ABSORPTION SPECTRA FROM TDDFT: DO HYBRID FUNCTIONALS ACCOUNT FOR EXCITONIC EFFECTS?

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MOTIVATION

- Accurate calculation of optical absorption and electron energy loss spectra of extended systems
- Still a challenging task in solid state theory
- Hybrid functionals yield truly impressive band gaps
- Do hybrid functionals improve the description of the optical absorption spectra and related properties?
- Time-dependent HSE approach
OVERVIEW

- Limitations of ab initio methods
- Introduction of hybrid functionals
- Assessment of hybrid functionals
- Theoretical approaches for calculating excitation spectra:
  - MBPT ($GW$ and the Bethe-Salpeter equation)
  - TD-DFT
  - TD-HSE
- TD-HSE results for Si, GaAs, C, SiC, and LiF
  - Absorption spectra
  - Static dielectric constants
AB INITIO MODELING

- **Density functional theory (DFT)**
  - Ground state properties with good precision
  - KS-DFT is highly efficient (up to 1000 atoms possible)

- **Limitations stemming from (semi)-local density functionals LDA & GGA:**
  - Thermochemistry: up to 1 eV error
  - Structural properties: 2-3% error
  - Elastic constants: 10%
  - Strongly correlated systems (transition metal oxides)
  - Van der Waals bonding missing
  - Band gap problem
  - Description of electronic excitations
THE BAND GAP PROBLEM

- When the Kohn-Sham (KS) eigenvalue differences are interpreted as excitation energies
- The band gap is a well defined ground state property \underline{wrong using local and semi-local DFT}
- Fundamental gap

\[ E_g = (E[N+1] - E[N]) - (E[N] - E[N-1]) \]
\[ = -A + I \]
\[ = E_{CBMIN}[N] - E_{VBMAX}[N] \ldots \text{in LDA/GGA} \]

\underline{Large errors in LDA/GGA/HF}

- Lack of Integer-discontinuity in the LDA/GGA/HF
ALTERNATIVES

- Quantum Monte Carlo
- Post-Hatree-Fock methods (MP2, CI, CC)
- Many-body perturbation theory
  - $GW$ approximation
  - Bethe-Salpeter Equation (BSE)
- Time-dependent density functional theory
- Hybrid density functionals
  - Have been very successful in quantum chemistry for small molecules
  - E.g., polarizability and magnetic properties (NMR, etc.)
HYBRID FUNCTIONALS

- Characterized by the admixture of a certain amount of nonlocal Fock exchange energy to a part of (semi)local density functional exchange energy.

- Two groups:
  - PBE-based
  - B3-based

PERDEW-BURKE-ERNZERHOF HYBRID: PBE₀\textsuperscript{[1,2]}

- Fraction of $\frac{1}{4}$ non-local Fock exchange rationalized by the adiabatic connection theorem\textsuperscript{[3]}.
- Remainder of $\frac{3}{4}$ is PBE exchange.
- PBE correlation is straightforwardly added.

\[
E_{xc}^\text{PBE₀} = \frac{1}{4}E_x^\text{HF} + \frac{3}{4}E_x^\text{PBE} + E_c^\text{PBE}
\]

**Heyd-Scuseria-Ernzerhof Hybrid: HSE**$$^{[1,2]}$$

$$E_{xc}^{HSE} = \frac{1}{4}E_{x}^{HF,SR}(\mu) + \frac{3}{4}E_{x}^{PBE,SR}(\mu) + E_{x}^{PBE,LR}(\mu) + E_{c}^{PBE}$$

**Screened Coulomb –kernel (μ= range separation)**

$$\frac{1}{r} = S_{\mu}(r) + L_{\mu}(r) = \frac{\text{erfc}(\mu r)}{r} + \frac{\text{erf}(\mu r)}{r}$$

where $$r = |r - r'|$$

Screened Coulomb kernel accelerates the convergence of two-electron integrals!
Favorite hybrid functional in quantum chemistry.
A three parameter functional – fitted to atomization energies, ionizaton potentials, proton affinities of the G2 test set of molecules.
Does not fulfill the uniform electron gas limit (failure of the LYP-correlation energy functional).

Agreement between PAW and GTO calc. for both, PBE and PBE0 is excellent: difference < 1.5 kcal/mol.

Compared to EXPT.: PBE: MAE = 8.6 kcal/mol PBE0: MAE = 3.7 kcal/mol

ASSESSMENTS HYBRIDS: ATOMIZATION ENERGIES OF SOLIDS\textsuperscript{[1,2]}

- PBE outperforms HF/DFT hybrid functionals!
- MARE of 3.4\% (PBE) compared to 7.4\% (PBE0), 6.3\% (HSE), and 17.6\% (B3LYP).

ATOMIC ENERGY OF SOLIDS

Increasing band gaps

HF exchange causes an overestimation of the exchange splitting in d elements. 
increase in spin-polarization energy
underestimation of the atomization energy
Increasing itinerant character

B3LYP performs badly for all metals

- 2/3 are related to the LYP correlation energy
- 1/3 due to the choice of the three parameters
ASSESSMENTS HYBRIDS: LATTICE CONSTANTS\[1\]

- Overall agreement between PBE and experiment is satisfactory
- PBE0 and HSE significantly improve upon PBE
- B3LYP performs equally well as PBE, except for d metals

ASSESSMENTS HYBRIDS: BULK MODULI

- Very sensitive to the calculated equilibrium volume
- Underestimation of bulk moduli due to overestimation of the lattice constants.
- Best description by PBE0 closely followed by HSE

### ASSESSMENTS HYBRIDS: TMOs\textsuperscript{[1]}

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>HSE</th>
<th>B3LYP</th>
<th>EXPT.</th>
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<tr>
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- Hybrids substantially improve upon LDA
- HSE latt. const. and local spin mag. moments are excellent
- CoO: much too small $M_s$ due to neglect of SOC (no contribution from the orbital moment)

ASSESSMENTS HYBRIDS: BAND GAPS$^{[1,2]}$

- Usual underestimation by PBE
- PBE0 and HSE yield improved band gaps
- HSE performs best for small- to medium-gap systems
- In large-gap systems (weak dielectric screening) 25% of HF exchange is not enough!

ASSESSMENTS HYBRIDS: CONCLUSIONS

- **HSE:**
  - Lattice constants & bulk moduli are clearly improved for insulators and semiconductors.
  - Band gaps are excellent for wide range of semiconductors, except for very large gap systems.
  - Transition metals are problematic, at least in terms of bulk moduli.
  - Atomization energies not improved compared to PBE.

- **B3LYP:**
  - The structural properties are slightly worse than PBE.
  - Atomization energies extremely poor for metals (HEG limit not fulfilled!)
MANY-BODY PERTURBATION TECHNIQUES\cite{1}

- **Hedin's equations:**

\[ \Sigma(1,2) = i \int G(1,3) \Gamma(3,2;4) W(4,1) d(3,4) \]

\[ W(1,2) = v(1,2) + \int v(1,3) P(3,4) W(4,2) d(3,4) \]

\[ \chi(1,2) = -i \int G(1,3) G(4,1) \Gamma(3,4;2) d(3,4) \]

\[ \Gamma(1,2;3) = \delta(1,2) \delta(1,3) + \int \frac{\delta \Sigma(1,2)}{\delta G(3)} G(4,5) G(7,5) \Gamma(6,7;3) d(4,5;6,7) \]

- **Dyson equation: Links \( G \) and \( \Sigma \)**

\[ G(1,2) = G_0(1,2) + \int G_0(1,3) \Sigma(4,3) G(4,2) d(3,4) \]

Interacting Green's function

motion of free electrons in the electro-static Hartree potential

MANY-BODY PERTURBATION TECHNIQUES[1]

- Hedin‘s equations together with the Dyson‘s equation form a set that in principles must be solved self-consistently for $G$.
- Can be omitted in $GW$ approximation: $G_0 W_0$ and $GW_0$ calculations.

- $GW$ approximation:
  $$\Sigma(1,2) = iG(1,3)W(3,1)$$
  $$W(1,2) = v(1,2) + \int v(1,3) P(3,4) W(4,2) d(3,4)$$
  $$\chi(1,2) = -iG(1,2)G(2,1^+)$$
  $$\Gamma(1,2;3) = \delta(1,2) \delta(1,3)$$

**The $GW$ Approximation**[^1]

- Vertex corrections are neglected
- Simple expression for the self-energy $\Sigma$, that allows to calculate the interacting Green's function $G$ from an independent-particle system $G_0$.
- Extends the Hartree-Fock approximation by replacing the bare Coulomb $v$ potential by the dynamically screened one $W$.

$$\Sigma_x = iGv \quad \rightarrow \quad \Sigma_{GW} = iGW$$

- Static approximation of the $GW$ self-energy: COHSEX
  - Coulomb hole term (local): $\frac{1}{2}v(\varepsilon^{-1}-1)$
  - Screened exchange term: $W(r,r') = \varepsilon^{-1}v$

**GW HISTORY AND CHALLENGES:**

- GW is a rather “old” method but computationally very demanding

- **Foundation of GW:**
  L. Hedin, Phys. Rev. 139, A796 (1965)

- **First Pseudopotential GW using LDA wavefunctions**
  + 1st order perturbation theory using GW
  \[ G = G_{LDA}, \quad W = \epsilon_{LDA} v \]
  M. S. Hybertsen, S. G. Louie, Phys. Rev. B 34, 5390 (1986), Sham and Schlüter

- **Efficient implementations using pseudo-potentials**

- **Full potential (all electron) + self-consistency**

- **Excitons taken into account for construction of W**
ONE-ELECTRON THEORIES

- **Density functional theory**

\[
\left(-\frac{\hbar^2}{2m_e} \Delta + V^{\text{ion}}(r) + V^{\text{el}}(r) + V^{\text{xc}}(r) \right) \varphi_n(r) = E_n \varphi_n(r)
\]

- **Hartree Fock theory**

\[
\left(-\frac{\hbar^2}{2m_e} \Delta + V^{\text{ion}}(r) + V^{\text{el}}(r) \right) \varphi_n(r) + \int V^{x}(r,r') \varphi_n(r') d^3r' = E_n \varphi_n(r)
\]

- **GW**

\[
\left(-\frac{\hbar^2}{2m_e} \Delta + V^{\text{ion}}(r) + V^{\text{el}}(r) \right) \varphi_n(r) + \int \Sigma^{xc}(r,r',\omega) \varphi_n(r') d^3r' d\omega = E_n \varphi_n(r)
\]
**GW ESSENTIALS**

- **Hartree-Fock**: bare nonlocal Fock exchange

\[ V^x(r, r') = \sum_{occ} \varphi_m(r) \varphi_m^*(r') \times -\frac{e^2}{|r - r'|} \]

- **GW**: replace bare \( 1/|r-r'| \) by dynamically screened Coulomb operator

\[ \Sigma^x(r, r', E) = \int_{-\infty}^{\infty} d\omega \sum_{all} \frac{\varphi_m(r) \varphi_m(r')}{\omega - E - E_m + i\delta \text{sgn}\left[ E_m - E_{\text{Fermi}} \right]} \times \]

\[ \mathcal{G} \]

\[ \mathcal{W} \]

\[ \mathcal{I} - e^2 \int dr'' \frac{\mathcal{F}^{-1}(r, r'', \omega)}{|r'' - r'|} \]
THE GW APPROXIMATION APPLIED

\( G_0 W_0 \) calculations:

- Start with KS-LDA/GGA wavefunctions and eigenvalues to construct \( G_0 \)
- Determine \( \chi^0, \varepsilon^{-1} \) within RPA and \( W_0 \)
- Calculate \( \Sigma_{GW} = i G_0 W_0 \)
- Determine the first-order change of energies, i.e., quasi-particle energies
  \[
  \langle \varphi_n | -\frac{\hbar^2}{m_e} \Delta + V_{\text{ion}} + V_{\text{el}} + \Sigma_{xc}(E_n) | \varphi_n \rangle = E_n
  \]

\( GW_0 \) calculations: partial self-consistency in \( G \):

\[
G(r, r') = \sum_m \frac{\varphi_m(r) \varphi_m(r')}{\omega - E - E_m + i\delta \text{ sgn} [ E_m - E_{\text{Fermi}} ]}
\]

\( W_0 \) is kept fixed!

Self-consistent \( GW \) calculations:

Inclusion of electron-hole (e-h) attraction by to \( \delta \Sigma / \delta G \)
COMPARISON HSE AND $GW$: BAND GAPS$^{[1,2]}$

- $G_0W_0$ gaps are larger than PBE ones, but consistently underestimated compared to EXPT.
- $GW_0$ further increases the gaps (roughly 7%)
- Throughout the series more accurate gaps than HSE
  - $G_0W_0$ MARE: 8.5%
  - $GW_0$ MARE: 4.5%
  - HSE MARE: 21%

Why is this not good enough?

- Screening properties are calculated using density functional theory
  - In some cases DFT is utterly wrong

\[
\text{ZnO: } \varepsilon_{\text{DFT}} \approx 5.2 \quad \quad \quad \varepsilon_{\text{EXP}} \approx 3.5
\]

- Wavefunctions are from density functional theory
  - DFT always yields too weak localization due to Coulomb selfinteraction (electrons experience their own electrostatic potential)
  - Not able to predict localization versus dislocalization
  - Much too shallow d states in ZnO and GaAs with wrong hybridization between d states and conduction band electrons
SELF-CONSISTENT QPGW BAND GAPS\textsuperscript{[1,2]}

- scQPGW (no e-h): Significant overestimation
- Much worse than $GW_0$
- Static dielectric constants are now 20% too small
- Inclusion of vertex corrections (electron-hole interaction) in $W$ required

SELF-CONSISTENT \( \text{QPGW}^{\text{TC-TC}} \) BAND GAPS\textsuperscript{[1,2]}

- \( \text{scQPGW} \) (with e-h): excellent results across all materials
  - MARE: 3.5%
- Further slight improvement over \( GW_0 \)
- Too expensive for large scale applications, but fundamentally important

OPTICAL PROPERTIES OF SOLIDS

- **Linear Response Theory**[1,2]:
  - Field strength of the incident radiation is weak
  - The induced polarization is linearly dependent on the electric field
  - Linear response functions $\chi(\omega)$ and $\varepsilon(\omega)$ describe the linear responses of a medium to an external field

DIELECTRIC MATRIX

- Random phase approximation (RPA)$^{[1]}$:
  - electrons and holes move independently in a self-consistent potential: $V_{tot}(r,t) = V_{ext}(r,t) + V_{ind}(r,t)$
  - Exchange and correlation effects on the response are neglected
  - Polarizability $\chi_0$ directly yields the dielectric matrix $\varepsilon$:
    \[
    V_{tot}(r) = \int dr' \varepsilon^{-1}(r, r') V_{ext}(r') \\
    \varepsilon_{RPA} = 1 - v\chi_0
    \]

- Dielectric response within DFT$^{[2]}$:
  \[
  V_{tot} = V_{ext} + V_{ind} + V_{XC} \\
  \varepsilon_{LDA} = 1 - v\chi_0(1 - f_{XC}\chi_0)^{-1}
  \]

DIELECTRIC MATRIX

- Irreducible polarizability matrix:
  \[ \chi^0_{G,G'}(q, \omega) = \frac{1}{\Omega} \sum_{n,n',k} 2w_k (f_{n',k+q} - f_{n,k}) \times \frac{\langle \psi_{n',k+q} | e^{i(q+G)r} | \psi_{n,k} \rangle \langle \psi_{n',k} e^{-i(q+G')r} | \psi_{n',k+q} \rangle}{E_{n',k+q} - E_{n,k} - \omega - i\eta} \]

- Microscopic dielectric matrix:
  \[ \varepsilon_{G,G'}(q, \omega) = \delta_{G,G'} - \frac{4\pi e^2}{|G+q||G'+q|} \chi^0_{G,G'}(q, \omega) \]

- Macroscopic dielectric matrix:
  \[ \varepsilon_{\infty}(q, \omega) = \lim_{q \to 0} \frac{1}{\varepsilon^{-1}_{00}(q, \omega)} \]

A) Calculation of the irreducible polarizability in RPA
B) Calculation of the microscopic DM
C) Inversion of the microscopic DM

LOCAL FIELD EFFECTS (LFE)\(^{[1,2]}\)

- The system is non-homogeneous on the microscopic scale (the total perturbing potential \(V_{tot}(r,t)\) varies, since \(V_{ind}(r,t)\) varies on the atomic scale)

- Thus: the microscopic DM is not diagonal in reciprocal space (depends explicitly on \(r\) and \(r'\), and not simply on |\(r-r'|\):

\[
\varepsilon_{G,G'}(q, \omega) = \delta_{G,G'} - v(q+G') \chi_{G,G'}^0(q, \omega)
\]

- Neglecting the LFE (\(G=G'=0\) component of \(\chi\) only):

\[
\varepsilon_{\infty}(q, \omega) = \lim_{q \to 0} \varepsilon_{G=0,G'=0}(q, \omega)
\]

No matrix inversion required!

BEYOND THE RPA:

- So far: Interaction between electrons (and holes) are lacking!
- Going beyond RPA allows for the inclusion of the electron-hole (e-h) interaction
  - Many-body perturbation techniques, in particular $GW$ in combination with the Bethe-Salpeter equation (BSE)
  - Time-dependent density functional theory (TD-DFT)
  - TD-HSE approach?

09/13/08
Absorption spectra from TDDFT-HSE
OPTICAL PROPERTIES IN MBPT: BSE[1]

- Green's function theory to study two-particle excited states (e-h pairs)
- Key quantity is the polarizability $\chi$, where the vertex corrections $\Gamma$ (e-h attraction) is included
- BSE for the polarizability $\chi$:

$$\chi = \chi_0 + \chi_0 K \chi$$

with

$$K(1,2;3,4) = \delta(1,2)\delta(3,4)\nu(1,3) - \delta(1,3)\delta(2,4)W(1,2)$$

THE BETHE-SALPETER EQUATION[1]

- Four-point kernel
- Effective two-particle equation with an effective two-particle hamiltonian with an effective potential having
  - local contributions that depend on the density
  - non-local contributions that are directly proportional to the density matrix $\rho(r,r',t)$
- BSE diagramm:

TIME-DEPENDENT DFT

- Evolution of the system under influence of a time-dependent external potential
- Runge-Gross Theorem\textsuperscript{[1]}: one-one mapping between time-dependent densities and the external potentials
- Time-dependent Kohn-Sham equations\textsuperscript{[2]}:

\[
\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(r,t)\right] \psi_i(r,t) = i \frac{\partial}{\partial t} \psi_i(r,t)
\]

\[
\rho(r,t) = \sum_{i=1}^{N} |\psi_i(r,t)|^2
\]

\[
V_{\text{eff}}(r,t) = V_H(r,t) + V_{XC}(r,t) + V_{\text{ext}}(r,t)
\]

All many-body effects are included in the time-dependent local exchange-correlation potential $V_{XC}(r,t)$

Excitation energies in TD-DFT[1]

- Dyson-like equation for the linear density response $\chi$ of an interacting many-electron system in terms of the non-interacting KS response $\chi_0$

- Only local potentials!
  Allows to work with two-point functions.

$$\chi(r,t; r', t') = \frac{\delta \rho(r, t)}{\delta V_{\text{ext}}(r', t')} |_{V_{\text{ext}} = 0} \quad \chi_0(r, t; r', t') = \frac{\delta \rho(r, t)}{\delta V_{\text{eff}}(r', t')} |_{V_{\text{eff}} = 0}$$

$$\chi(r, r' \omega) = \chi_0(r, r' \omega) + \int dr_1 dr_2 \chi_0(r, r_1, \omega) K(r_1, r_2, \omega) \chi_0(r_2, r', \omega)$$

$$K(r_1, r_2, \omega) = \frac{1}{|r_1 - r_2|} + f_{\text{XC}}(r_1, r_2, \omega)$$

ANALOGIES BETWEEN BSE & TD-DFT$^1$

\[ S = S_0 + S_0 KS \]

**BSE: four-point quantities**

- \( S = \) two-particle correlation function \( L \)
- \( S_0 = L_0 \) (indep. quasi-particle response)
- \( K = \nu + F^{BSE} \)
  
  \[ F^{\text{BSE}}_{(n_1 n_2)(n_3 n_4)} = -\int drdr' \psi_{n_1}(r) \psi_{n_3}^\dagger(r) \times W(r',r) \psi_{n_2}(r') \psi_{n_4}(r') \]

**TD-DFT: two-point quantities**

- \( S = \) two-point polarizability \( \chi \)
  
  \[ \varepsilon^{-1} = 1 + \nu \chi \]
- \( S_0 = \chi \) (indep. particle response)
- \( K = \nu + F^{TD-DFT} \)
  
  \[ F^{\text{TD-DFT}}_{(n_1 n_2)(n_3 n_4)} = \int drdr' \psi_{n_1}(r) \psi_{n_2}^\dagger(r) \times f_{XC}(r,r') \psi_{n_3}^\dagger(r') \psi_{n_4}(r') \]

HOW TO SOLVE THE DYSON EQUATION \cite{1,2}

- Basis transformation from space to orbital space: $r \rightarrow \psi_{n,k}(r)$ \textit{i.e.}, a basis of pairs of occupied and empty states

- Dyson equ. can be transformed to an effective two-particle Hamiltonian equation:

$$H^{2p}_{(n_1n_2)(n_3n_4)} = (E_{n_2} - E_{n_1}) \delta_{n_1n_3} \delta_{n_2n_4} + (f_{n_1} - f_{n_2}) K_{(n_1n_2)(n_3n_4)}$$

$$S_{(n_1n_2)(n_3n_4)} = \left[H^{2p} - I\omega\right]^{-1}_{(n_1n_2)(n_3n_4)} (f_{n_4} - f_{n_3})$$

OPTICAL SPECTRA FROM TD-DFT\textsuperscript{[1-4]}

- Including excitonic effects
- Without solving the BSE
- Response function: \[ \chi = \chi_c (\chi_c - \chi_v \chi_f - \chi_r)^{-1} \chi. \]

For vertical transitions \( \nu k \) to \( c k \) \((t=\{\nu c k\})\):

\[ T_{GG}(\omega) = \frac{1}{N_k} \sum_t \frac{\Phi^i(t;G) \Phi(t;G')}{(E_{ck}^{\text{KS}} - E_{vk}^{\text{KS}} - \omega)^2} \left[ \Delta E_{ck}^{GW} - \Delta E_{vk}^{GW} \right] + \frac{1}{N_k^2} \sum_{tt'} \frac{\Phi^i(t;G)}{E_{ck}^{\text{KS}} - E_{vk}^{\text{KS}} - \omega} F_{tt'}^{\text{BSE}} \frac{\Phi(t';G')}{E_{c'k'}^{\text{KS}} - E_{v'k'}^{\text{KS}} - \omega} \]

\[ T_1 \quad + \quad T_2 \]

OPTICAL SPECTRA FROM TD-DFT$^{[1-4]}$

- **$T$-matrix:**

\[
T_{GG'}(\omega) = \frac{2}{N_k} \sum_t \frac{\Phi^i(t;G) \Phi(t;G')}{(E_{ck}^{KS} - E_{vk}^{KS} - \omega)^2} \left[ \Delta E_{ck}^{GW} - \Delta E_{vk}^{GW} \right] + \frac{2}{N_k^2} \sum_{tt'} \frac{\Phi^i(t;G)}{E_{ck}^{KS} - E_{vk}^{KS} - \omega} F_{tt'}^{BSE} \frac{\Phi(t';G')}{E_{c'k'}^{KS} - E_{v'k'}^{KS} - \omega}
\]

- **Contribution $T_1$** acts as an effective self-energy shift

- **$T_2$** contains the e-h contribution by the screened Coulomb interaction $W(r,r')$:

\[
F_{tt'}^{BSE} = - \int drdr' \Phi(vk,v'k';r) W(r',r) \Phi^i(ck,c'k';r')
\]

- **Inclusion of whole $T$ yields spectra identical to BSE results$^{[3]}$**

THE TD-HSE APPROACH\cite{1}

- Effective XC kernel from the frequency-dependent non-local exchange term $f_{x-nl}$
- Similar $T$-matrix: $T = \chi_0 f_{X-nl} \chi_0$
- The $T(r', r)$-matrix captures the following process:
  - Change of the external potential at $r$
  - Linear response of orbitals
  - Change of the non-local exchange potential
  - Linear response of orbitals and resultant charge density change at $r'$
- Hartree potential and the local XC potential are accounted for by:
  $\chi_0 (\nu + f_{XC-l}) \chi_0$

\[ f_{XC-l} = \delta(r-r') \frac{\delta^2 E_{XC-l}[n(r)]}{\delta n(r) \delta n(r')} \]

THE TD-HSE APPROACH APPLIED\textsuperscript{[1]}

- Neglect frequency dependence of $f_{X-nl}$ and determine it only once at zero frequency
- Two-electron terms related to the coupling between resonant and antiresonant parts of the $T$-matrix are included
- Occupied and empty one-electron states are calculated using the HSE functional
- \textbf{Screened} Coulomb interaction $W(r,r')$ as in BSE is replaced by $\frac{1}{4}$ of the non-local exchange term

\textbf{THUS:} excitonic effects can and should be approximately captured by hybrid functionals!

OPTICAL ABSORPTION: BULK SILICON[1]

LDA: independent

HSE: independent

\[ \varepsilon_{RPA}^{-1} = 1 + \nu \chi_0 \]

Band gap opens in the case of HSE;
Similar to a scissors-corrected DFT approach!

Inclusion of the many-body effects via $f_{X-nl}$ causes a red-shift of the spectrum and a pronounced increase of the cross section at low energies.

TD-HSE improves upon IP-HSE, but fails to describe the first exciton!

Limited interaction range of the HSE functional fails to account for all long-range excitonic effects?

Optical Absorption of Semiconductors\cite{1}

- Reducing the range separation parameter $\mu$ means that exchange is enhanced for small $q$.
- This has the following effects on the spectra:
  - Slight opening of the gap resulting in a blue-shift of the absorption.
  - Increase of the excitonic effects through $f_{X-nl}$.
- Agreement with experiment is satisfactory!

## Static Dielectric Constants[1]

<table>
<thead>
<tr>
<th></th>
<th>LDA $\varepsilon_\infty^{RPA}$</th>
<th>TD-LDA $\varepsilon_\infty$</th>
<th>HSE $\varepsilon_\infty^{RPA}$</th>
<th>TD-HSE $\varepsilon_\infty$</th>
<th>EXPT.</th>
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<tbody>
<tr>
<td>Si</td>
<td>14.1</td>
<td>13.35</td>
<td>10.94</td>
<td>11.31</td>
<td>11.9</td>
</tr>
<tr>
<td>GaAs</td>
<td>14.81</td>
<td>13.98</td>
<td>10.64</td>
<td>10.95</td>
<td>11.1</td>
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<tr>
<td>AlP</td>
<td>9.12</td>
<td>8.30</td>
<td>7.27</td>
<td>7.35</td>
<td>7.54</td>
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<tr>
<td>SiC</td>
<td>7.29</td>
<td>6.96</td>
<td>6.17</td>
<td>6.43</td>
<td>6.52</td>
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<tr>
<td>C</td>
<td>5.94</td>
<td>5.80</td>
<td>5.21</td>
<td>5.56</td>
<td>5.7</td>
</tr>
<tr>
<td>ZnO (c)</td>
<td>5.31</td>
<td>5.15</td>
<td>3.39</td>
<td>3.55</td>
<td>3.78</td>
</tr>
<tr>
<td>ZnO (a)</td>
<td>5.28</td>
<td>5.11</td>
<td>3.35</td>
<td>3.51</td>
<td>3.70</td>
</tr>
<tr>
<td>LiF</td>
<td>2.06</td>
<td>2.02</td>
<td>1.78</td>
<td>1.84</td>
<td>1.9</td>
</tr>
</tbody>
</table>

- **LDA**: overestimates the screening in RPA; **REDUCTION** due to inclusion of two-particle interaction (repulsive action of the Hartree kernel $v$).
- **HSE**: red-shift of the spectra and the increase of intensity at low frequencies causes an **INCREASE** of the static dielectric constant.

CONCLUSIONS TD-HSE

- Dielectric constants remain somewhat too small.
- Average deviation between theory and EXPT. decreases from 10% (LDA) to 3% (TD-HSE).
- Absorption spectra show reasonable agreement with experiment.
- Not as universal as GW/BSE! Works best for medium-gap semiconductors.
- Hybrid functionals are an overall better compromise for semiconductors than purely local functionals.
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Meeting on Optical Response of Extended systems
November 19-21 2008
Vienna, Austria

- **Scope:**
  - Bringing together experimentalists and theoreticians
  - Form a platform for leading experts to discuss and exchange their recent results and scientific concepts

- **Invited speakers:**
  - C. Ambrosch-Draxl
  - F. J. Garcia de Abajo
  - R. Gomez-Abal
  - M. Kociak
  - G. Kresse
  - A. Marini
  - L. Reining
  - A. Rubio
  - P. Schattenschneider
  - W. Sigle
  - J. Verbeeck
  - W. Werner
  - P. Zeppenfeld

- **Registration:**
  - [www.physics.at](http://www.physics.at)

- **deadline:** October 19 2008