\left[H(\tau_1)H(\tau_2)\cdot\cdot H(\tau_n)\right]$$

Time evolution operator

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$$U(t,t_0) = 1 + \sum_{n=1}^{\infty}\frac{(-i)^n}{n!}\int_{t_0}^{t} d\tau_1\int_{t_0}^{t} d\tau_2\cdots\int_{t_0}^{t} d\tau_n\mathcal{T}\left[H(\tau_1)H(\tau_2)\cdots H(\tau_n)\right]$$

$$U(t,t_0) = \mathcal{T}e^{-i\int_{t_0}^{t} d\tau H(\tau)}$$

Time evolution operator

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time integrators problem

second-order differencing
Crank-Nicholson implicit midpoint
predictor-corrector
splitting techniques
Magnus expansion
exponential midpoint

exponential operator

Taylor expansion

Chebychev polynomials

Lanczos iterative scheme

Castro *et al.* Lect. Notes Phys. **706**, 197 (2004)

✓ approximate $V_{\mathrm{xc}}[n, \Psi^0, \Phi^0](\mathbf{r}, t)$

✓ solve the TD Kohn-Sham equations

C look at some observables

C look at some observables

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}[n, \Phi^0](\mathbf{r}, t)\right] \psi_i(\mathbf{r}, t) = i\frac{\partial \psi_i(\mathbf{r}, t)}{\partial t}$$

$$\boldsymbol{n(\mathbf{r}, t)} = \sum_{\mathrm{occ}} |\boldsymbol{\psi_i(\mathbf{r}, t)}|^2$$

Time resolved
X-ray Crystallography
of a protein

Schotte *et al.* Science **300**, 1944(2003)

$$n(\mathbf{r}, t)$$

$$\int d\mathbf{r}\; n(\mathbf{r}, t) = N_{\text{electrons}}$$

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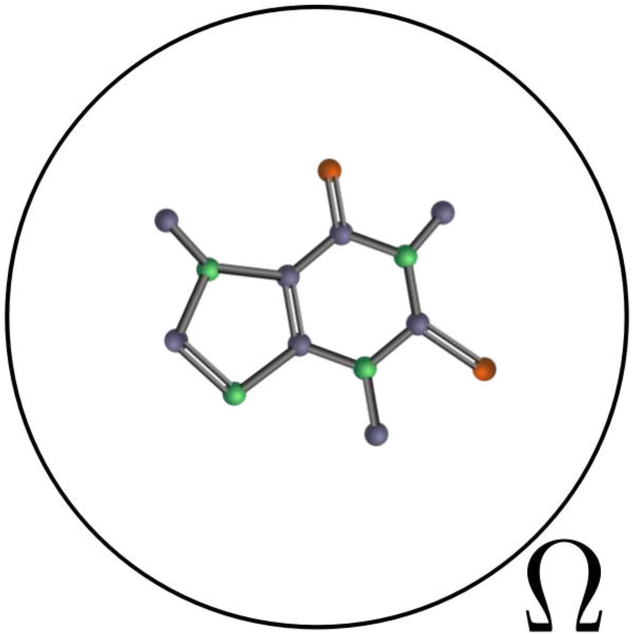

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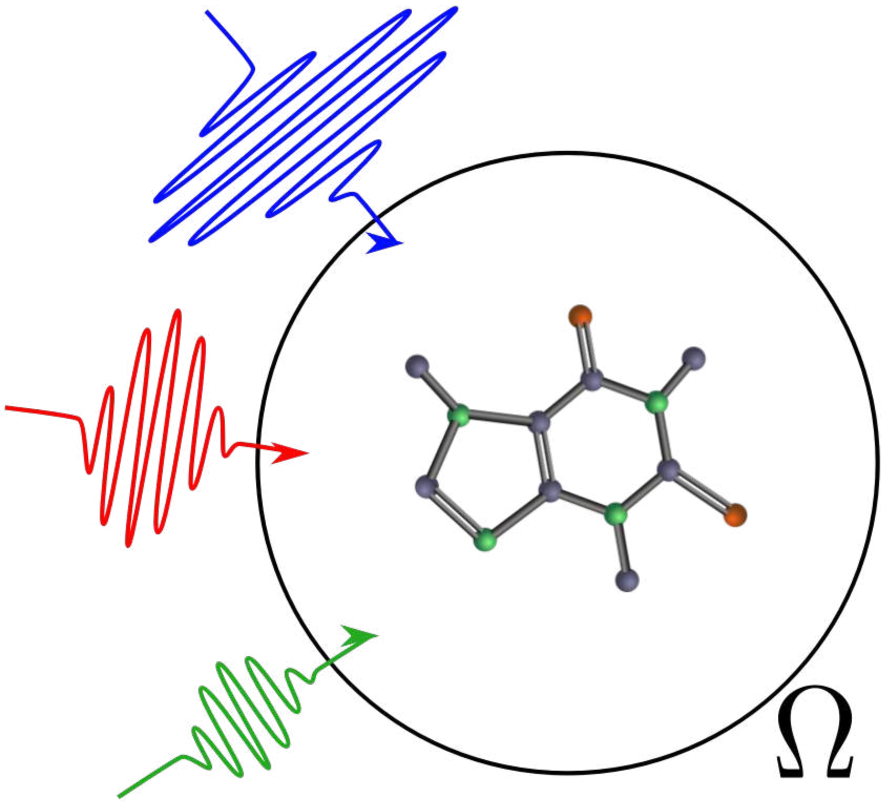

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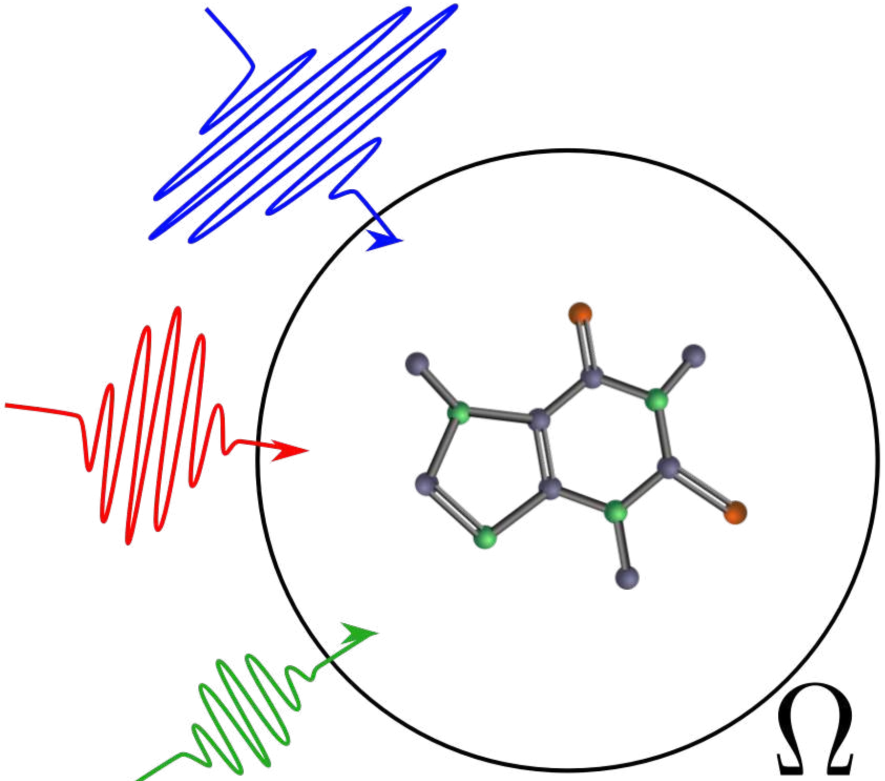

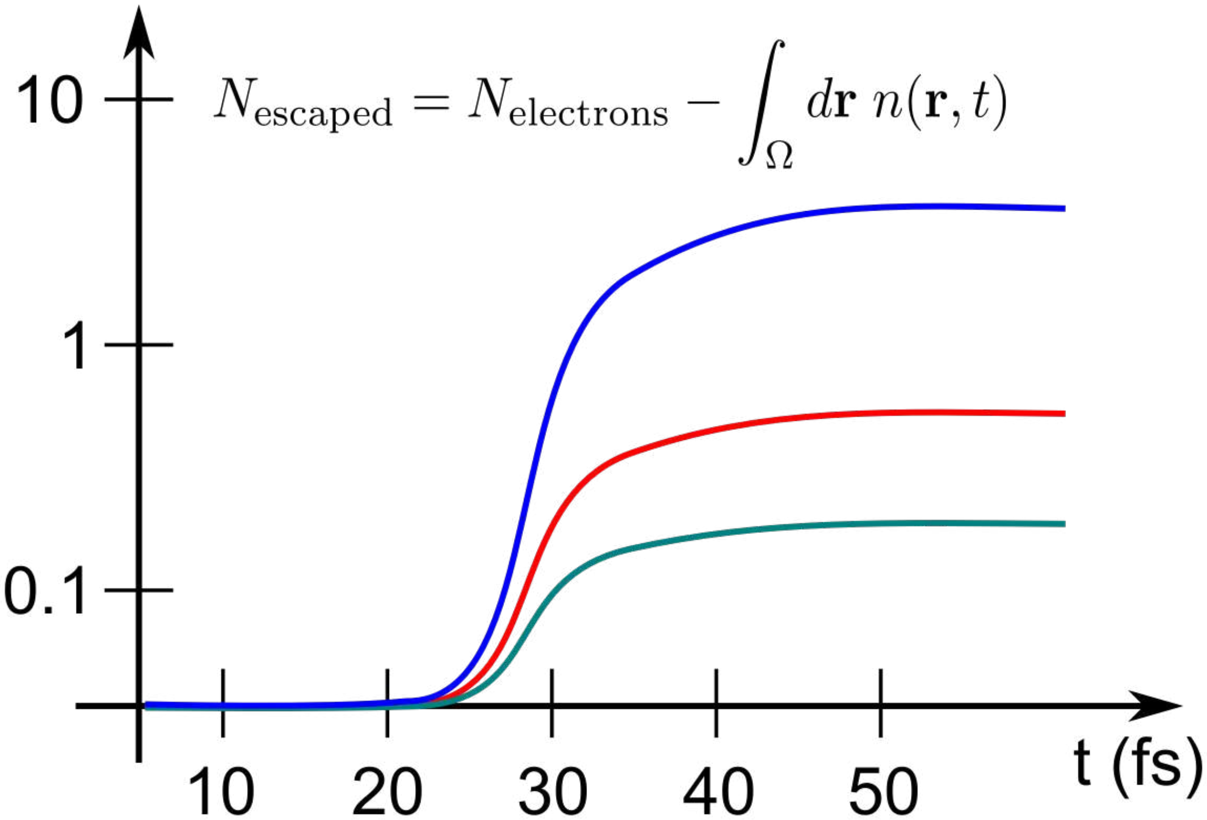

C.Ullrich *et al.*, J. Phys. B: At. Mol. Opt. Phys. **30**, 5043 (1997)

Time Dependent ELF

$$ELF(\mathbf{r},t) = \left[1 + D^0 \left(\sum_i |\nabla \psi_i(\mathbf{r},t)| - \frac{1}{4}\frac{[\nabla n(\mathbf{r},t)]^2}{n(\mathbf{r},t)} - \frac{1}{2}\frac{j^2(\mathbf{r},t)}{n(\mathbf{r},t)} \right)^2 \right]^{-1}$$

T. Burnus, M. A. L. Marques, and E. K. U. Gross, Phys. Rev. A **71**, 010501(R) (2005)

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T. Burnus, M. A. L. Marques, and E. K. U. Gross, Phys. Rev. A **71**, 010501(R) (2005)

One-particle operator

$$\langle \Psi(t)|\hat{O}|\Psi(t)\rangle = \int O(\mathbf{r})\, n(\mathbf{r},t) d\mathbf{r}$$

Some observables

$$\alpha(t) = \int \mathbf{r}\, n(\mathbf{r},t) d\mathbf{r}$$

$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

Some observables

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Photo-absorption cross section

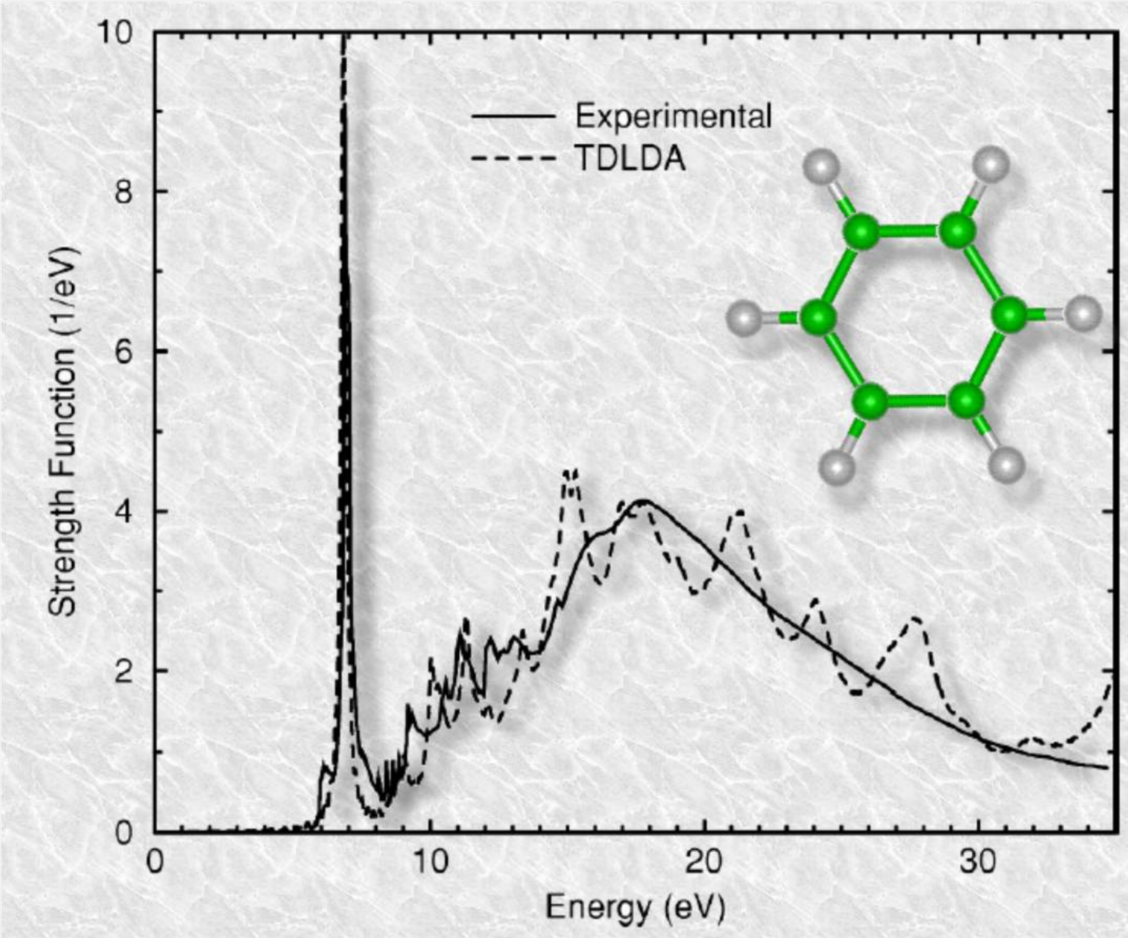
$$M_{lm}(t) = \int r^l\, Y_{lm}(r)\, n(\mathbf{r},t)\, d\mathbf{r}$$

Multipoles

$$L_z(t) = \sum_i \int \psi_i(\mathbf{r},t) i(\mathbf{r}\times\nabla)_z \psi_i(\mathbf{r},t)\, d\mathbf{r}$$

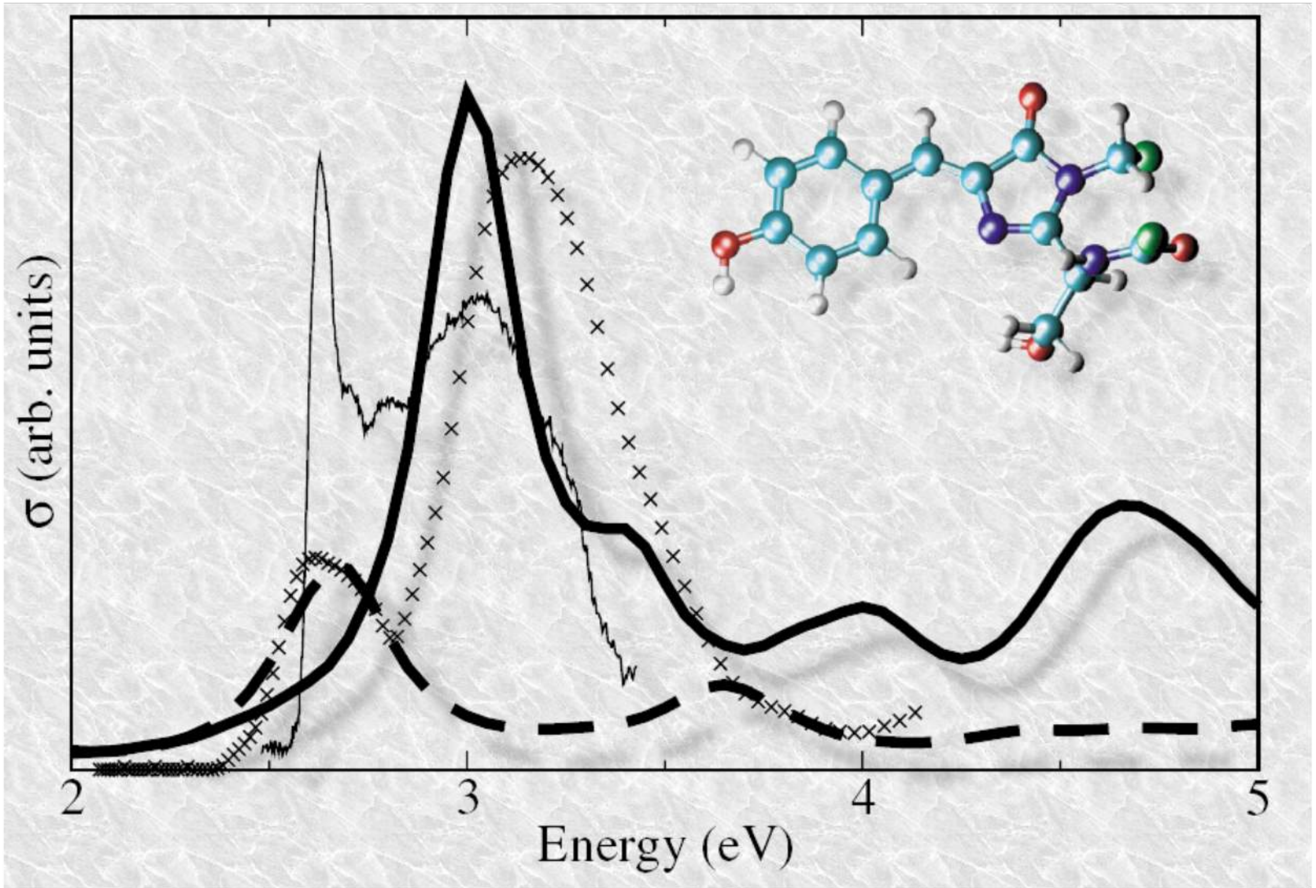
Angular Momentum

Benzene



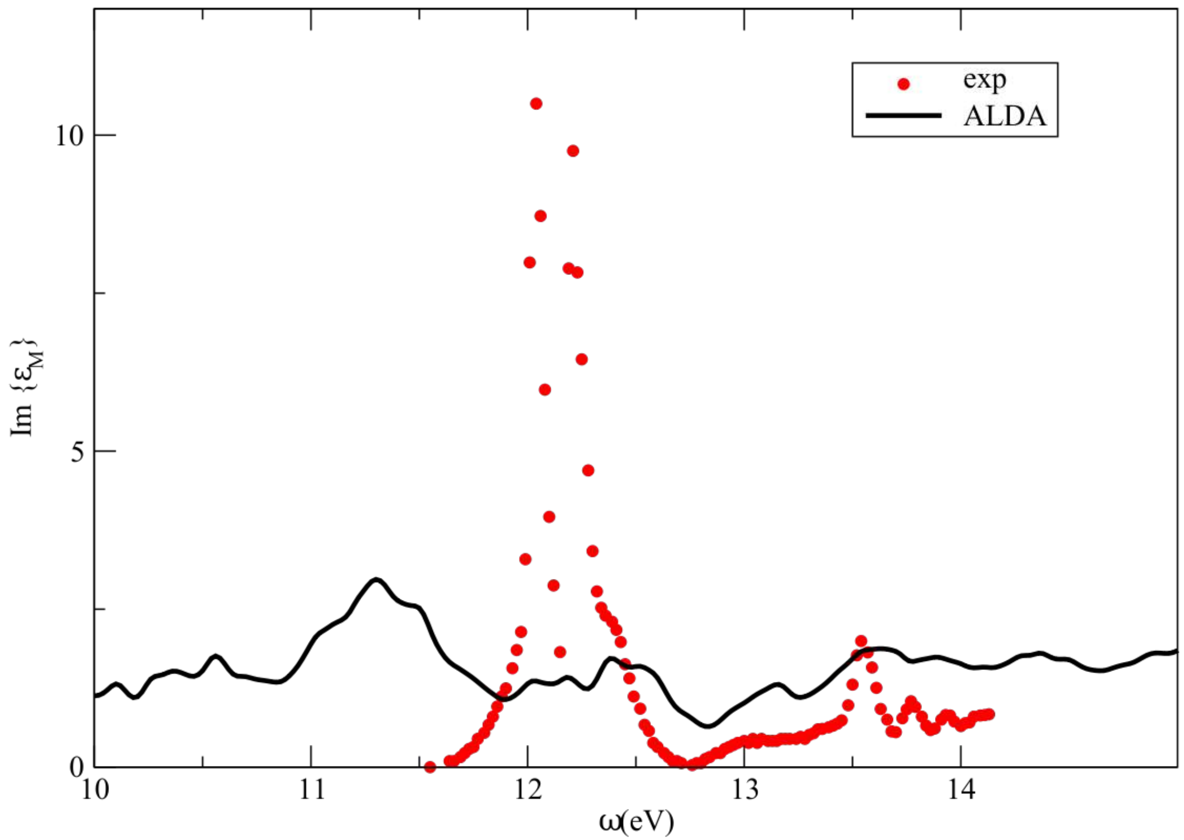
Yabana and Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

GFP



 M.Marques *et al.* Phys.Rev.Lett. **90**, 258101 (2003)

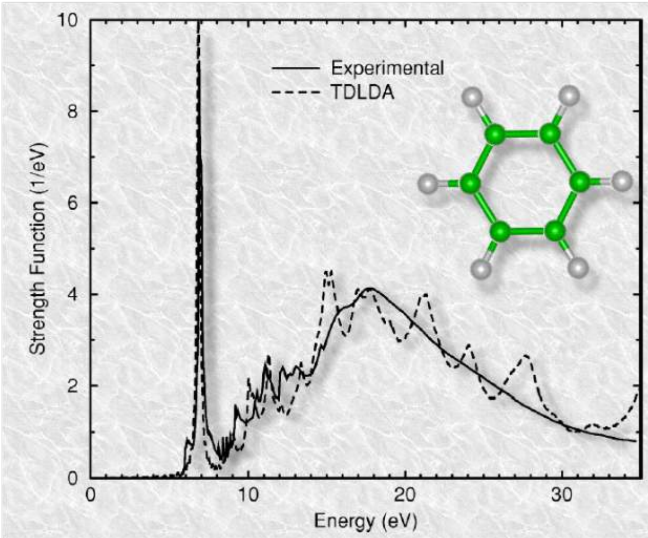
Solid Argon



Marsili *et al.* Phys. Rev. B **76**, 161101(R) (2007)

Photo-absorption cross section

Benzene



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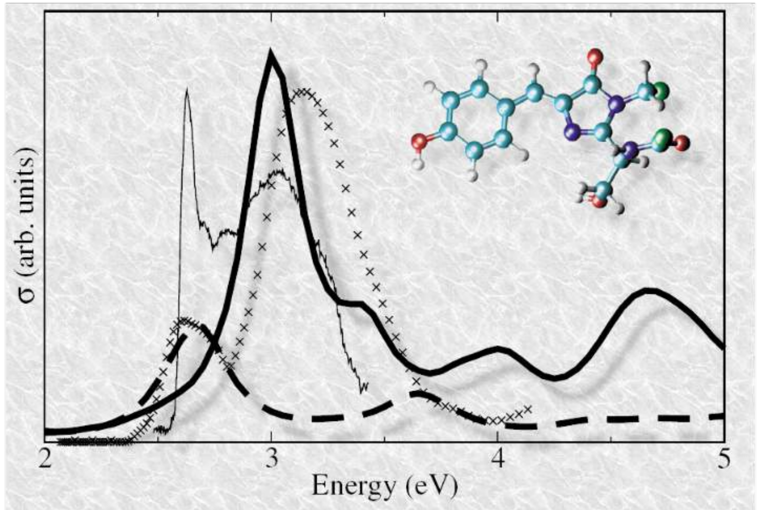

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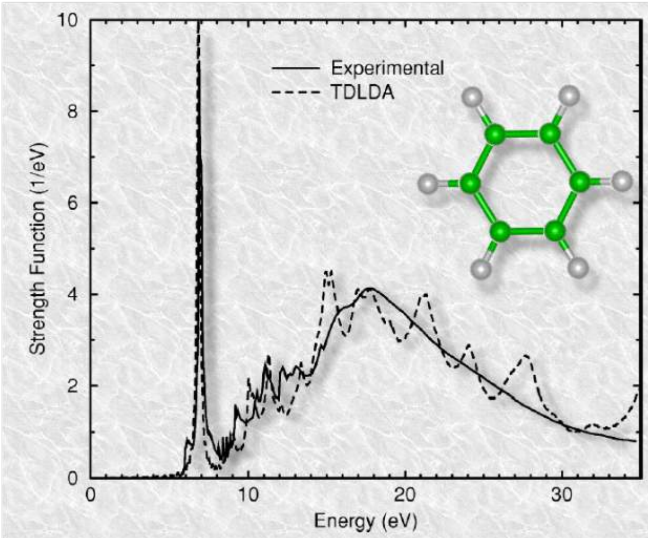
$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

Benzene



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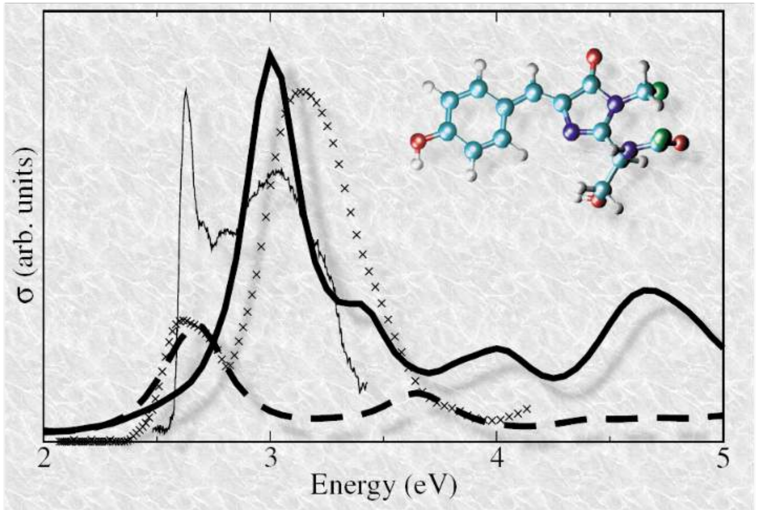

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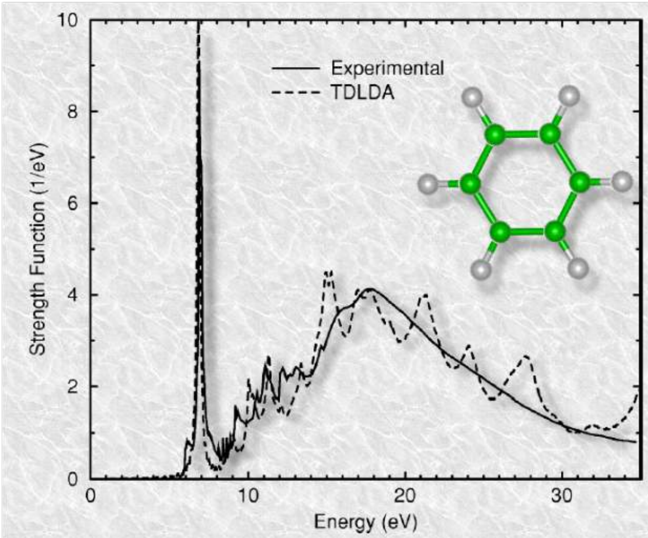

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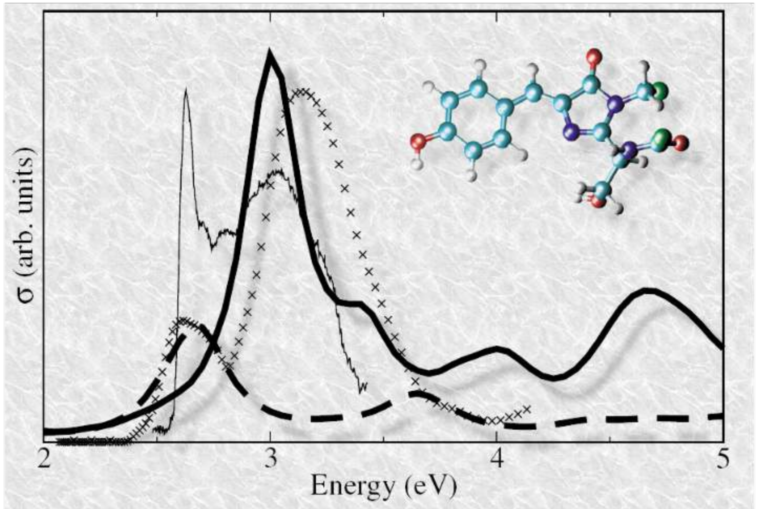

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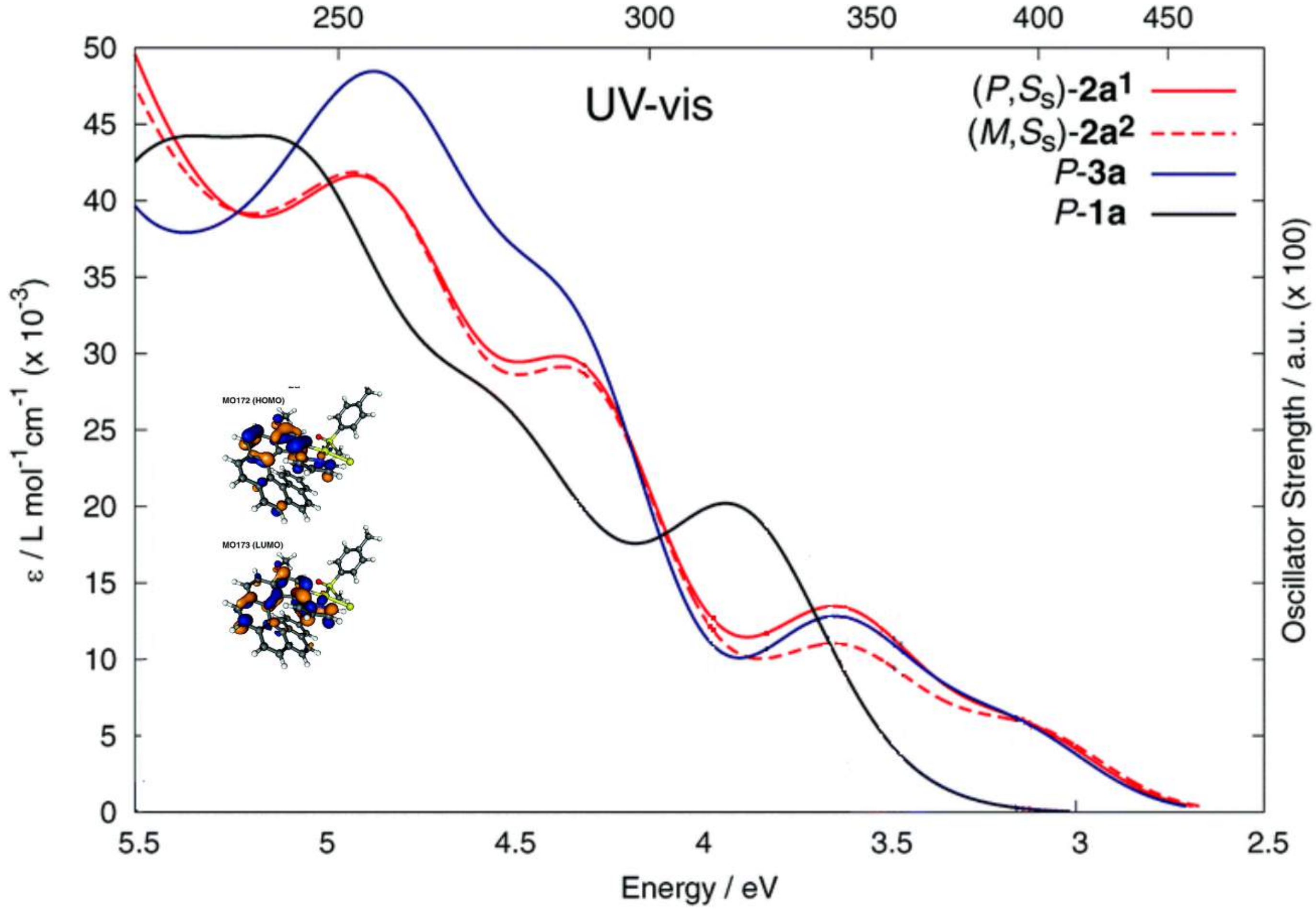
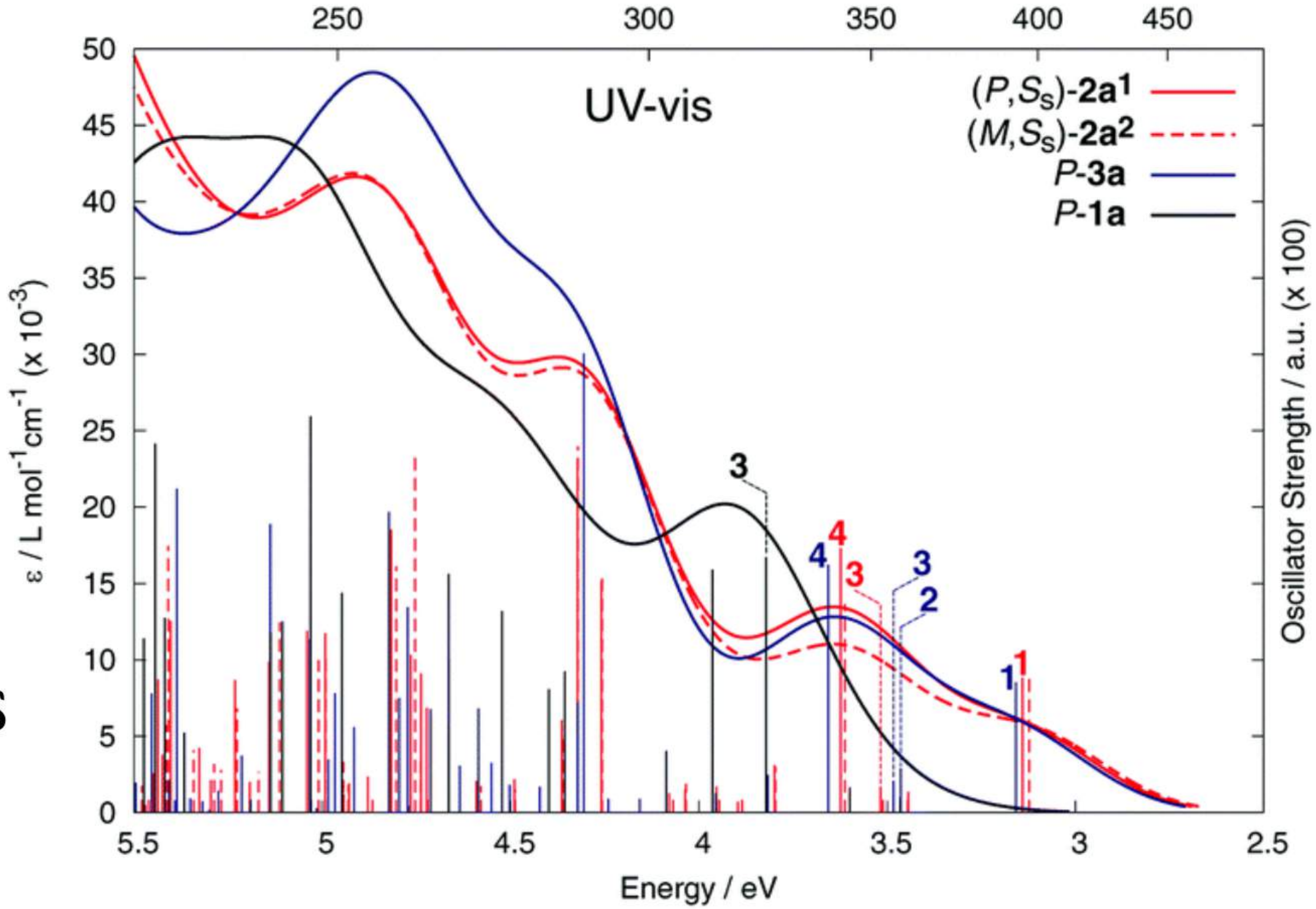
$$V_{\mathrm{ext}}(\mathbf{r},t) = V_{\mathrm{ext}}^{nucl}(\mathbf{r}) + \delta(t)\eta$$

Absorption of cycloplatinated helicenes



Shen *et al.* Chem. Sci. **5**, 1915 (2014)

Absorption of cycloplatinated helicenes



excitations
energies

Shen *et al.* Chem. Sci. **5**, 1915 (2014) can we exploit perturbation theory ? $\delta V_{\mathrm{ext}} \to 0$

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how to access excitation energies ?

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what about other spectroscopies ?

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