Excited States:

Manybody Perturbation Theory

& Time-dependent DFT

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Open Problems

- Interpretation of Kohn-Sham states
- Band gap problem
- Functionals
- Excited states

Concepts

- Manybody perturbation theory (MBPT): GW & BSE
- Time-dependent density functional theory (TDDFT)

Technicalities

- LAPW - specific problems & advantages
- Implementation

Results

Contents

Sources of discrepancies

Ground state:

$$V_{xc}(\mathbf{r}) = \frac{dE_{xc}[\rho(\mathbf{r})]}{d\rho(\mathbf{r})}$$

Local Density Approximation (LDA)
Generalized Gradient Approximation (GGA)

Excited state:

Interpretation within one-particle picture
Interpretation of excited states in terms of ground state properties

Response function:

Random phase approximation ignores electron-hole interaction
Manybody treatment needed

Excited States Based on DFT?

Hohenberg-Kohn theorem:

$$E = F[\rho(\mathbf{r})] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

Kohn-Sham equation:

$$\left\{-\nabla^2 + V_{ext}(\mathbf{r}) + V_C(\rho(\mathbf{r})) + V_{xc}(\rho(\mathbf{r}))\right\}\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i f_i\;|\psi_i(\mathbf{r})|^2$$

DFT Basics

Hartree-Fock:

ε_i ionization energies

$$\varepsilon_i = E(n_1, n_2, \ldots, n_i, \ldots, n_N) - E(n_1, n_2, \ldots, n_{i-1}, \ldots, n_N)$$

Koopman's theorem

DFT:

ε_i Lagrange parameters

$$\varepsilon_i(n_1, n_2, \ldots, n_i, \ldots, n_N) = \frac{dE}{dn_i}$$ Janak's theorem

$\psi_i(\mathbf{r})$ auxiliary functions $\rho(\mathbf{r}) = \sum_i f_i\;|\psi_i(\mathbf{r})|^2$

Interpretation of KS States

Ionization energy $\varepsilon_N(N) = -I$

Electro-affinity $\varepsilon_{N+1}(N+1) = -A$

Band gap $E_g = I - A = \varepsilon_{N+1}(N+1) - \varepsilon_N(N)$

$$E_g = \underbrace{\varepsilon_{N+1}(N) - \varepsilon_N(N)}_{\varepsilon_g} + \underbrace{\varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N)}_{\Delta_{xc}}$$

$$E_g = \varepsilon_g + \Delta_{xc}$$

- Even the exact KS solutions don't have to provide good band gaps!

Δ_{xc} shift of conduction bands: scissors operator
manybody perturbation theory: GW approach

The Band Gap Problem

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int d\omega' \, G(\mathbf{r},\mathbf{r}',\omega-\omega')W(\mathbf{r},\mathbf{r}',\omega)$$

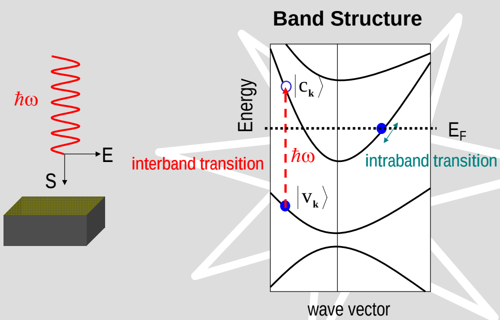
Quasiparticle band structure:

$$\epsilon^{QP}_{n\mathbf{k}} = \epsilon^{LDA}_{n\mathbf{k}} - \langle n\mathbf{k}|\Sigma(\epsilon^{QP}_{n\mathbf{k}}) - V^{LDA}_{xc}|n\mathbf{k}\rangle$$

- Shift of conduction bands nearly independent of **k**.

M. S. Hybertson and S. G. Louie, Phys. Rev. Lett. 55, 1418 (1985).
M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986).

The GW Approach



$$\mathrm{Im}\,\varepsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2}\sum_{c,v}\int d\mathbf{k}\,\langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle\,\delta(\varepsilon_{c_\mathbf{k}}-\varepsilon_{v_\mathbf{k}}-\omega)$$ RPA

Light Scattering

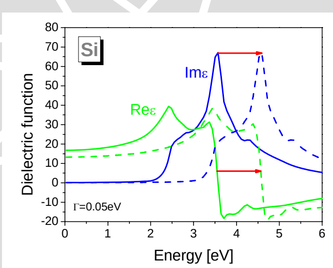
$$\mathrm{Im}\,\varepsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2}\sum_{c,v}\int d\mathbf{k}\,\langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle\,\delta(\varepsilon_{c_\mathbf{k}}-\varepsilon_{v_\mathbf{k}}-\omega)$$

$(\omega-\Delta)^2$ $\qquad$ $\varepsilon_{c_\mathbf{k}}+\Delta$

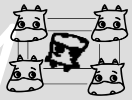
R. del Sole and R. Girlanda, Phys. Rev. B 48, 11789 (1993).

- Spectra: shift Imε not band energies!
- Exact within RPA & GW
- Matrix elements rescaled
- Sumrule violated

$$\int_0^\omega \sigma(\omega')\,\omega'\,d\omega' = N_{eff}(\omega)$$



The Selfenergy Correction



Two-particle wave function:

$$\Phi^\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{v c \mathbf{k}} A^\lambda_{vc\mathbf{k}} \psi^*_{v\mathbf{k}}(\mathbf{r}_h) \psi_{c\mathbf{k}}(\mathbf{r}_e)$$

KS states from GS calculation

Effective two-particle Schrödinger equation:

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^\lambda_{v'c'\mathbf{k}'} = E_\lambda A^\lambda_{vc\mathbf{k}}$$

BSE

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^\lambda_{v'c'\mathbf{k}'} = E_\lambda A^\lambda_{vc\mathbf{k}}$$

$$H^{e-h} = H^{diag} + H^{dir} + H^{x}$$

$$\Phi^\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{v c \mathbf{k}} A^\lambda_{vc\mathbf{k}} \psi^*_{v\mathbf{k}}(\mathbf{r}_h) \psi_{c\mathbf{k}}(\mathbf{r}_e)$$

$$H^{diag}_{vc\mathbf{k},v'c'\mathbf{k}'} = (\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}}) \delta_{vv'} \delta_{cc'} \delta_{\mathbf{k}\mathbf{k}'}$$

$$H^{dir}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \psi_{v\mathbf{k}}(\mathbf{r}) \psi^*_{c\mathbf{k}}(\mathbf{r}') \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \psi^*_{v'\mathbf{k}'}(\mathbf{r}) \psi_{c'\mathbf{k}'}(\mathbf{r}') d\mathbf{r}\, d\mathbf{r}'$$

$$H^{x}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \frac{\psi^*_{v'\mathbf{k}'}(\mathbf{r}') \psi^*_{c\mathbf{k}}(\mathbf{r}) \psi_{v\mathbf{k}}(\mathbf{r}) \psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}'$$

$$\mathrm{Im}\,\epsilon_{xx}(\omega) = \frac{8\pi^2}{\Omega} \sum_\lambda \left| \sum_{v,c,\mathbf{k}} A^\lambda_{vc\mathbf{k}} \frac{\langle v_\mathbf{k} | p^x | c_\mathbf{k} \rangle^{QP}}{\varepsilon_{c_\mathbf{k}} - \varepsilon_{v_\mathbf{k}}} \right|^2 \delta(E_\lambda - \omega)$$

BSE

$$H^{dir}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \psi_{v\mathbf{k}}(\mathbf{r}) \psi^*_{c\mathbf{k}}(\mathbf{r}') \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \psi^*_{v'\mathbf{k}'}(\mathbf{r}) \psi_{c'\mathbf{k}'}(\mathbf{r}') d\mathbf{r}\, d\mathbf{r}'$$

$$\frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{\Omega} \sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} \frac{4\pi\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|} e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}$$

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

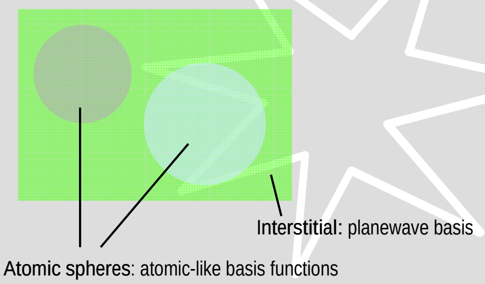
$$H^{dir}_{vc\mathbf{k},v'c'\mathbf{k}'} = -\frac{1}{\Omega} \sum_{\mathbf{G}\mathbf{G}'} W_{\mathbf{G}\mathbf{G}'}(\mathbf{k}'-\mathbf{k}) M^{\mathbf{G}}_{cc'}(\mathbf{k},\mathbf{q}) [M^{\mathbf{G}'}_{vv'}(\mathbf{k},\mathbf{q})]^*$$

$$M^{\mathbf{G}}_{nn'}(\mathbf{k},\mathbf{q}) = \langle n\mathbf{k} | e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} | n'\mathbf{k}' \rangle$$

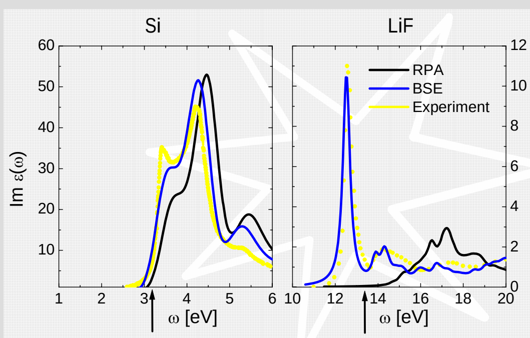
$$\mathbf{k}' = \mathbf{k} + \mathbf{q}$$

BSE: Implementation

$$M_{nn'}^{\mathbf{G}}(\mathbf{k},\mathbf{q}) = \langle n\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|n'\mathbf{k}'\rangle$$



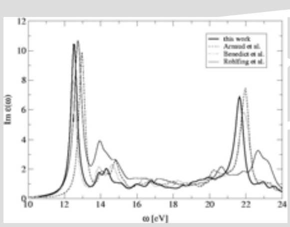
Implementation: the LAPW Method



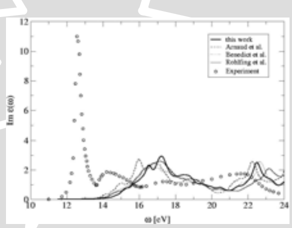
Peter Puschnig, PhD Thesis, 2002.

Beyond RPA: Examples

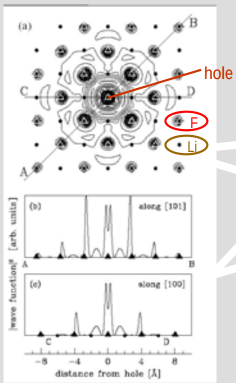
BSE



RPA



Solving BSE: LiF

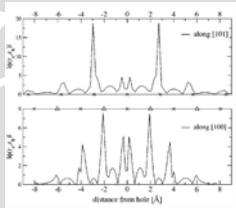


Pseudopotential results:

M. Rohlfing and S. G. Louie, Phys. Rev. Lett. 81, 2313 (1998).

LAPW (all-electron) results:

P. Puschnig and C. Ambrosch-Draxl, Phys. Rev. B 66, 165105 (2002).

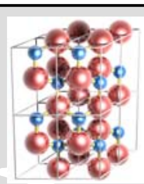


Solving BSE: LiF

Inorganic semiconductors

- Small binding energies
  a few tens meV
- High precision needed
  many k-points in small region of BZ
- Huge BSE matrices
  e.g. for GaN: 55000 x 55000

Computational Effort

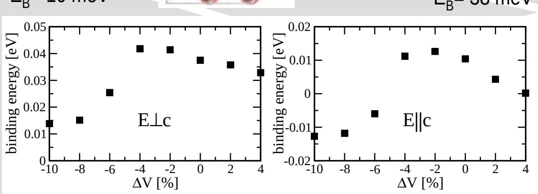


hexagonal, wurzite

E_g = 3.4 eV

E_B= 10 meV

E_B= 38 meV



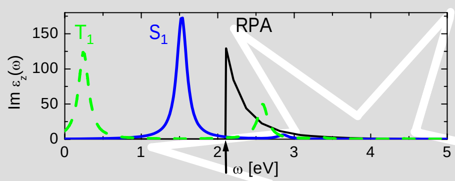
R. Laskowski, N. E. Christensen, G. Santi, and CAD , Phys. Rev. B 72, 035204 (2005).

GaN

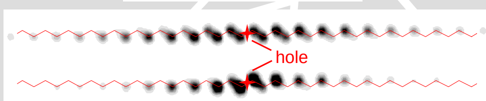
Organic semiconductors

- Localized states in real space
- Higher exciton binding energies
  values up to 1 eV
- Huge BSE matrices due to big unit cells
  order of magnitude: 100 atoms

Computational Effort

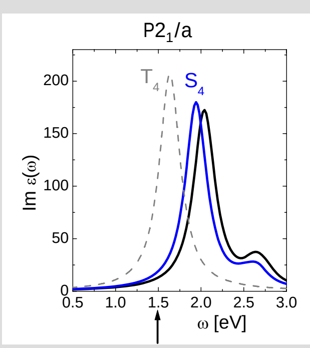


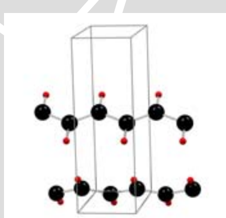
$$\Phi^\lambda(\mathbf{r}_e,\mathbf{r}_h)=\sum_{vc\mathbf{k}} A^\lambda_{vc\mathbf{k}}\psi^*_{v\mathbf{k}}(\mathbf{r}_h)\psi_{c\mathbf{k}}(\mathbf{r}_e)$$



P. Puschnig, PhD Thesis, University Graz, 2002.

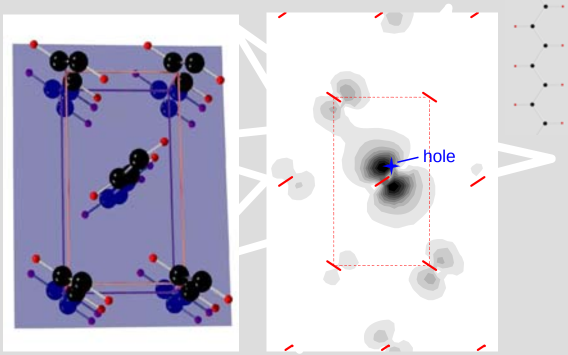
Solving BSE: 1D Polyacetylene





P. Puschnig and C. Ambrosch-Draxl, Phys. Rev. Lett. 89, 056405 (2002).

Solving BSE: 3D Polyacetylene



Exciton Wavefunction: $(CH)_x$

MBPT:

- Mixing of concepts
- GW & BSE determined by 4 point functions
- Computationally very demanding

TDDFT:

- Keep the spirit of DFT
- TDDFT involves 2 point functions only
- Computationally less costly
- TDDFT more generally applicable than GW / BSE: applications in the linear-response regime & beyond (e.g. strong laser fields)

G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002).

MBPT versus TDDFT

Fundamentals of DFT:

- The electron density is the fundamental quantity.
- The density determines the potential up to a constant.
- The potential determines the Hamiltonian.
- The Hamiltonian determines the wavefunction.
- Every observable is a functional of the density.
- Replace the system of interacting electrons by a fictitious system of non-interacting electrons with the same density

(TD)-DFT

Runge-Gross theorem:

Consider N electrons in a time-dependent external potential. Densities ρ and ρ' evolving from a common initial state under the influence of two potentials V and V' (both Taylor expandable about the initial time t_0) are always different provided that the potentials differ by more than a purely time-dependent function:

$$V(\mathbf{r},t) \neq V'(\mathbf{r},t) + c(t)$$

Thus there is a one-to-one mapping between densities and potentials.

$$V(\mathbf{r},t) \longleftrightarrow \rho(\mathbf{r},t)$$

E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

TDDFT Basics

TD Kohn-Sham equation:

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

$$V_{eff}[\rho](\mathbf{r},t) = V_{ext}(\mathbf{r},t) + \int d\mathbf{r}'\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + V_{xc}[\rho](\mathbf{r},t)$$

$$\rho(\mathbf{r},t) = \sum_j |\phi_j(\mathbf{r},t)|^2$$

TDDFT Basics

DFT:	TDDFT:
Hohenberg-Kohn theorem	Runge-Gross theorem
Kohn-Sham system	TD-Kohn-Sham system
Kohn-Sham equation	TD Kohn-Sham equation
Density	Response function
Approximate xc-potential	Approximate xc-kernel

$$f_{xc}(\mathbf{r},t;\mathbf{r}',t') = \frac{\delta V_{xc}[\rho](\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')}\Big|_{\rho=\rho_0}$$

Use same level of approximation!

(TD)-DFT

TDDFT in Linear-Response Regime

$$V_{ext}(\mathbf{r},t) = V_0(\mathbf{r}) + V_1(\mathbf{r},t)\Theta(t-t_0)$$

$$\rho(\mathbf{r},t) = \rho_0(\mathbf{r}) + \rho_1(\mathbf{r},t) + \dots$$

First-order density response:

$$\rho_1(\mathbf{r},t) = \int dt' \int d\mathbf{r}'\, \chi(\mathbf{r},t;\mathbf{r}',t')V_1(\mathbf{r}',t')$$

Response function:

$$\chi(\mathbf{r},t;\mathbf{r}',t') = \frac{\delta\rho(\mathbf{r},t)[V_{ext}]}{\delta V_{ext}(\mathbf{r}',t')}\Big|_{V_0}$$

TDDFT in Linear-Response Regime

Kohn-Sham response function:

$$\chi_0(\mathbf{r},t;\mathbf{r}',t') = \frac{\delta\rho(\mathbf{r},t)[V_{eff}]}{\delta V_{eff}(\mathbf{r}',t')}\Big|_{V_{eff}[\rho_0]}$$

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{i,j}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}$$

$$\chi = \chi_0 + \chi_0\,[\,V_C + f_{xc}\,]\,\chi$$

$$f_{xc}(\mathbf{r},t;\mathbf{r}',t') = \frac{\delta V_{xc}[\rho](\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')}\Big|_{\rho=\rho_0}$$

TDDFT: xc Kernels

$$f_{xc}(\mathbf{r},t;\mathbf{r}',t') = \frac{\delta V_{xc}[\rho](\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')}\Big|_{\rho=\rho_0}$$

- Universal!
- Contains all manybody effects
- Replaces GW & BSE

TDDFT:

- TD-LDA
- TD-EXX
- .....

DFT:

- LDA
- EXX
- .....

Thank you for your attention!