A real-time approach to optical properties in solids: time-dependent Bethe-Salpeter equation

C. Attaccalite1, M. Grüning2 and A. Marini3
1) Institut Neél, CNRS/UJF, Grenoble(France)  
2) Physics Department, University of Coimbra (Portugal)  
3) Dipartimento di Fisica, Università “Tor Vergata”, Roma(Italy)

The electronic and optical properties of semiconductors are well understood in terms of many-body effects. However there is a lack of a first-principles approach capable of prediciting the influence of Coulomb correlations in light-matter interaction beyond the linear optics. In this work we extend the well established many-body techniques in frequency space to real time domain, in such a way to describe phenomena beyond the linear regime. We report as example the calculations of dielectric constants in bulk materials and nanostructures.

Electron-light interaction

\[ H = H_0 + H_{\text{ex}} + H_{l} \]  
\[ H_0 = T + V_{\text{F}}(r) + V_{\text{e}}(r) + V_{\text{ex}}(r) \]  
\[ H_{\text{ex}} = -\sum_{<ij>} \left| r_i - r_j \right| \]  
\[ H_{l} = -\mathbf{r} \cdot \mathbf{E}(t) \]

where we chose as \( H_0 \) the Kohn-Sham Hamiltonian, that has been shown to be a very good starting point for many-body perturbation theory, and doesn't require any additional parameter except the atomic positions. The operator \( T \) is the kinetic operator, \( V_{\text{F}} \) the electron-ion interactions, where ions have been replaced by norm-conserving pseudopotentials and \( V_{\text{e}} \) the exchange correlation functional. The interaction with the external field \( H_{l} \) has been treated in direct coupling or length gauge.

The Kadanoff-Baym equations

The equation of motion of the system coupled with the external field, deriving from eq. 1, can be described in terms of the non-equilibrium Green's functions, which we expand in the eigenstates of the \( H_0 \) Hamiltonian:

\[ \frac{\partial}{\partial t} G_{n\text{m},k}(t_1, t_2) = \delta(t_1 - t_2)\delta_{n,m} + H_{n\text{m},k}(t_1)G_{n\text{m},k}(t_1, t_2) + \sum_{n'} U_{n\text{m},k}(t_1)G_{n',m, k}(t_1, t_2) \]

\[ + \sum_{n'} \int dt_3 \left( \Sigma^{\text{a}}_{n\text{m}, k}(t_1, t_3)G_{n',m, k}(t_3, t_2) + \Sigma^{\text{c}}_{n\text{m}, k}(t_3, t_2)G_{n',m, k}(t_1, t_3) \right) \]

In addition to this equation there is also the adjoint one for \( \chi \). However in general the equation for \( G^\dagger \) is not closed because both the self-energies \( \Sigma^\dagger, \Sigma \) and the \( G^\dagger \) depend on the \( G^\dagger \).

\[ \chi(t_1, t_2) \simeq \sum_{\text{COULomb plus screened-exchange self-energy}} \Sigma_{\text{COULomb plus screened-exchange self-energy}}(t_1 - t_2) \]

Within this approximation eq. 2 doesn't depend anymore on \( G^\dagger \) and moreover it reduces to its diagonal, in time, part only. (no dynamical effects \& no memory)

\[ \frac{\partial}{\partial t} G_{n\text{m},k}(t) = \left[ H_0 + U(t) + \Sigma_{\text{COULomb plus screened-exchange self-energy}}(t, G^\dagger(t)) \right]_{n\text{m},k} \]

Time-dependent Bethe-Salpeter eq.

Disregarding dynamical effects corresponds to a too strong approximation. In fact even if it has been shown that they are not so relevant for the optical response in solids (\( H_0 \) cancel with the quasi-particle renormalization factors), their effect is extremely important for the quasi-particle properties. Therefore we decided to modify eq. 3 in such a way to catch the most relevant effects of the dynamical self-energy.

\[ \frac{\partial}{\partial t} G_{n\text{m},k}(t) = \left[ H_0 + U + \Delta H_0 + V_{\text{F}}(\mathbf{r}(t)) - V_{\text{e}}(\mathbf{r}(t)) \right] + \Sigma_{\text{COULomb plus screened-exchange self-energy}}(G^\dagger(t), G^\dagger(t)) \]

where \( \rho(t, \mathbf{r}) \) is the density, and \( \Delta H_0 \) is a scissor operator to apply the \( GW \) correction to the Kohn-Sham eigenvalues. Eq. 4 is equivalent to assume that the quasi-particle correction just modifies the single particle eigenvalues leaving unchanged the Kohn-Sham wave-functions.

\[ G^\dagger_{n\text{m}, k}(t_2) = -i\epsilon_{\text{m}, k}(t_2) \delta_{n, m} \]

This equation has the following features:
- it includes quasi-particle corrections, including dynamical effects
- it reduces to the standard Bethe-Salpeter equation on top of \( GW \) quasi-particles for weak perturbations
- it includes electron-hole interaction though the variation of the self energy respect to the \( G^\dagger \): \( \partial\Sigma/\partial G^\dagger \)

Illustration of the methodology

We present numerical studies to illustrate the methodology just presented. We start with the calculation of the dielectric constant of a bulk material, the hexagonal Boron-Nitride (hBN). hBN is a wide gap insulator, which optical properties are strongly renormalized by the excitonic effects and for which all necessary parameters, crystal lattice etc. are well known.

Theoretical Spectroscopy

By using the Maxwell equations it is possible to derive a relation between the induced polarization \( P(r, t) \), the electric displacement \( D(r, t) \) and the electric field \( E(r, t) \), the so called material equation:

\[ D(r, t) = -\varepsilon_0 E(r, t) + P(r, t) \]

In linear response the electric displacement \( D(r, t) \) is directly proportional, in frequency space, to the electric field as \( D(\omega) = \varepsilon(\omega) E(\omega) \) or equivalently \( P(\omega) = \varepsilon_\text{e}(\omega) - \varepsilon_\text{i}(\omega) E(\omega) \) and the macroscopic polarization \( P(\omega) \) can be obtained from the \( \varepsilon(\omega) \) as:

\[ P(\omega) = -\frac{1}{\varepsilon_0} \sum_{n,m,k} (\varepsilon_{n,m,k}(\omega) G_{n,m,k}^\dagger(\omega) - \varepsilon_{n,m,k}(\omega) G_{n,m,k}(\omega)) \]

Conclusions:

We present a new way to study optical properties in bulk materials and nanostructures, by using a time-dependent version of the Bethe-Salpeter equation. Our method has the flexibility of the real-time approaches, combined with the strength of many body perturbation theory.

what next:

The time-dependent Bethe-Salpeter equation allows to simulate phenomena beyond the linear optics as:
- non-linear response
- four-wave mixing
- Fourier spectroscopy
- pump and probe

with an affordable computational cost.

A real-time approach to optical properties in solids: Time-dependent Bethe-Salpeter equation
C. Attaccalite, M. Grüning and A. Marini, submitted(2011)

Illustration of the methodology

Time-dependent Bethe-Salpeter equation

To probe our system we used a delta function, in time, homogenous electric field that excites all the frequencies with the same intensity.

\[ E(t) = \delta(t) \]

By using the Maxwell equations it is possible to derive a relation between the induced polarization \( P(\omega) \), the electric displacement \( D(\omega) \) and the electric field \( E(\omega) \), the so called material equation:

\[ D(\omega) = -\varepsilon_0 E(\omega) + P(\omega) \]

In linear response the electric displacement \( D(\omega) \) is directly proportional, in frequency space, to the electric field as \( D(\omega) = \varepsilon(\omega) E(\omega) \) or equivalently \( P(\omega) = \varepsilon_\text{e}(\omega) - \varepsilon_\text{i}(\omega) E(\omega) \) and the macroscopic polarization \( P(\omega) \) can be obtained from the \( \varepsilon(\omega) \) as:

\[ P(\omega) = -\frac{1}{\varepsilon_0} \sum_{n,m,k} (\varepsilon_{n,m,k}(\omega) G_{n,m,k}^\dagger(\omega) - \varepsilon_{n,m,k}(\omega) G_{n,m,k}(\omega)) \]

Conclusions:

We present a new way to study optical properties in bulk materials and nanostructures, by using a time-dependent version of the Bethe-Salpeter equation. Our method has the flexibility of the real-time approaches, combined with the strength of many body perturbation theory.

what next:

The time-dependent Bethe-Salpeter equation allows to simulate phenomena beyond the linear optics as:
- non-linear response
- four-wave mixing
- Fourier spectroscopy
- pump and probe

with an affordable computational cost.

A real-time approach to optical properties in solids: Time-dependent Bethe-Salpeter equation
C. Attaccalite, M. Grüning and A. Marini, submitted(2011)