

Bethe-Salpeter Equation in ABINIT

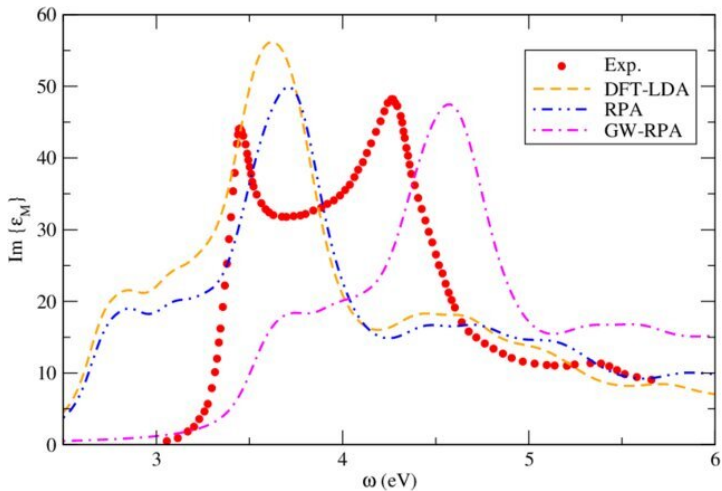
adapted (without permission) from

<https://docs.abinit.org/theory/bse/>

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Motivation

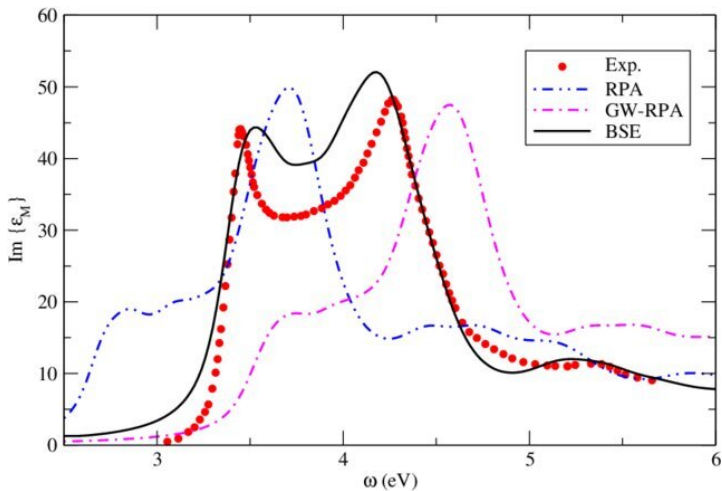
Silicon optical spectrum



from F. Sottile

Motivation

Silicon optical spectrum

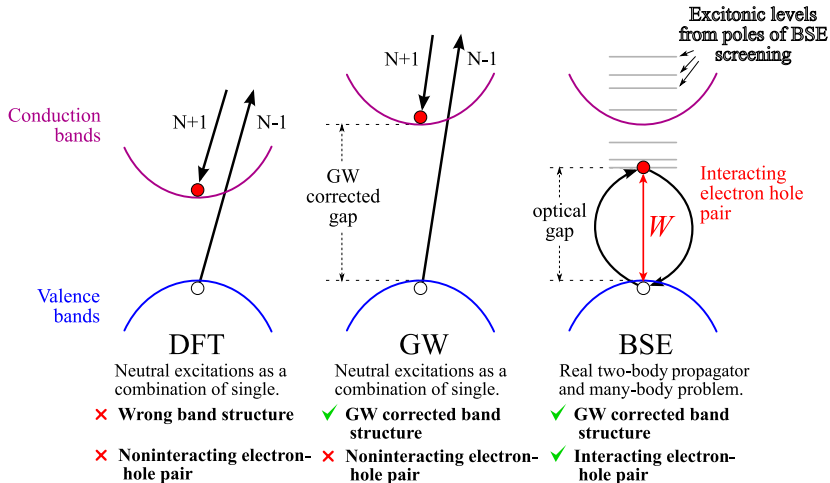


from F. Sottile

Accurate prediction of optical spectra requires many-body theory.

- Independent-particle approaches such as RPA neglect electron–hole interaction
- GW improves quasiparticle energies but does not include excitons
- The Bethe–Salpeter Equation (BSE) provides a formalism for neutral excitations
- BSE describes excitons

DFT – GW – BSE physical content



Conceptual relation between independent-particle, GW, and BSE descriptions.

Microscopic/macroscopic dielectric functions

The microscopic dielectric matrix is defined as

$$\varepsilon_{\mathbf{G}_1\mathbf{G}_2}(\mathbf{q}, \omega) = \delta_{\mathbf{G}_1\mathbf{G}_2} - v(\mathbf{q} + \mathbf{G}_1) \tilde{\chi}_{\mathbf{G}_1\mathbf{G}_2}(\mathbf{q}, \omega)$$

where

- $v(\mathbf{q}) = \frac{4\pi}{|\mathbf{q}|^2}$ is the Coulomb potential
- $\tilde{\chi}$ is the reducible polarizability

$$\varepsilon_M(\omega) = \lim_{\mathbf{q} \rightarrow 0} \frac{1}{\varepsilon_{00}^{-1}(\mathbf{q}, \omega)}$$

This formula includes the “local-field effects” that arise from microscopic inhomogeneity of the system.

Optical spectra are obtained from $\Im \{\varepsilon_M(\omega)\}$

Two-Particle Green's Function

The BSE introduces an effective two-particle interaction.

Remember the 2-particle Green's function from previous lesson:

$$G_2(1, 2, 3, 4) = \langle N, 0 | T[\Psi(1)\Psi(2)\Psi^\dagger(3)\Psi^\dagger(4)] | N, 0 \rangle$$

It describes 2 particles at the same time.

In practice, optical excitations only need the susceptibility χ , therefore one introduces the two-particle propagators:

$$L(1, 2; 3, 4) = -G_2(1, 2, 3, 4) + G(1, 3)G(2, 4)$$

and its non-interacting version

$$L_0(1, 2; 3, 4) = G(1, 4)G(3, 2)$$

Polarizabilities are contractions of these quantities:

$$\chi_0(1, 2) = L_0(1, 1; 2, 2), \quad \chi(1, 2) = L(1, 1; 2, 2)$$

BSE is a Dyson-like equation

The interacting propagator satisfies

$$L(1, 2; 3, 4) = L_0(1, 2; 3, 4) + \int d5678 L_0(1, 2; 3, 4) K(5, 7; 6, 8) L(8, 2; 7, 4)$$

which can be solved formally as

$$L = [1 - L_0 K]^{-1} L_0$$

K is the Bethe–Salpeter kernel that contains the electronic interactions.

The BSE kernel consists of two terms:

$$K(1, 2; 3, 4) = i \frac{\delta [v_H(1)\delta(1, 2) + \Sigma(1, 2)]}{\delta G(3, 4)}$$

Introducing $\Sigma \approx iGW$,

$$K(1, 2; 3, 4) \approx \delta(1, 2)\delta(3, 4) v(1, 3) - \delta(1, 3)\delta(2, 4) W(1, 2)$$

where

- v : time-dependent Hartree (responsible for local-field effects)
- $W \approx W(\omega = 0)$: statically screened Coulomb interaction
- Taking $W(\omega = 0) \approx v$ recovers time-dependent Hartree-Fock

Transition Space Representation

In practice, the problem is expanded in the basis of electron-hole transitions:

$$|v\mathbf{c}\mathbf{k}\rangle \equiv \psi_{c\mathbf{k}}(\mathbf{r})\psi_{v\mathbf{k}}^*(\mathbf{r})$$

The independent-particle polarizability becomes

$$\chi_{0,(v\mathbf{c}\mathbf{k})(v'\mathbf{c}'\mathbf{k}')}(\omega) = \frac{f_{c\mathbf{k}} - f_{v\mathbf{k}}}{\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}} - \omega} \delta_{vv'} \delta_{cc'} \delta_{\mathbf{k}\mathbf{k}'}$$

Remember we had:

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{nn'\mathbf{k}} (f_{n\mathbf{k}} - f_{n'\mathbf{k}}) \frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi_{n'\mathbf{k}}^*(\mathbf{r})\psi_{n'\mathbf{k}}(\mathbf{r}')\psi_{n\mathbf{k}}^*(\mathbf{r}')}{\omega - (\varepsilon_{n'\mathbf{k}} - \varepsilon_{n\mathbf{k}}) + i\eta}$$

Excitonic Hamiltonian

The inversion problem for each frequency

$$L = [1 - L_0 K]^{-1} L_0$$

can be replaced by a single diagonalisation problem

$$L^{-1}(\omega) = L_0^{-1}(\omega) - K$$

since

$$L_0^{-1}(\omega) = (\omega - \varepsilon_{c\mathbf{k}} + \varepsilon_{v\mathbf{k}}) \delta_{vv'} \delta_{cc'} \delta_{\mathbf{k}\mathbf{k}'}$$

We can define an 2-particle Hamiltonian:

$$H = (\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}}) \delta_{vv'} \delta_{cc'} \delta_{\mathbf{k}\mathbf{k}'} + K_{vck}^{v'c'\mathbf{k}'}$$

Tamm–Dancoff Approximation

The full Hamiltonian has block form

$$H = \begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}$$

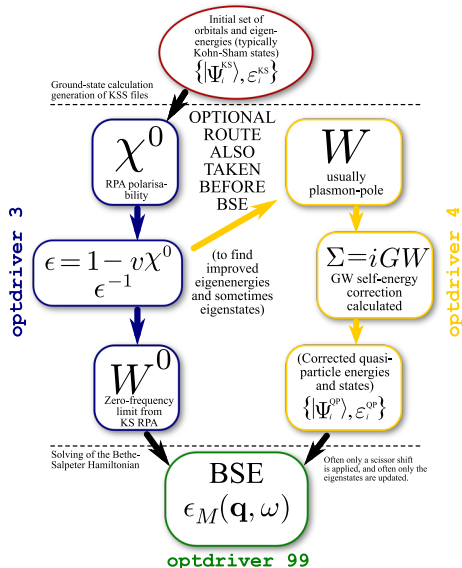
In solids, coupling block C is often small.

Under the Tamm–Dancoff approximation:

$$H = \begin{pmatrix} R & 0 \\ 0 & -R^* \end{pmatrix}$$

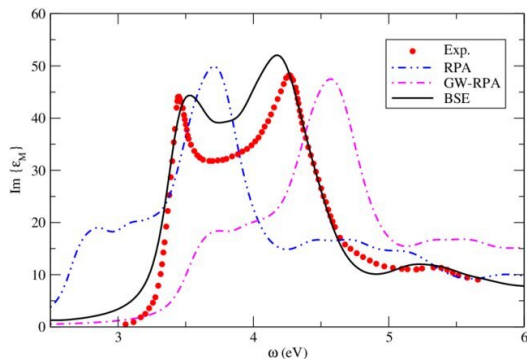
which is block-diagonal and leading to a Hermitian eigenvalue problem $RX = X\Omega$.

Workflow in ABINIT



- Sometimes the *GW* step skipped: use of a simple scissor
- Several diagonalization schemes: full diago, iterative diago

Final result for silicon



What does it take to obtain this plot?

- 1 low energy: few bands.
Here 3 occupied, 3 empty
- 2 smoothness: dense randomly-shifted k-point grid. Here 864 k-points
- 3 transition space:
 $3 \times 3 \times 864 \approx 8000$

Third peak of silicon and k-point sampling

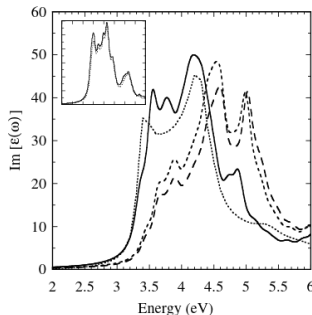


FIG. 1. Absorption spectra of Si. Inset: calculation according to Eq. (9) with 864 **k** points in the BZ, using eight bands (continuous curve) or only six bands (dotted curve). Main part: Calculation according to Eq. (9) with 2048 **k** points in the BZ, six bands and the diagonal approximation to ϵ^{-1} ; with both electron-hole attraction and local field effects in the Hamiltonian (continuous curve), inclusion of local field effects alone (long-dashed curve) and RPA with QP shifts only (short-dashed curve). Experimental curve (dots) [28].

Albrecht, Reining, Del Sole, Onida, PRL (1998)

Bound exciton in insulators

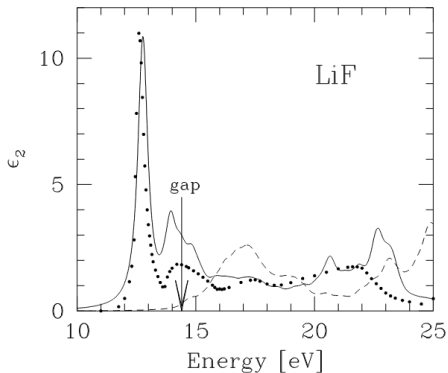


FIG. 3. Same as Fig. 1, but for LiF. A broadening of 0.25 eV is included. The experimental data are from Ref. [17].

Rohlfing and Louie, PRL (1998)

- Rohlfing and Louie, Phys. Rev. Lett. (1998)
- Albrecht, Reining, Del Sole, Onida, Phys. Rev. Lett. (1998)
- Shirley Phys. Rev. Lett. (1998)
- Onida, Reining, Rubio, Rev. Mod. Phys. (2002)
- ABINIT BSE Documentation