

Nonlinear optical Spectra from real-time Bethe Salpeter Equation

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I. NONLINEAR SPECTRA: TIME-DEPENDENT SCHRÖDINGER'S EQUATION

The time-development of occupied states $|\nu_{n\mathbf{k}}\rangle$ can be obtained from a time-dependent Schrödinger's equation as [1]

$$i\hbar \frac{d}{dt} |\nu_{n\mathbf{k}}\rangle = \left[\mathcal{H}_{\mathbf{k}}^{system} + i\mathcal{E}(t) \cdot \tilde{\partial}_{\mathbf{k}} \right] |\nu_{n\mathbf{k}}\rangle \quad (1)$$

in which $\mathcal{H}_{\mathbf{k}}^{system}$ is the system Hamiltonian and $\mathcal{E}(t) \cdot \tilde{\partial}_{\mathbf{k}}$ is the coupling of the electrons with the external field. If the system is periodic, the Born-von Kármán periodic boundary condition impose the operator $\tilde{\partial}_{\mathbf{k}} \equiv \frac{\partial}{\partial \mathbf{k}}$. The solutions to this equation are then gauge invariant under unitary transformations of the Bloch state $|k\rangle$.

Instead of a perturbative way (i.e., in the Fourier transformed domain), Eqn. (1) is solved directly in the real-time (RT) domain. The reasons are straightforward. A perturbative scheme is always computationally very expensive whereas in RT, the many-body effects can be efficiently added in the Hamiltonian.

In order to find the macroscopic polarization, we follow the modern theory of polarization by King-Smith and Vanderbilt [2]. These authors argued that the Berry's phase change generated by a closed path in \mathbf{k} -space correctly defines the macroscopic polarization of a periodic system. When the states $|\nu_{n\mathbf{k}}\rangle$ are known, the in-plane macroscopic polarization along the lattice vector a can then be evaluated from [1, 2]

$$\mathcal{P}_{\parallel} = -\frac{eg_s}{2\pi\Omega} \frac{|a|}{N_{\mathbf{k}_{\perp}}} \sum_{\mathbf{k}_{\perp}} \Im \log \prod_{\mathbf{k}_{\parallel}}^{N_{\mathbf{k}_{\parallel}}-1} \det S(\mathbf{k}, \mathbf{k} + \mathbf{q}_{\parallel}) \quad (2)$$

in which e is the electronic charge, g_s is the spin degeneracy, $S(\mathbf{k}, \mathbf{k} + \mathbf{q}_{\parallel})$ is the overlap matrix between the states $|\nu_{n\mathbf{k}}\rangle$ and $|\nu_{m\mathbf{k}+\mathbf{q}_{\parallel}}\rangle$, $N_{\mathbf{k}_{\parallel}}$ and $N_{\mathbf{k}_{\perp}}$ are the respective in-plane and out-of plane \mathbf{k} -points to the polarization direction with $q_{\parallel} = \frac{2\pi}{N_{\mathbf{k}_{\parallel}}}$.

The system Hamiltonian in Eqn. (1) can now be constructed as follows: In the independent-particle approximation, the energy eigenvalues are simply evaluated from the Kohn-Sham DFT Hamiltonian [1]

$$\mathcal{H}_{\mathbf{k}}^{system} = \mathcal{H}_{\mathbf{k}}^{DFT} \quad (3)$$

Next, the G_0W_0 corrections can be added to this IPA Hamiltonian as either by a scissor operator [1]

$$\mathcal{H}_{\mathbf{k}}^{system} = \mathcal{H}_{\mathbf{k}}^{DFT} + \Delta \mathcal{H}^{scissor} = \mathcal{H}_{\mathbf{k}}^{DFT} + \sum_{n\mathbf{k}} \Delta_{n\mathbf{k}} |v_{n\mathbf{k}}^0\rangle \langle v_{n\mathbf{k}}^0| \quad (4)$$

or directly by $\Delta_{n\mathbf{k}} = E_{n\mathbf{k}}^{G_0W_0} - E_{n\mathbf{k}}^{DFT}$ from an *ab-initio* computation.

The next hierarchy is the TD-DFT, where the system Hamiltonian is [1, 3]

$$\mathcal{H}_{\mathbf{k}}^{system} = \mathcal{H}_{\mathbf{k}}^{DFT} + V_H [\Delta\rho(r, t)] + V_{xc}(r) [\Delta\rho(r, t)] \quad (5)$$

in which V_H is the self-consistent Hartree potential, and V_{xc} is the exchange-correlation potential at the level of Kohn-Sham DFT, now calculated quasi-statically within LDA or GGA. These two potentials are dependent on the time-varying electronic density $\rho(r, t)$. Random phase approximation is the condition when V_{xc} is neglected in the system Hamiltonian. The change $\Delta\rho(r, t) = \rho(r, t) - \rho(r, 0)$ is the electronic density variation and is responsible for the local-field effects due to the inhomogeneity in the system.

The next level of hierarchy is the incorporation of scissor-corrected SEX interaction in the Hamiltonian. This is usually known as TD-BSE [1]

$$\mathcal{H}_{\mathbf{k}}^{system} = \mathcal{H}_{\mathbf{k}}^{DFT} + \Delta \mathcal{H}_{\mathbf{k}}^{scissor} + V_H [\Delta\rho(r, t)] + \sum_{SEX} [\Delta\gamma] \quad (6)$$

in which $\Delta\gamma(r, r', t) = \gamma(r, r', t) - \gamma(r, r', 0)$ is the density fluctuation matrix induced by the external field. The self-energy \sum_{SEX} is the convolution between the statically screened interaction W and $\Delta\gamma(r, r', t)$.

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The EOM, Eqn. (1), is now numerically solved for $|\nu_{nk}\rangle$ using the following algorithm developed by Crank and Nicholson [4] for both Hermitian and non-Hermitian type Hamiltonians

$$|v_{nk}(t + \Delta t)\rangle = \frac{I - i(\Delta t/2)\mathcal{H}_{\mathbf{k}}^{system}(t)}{I + i(\Delta t/2)\mathcal{H}_{\mathbf{k}}^{system}(t)} |v_{nk}(t)\rangle \quad (7)$$

in which I is the identity element. The operation is strictly unitary for any value of time-step Δt . It turns out that if the applied field is a Dirac delta-type, the Fourier transformed responses can be evaluated at all frequencies. In case of a low intensity, one can show that the solution of Eqn. (1) asymptotically tends to time-independent BSE [5]. The extraction of the nonlinear response function is a post-processing computation. The sudden switching of a monochromatic $\mathcal{E}(t)$ induces spurious fluctuations at the initial stage. In order to calculate the $\mathcal{P}(t)$ from a clean signal, we add a dephasing time-constant. This would essentially mean that after say 5 time-constants these spurious fluctuations are sufficiently cleared out from $\mathcal{P}(t)$ and the nonlinear responses can be obtained between this time and the total simulation time. There are two approaches by which nonlinear χ can be evaluated. Either, the field may be applied in a quasi-static way, so that the spurious fluctuations do not appear. However calculating \mathcal{P} in this way takes a long time to simulate [1]. The other way is to use the previous sudden approximation and change the following Fourier series into a system of linear equations. The polarization Fourier series is [1]

$$\mathcal{P}(t) = \sum_{n=-\infty}^{n=\infty} p_n e^{-i\omega_n t} \quad (8)$$

This series is truncated [1] to an order \mathcal{S} larger than the response we are interested to calculate. With a laser frequency ω_L , we find the time-period T_L and within this we sample the signal to $2\mathcal{S} + 1$ values. Eqn. (8) can now be transformed in a system of linear equation

$$\mathcal{F}_{lin} p_n^\alpha = \mathcal{P}_i^\alpha \quad (9)$$

in which α is the polarization direction. By Fourier inversion of the $(2\mathcal{S} + 1) \times (2\mathcal{S} + 1)$ matrix (done on sampled times t_i) ($\mathcal{F}_{lin} \equiv e^{-i\omega_n t_i}$), each component p_n^α of the coefficients p_n can be obtained.

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