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

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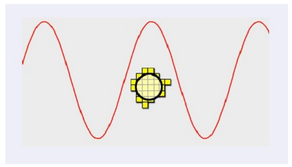
The electronic and optical properties of semiconductors are well understood in term of many-body effects. However there is a lack of a first-principles approach capable of predicting the **influence of Coulomb correlations in light-matter interaction beyond the linear optics**. In this work we extend 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.

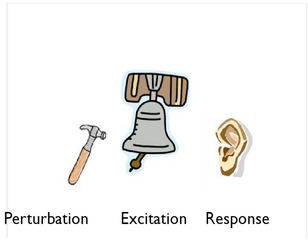
## *Electron-light interaction*



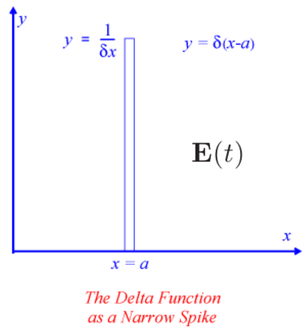
$$H = H_0 + H_{ee} + H_I \qquad (1)$$
$$H_0 = T + V_H(\mathbf{r}) + V_{eI}(\mathbf{r}) + V_{xc}(\mathbf{r})$$
$$H_{ee} = -\sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$H_I = -\mathbf{r}\cdot\mathbf{E}(t)$$

**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 The operator T is the kinetic operator, $V_{el}$ the electron-ion interactions, where ions have been replaced by norm-conserving pseudopotentials and $V_{xc}$ the exchange correlation functional. The interaction with the external field $H_I$ has been treated in direct coupling or length gauge.**

## Theoretical Spectroscopy




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




*The Delta Function as a Narrow Spike*

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:

$$\mathbf{D}(r,t) = \epsilon_0\mathbf{E}(r,t) + \mathbf{P}(r,t)$$

In linear response the electric displacement **D(r, t)** is directly proportional, in frequency space, to the electric field as **$D(\omega) = \epsilon(\omega) E(\omega)$**. or equivalently **$P(\omega) = \epsilon_0(\epsilon(\omega) - I)E(\omega)$**
and the macroscopic polarization **P(t)** can be obtained from the **$G^<$** as:

$$\mathbf{P}(t) = -\frac{1}{V}\sum_{n,m,\mathbf{k}} \langle m,\mathbf{k}|\mathbf{r}|n,\mathbf{k}\rangle G^<_{n,m,\mathbf{k}}(t)$$

… then … $\chi(\omega) = \frac{P(\omega)}{\varepsilon_0 E(\omega)}$ … and … $\varepsilon(\omega) = I + \chi(\omega)$

## 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:**

L. Kadanoff G. Baym

$$i\hbar\frac{\partial}{\partial t_1}G^<_{n_1n_2\mathbf{k}}(t_1,t_2) = \delta(t_1-t_2)\delta_{n_1n_2} \qquad (2)$$
$$+H^o_{n_1n_1\mathbf{k}}(t_1)G^<_{n_1n_2\mathbf{k}}(t_1,t_2) + \sum_{n_3} U_{n_1n_3\mathbf{k}}(t_1)G^<_{n_3n_2\mathbf{k}}(t_1,t_2)$$
$$+\sum_{n_3}\int \mathrm{d}t_3\big(\Sigma^{\mathrm{r}}_{n_1n_3\mathbf{k}}(t_1,t_3)G^<_{n_3n_2\mathbf{k}}(t_3,t_2)$$
$$+\Sigma^<_{n_1n_3\mathbf{k}}(t_1,t_3)G^{\mathrm{a}}_{n_3n_2\mathbf{k}}(t_3,t_2)\big).$$

**In addition to this equation there is also the adjoint one for $t_2$ . However in general the equation for $G^>$ is not closed because both the self-energies $\Sigma^r$, $\Sigma^<$ and the $G^a$ depend on the $G^>$.**

**Approximation:** $\begin{cases}\Sigma^{\mathrm{r}}(t_1,t_2) \simeq \Sigma^{\mathrm{COHSEX}}(t_1)\delta(t_1-t_2) \\ \Sigma^<(t_1,t_2) = 0\end{cases}$ $\Sigma^{\mathrm{COHSEX}}$

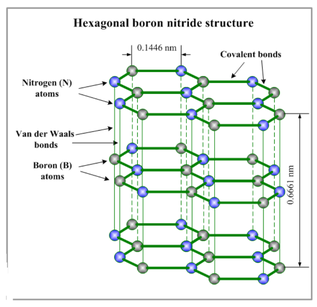
**Coulomb-hole plus screened-exchange self-energy**

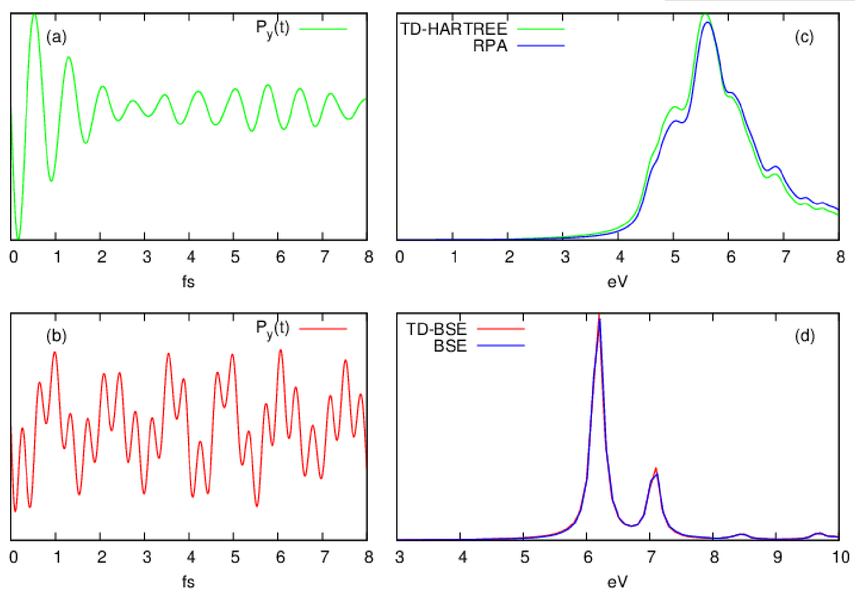
**Within this approximation eq. 2 doesn't depend anymore on $G^>$ and moreover it reduces to its diagonal, in time, part only. (no dynamical effects = no memory)**

$$i\hbar\frac{\partial}{\partial t}G^<_{n_1n_2\mathbf{k}}(t) = \left[H_o + U(t) + \Sigma^{\mathrm{COHSEX}}(t), G^<(t)\right]_{n_1n_2\mathbf{k}} \qquad (3)$$

## 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.**




## 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 (they 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.**

$$i\hbar\frac{\partial}{\partial t}G^<_{n_1n_2\mathbf{k}}(t) = \big[H_0 + U + \Delta H_0 + V_h(\rho^0(t_0)) - V_h(\rho(t))$$
$$+\Sigma^{COHSEX}(\tilde{G}^<(t_0)) - \Sigma^{COHSEX}(G^<(t))\big]_{n_1n_2\mathbf{k}} \qquad (4)$$

time-depent Bethe-Salpeter equation

**where ρ(r, t) is the density, and $\Delta H_0$ is a scissor operator to apply the $G_0W_0$ 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.**

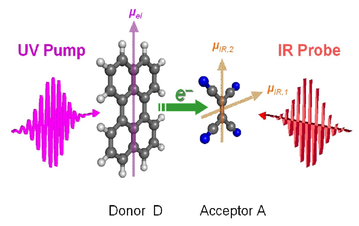
$\tilde{G}^<_{nn'}(t_0) = -if(e^0_n)\delta_{nn'}$ **is Green's function solution of eq. (3) with Σ=0**

**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 $G_0W_0$ quasi-particles for weak perturbations**
- **it includes electron-hole interaction though the variation of the self energy respect to the $G^<$:** $\partial\Sigma/\partial G^<$

## Conclusions:

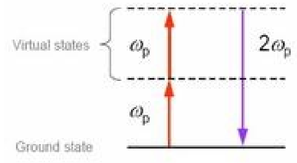
**We present a new way to study optical properties in bulk materials and nanostructures, by using a time-dependent version of the Bethe-Sapeter equation. Our method has the flexibility of the real-time approaches, combined with the strength of many body perturbation theory.**

***what next:***




**The time-dependent Bethe-Sapeter equantion allows to simulate phenomenas beyond the linear optics as:**
- **non-linear response**
- **four-wave mixing**
- **Fourier spectroscopy**
- **pump and probe**

**with an affordable computational cost.**

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