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International Centre for Theoretical Physics

United Nations
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2220-13

15th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

13 - 15 January 2011

Berthe-Salpeter equation without empty electronic states applied to charge-transfer excitations

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Solution of the Bethe-Salpeter equation without empty electronic states applied to charge transfer excitations

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Acknowledgments

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- Huy-Viet Nguyen (UC Davis)
- Tuan Anh Pham (UC Davis)
- Giulia Galli (UC Davis)

This work was supported by NSF-CHE-0802907 grant and DOE-BES-FG02-06ER46262 grant.

Outline

- Density matrix formulation of the Bethe-Salpeter equation
- The standard electron-hole representation of density matrices
- Elimination of the empty states
- Calculation of dielectric matrices and GW energy levels
- Practical implementation
- Optical spectra of bulk materials: Silicon and diamond
- Application to a 1nm silicon nanocluster
- Application to charge-transfer excitations
- Preliminary GW results

Density matrix formulation of the Bethe-Salpeter equation

The starting point of our derivation is the Quantum-Liouville equation for the COHSEX density matrix:

$$i\frac{d\hat{\rho}(t)}{dt} = \left[\hat{H}_{COHSEX}(t), \hat{\rho}(t)\right]$$

where the Hamiltonian contains a non-local self-energy:

$$\begin{aligned}\hat{H}_{COHSEX}(t)\phi_i(\mathbf{r},t) &= \left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r},t) + v_{ext}(\mathbf{r},t)\right]\phi_i(\mathbf{r},t) \\ &+ \int \Sigma_{COHSEX}(\mathbf{r},\mathbf{r}',t)\phi_i(\mathbf{r}',t)d\mathbf{r}'\end{aligned}$$

COHSEX=Coulomb Hole (plus) Screened Exchange

See D. Rocca, D. Lu, and G. Galli, J. Chem. Phys. 133, 164109 (2010); D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. 128, 154105 (2008)

Linearization of the Quantum-Liouville equation

For a small external perturbation we have

$$i\frac{d\hat{\rho}'(t)}{dt} = \left[\hat{H}_{COHSEX}, \hat{\rho}'(t)\right] + \left[\hat{\Sigma}'_{COHSEX}[\hat{\rho}'](t), \hat{\rho}_0\right] + \left[\hat{v}'_{ext}(t), \hat{\rho}_0\right]$$

that can be formally written as

$$i\frac{d\hat{\rho}'(t)}{dt} = \mathcal{L}\cdot\hat{\rho}'(t) + \left[\hat{v}'_{ext}(t), \hat{\rho}_0\right]$$

By Fourier analyzing we obtain

$$\boxed{(\omega - \mathcal{L})\cdot\hat{\rho}'(\omega) = [\hat{v}'_{ext}(\omega), \hat{\rho}_0]}$$

The eigenvalues of $\mathcal{L}$ are the EXCITATION ENERGIES of the system.

Electron-hole representation of density matrices

$$\hat{\rho}' = \sum_v \left[|\phi_v\rangle\langle\phi'_v(-\omega)| + |\phi'_v(\omega)\rangle\langle\phi_v| \right]$$

Since ϕ'_v orbitals are orthogonal to the ground-state orbitals ϕ_v, ONLY the elements of $\hat{\rho}'$ between valence and conduction states (and vice versa) are different from zero.

Electron-hole representation:

$$\begin{aligned} P_{vc} &= \langle\phi_v|\hat{\rho}'|\phi_c\rangle \\ P_{cv} &= \langle\phi_c|\hat{\rho}'|\phi_v\rangle \end{aligned}$$

Explicit representation of density matrices and operators: DFPT

$$\hat{\rho}' = \sum_v \left[|\phi_v\rangle\langle\phi'_v(-\omega)| + |\phi'_v(\omega)\rangle\langle\phi_v| \right]$$

Instead of using explicitly the conduction states we use the PROJECTOR onto the conduction state subspace

$$\hat{Q} = 1 - \sum_v |\phi_v\rangle\langle\phi_v|.$$

Density Functional Perturbation Theory representation:

$$\begin{aligned} x_v^x(\mathbf{r}) &= \hat{Q}\hat{\rho}'\phi_v(\mathbf{r}) = \sum_c \phi_c(\mathbf{r}) P_{cv} \\ x_v^y(\mathbf{r}) &= \left(\hat{Q}\hat{\rho}'^{\dagger}\phi_v(\mathbf{r})\right)^* = \sum_c \phi_c^*(\mathbf{r}) P_{vc}. \end{aligned}$$

See Baroni *et al.*, Rev. Mod. Phys. 73, 515 (2001)

Dielectric matrix calculation

In order to solve the BSE we need to compute the screened Coulomb potential:

$$W(\mathbf{r},\mathbf{r}') = \int \epsilon^{-1}(\mathbf{r},\mathbf{r}'')v_c(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''$$

The standard approach to compute ϵ^{-1} requires a SUMMATION OVER EMPTY STATES.
We efficiently compute ϵ^{-1} using an iterative method based on DFPT which DOES NOT require calculations of empty states and allows to obtain the eigenvalue decomposition of ϵ:

$$\widetilde{\epsilon} = \sum_{i=1}^{N} \lambda_i |\mathbf{u}_i\rangle\langle\mathbf{u}_i|.$$

See:

H. F. Wilson, F. Gygi, and G. Galli, Phys. Rev. B 78, 113303 (2008)
H.-V. Nguyen and S. de Gironcoli, Phys. Rev. B 79, 205114 (2009)
D. Rocca, D. Lu, and G. Galli, J. Chem. Phys. 133, 164109 (2010)

Calculation of GW quasi-particle energies

The eigenvalue decomposition of the dielectric matrix

$$\widetilde{\epsilon}(i\omega) = \sum_{i=1}^{N} \lambda_i(i\omega)|\mathbf{u}_i\rangle\langle\mathbf{u}_i|.$$

can be used to express the expectation value of the GW self-energy $\Sigma_{GW} = \Sigma_X + \Sigma_C$ as

$$\langle\Sigma_C(i\omega)\rangle_n = \frac{1}{2\pi}\sum_{i=1}^{N}\int d\omega'(\lambda_i^{-1}(i\omega') - 1) \times\langle\phi_n(v_c^{\frac{1}{2}}\mathbf{u}_i)|(H^0 - i(\omega-\omega'))^{-1}|\phi_n(v_c^{\frac{1}{2}}\mathbf{u}_i)\rangle$$

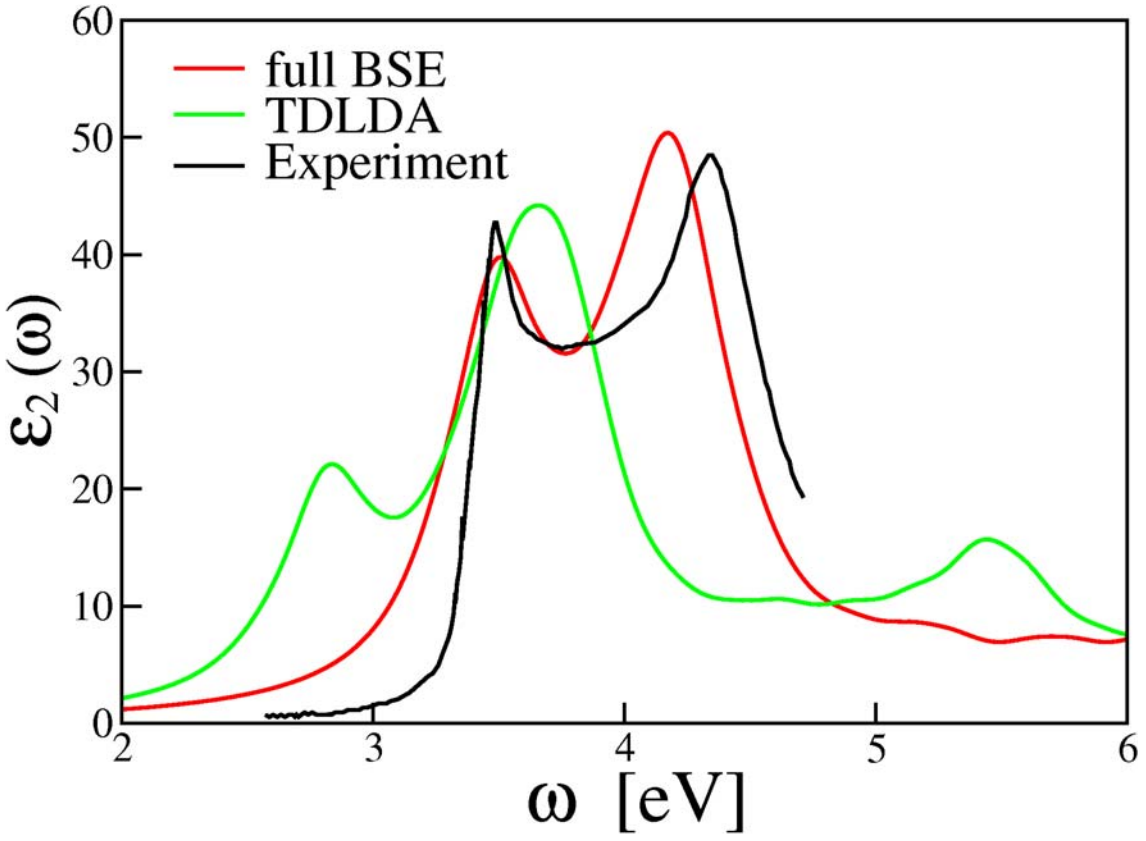
- Real frequency results are obtained through analytic continuation
- The matrix elements can be efficiently computed using the Lanczos algorithm
- NO empty states are explicitly required

Practical implementation

- We compute explicitly the absorption spectra using a generalization of the non-Hermitian Lanczos iterative algorithm. More details in:
  D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. 128, 154105 (2008)
- The new method has been implemented in the QUANTUM ESPRESSO package, which uses a plane-wave basis-set and pseudopotentials
- The current implementation uses a scissor operator: $\hat{H}_{QP} \approx \hat{H}_{KS} + \Delta\, \hat{Q}$
- Work is in progress to introduce GW quasi-particle corrections
- Details in:
  D. Rocca, D. Lu, and G. Galli, J. Chem. Phys. 133, 164109 (2010)

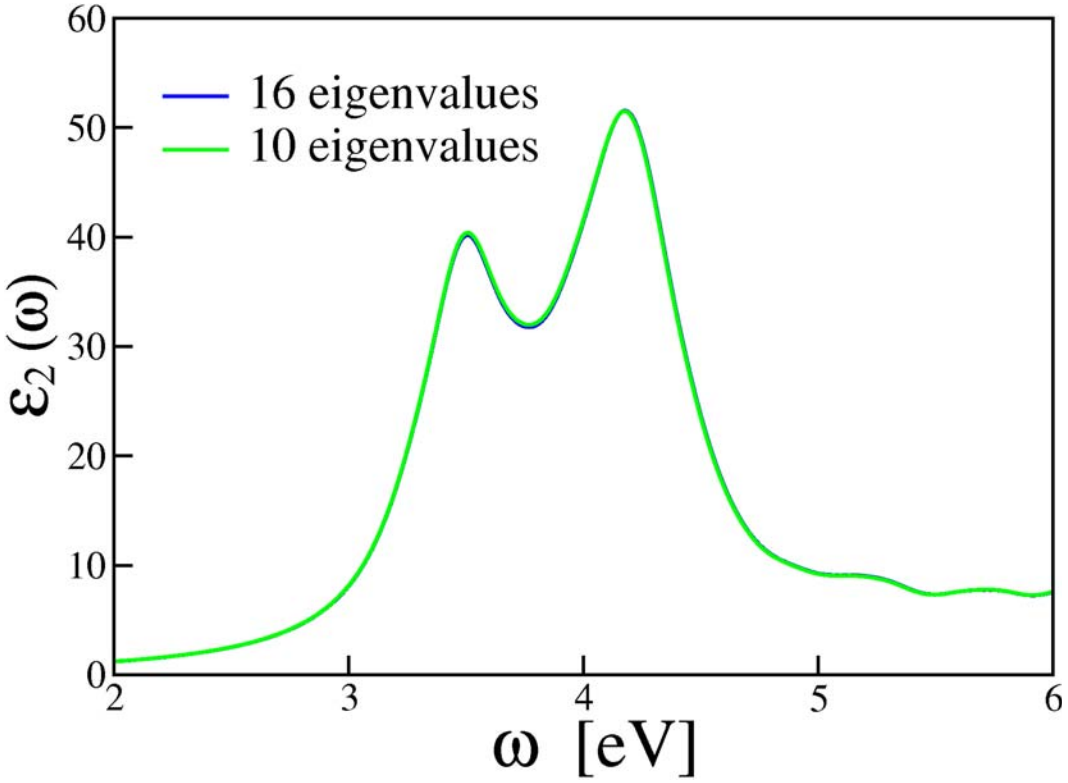
Optical spectra of bulk materials: Silicon

- $8 \times 8 \times 8$ k mesh
- 18 Ry cut-off

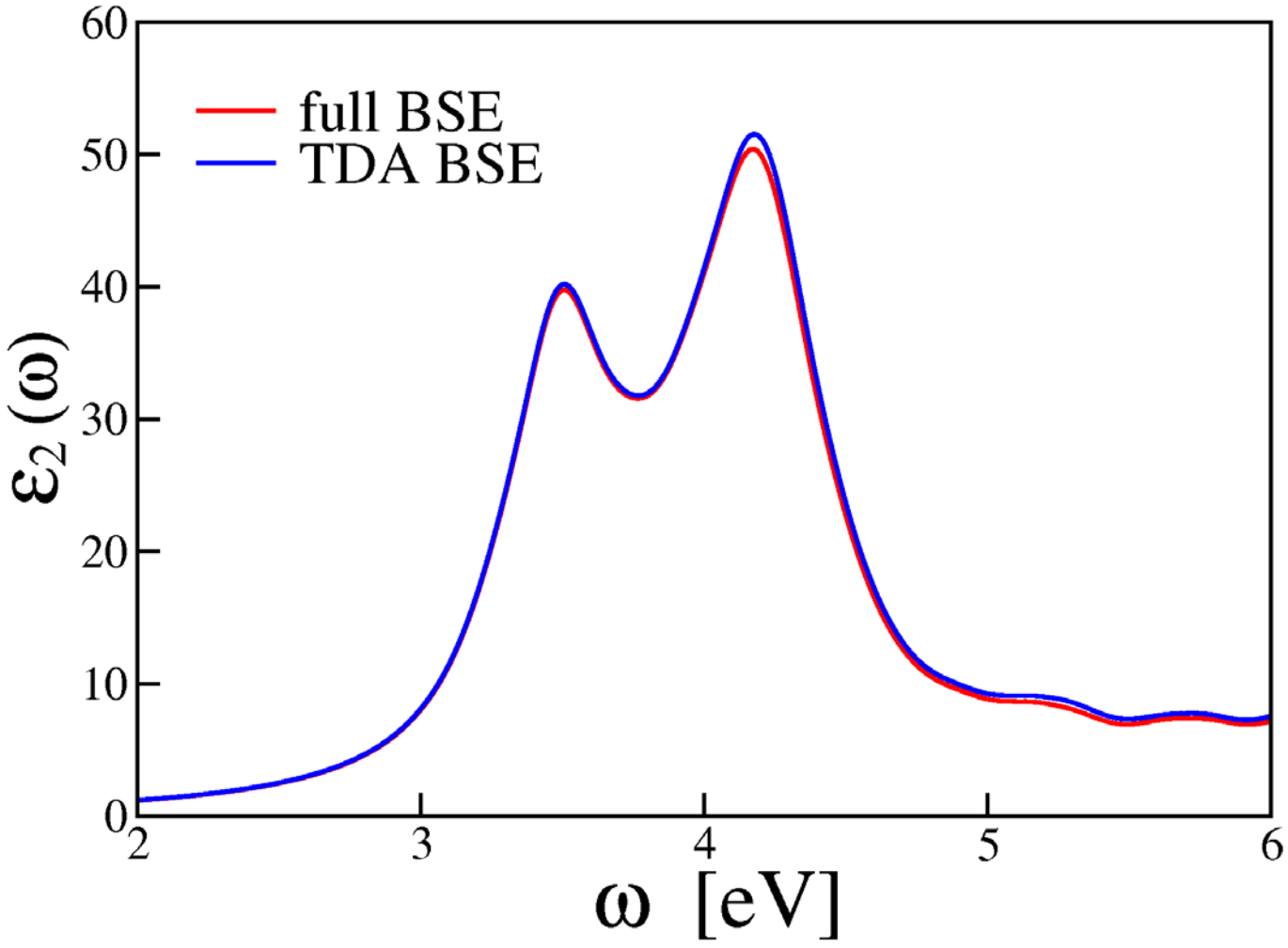


Convergence with respect to the number of eigenvalues in the dielectric matrix

$$\widetilde{\epsilon} = \sum_{i=1}^{N} \lambda_i |\mathbf{u}_i\rangle\langle\mathbf{u}_i|$$

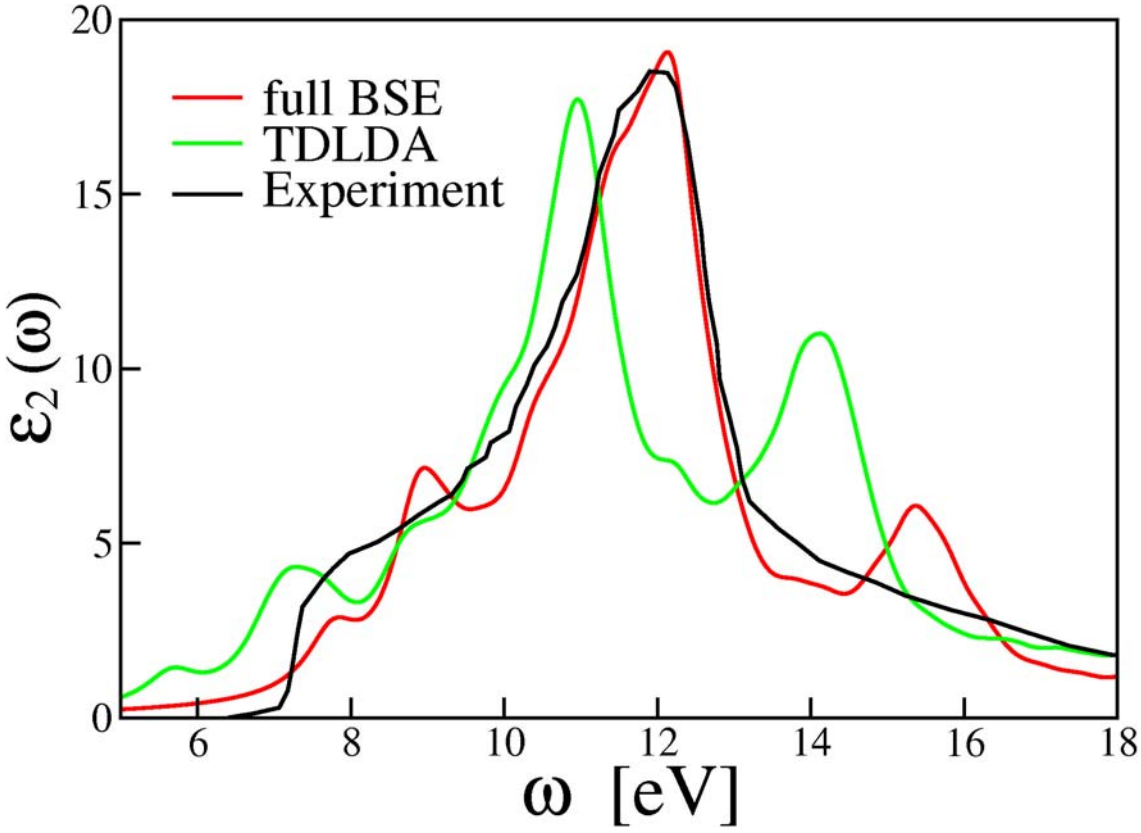


Tamm-Dancoff approximation (TDA)



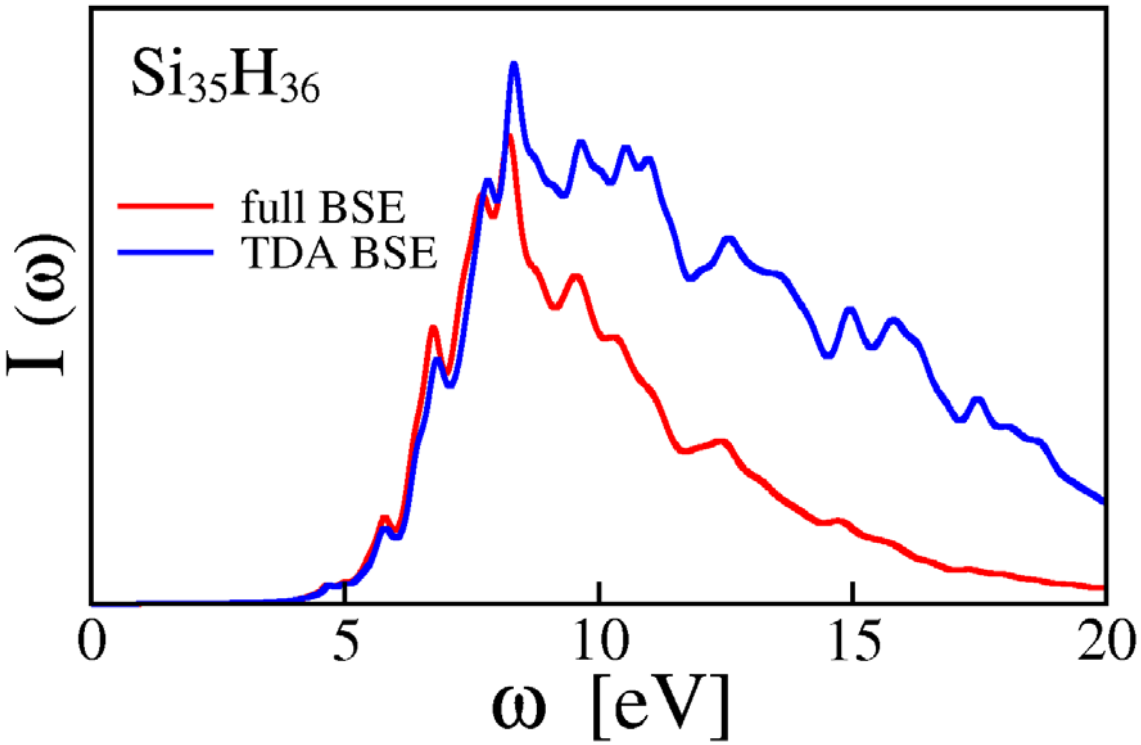
Optical spectra of bulk materials: Diamond

- $8 \times 8 \times 8$ k mesh
- 40 Ry cut-off



A large system application: absorption spectrum of a 1nm silicon nanocluster

- 176 electrons
- $40 \times 40 \times 40$ a_0^3 supercell
- 20 Ry cut-off
- 80 Ry for ϵ

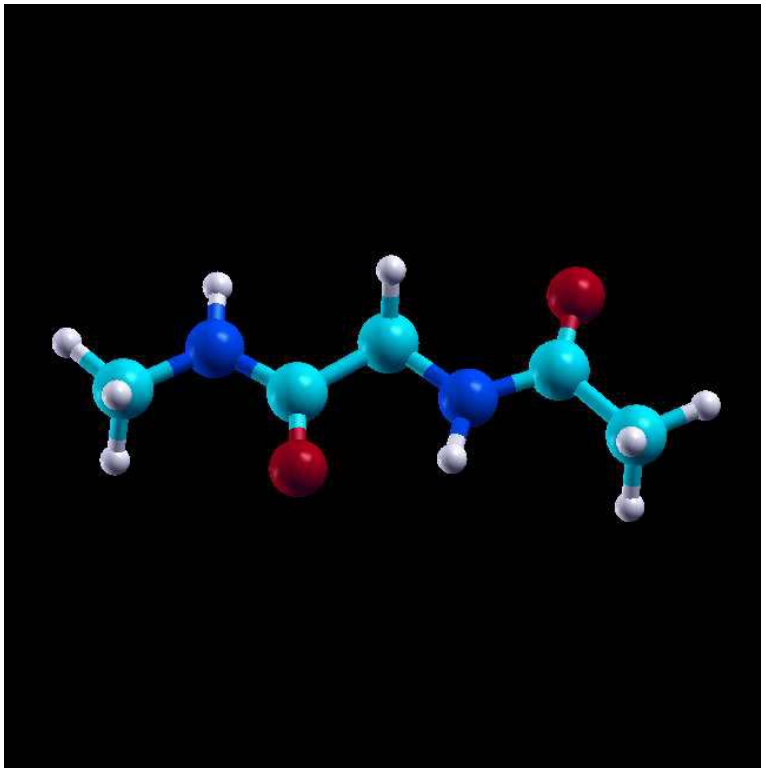


TDA = Tamm-Dancoff approximation (Hermitian approximation)

Charge transfer excitations: Study of a dipeptide model

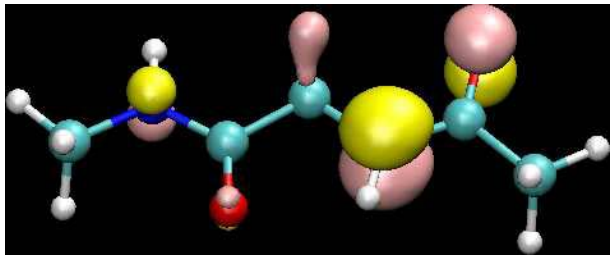
In order to describe charge-transfer excitations:

- Non-local exchange in the kernel is necessary (JCP 119, 2943 (2003))
- A proper description of the screening has to be included (Bethe-Salpeter equation)

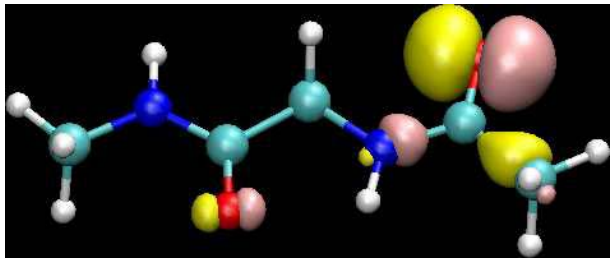


Dipeptide orbitals

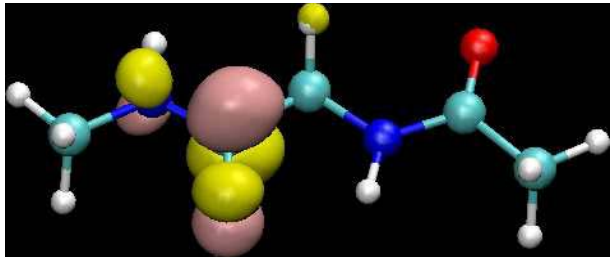
HOMO-1



HOMO



LUMO



Failure of TDLDA to describe charge-transfer excitations

Optical Excitation	TDLDA (TDA)	TDLDA	CASPT2[1]
HOMO $\rightarrow$ LUMO (CT)	4.61	4.61	8.07
HOMO-1 $\rightarrow$ LUMO (CT)	5.16	5.15	7.18
HOMO$\rightarrow$LUMO+2 (L)	5.30	5.30	5.62
HOMO-2$\rightarrow$ LUMO (L)	5.67	5.66	5.79

TDA = Tamm-Dancoff approximation (Hermitian approximation)

CT = Charge-transfer excitation

L = Local excitation

CASPT2 = Complete Active Space with Second-order Perturbation Theory

[1] JACS 1998, 120, 10912.

Dipeptide excitation energies: Bethe-Salpeter equation (BSE)

Optical Excitation	BSE (TDA)	BSE	CASPT2[1]
HOMO $\rightarrow$ LUMO (CT)	o.s.≈ 0	o.s.≈ 0	8.07 (o.s.≈ 0)
HOMO-1 $\rightarrow$ LUMO (CT)	7.20	7.05	7.18
HOMO$\rightarrow$LUMO+2 (L)	5.33	5.30	5.62
HOMO-2$\rightarrow$ LUMO (L)	5.63	5.60	5.79

TDA = Tamm-Dancoff approximation (Hermitian approximation)

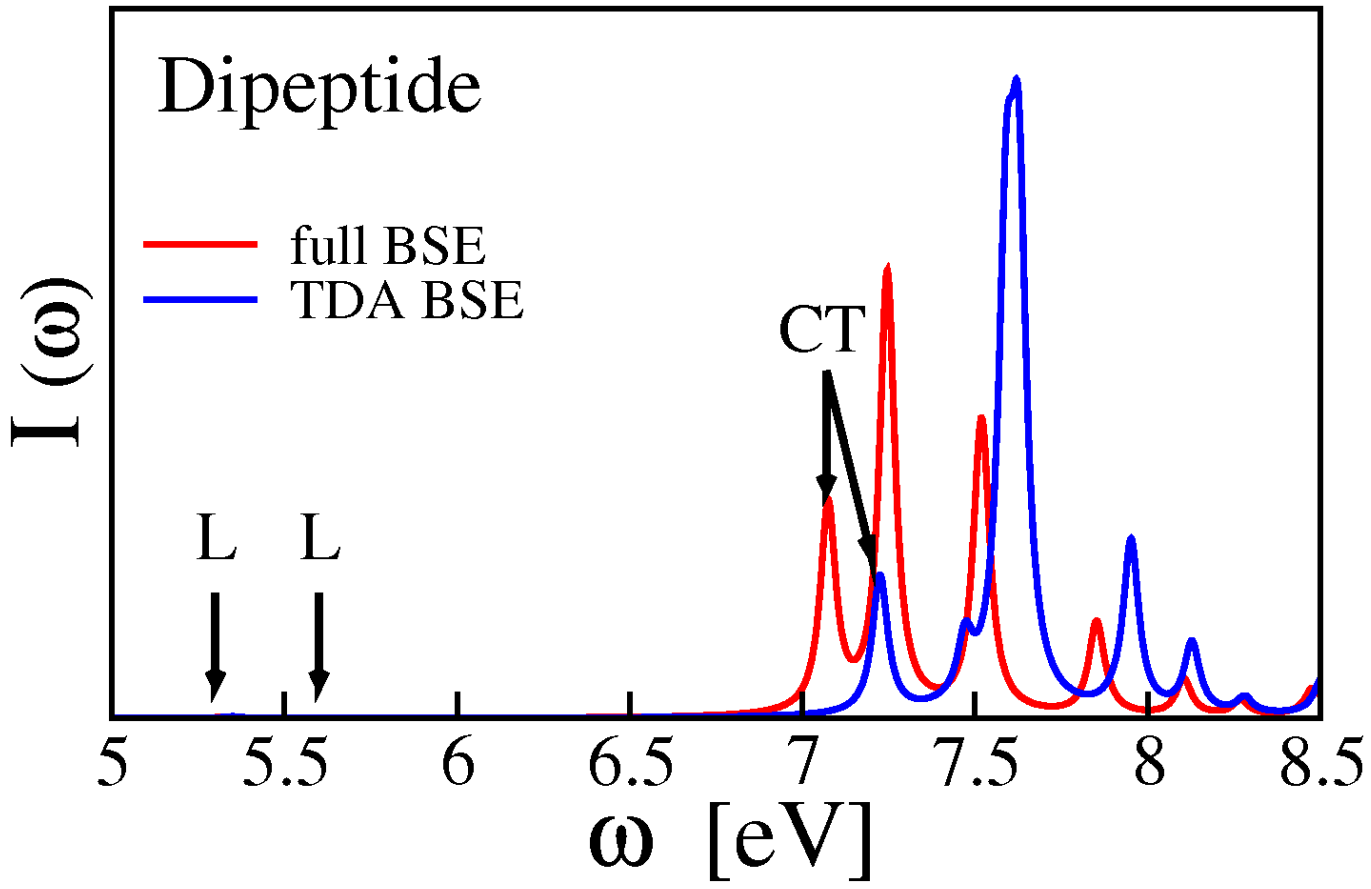
CT = Charge-transfer excitation

L = Local excitation

CASPT2 = Complete Active Space with Second-order Perturbation Theory

[1] JACS 1998, 120, 10912.

Dipeptide absorption spectrum



TDA = Tamm-Dancoff approximation (Hermitian approximation)

Preliminary GW results: IP for small molecules (eV)

Molecule	LDA	PBE [1]	G_0W_0	G_0W_0 [1]	Exp. [1]
CH_4	9.44	9.43	13.95	14.40	13.60
NH_3	6.29	6.16	10.59	10.60	10.82
H_2O_2	6.53	6.38	11.05	11.10	11.70
H_2O	7.31	7.24	12.25	11.90	12.62

[1] C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen, PRB 81, 085103 (2010)

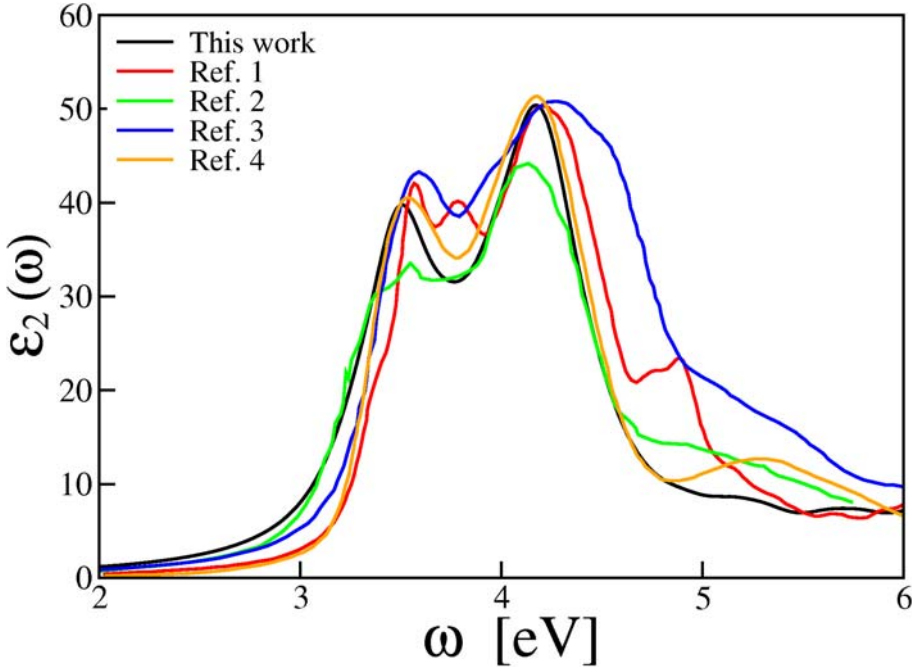
Work is in progress to interface the BSE and GW codes.

Conclusions

- We have introduced a new method in which:
  - Only calculations of occupied states are needed
  - The numerical scalability is comparable to ground-state Hartree-Fock calculations
  - The equations are solved without relying on the Tamm-Dancoff approximation (Hermitian approximation)
  - The spectrum can be calculated in an energy range much larger than with standard approaches
  - Dielectric matrices are obtained using an iterative method based on DFPT (easy storage and inversion)
- The new method as been successfully applied to the description of bulk solids, nanoclusters and charge-transfer excitations

D. Rocca, D. Lu, and G. Galli, J. Chem. Phys. 133, 164109 (2010)

Comparison with the literature



[1] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, PRL 80, 4510 (1998)
[2] L. X. Benedict, E. L. Shirley, and R. B. Bohn, PRB 57, R9385 (1998)
[3] M. Rohlfing and S. G. Louie, PRB 62, 4927 (2000)
[4] L. Reining, V. Olevano, A. Rubio, and G. Onida, PRL 88, 066404 (2002)