Linear-response and real-time TDDFT for excitons in solids

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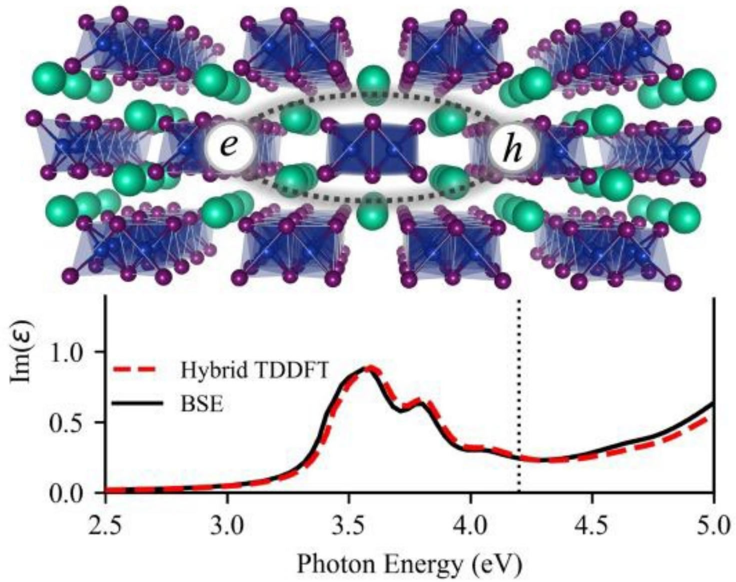
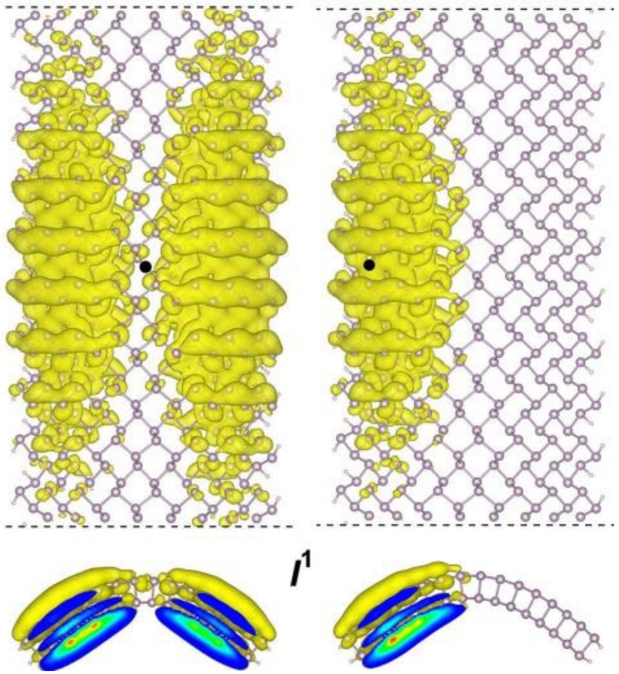
University of Missouri



HoW exciting! 2023
August 8, 2023



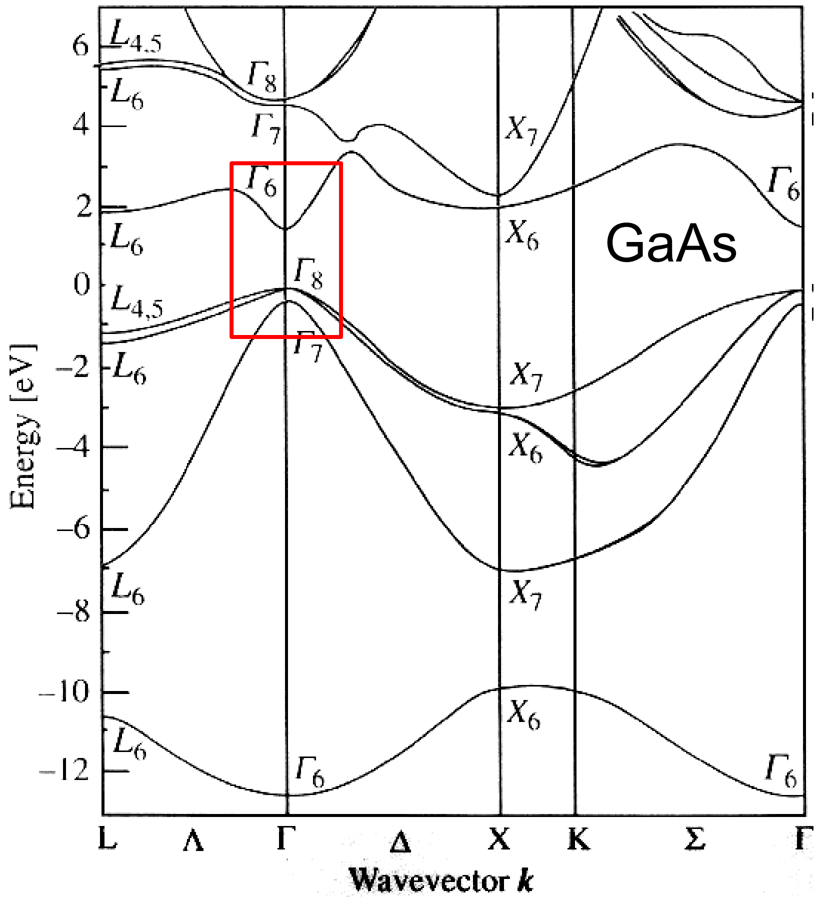
TDDFT for excitons in periodic solids:

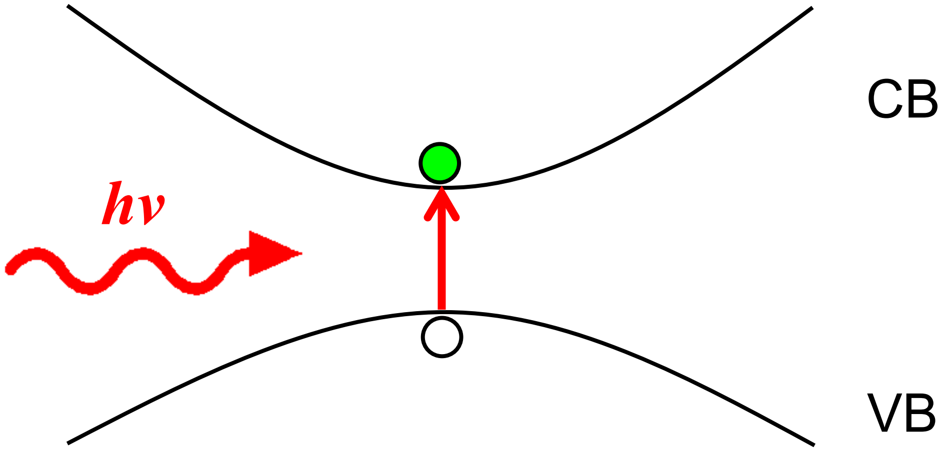
1. **Which exchange-correlation functional(s) can capture excitonic effects in LR and RT?**
   - *LRC functional, screened hybrid functional*

2. **How to visualize/characterize excitons?**
   - *time-dependent exciton wave function*

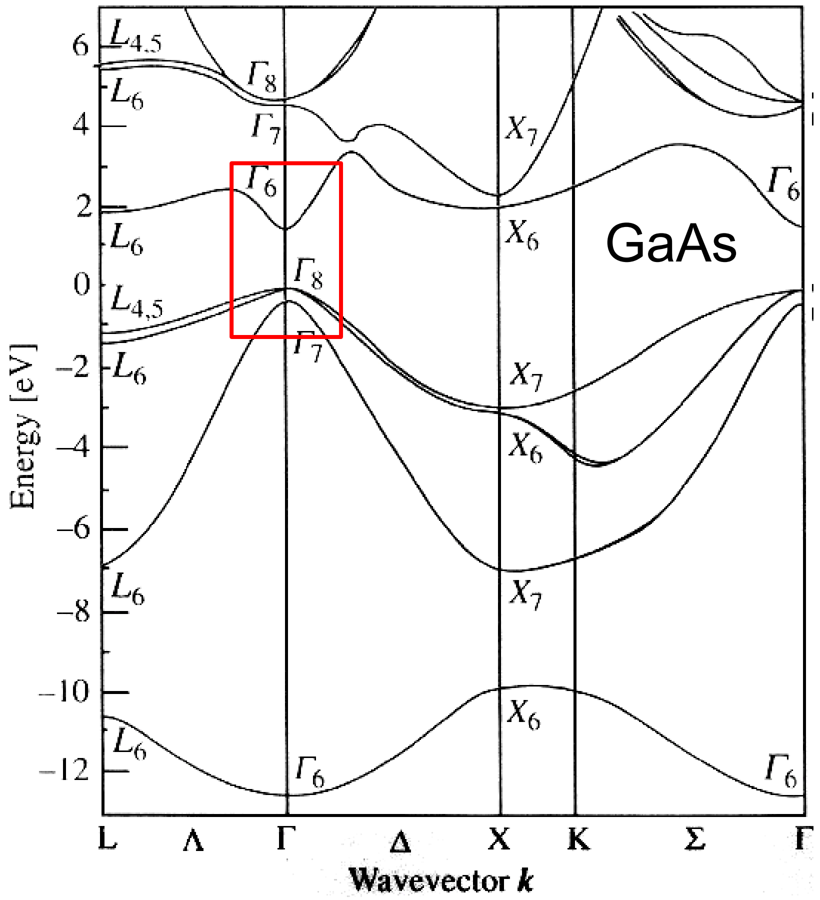
J. R. Williams, N. Tancogne-Dejean, and C. A. Ullrich, JCTC **17**, 1795 (2021)
J. Sun and C. A. Ullrich, Phys. Rev. Materials **4**, 095402 (2020)
J. Sun, J. Yang, and C.A. Ullrich, Phys. Rev. Research **2**, 013091 (2020)
J. Sun, C.-W. Lee, A. Kononov, A. Schleife, and C. A. Ullrich, PRL **127**, 077401 (2021)

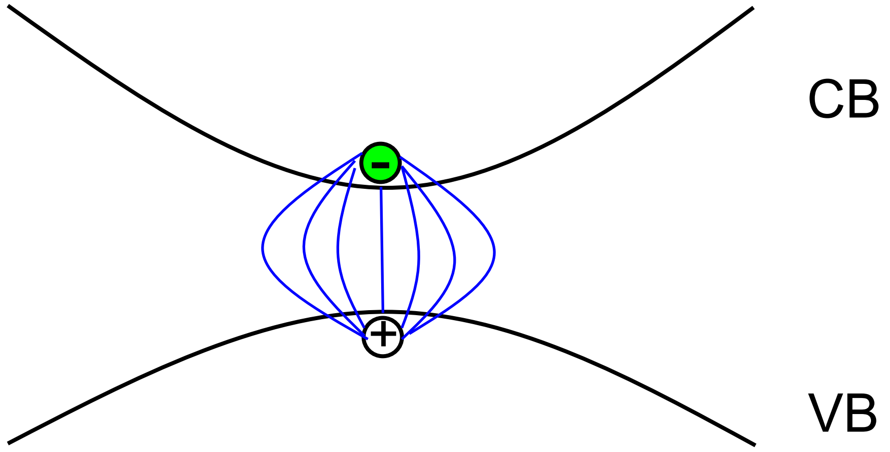
Absorption of light across the band gap





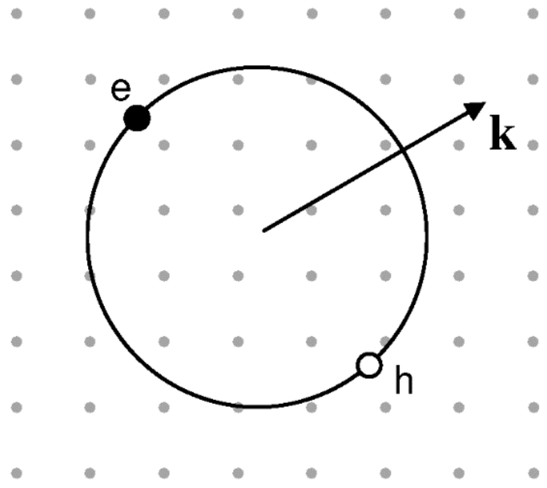
Absorption of light across the band gap





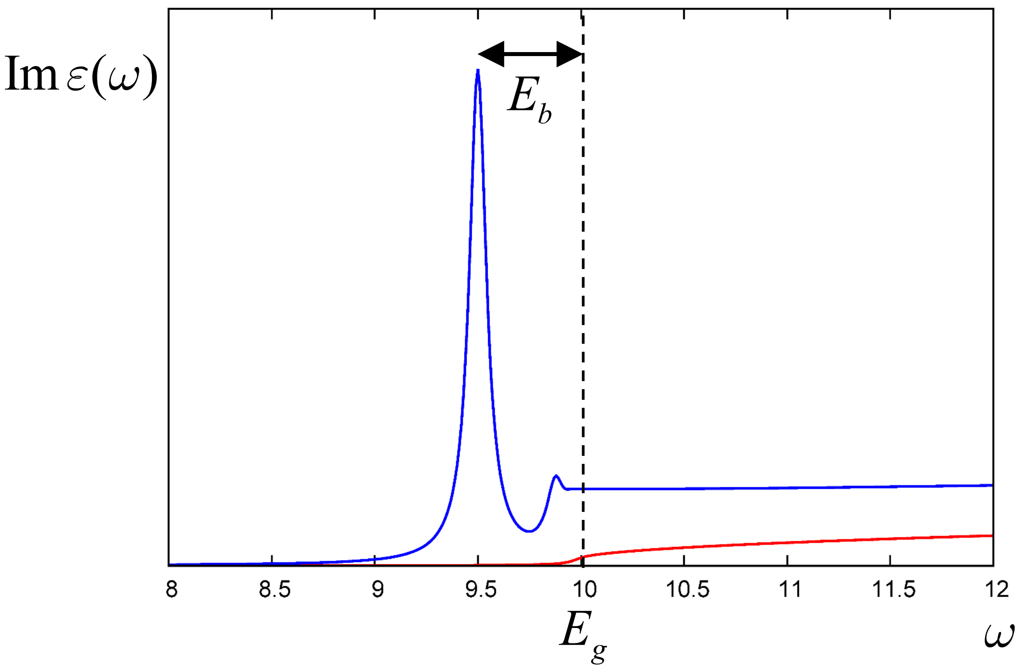
Excitons: bound e-h pairs

Excitons: the Wannier equation



$$\left[-\frac{\hbar^2\nabla^2}{2m_{eh}}-\frac{e^{*2}}{4\pi\varepsilon_0 r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$\frac{1}{m_{eh}}=\frac{1}{m_e^*}+\frac{1}{m_h^*}$$



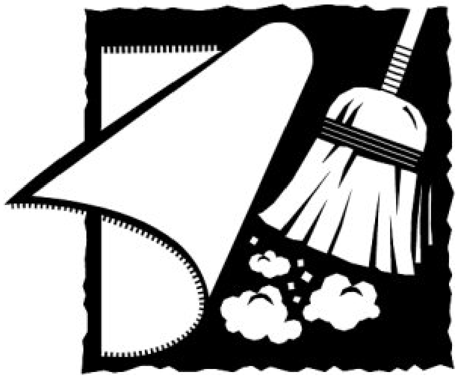
$$E_n^*=-\frac{m_{eh}}{2\hbar^2 n^2}\left(\frac{e^{*2}}{4\pi\varepsilon_0}\right)^2$$

Exciton binding energy for GaAs:

$$E_0^*=4.75\ meV$$

Experiment: $E_0^*=3.3\ meV$

Beyond the simple picture



So far so good…. but what did we sweep under the rug?

- ► Effective-mass approximation too simplistic: need details of the **electronic band structure**
- ► **Electron-electron interactions and screening from first principles**
- ► **Real-time dynamics: nonlinear effects?**

(► Phonons, EM propagation effects....)

Many-body perturbation theory vs TDDFT

Hybrid functionals

Quasiparticle-based:

electron addition+removal (GW)

e-h interaction+screening (BSE)

Density-based:

ground state KS: $V_{xc}(\mathbf{r})$

linear response: $f_{xc}(\mathbf{r},\mathbf{r}',\omega)$

Onida, Reining & Rubio, RMP **74**, 601 (2002)
S. Sharifzadeh, J. Phys. Condens. Matter **30**, 153002 (2018)

C. A. Ullrich and Z.-H. Yang, Topics in Current Chem. **368** (2015)

Linear-response (LR) TDDFT

$$\delta n(\mathbf{r},\omega) = \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',\omega)\delta V(\mathbf{r}',\omega)$$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi_s(\mathbf{r},\mathbf{r}',\omega) + \int d\mathbf{x} \int d\mathbf{x}' \chi_s(\mathbf{r},\mathbf{x},\omega) \left\{ \frac{1}{|\mathbf{x}-\mathbf{x}'|} + f_{xc}(\mathbf{x},\mathbf{x}',\omega) \right\} \chi(\mathbf{x}',\mathbf{r}',\omega)$$

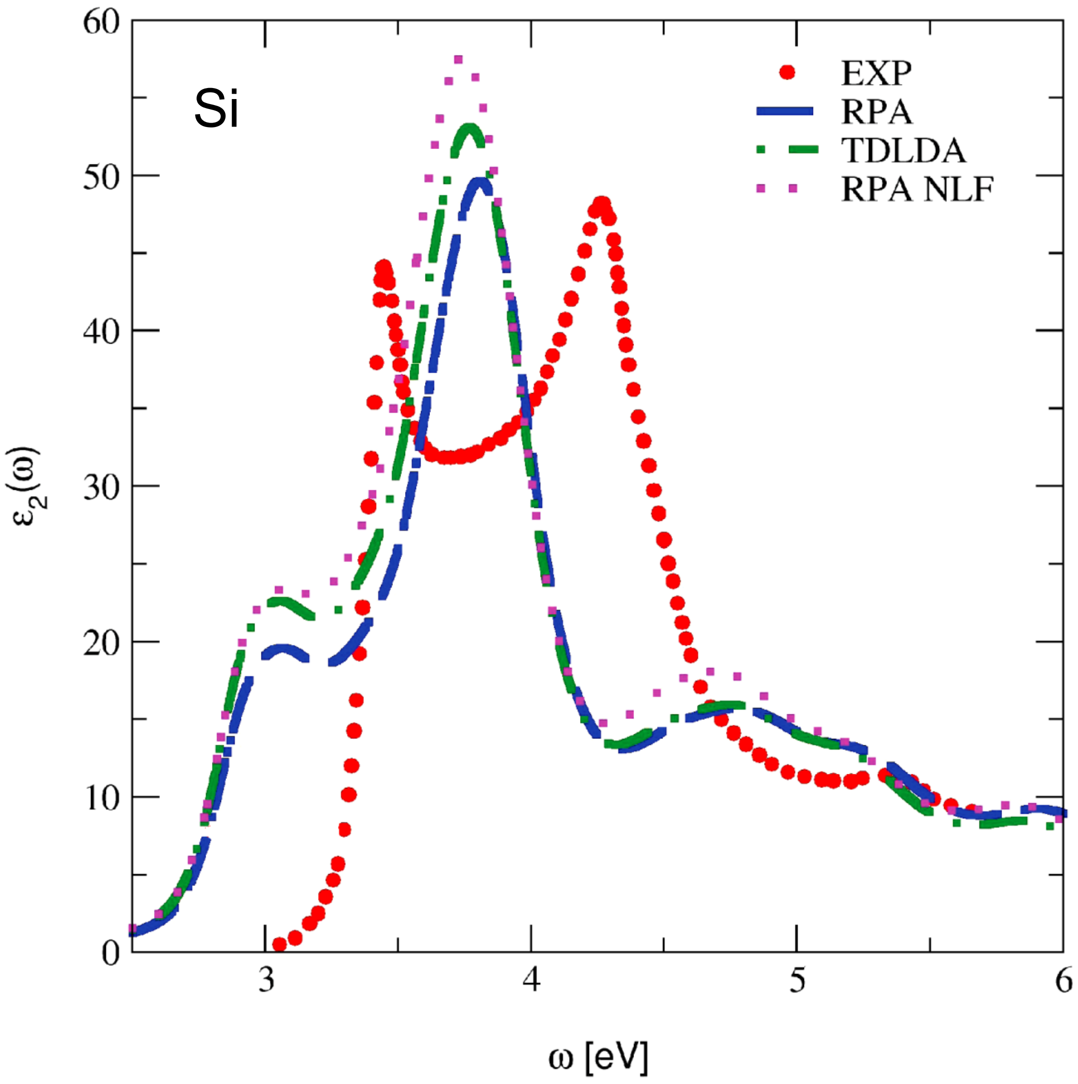
dielectric function in a periodic system:

$$\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}'} + \frac{4\pi}{|\mathbf{q}+\mathbf{G}|} \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$$

macroscopic dielectric function (determines optical absorption):

$$\varepsilon_{mac}(\omega) = 1 - \lim_{q\to 0} \frac{4\pi}{q^2} \bar{\chi}_{00}(\mathbf{q},\omega)$$

Failure of the LDA



Why does the LDA fail??

- ► **gap too small**
- ► **lacks long spatial range**
- ► **need new classes of xc functionals**

G. Onida, L. Reining, A. Rubio, RMP **74**, 601 (2002)
S. Botti, A. Schindlmayr, R. Del Sole, L. Reining, Rep. Prog. Phys. **70**, 357 (2007)

Which exchange-correlation functional to choose?

No excitons with standard functionals (LDA, GGA)!

Long-range corrected (LRC):

$$f_{xc}^{LRC}(\mathbf{r},\mathbf{r}') = -\frac{\alpha(n)}{4\pi|\mathbf{r}-\mathbf{r}'|}$$

- ►model parameters/empirical fitting
- ►Computationally simple, but less accurate
- ►Other functionals reduce to same basic type

Botti *et al.*, PRB **69**, 155112 (2004)
Sharma, Dewhurst, Sanna & Gross, PRL **107**, 186401 (2011)
Rigamonti et al., PRL **114**, 146402 (2015)
Trevisanutto *et al.*, PRB **87**, 205143 (2013)
Berger, PRL **115**, 137402 (2015)
Cavo, Berger & Romaniello, PRB **101**, 115109 (2020)
Byun, Sun & Ullrich, Electron. Struct. **2**, 023002 (2020)

Screened hybrid:

$$K_{xc}^{hybrid} = \gamma K_{x}^{XX} + (1-\gamma)K_{xc}^{ALDA}$$

- ►Generalized TDDFT (includes nonlocal exchange)
- ►Computationally more demanding
- ►More accurate (comparable to BSE)

Refaely-Abramson *et al.*, PRB **92**, 081204 (2015)
Wing *et al.*, PRMat **3**, 064603 (2019)
Tal, Liu, Kresse & Pasquarello, PRRes **2**, 032019 (2020)
Zivkovic, de Leeuw, Searle & Bernasconi, JPC C **124**, 24995 (2020)
Sun, Li & Liang, PCCP **21**, 16296 (2021)

Excitation spectra from TDDFT vs BSE

$$\left[(E_{c\mathbf{k}} - E_{v\mathbf{k}'})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{kk}'} + K_{cv\mathbf{k}',c'v'\mathbf{k}'}\right]\mathbf{Y}_n = \Omega_n \mathbf{Y}_n$$

TDDFT coupling matrix contains xc kernel: $f_{xc,\mathbf{GG}'}$

BSE coupling matrix contains screened Coulomb interaction:

$$W_{\mathbf{GG}'}(\mathbf{q}) = -4\pi \frac{\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega=0)}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}$$

Hybrid functional:

$$W_{\mathbf{GG}'}(\mathbf{q}) = -4\pi \frac{\gamma}{|\mathbf{q}+\mathbf{G}'|^2}\delta_{\mathbf{GG}'}$$

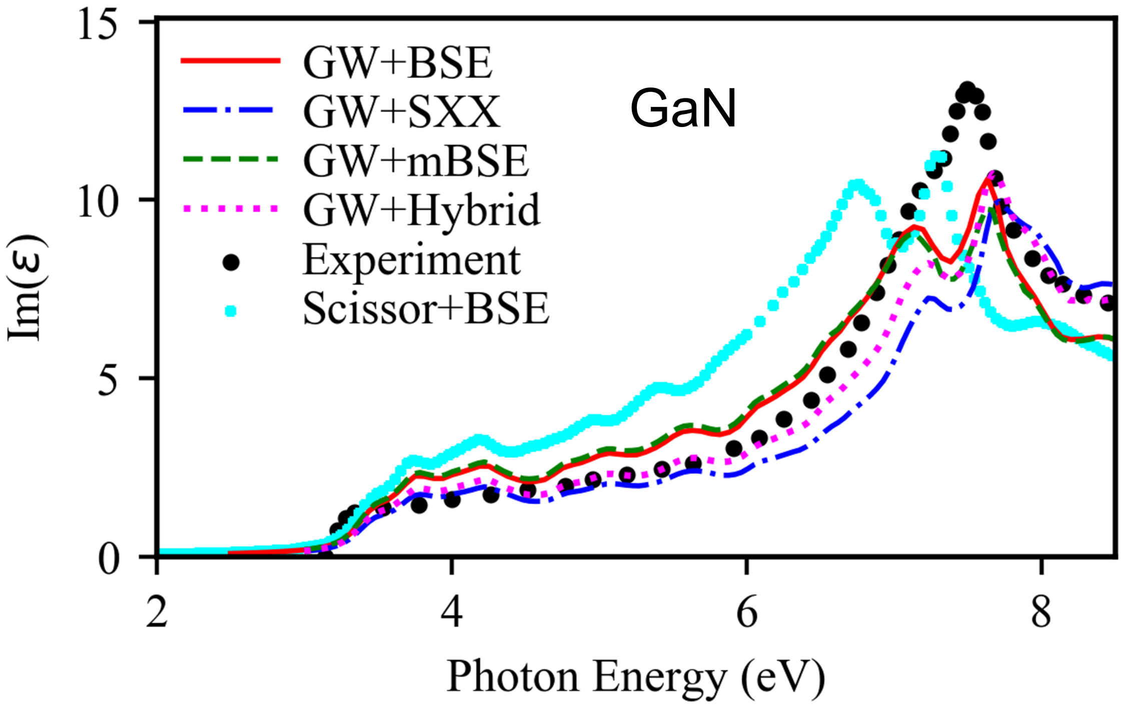
$$\gamma = \varepsilon^{-1}_{00}(0,0)$$

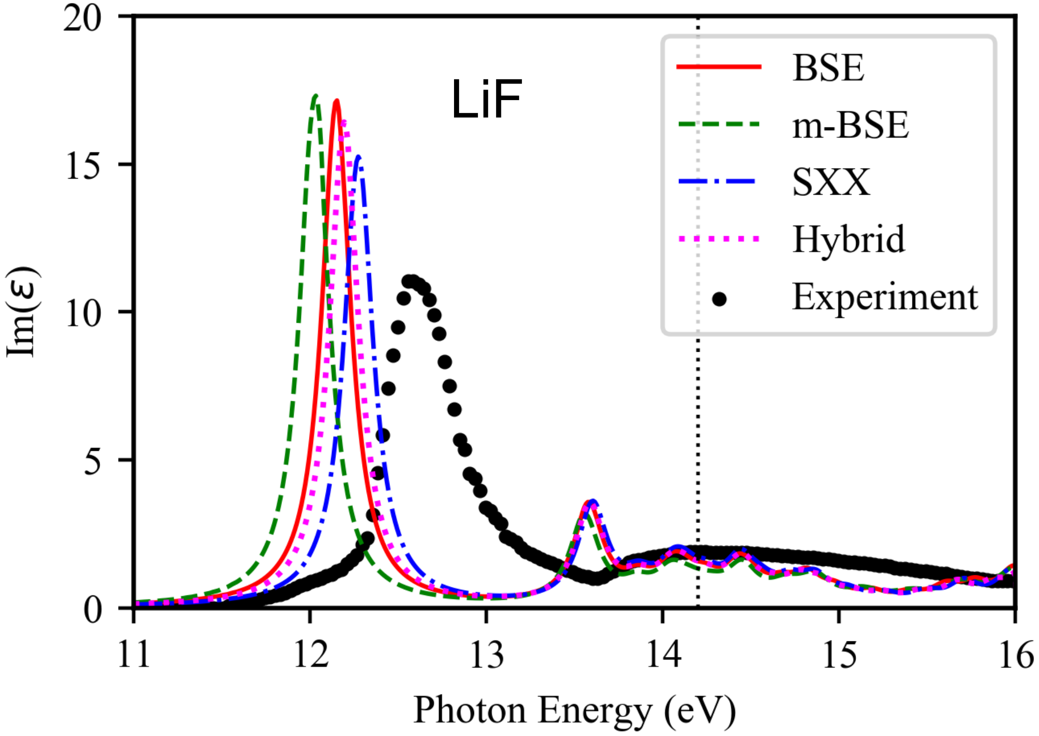
Calculated with RPA

Dielectrically screened hybrid functional

$$K_{xc}^{hybrid} = \gamma K_x^{XX} + (1-\gamma) K_{xc}^{ALDA}$$

$$\gamma = \varepsilon_{00}^{-1}(0,0)$$

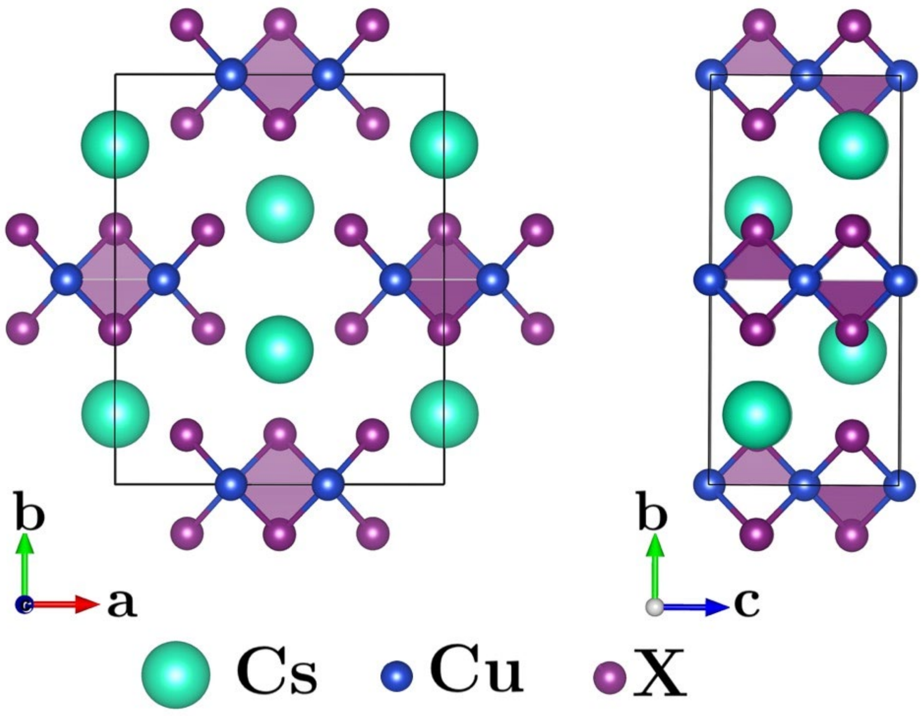


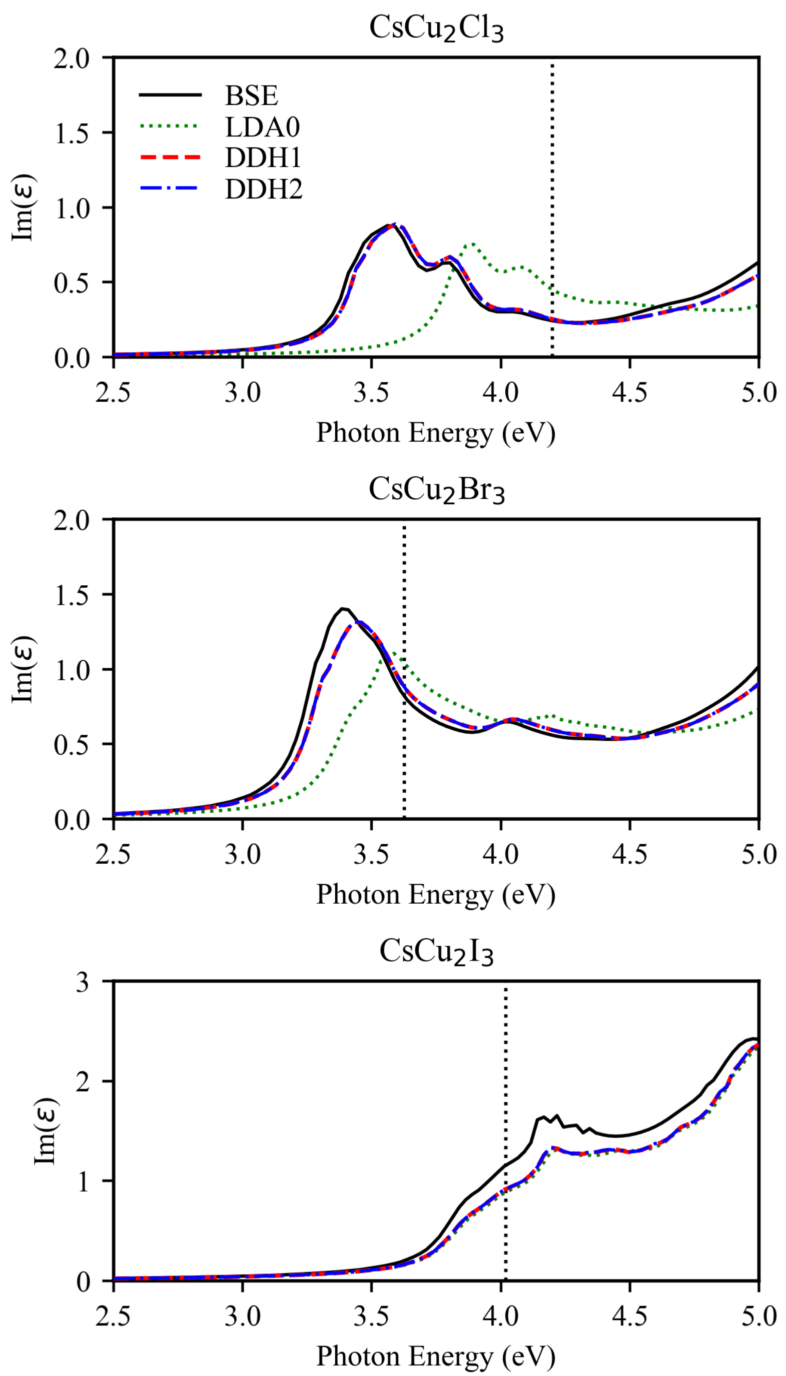


J. Sun, J. Yang, and C.A. Ullrich, Phys. Rev. Research **2**, 013091 (2020)
Z. Yang, F. Sottile and C.A. Ullrich, PRB **92**, 035202 (2015)

$CsCuX_3$: hybrid vs BSE

J. Sun and C. A. Ullrich, Phys. Rev. Materials **4**, 095402 (2020)

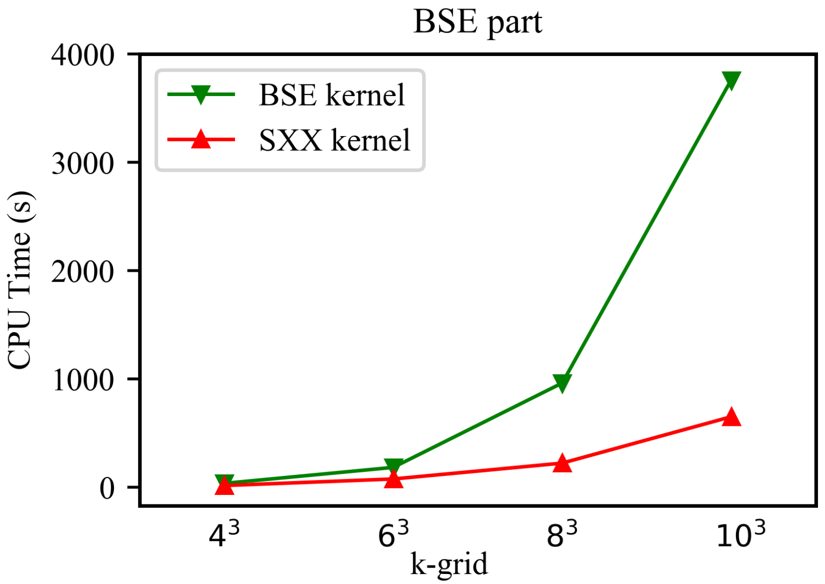


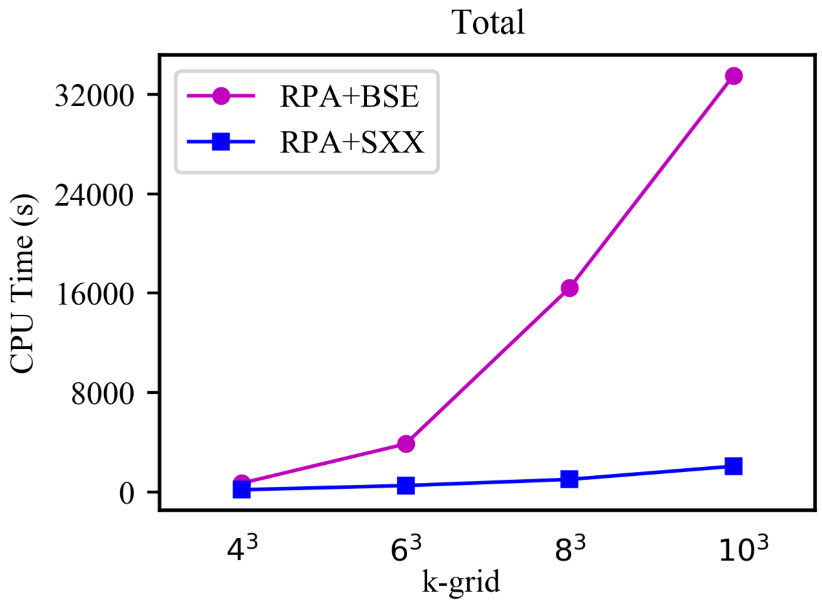


►**Good agreement between BSE and hybrid-TDDFT**

►**Calculation much faster using hybrid-TDDFT**

$CsPbBr_3$: speedup of hybrid vs BSE





acceleration from $\delta_{\mathbf{GG}'}$
in coupling matrix

acceleration from not having
to calculate $(\varepsilon^{RPA})^{-1}_{\mathbf{GG}'}(\mathbf{q},0)$

Using Yambo 4.3.2 in most memory-efficient configuration
(not most efficient parallelization)

Real-time electron dynamics in solids: codes

- Ultrafast magnetization dynamics, femtomagnetism
  ELK (Full-potential LAPW)
  Krieger, Dewhurst, Elliott, Sharma & Gross, JCTC. **11**, 4870 (2015)
- High-harmonic generation, magnons
  Octopus (real-space grid)
  N. Tancogne-Dejean, O.D. Mücke, F.X. Kärtner, & A. Rubio, PRL **118**, 087403 (2017)
- Core-level spectroscopy.
  SIESTA (LCAO)
  Pemmaraju, Vila, Kas, Sato, Rehr, Yabana & Prendergast, Comput. Phys. Comm. **226**, 30 (2018)
- Ultrafast nonlinear spectroscopy, coherent phonons.
  Salmon (real-space grid, norm-conserving PP)
  Noda, Ishimura, Nobusada, Yabana & Boku, J. Comput. Phys. **265,** 145 (2014)
- Stopping power of materials under ion impact.
  Qb@ll, INQ (plane waves)
  Schleife, Kanai & Correa, Phys. Rev. B **91**, 014306 (2015)
  Andrade et al. JCTC 17, 7447 (2021)

exciting

pyscf

B. Wong (2023)

...and there are more.....

Excitons with real-time TDDFT

$$i\frac{\partial}{\partial t}\varphi_j(\mathbf{r},t)=\left[\frac{1}{2}\left(\frac{\nabla}{i}+\mathbf{A}_{laser}(\mathbf{r},t)+\mathbf{A}_{xc}(\mathbf{r},t)\right)^2+V_{nuc}(\mathbf{r})+V_{Hxc}(\mathbf{r},t)\right]\varphi_j(\mathbf{r},t)$$

$$f_{xc}^{LRC}(\mathbf{r},\mathbf{r}')=-\frac{\alpha}{4\pi|\mathbf{r}-\mathbf{r}'|} \quad \Rightarrow \quad V_{xc}^{LRC}(\mathbf{r},t)=-\int f_{xc}^{LRC}(\mathbf{r},\mathbf{r}')\delta n(\mathbf{r}',t)d\mathbf{r}'$$

Long-range part is ill defined!
Make gauge transformation:

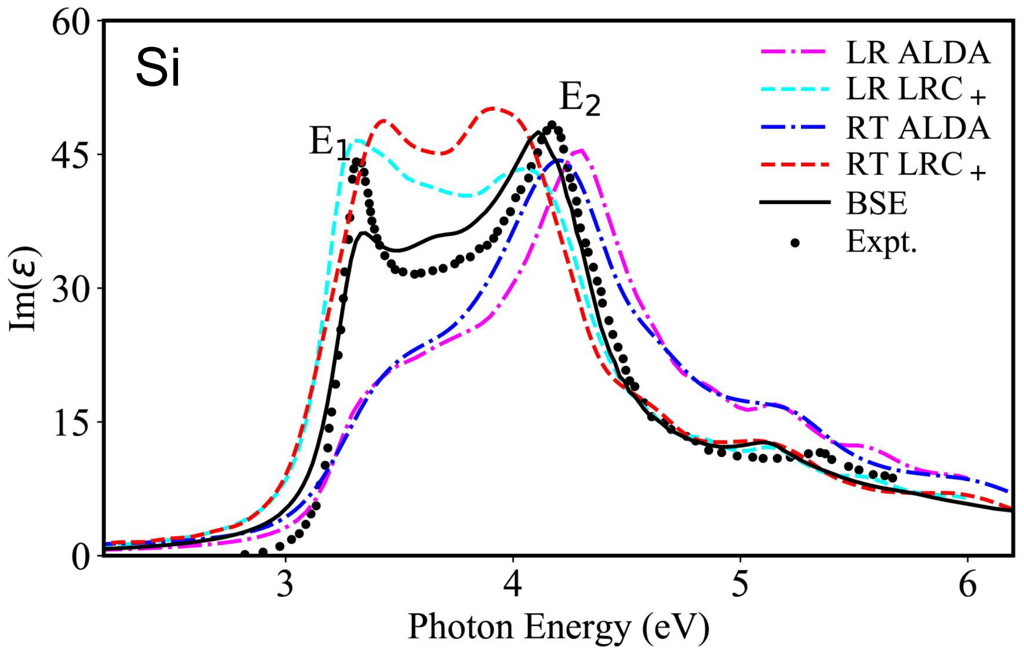
$$\nabla\cdot\mathbf{j}=-\dot{n} \qquad -\nabla V_{xc}^{LRC}=\dot{\mathbf{A}}_{xc}^{LRC}$$

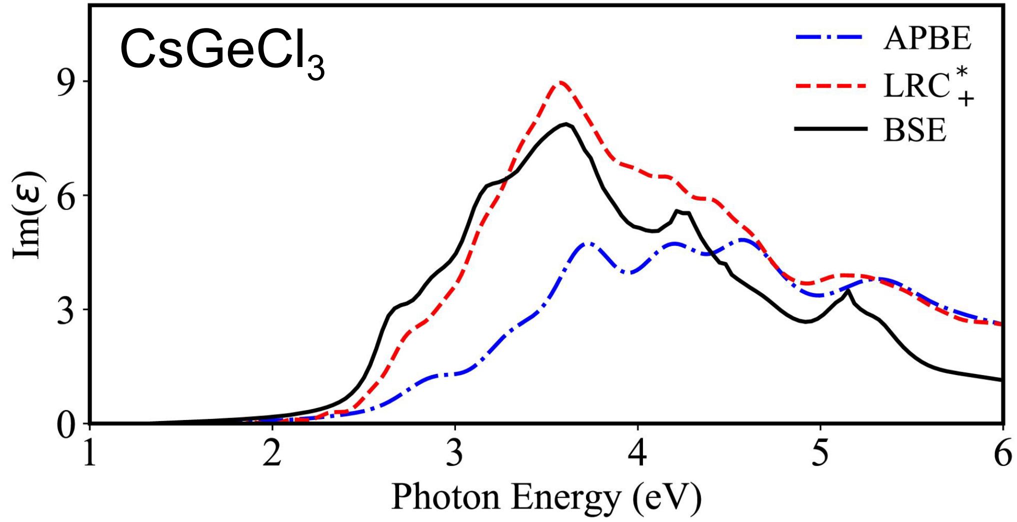
Head-only approximation:

$$\mathbf{A}_{xc}^{LRC}(\mathbf{r},t)=-\frac{\alpha}{4\pi}\int_0^t dt'\int_0^{t'} dt''\nabla\int dr'\frac{\nabla'\cdot\mathbf{j}(\mathbf{r}',t'')}{|\mathbf{r}-\mathbf{r}'|}$$

$$\frac{d^2}{dt^2}\mathbf{A}_{xc,\mathbf{G}=0}^{LRC}(t)=\alpha\,\mathbf{j}_{mac}(t)$$

Optical spectra from real-time TDDFT





Calculations done using Qb@ll code (including LRC vector potential).

$$\mathbf{j}_{mac}(t) = \frac{e}{\Omega} \int_{\Omega} \mathbf{j}(\mathbf{r}, t) d\mathbf{r}$$

conductivity:

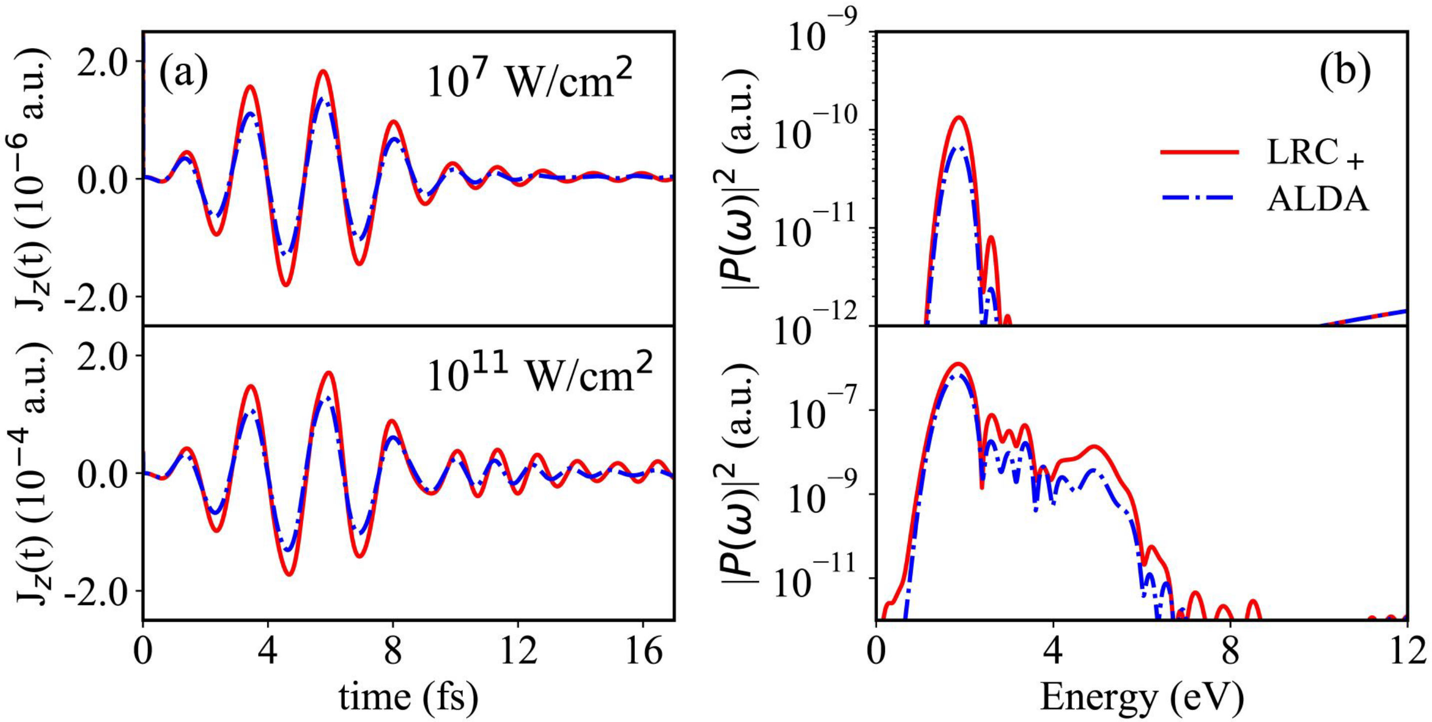
$$\sigma_{ij}(\omega) = -\frac{c}{A_j} \int_0^T e^{i\omega t} f(t) j_{mac,i}(t) dt$$

dielectric function:

$$\varepsilon(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega}$$

Nonlinear effects

Si

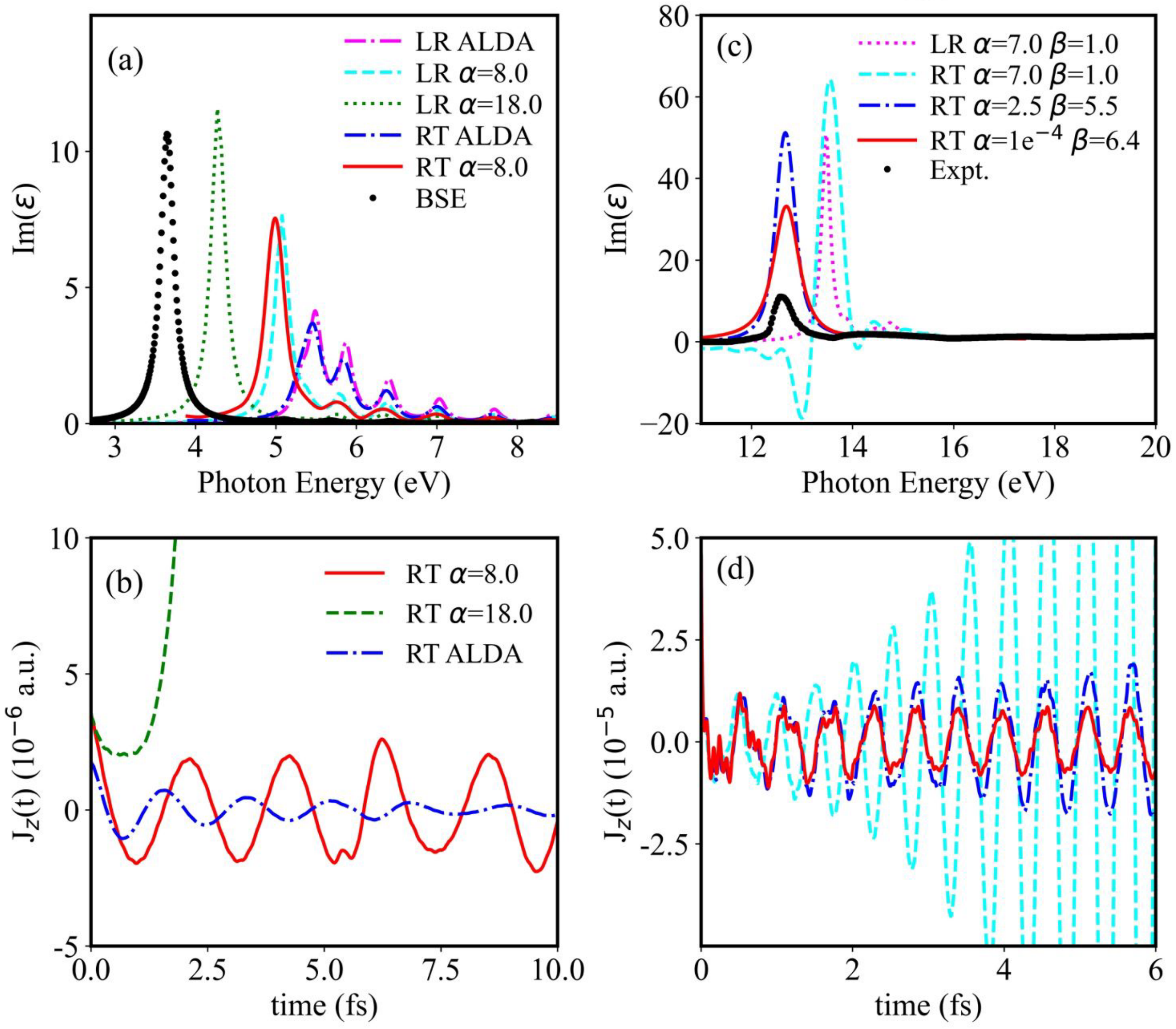


Excitonic effects enhance nonlinear response in Si (3^{rd} harmonic generation)

J. Sun, C.-W. Lee, A. Kononov, A. Schleife, and C. A. Ullrich, PRL **127**, 077401 (2021)

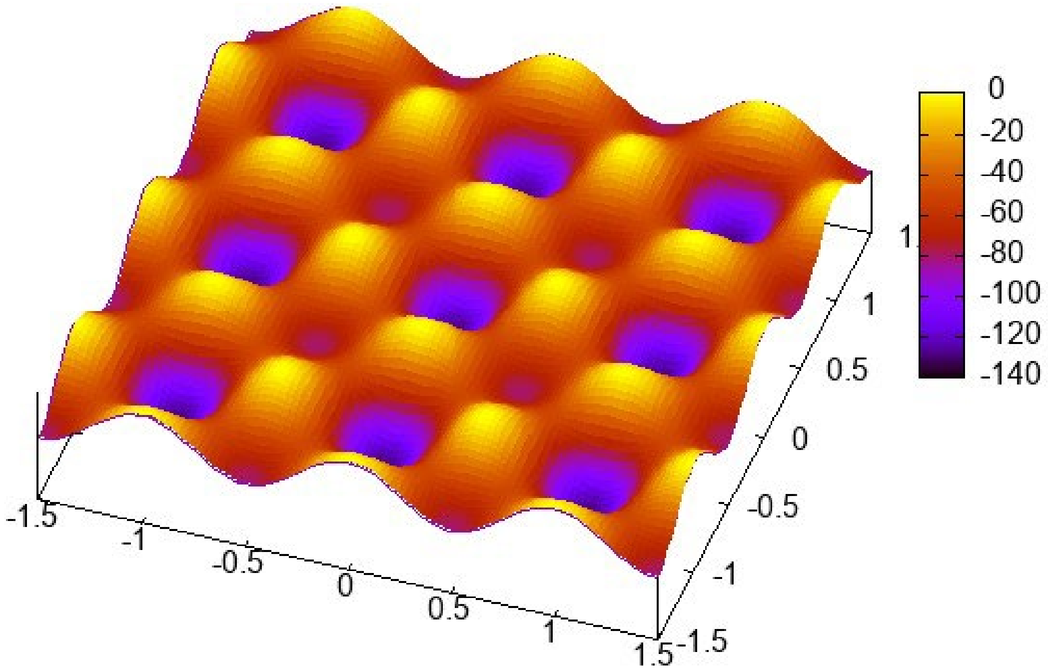
Strongly-bound excitons from real-time TDDFT

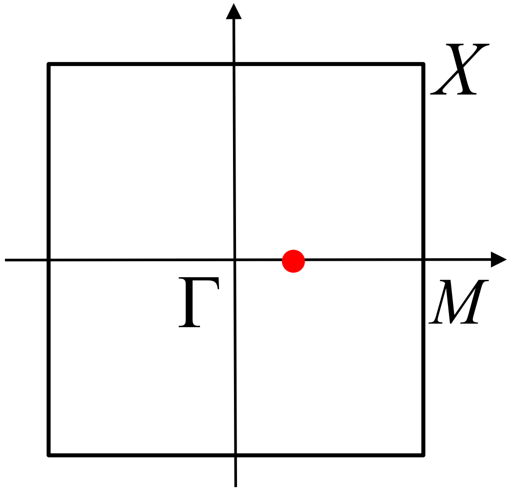
H_2 chain LiF

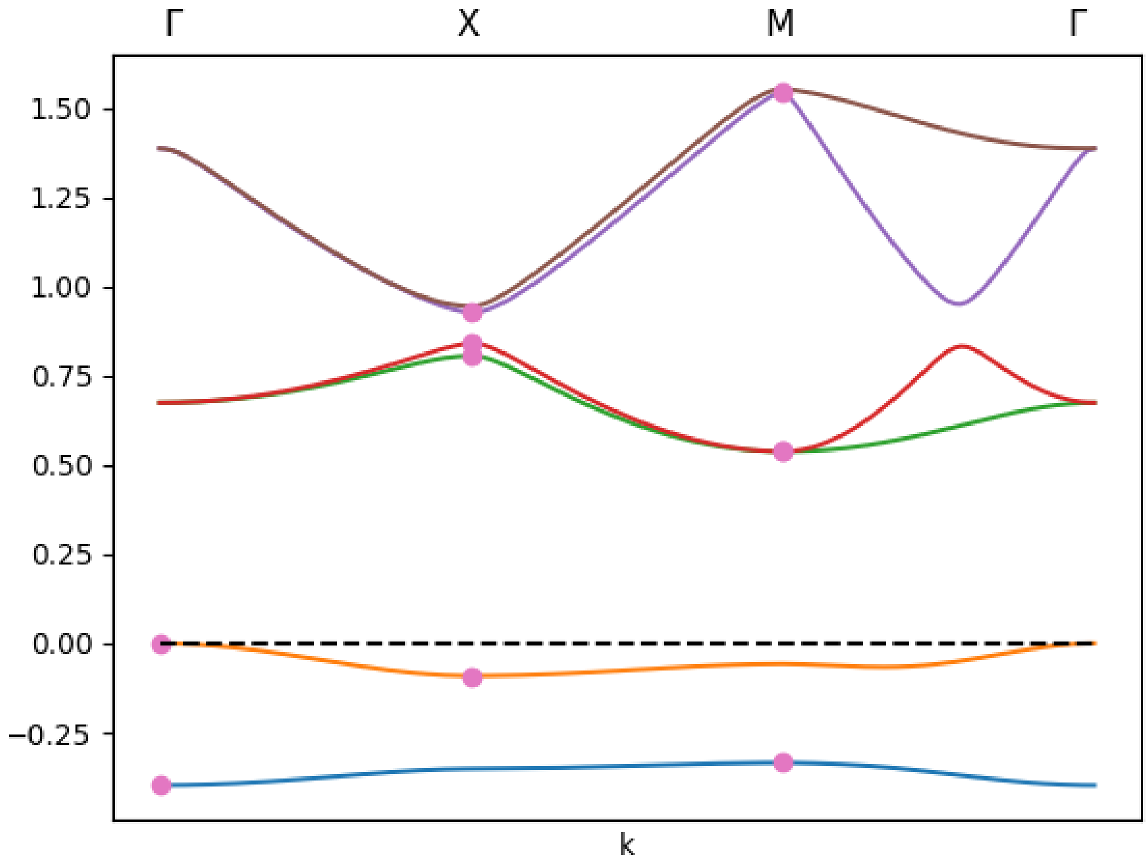


- ► Strongly bound excitons: LRC develops **instabilities.**
- ► **quick and dirty fix:** e-h binding through local-field effects
- ► **Questions:**
  - **Can TD-LRC be stabilized?**
  - **What else can one do?**

2D model solid to study LR- and RT-TDDFT





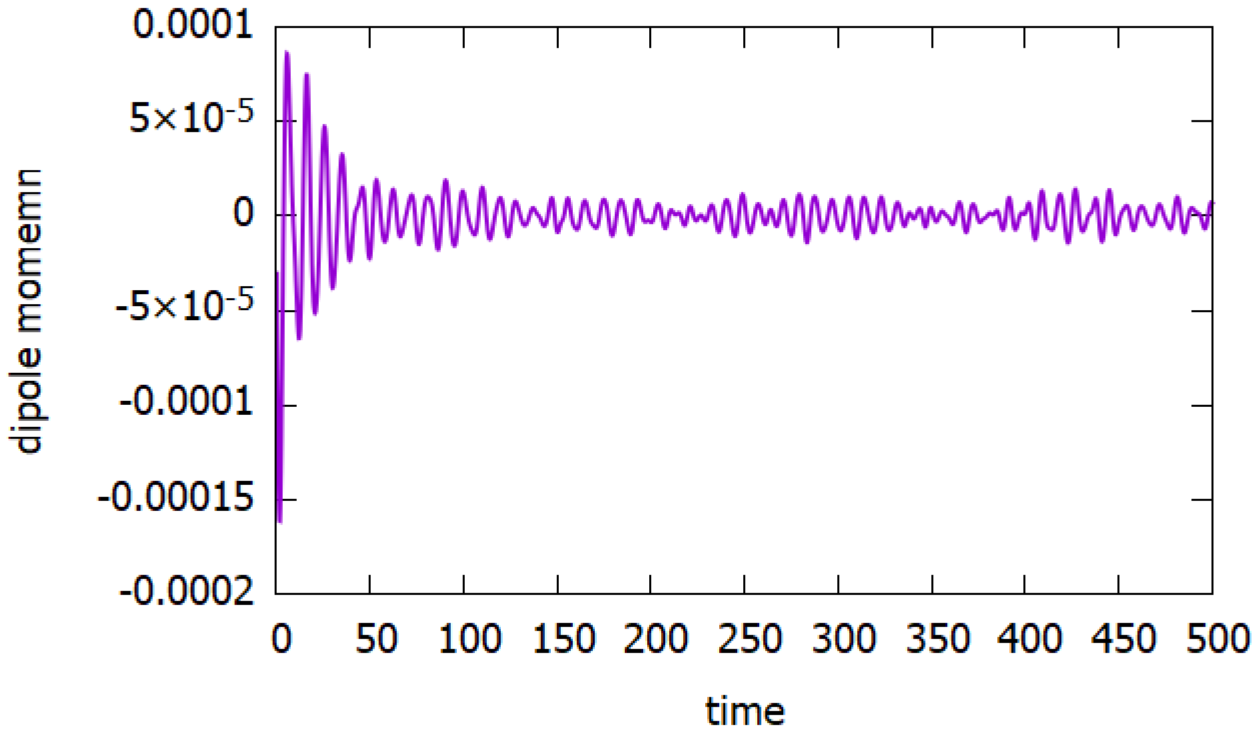


- 4 electrons per unit cell
- two lowest valence bands are occupied
- use simple plane-wave basis
- Consider response at finite q

RT-TDDFT for optical spectra

$$i\frac{\partial}{\partial t}\varphi_j(\mathbf{r},t)=\left[\frac{1}{2}\left(\frac{\nabla}{i}+\mathbf{A}(t)\right)^2+V_{eff}(\mathbf{r},t)\right]\varphi_j(\mathbf{r},t)$$

"delta-kick": $V(\mathbf{r},t)=\mathbf{E}_0\mathbf{r}\delta(t-t_0)$ ⇒ $\mathbf{A}(t)=\mathbf{E}_0\theta(t-t_0)$

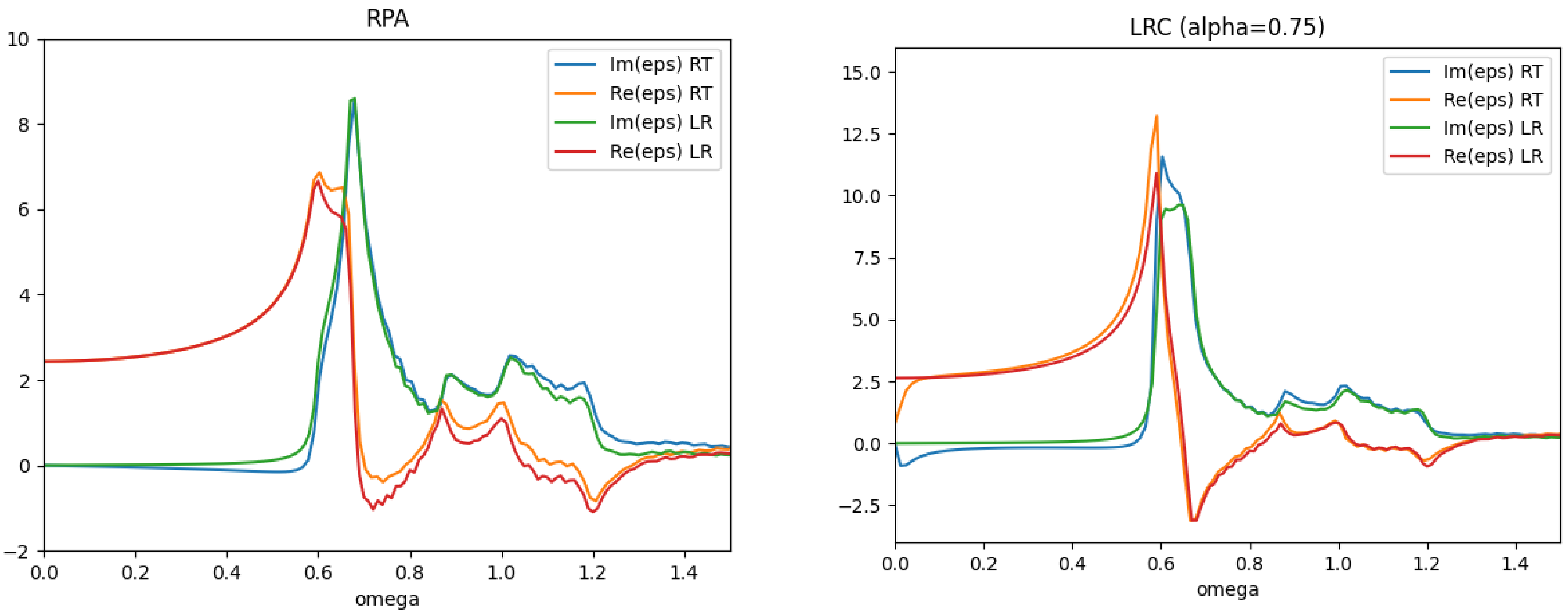


$$d(\omega)=\int dt\, d(t)e^{-i\eta t}e^{i\omega t}$$

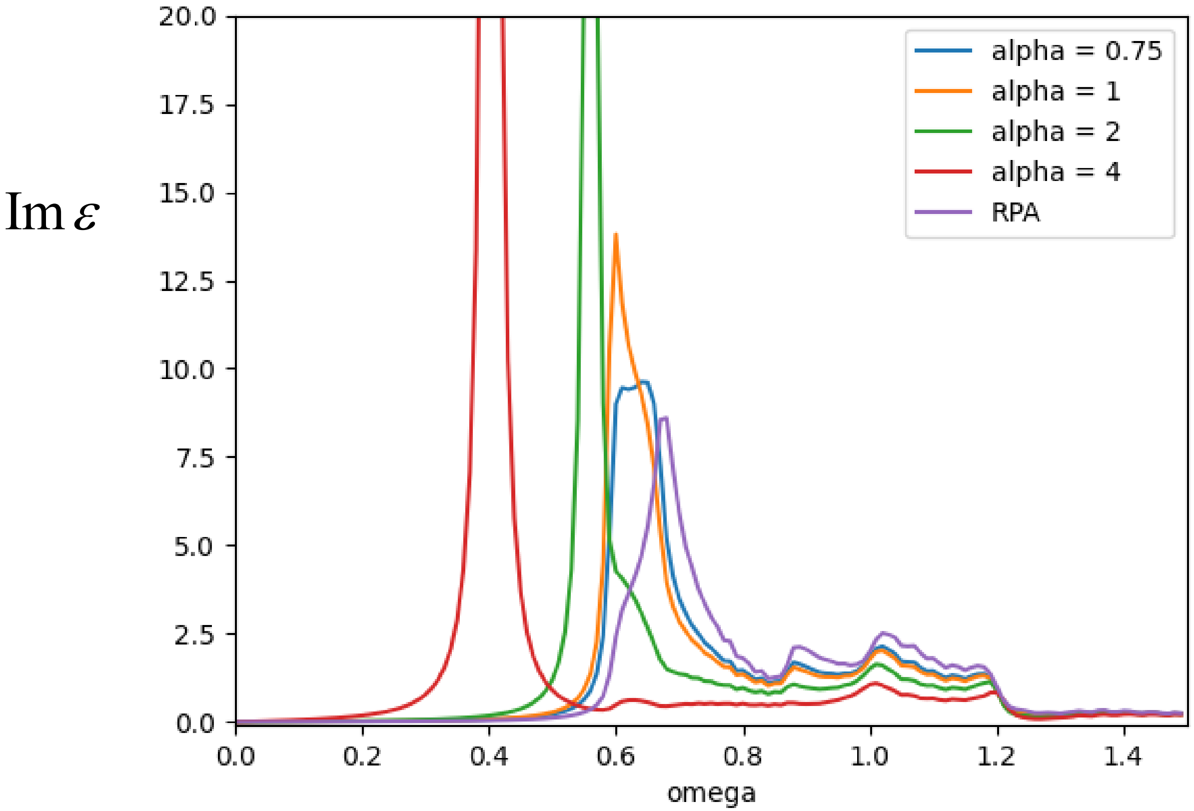
$$\varepsilon_{mac}(\omega)=1-\frac{4\pi}{E_0}d(\omega)$$

T. Sander and G. Kresse, JCP **146**, 064110 (2017)

Equivalence of LR- and RT-TDDFT for optical spectra



Stability of time-dependent LRC



From LR-TDDFT:
- ► excitons have huge oscillator strength
- ► Rydberg series condensed in 1 peak

From RT-TDDFT:
Dipole oscillations blow up for large α_{xc} !

► Need more G-vectors to stabilize

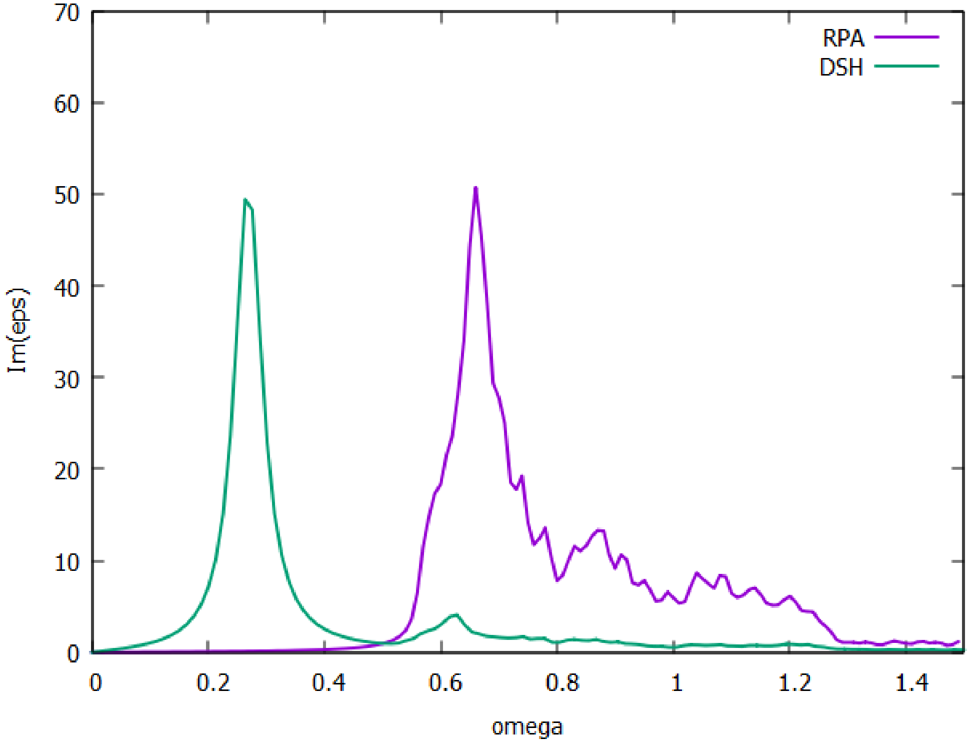
► Zero-force theorem? We are currently testing this... seems to help somewhat.

►Key issue: stability of $\frac{d^2}{dt^2}\mathbf{A}_{LRC} = \alpha\,\mathbf{j}_{mac}$

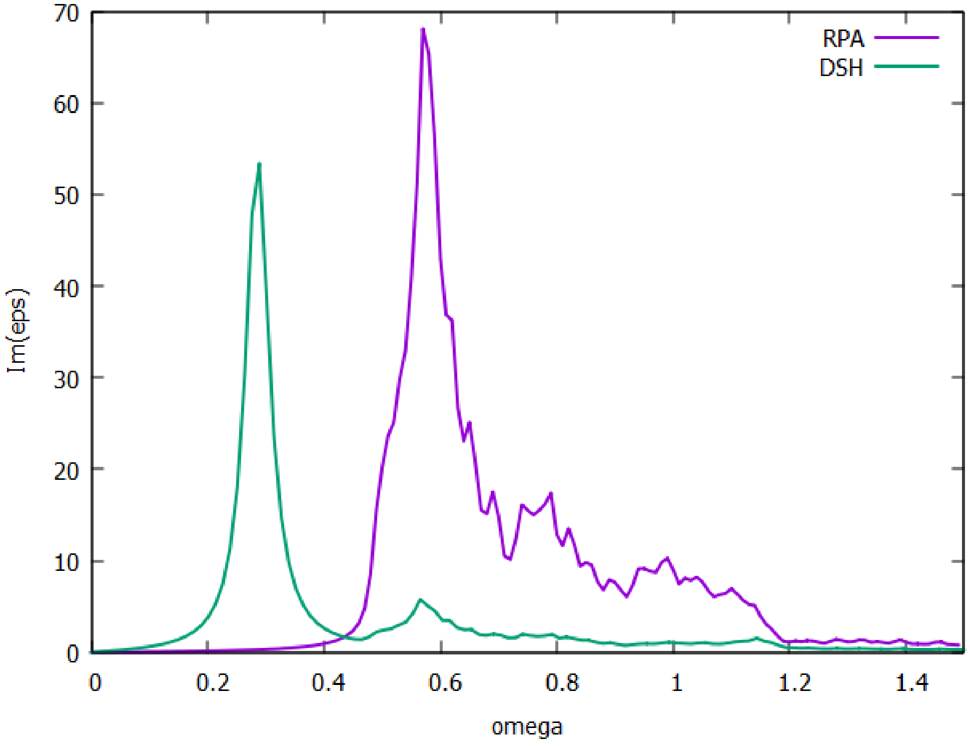
currently testing 4th order Runge-Kutta.

Time-dependent screened HF

ε=4



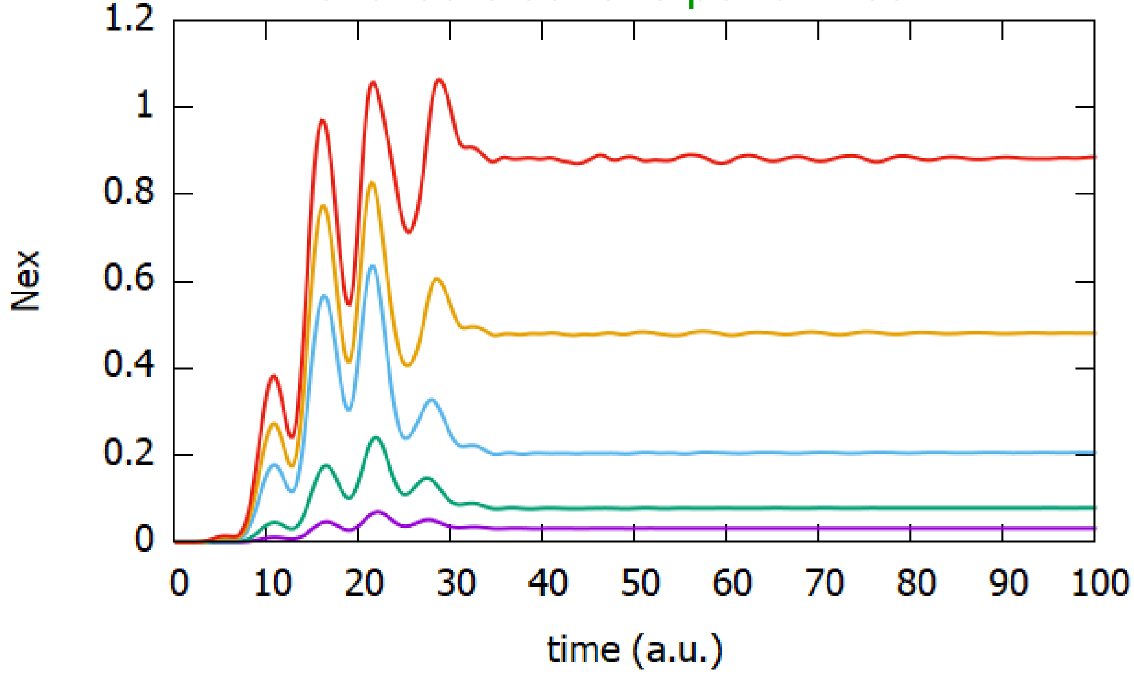
ε=10



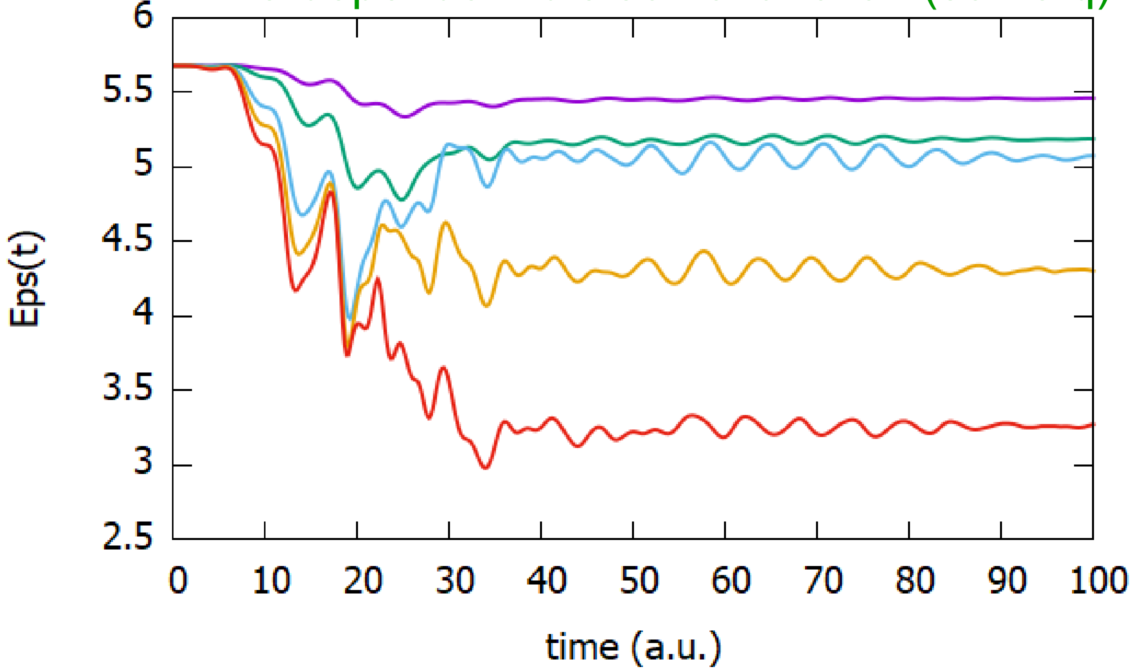
- Time propagation is **stable**, even for strongly bound excitons
- Use same approach for ground state and response/time propagation.
- This is preliminary... will need ε(**q**) for 2D systems.

Time-dependent screening (following 3-cycle pulse)

excited electrons per unit cell



time-dependent dielectric function (some q)

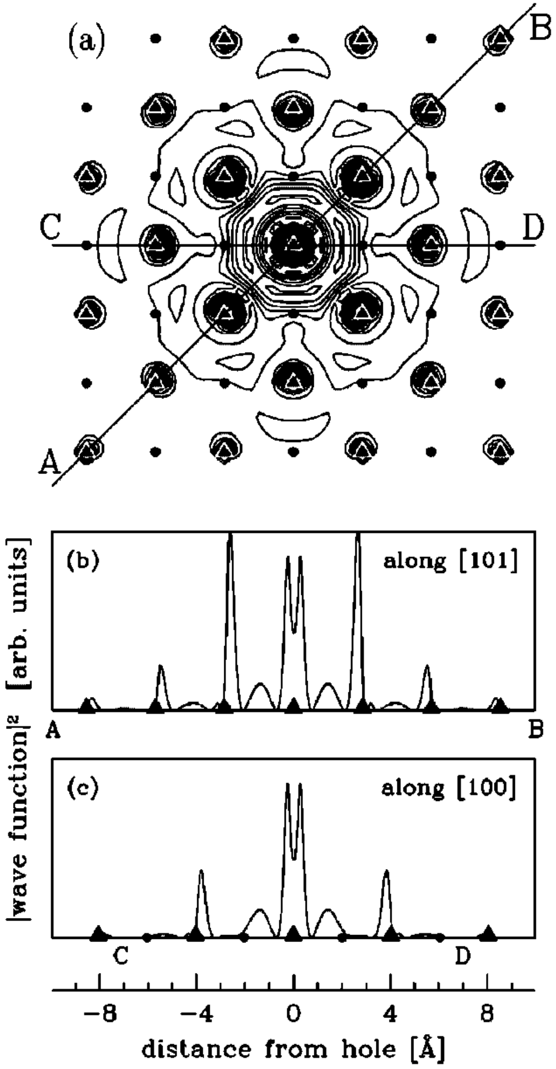


- ►Quasistatic approximation (projecting TDKS orbitals on instantaneous band structure)
- ►Population transfer into higher bands reduces the screening significantly
- ►Interband screening dominant at fast time scales
- ►Intraband screening should kick in at time scales $\sim \omega_p^{-1}$

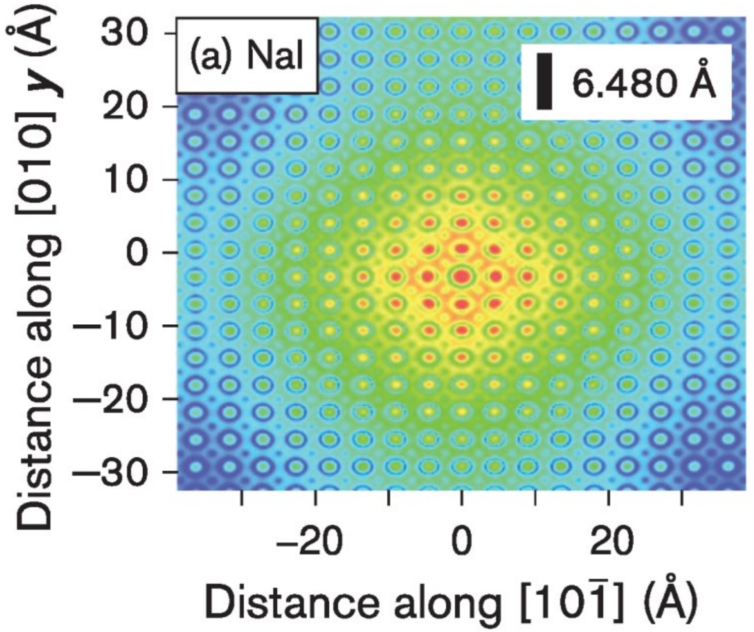
Huber, Tauser, Brodschelm, Bichler, Abstreiter & Leitenstorfer, Nature **414**, 286 (2001)

Exciton wave functions in 3D solids

LiF



Rohlfing and Louie, PRB **62**, 4927 (2000)



GW-BSE

Erhart, Schleife, Sadigh and Aberg, PRB **89**, 075132 (2014)

Can we get exciton wave function from TDDFT?
Can we make it time-dependent?

Transition Density Matrix (TDM)

TDM associated with a specific excitation $\Psi_0 \to \Psi_n$:

$$\Gamma_n(\mathbf{r},\mathbf{r}') = \left\langle \Psi_n \left| \hat{\rho}(\mathbf{r},\mathbf{r}') \right| \Psi_0 \right\rangle$$

Many-body eigenstates: $\hat{H}_0 \Psi_n = E_n \Psi_n$

1-body density matrix operator: $\hat{\rho}(\mathbf{r},\mathbf{r}') = \hat{\psi}^+(\mathbf{r}')\hat{\psi}(\mathbf{r})$

R. McWeeny, RMP **32**, 335 (1960)
F. Furche, JCP **114**, 5982 (2001)
F. Plasser, M. Wormit and A. Dreuw, JCP **141**, 024106 (2014)

TDM = exciton wave function

Kohn-Sham TDM

S. Tretiak and S. Mukamel, Chem. Rev. **102**, 3171 (2002)
F. Furche, JCP **114**, 5982 (2001)

$$\Gamma_n^{KS}(\mathbf{r},\mathbf{r}') = \sum_{ia}\left[\varphi_a^*(\mathbf{r})\varphi_i(\mathbf{r}')X_{ia}(\Omega_n) + \varphi_i^*(\mathbf{r})\varphi_a(\mathbf{r}')Y_{ia}(\Omega_n)\right]$$

Diagonal elements: transition densities

$$\Gamma_n^{KS}(\mathbf{r},\mathbf{r}) = \Gamma_n(\mathbf{r},\mathbf{r}) = \delta n(\mathbf{r},\Omega_n)$$

Off-diagonal elements **not** in principle exact, but still usefully accurate:

$$\Gamma_n^{KS}(\mathbf{r},\mathbf{r}') \neq \Gamma_n(\mathbf{r},\mathbf{r}'), \quad \mathbf{r} \neq \mathbf{r}'$$

Time-dependent TDM

Y. Li and C.A. Ullrich, Chem. Phys. **391**, 157 (2011)
Y. Li and C.A. Ullrich, JCP **145**, 164107 (2016)

weakly perturbed system: $\Psi(t) = \Psi_0 e^{-iE_0 t} + \delta\Psi(t)$

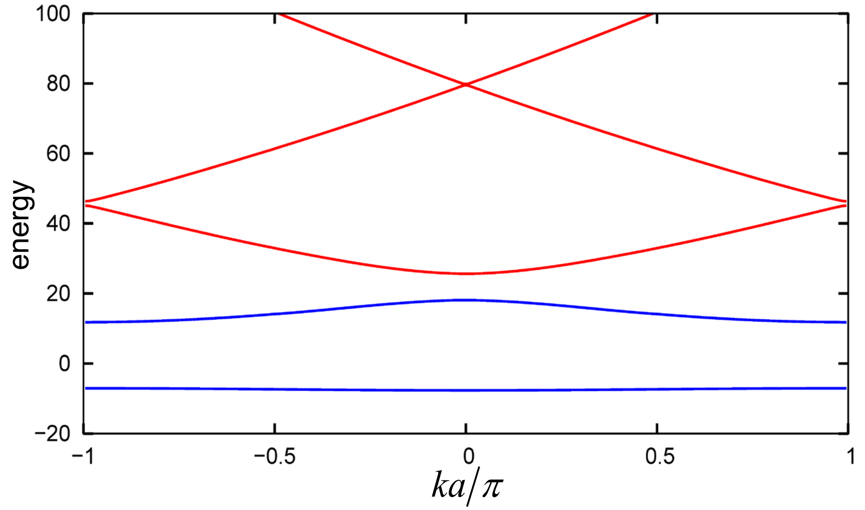
Time-dependent TDM:

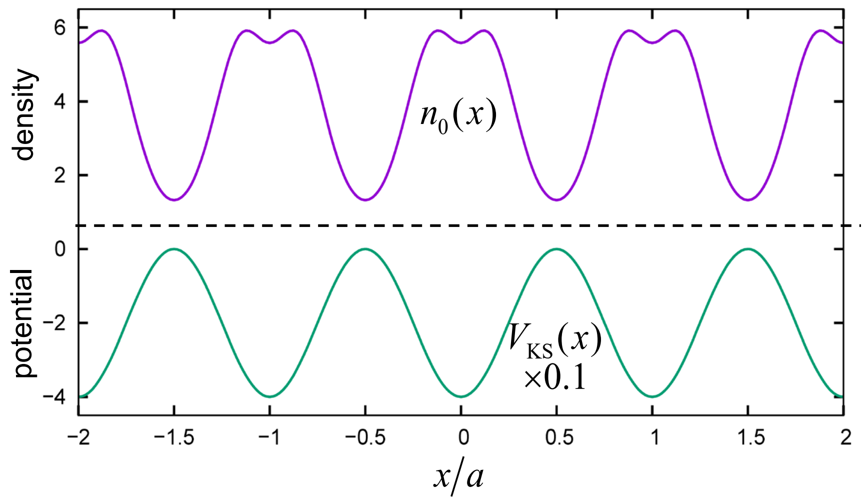
$$\Gamma(\mathbf{r},\mathbf{r}',t) = \left\langle \delta\Psi(t) \middle| \hat{\rho}(\mathbf{r},\mathbf{r}') \middle| \Psi_0 e^{-iE_0 t} \right\rangle + \left\langle \Psi_0 e^{iE_0 t} \middle| \hat{\rho}(\mathbf{r},\mathbf{r}') \middle| \delta\Psi(t) \right\rangle$$

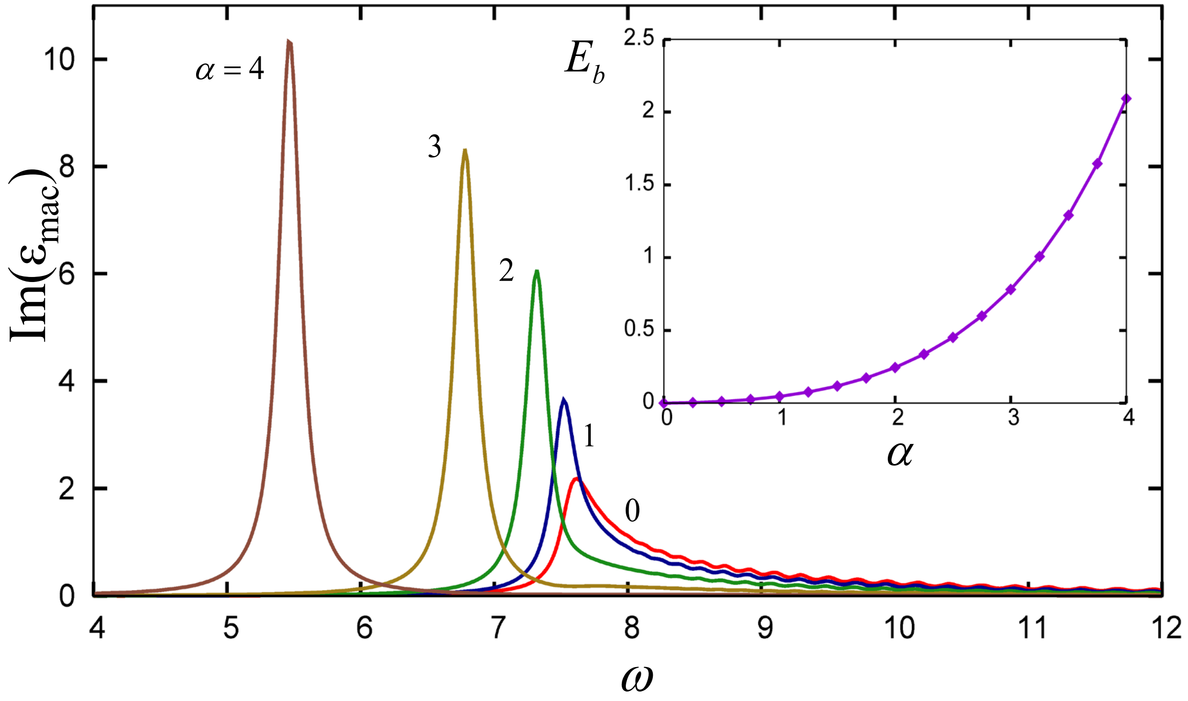
Kohn-Sham time-dependent TDM:

$$\Gamma_{KS}(\mathbf{r},\mathbf{r}',t) = \sum_j \left[\varphi_j(\mathbf{r},t)\varphi_j^*(\mathbf{r}',t) - \varphi_j^{(0)}(\mathbf{r})\varphi_j^{(0)*}(\mathbf{r}') \right]$$

Visualizing excitons in a 1D model solid

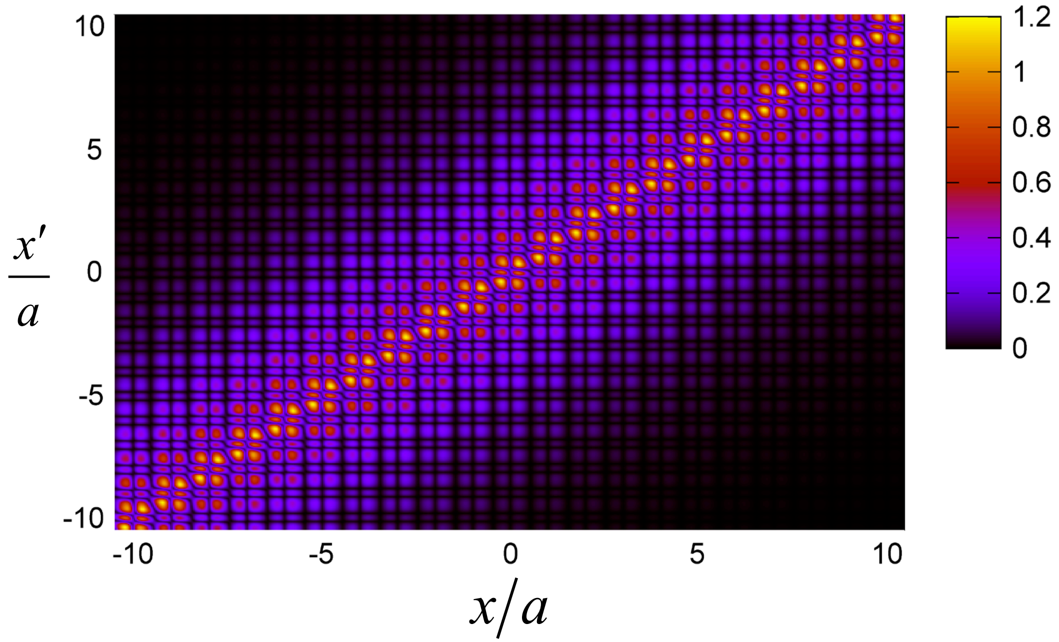


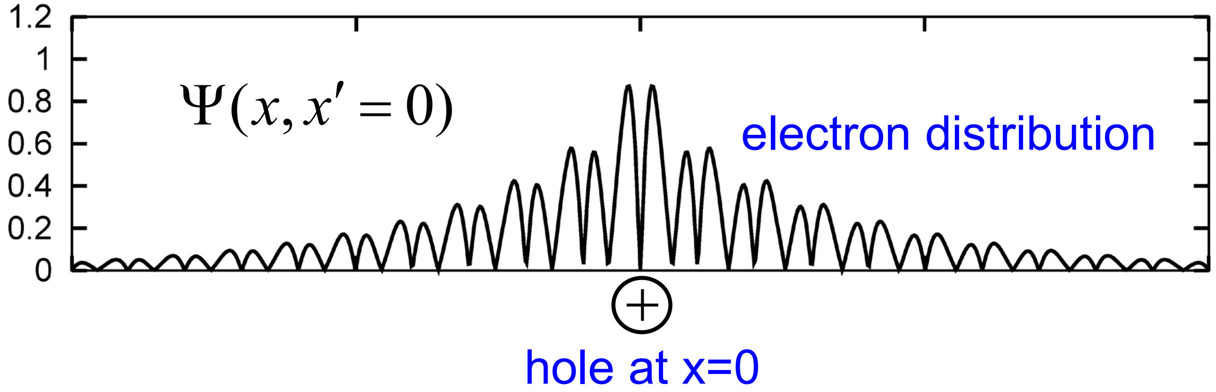




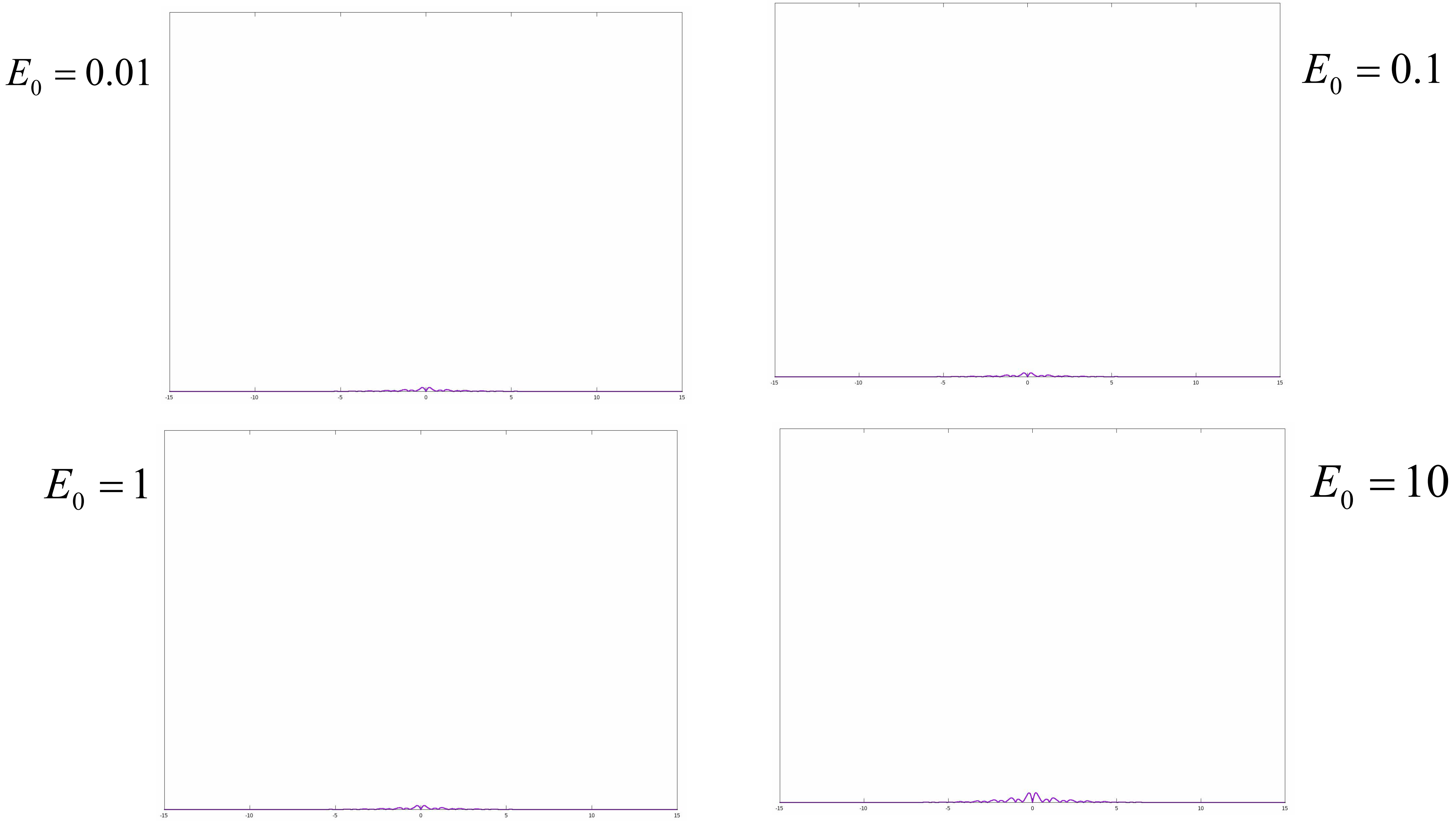
- "headless" LRC to avoid instabilities
- very strongly bound
- large oscillator strength
- agrees well with Wannier model

Exciton wave functions in 1D model solid

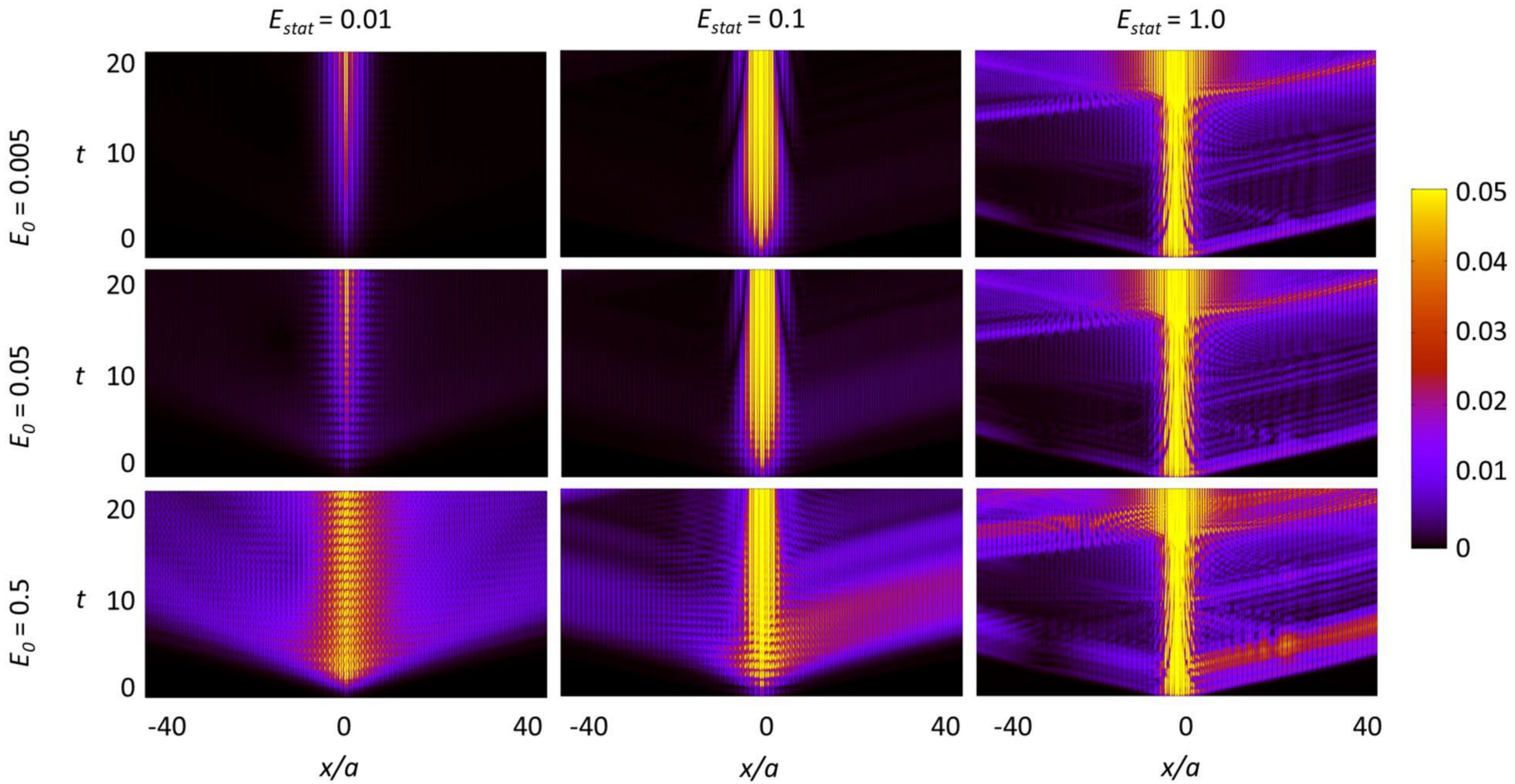




Real-time exciton wave functions (triggered by laser pulse)



Static field induced exciton dissociation



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Summary

► Excitonic effects in solids can be described in linear response or with time propagation.

► LRC approximation works for weakly bound excitons, but has problems

► Hybrid-TDDFT is competitive with BSE:
- optical spectra: as accurate, but cheaper
- real time: access to ultrafast, nonlinear effects

► Visualization: time-dependent exciton wave function

► Next step: applications to real materials in 3D and 2D

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