How pump–probe differential reflectivity at negative delay yields the perturbed-free-induction-decay: theory of the experiment and its verification

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Abstract
We present a simple but mathematically complete first-principles theory for the pump–probe differential reflectivity experiment at negative delay (probe preceding the pump) to show how it gives information about the perturbed-free-induction-decay of coherent polarization. The calculation, involving the optical Bloch equations to describe the induced polarization and the Ewald–Oseen idea to calculate the reflected signal as a consequence of the free oscillations of perturbed dipoles, also explicitly includes the process of lock-in detection of a double-chopped signal after it has passed through a monochromator. The theory giving a closed form expression for the measured signal in both time and spectral domains is compared with experiments on high quality GaAs quantum well sample. The dephasing time inferred experimentally at 4 K compares remarkably well with the inverse of the absorption linewidth of the continuous-wave photoluminescence excitation spectrum. Spectrally-resolved signal at negative delay calculated from our theoretical expression nicely reproduces the coherent spectral oscillations observed in our experiments, although exact fitting of the experimental spectra with the theoretical expression is difficult on account of multiple resonances.

Keywords: pump–probe theory and experiment, optical Bloch equations, Ewald–Oseen extinction theorem, perturbed-free-induction-decay, excitonic polarization dephasing

(Some figures may appear in colour only in the online journal)
wave vectors \( \vec{k}_{\text{pm}} \) (the pump beam) and \( \vec{k}_{\text{pr}} \) (the probe beam) are cofocused on to the sample. However, unlike FWM experiments, the PPDT/PPDR signal arising from the third order nonlinear optical effect is detected along the probe transmission/reflection direction, where a linear optical signal is also present. As this facilitates easy identification of the PPDT/PPDR signal direction, setting up these experiments becomes much easier compared to the nonlinear wave-mixing experiments. The pump–probe technique has been conventionally used to study incoherent processes such as energy relaxation and recombination dynamics in a large number of materials under conditions of positive delay (pump preceding the probe) [32–37]. While the theory of susceptibility at negative delays has long been developed [3, 31] and there are a few reports of measurements of the perturbed-free-induction-decay using negative delay pump–probe measurements [12–19], mostly in transmission geometry, its overall use has been limited. This is primarily because the interpretation of the measured signal is not quite transparent and has sometimes been controversial [38]. It is hard to intuitively understand why the spectrally-resolved, time-integrated PPDT/PPDR signal is non-zero at negative delays, how it carries information of polarization [38]. It is hard to intuitively understand why the spectrally-resolved, time-integrated PPDT/PPDR signal is non-zero at negative delays [12, 38]. A complete calculation of the measured signal accounting for all the optical and electronic components of the PPDR/PPDT experiments would be, we believe, useful.

In this paper we attempt to develop such a theoretical framework for the pump–probe differential reflectivity measurements at negative delay. The paper is organized as follows. First we present a description of a typical PPDR experimental setup to identify the important components of the experimental scheme. Then we develop our theoretical model of PPDR signal taking account of each of the important experimental components. Finally, we compare our theoretical model with the results of PPDR experiments on high quality GaAs/AlGaAs multi-quantum well sample at low temperature. The theory nicely reproduced the coherent spectral oscillations observed in low-temperature PPDR spectra at negative delays. The dephasing time estimated from the perturbed-free-induction-decay in the time-integrated PPDR signal measured at exciton peak at negative delay matches well with the inverse linewidth of the absorption spectra which is estimated from the photoluminescence excitation (PLE) spectroscopy [39]. This provides a strong evidence to the credibility of the pump–probe method.

2. Experimental

The schematic of a typical experimental setup for spectrally-resolved time-integrated PPDR measurements is shown in figure 1. A beam containing train of \(~100\) fs pulses at a repetition rate of \(80\) MHz from a mode-locked Ti:sapphire laser is split by a beam-splitter into pump and probe beams. The pulses in the pump beam are controllably delayed with respect to the corresponding pulses in the probe beam by a retroreflector-on-a-linear-translation-stage arrangement. The pump and probe beams are modulated at different frequencies, \(f_{\text{pm}} = 760\) Hz and \(f_{\text{pr}} = 912\) Hz respectively, by an opto-mechanical chopper having square-wave-like chopping profile with a 50% duty cycle. The pump and probe beams are incident on the sample at an angle of \(15^\circ\) and \(10^\circ\) respectively, from the normal to the sample surface and are denoted by the wave vectors \(\vec{k}_{\text{pm}}\) and \(\vec{k}_{\text{pr}}\) respectively. The reflected probe beam is spectrally dispersed by a monochromator with a narrow spectral band-pass of \(~0.1\) nm. The signal passing through the narrow band-pass of the monochromator is measured with a photomultiplier tube (PMT) detector. The signal from the PMT is fed to a lock-in amplifier which is locked to the sum frequency \(f_{\text{pm}} + f_{\text{pr}} = 1.67\) kHz [40]. Lock-in time-constant is set to be 300 ms. Locking to the sum (or difference) frequency allows for a direct measurement of the PPDR signal which is the change in the probe reflectivity due to the pump beam. One may measure either the PPDR spectrum at a given delay or measure the delay dependence of the PPDR signal at a given wavelength.

3. Theoretical calculations

The important steps in the calculation are (i) to write down the electric fields due to the pump and the probe pulse trains modulated by the square-wave chopping functions imparted by the opto-mechanical chopper, (ii) to calculate the relevant components of polarization (having the required wavevector combination) generated in the sample due to the pump and the probe electric fields, (iii) to calculate the radiated electric field in the probe-reflection direction due to the generated polarization within the sample, and (iv) to calculate the detected light intensity due the radiated electric filed in the probe-reflection direction, taking account of the effect of the spectral filtering.
by the monochromator, time integration of the detected light intensity by the slow detector that averages over many pulses, and phase-sensitive detection by the lock-in amplifier which is locked to the sum frequency of the pump and probe chopping.

To keep the treatment analytically tractable, we approximate the ∼100 fs pulses as periodic delta-functions with a time separation ∆ between consecutive pulses. The train of pulses in the pump and the probe beams arrive at the sample with a relative delay τ. In this calculation we are interested in negative delays where the probe pulse precedes the corresponding pump pulse. Thus, the electric field due to the probe and pump pulses are written, respectively, as

\[ \vec{E}^p(t) = \sum_{m} \{ \vec{E}^p(t - m\Delta) \exp[i(\vec{k}^p \cdot \vec{r} - \omega t)] \} + c.c. \]

and

\[ \vec{E}^m(t) = \sum_{m} \{ \vec{E}^m(t - m\Delta - \tau) \exp[i(\vec{k}^m \cdot \vec{r} - \omega t)] \} + c.c.; \quad \tau > 0 \]

where \( \vec{E}^p \) (\( \vec{E}^m \)) is the vector amplitude function which contains the area under the pulse temporal envelope and the unit vector describing the direction of the electric field for the probe (pump) beam, \( \vec{k}^p \) (\( \vec{k}^m \)) is the wavevector of the probe (pump) beam, \( \omega_t \) is the frequency of the laser beam which is same for the probe and the pump beams as they both are derived from the same laser, \( m \) is an integer, and c.c. stands for the complex conjugate. On account of a strict hierarchy of (almost) non-overlapping time scales, \( t_p \sim 100 \) fs (pulse width) \( \ll T_2 \sim 1 \) ps (polarization dephasing time) \( \ll \tau \sim 100 \) ps (population relaxation time) \( \ll \Delta \sim 10 \) ns (pulse-repetition period), the effect of each pair of pump and probe pulses in the pulse train may be treated independently.

Square-wave modulations of the probe and pump beams are incorporated by taking the Fourier expansions of the respective electric fields:

\[ \vec{E}^p(t) = \sum_{m} \{ \vec{E}^p(t - m\Delta) \exp[i(\vec{k}^p \cdot \vec{r} - \omega t)] \}
\]

\[ \times \left[ \frac{1}{2} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\sin(n\Omega_{pe} t + \theta_1)}{n} \right] + c.c. \]

\[ = \sum_{m} \vec{E}^p(t, \Omega_{pe}) \delta(t - m\Delta) \exp[i(\vec{k}^p \cdot \vec{r} - \omega t)] + c.c. \]

and

\[ \vec{E}^m(t) = \sum_{m} \{ \vec{E}^m(t - m\Delta - \tau) \exp[i(\vec{k}^m \cdot \vec{r} - \omega t)] \}
\]

\[ \times \left[ \frac{1}{2} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\sin(n\Omega_{pm} t + \theta_2)}{n} \right] + c.c. \]

\[ = \sum_{m} \vec{E}^m(t, \Omega_{pm}) \delta(t - m\Delta - \tau) \exp[i(\vec{k}^m \cdot \vec{r} - \omega t)] + c.c. \]

Here \( \vec{E}^p(t, \Omega_{pe}) \) and \( \vec{E}^m(t, \Omega_{pm}) \) are the field amplitudes including the Fourier series, \( \theta_1 \) and \( \theta_2 \) are the phase factors, and \( \Omega_{pe} = 2\pi f_{pe} \) and \( \Omega_{pm} = 2\pi f_{pm} \) are the chopping frequencies of the probe and pump beams, respectively. The signal-to-noise ratio in the double modulation case is superior as has been reported in the past [41, 42]. It is worth clarifying that whether one considers the chopper is modulating the electric field or the intensity of the incident beams depends on the phenomenon being probed. In the coherent regime, it is the electric field because the polarization of the dipoles couples to the field, whereas intensity modulation should be considered for studies in the incoherent regime dealing with carrier population. But note that in either case the Fourier expansion is essentially the same because the squares of equations (3) and (4) also yield the same Fourier frequency components (a square-wave train remains as a square-wave train upon squaring its amplitude). It is important to once again emphasize the well-separated time scales appearing in equations (3) and (4). The chopping frequencies are of the order of a few hundred Hz, and \( \omega_t \) is of the order of 10^{15} Hz. Also note that a ∼100 fs laser pulse still contains more than 20 cycles of the electric field at optical wavelengths.

Under the simplest approximation, the sample may be considered to contain an ensemble of identical noninteracting two-level systems. The interaction with the optical fields of the pump and the probe beams gives rise to macroscopic polarization, which has several components with different combination of wavevectors \( \vec{k}^p \) and \( \vec{k}^m \), depending upon the order of interaction considered in the calculation. The time-dependent polarization in turn gives rise to radiating electric fields in different directions depending on the embedded wavevector combinations. The standard framework for the calculation of the polarization in the given experimental condition is to solve the optical Bloch equations perturbatively to the required order [1, 6, 25].

For an ensemble of noninteracting two-level systems having an energy separation \( \hbar \omega_0 \), the optical Bloch equations obtained using the density matrix formalism, the Heisenberg equation for time evolution and the relaxation time approximation, are a set of coupled equations connecting the time evolution of the off-diagonal and diagonal elements of the density matrix. These in turn are related to the polarization and population density respectively. Since the formalism is very standard, we will use the notation and methodology as is given in the book by Meier et al [3] where the perturbative solution of the optical Bloch equations under the two-beam delta-pulse excitation up to third order in polarization using rotating wave approximation is also calculated. We pick up the terms having a phase factor \( \exp(-i\vec{k}^p \cdot \vec{r}) \). These are responsible for generating the radiated electric field in the probe reflection direction. We have one first- and one third-order terms with this phase factor and the total polarization (up to third order) \( \vec{P}_{\text{total}}(\vec{r}, t, \Omega_{pe}, \Omega_{pm}) \) can be written as

\[ \vec{P}_{\text{total}}(\vec{r}, t, \Omega_{pe}, \Omega_{pm}) \times (1 + \Theta(t) + \Theta(\tau) ) \]

\[ \Theta(t - \tau) e^{-\frac{t}{\tau}} \sin(\omega t - \vec{M} \cdot \vec{r}), \]

with

\[ \vec{M}(t, \Omega_{pe}) = \frac{2}{\hbar} \vec{E}^p(t, \Omega_{pe})/|\vec{M}_{\text{exc}}|^2 \]
and
\[ a_2(t, \Omega_{pr}, \Omega_{pm}) = \frac{2}{\hbar^2} \left| \tilde{e}_{0}(t, \Omega_{pm}) \right|^2 \tilde{e}_{0}(t, \Omega_{pr}) |\tilde{\mu}_{vc}|^2 e^{-\frac{\pi}{\tau}}. \] (7)

Here, \( \mu_{vc} \) is the relevant dipole matrix element, \( T_1 \) and \( T_2 \) respectively, are the energy and phase relaxation times, and \( \Theta \) is the Heaviside step function.

One can then take the Fourier transform of this polarization to get the expression for the third-order susceptibility which will be directly related to the dielectric constant measured in the absorption measurement. This is what is done in the treatment by Koch and coworkers [3]. We shall consider coherent reflection instead. The case of reflectivity measurement is slightly different and one needs to explicitly consider the emitted radiation due to this polarization. As mentioned above, note that the position dependent part (\( k_{ref} \cdot \hat{r} \)) of the phase of the oscillating polarization is responsible for the directionality of the emitted radiation.

In the absence of free charges, the current density \( \vec{J} = \partial \tilde{\mu}_{total}/\partial t \) generated in the sample due to the time-dependent polarization acts as the source for a vector potential of the radiated electric field. Note that the transition frequency \( \omega_0 \) between ground and excited states (here idealized as a two level system) for a typical semiconductor sample falls in the optical frequency range (\( \sim 10^{15} \) Hz). Thus the derivative of the \( \sin(\omega_0 t - k_{pr} \cdot \hat{r}) \) factor appearing in equation (5) will make a much larger contribution to the current density, compared to the other factors (the laser pulse width, the dipole oscillators’ dephasing time or the modulation time period from the chopper). Thus the current density may approximately be written as
\[ \vec{J}(\vec{r}, t, \Omega_{pr}, \Omega_{pm}) \approx \Re [\omega_0 \tilde{a}_1(t, \Omega_{pr}) \Theta(t) + \tilde{a}_2(t, \Omega_{pr}, \Omega_{pm}) \Theta(t - \tau) e^{-\Gamma t} e^{i(\omega_0 t - k_{pr} \cdot \hat{r})}] \]. (8)

Here \( \Gamma = T_2^{-1} \) and \( \Re \) denotes the real part of the expression. This current density is the source of the radiated field in the inhomogeneous wave equation (Helmholtz equation) [43]
\[ \vec{A}(\vec{r}, t, \Omega_{pr}, \Omega_{pm}) = \int_{\Omega} d^3r' \mu_0 \vec{J}(\vec{r}', t) G(|\vec{r} - \vec{r}'|), \] (9)
where \( \vec{A}(\vec{r}, t, \Omega_{pr}, \Omega_{pm}) \) is the vector potential, \( \mu_0 \) is the permeability of the vacuum and
\[ G(|\vec{r} - \vec{r}'|) = \frac{e^{-i\vec{k}' \cdot (\vec{r} - \vec{r}')}}{4\pi |\vec{r} - \vec{r}'|} \] (10)
is the Green’s function for the Helmholtz equation, namely,
\[ \nabla^2 G(|\vec{r} - \vec{r}'|) + k^2 G(|\vec{r} - \vec{r}'|) = -\delta^3(|\vec{r} - \vec{r}'|). \] (11)
Here the spatial coordinate carrying \( \vec{r}' \) denotes the plane of the sample. Taking the incident wavevector to be \( \vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z} \) and assuming that the sample spans the entire \( x-y \) plane at \( z = 0 \) and it has negligible thickness \( (L_z \to 0) \) along the \( z \) direction (figure 2), we can recast the integral of equation (9) as
\[ \vec{A}(\vec{r}, t, \Omega_{pr}, \Omega_{pm}) = \Re \left[ \lim_{L_z \to 0} \int_{-\infty}^{+\infty} dx' \int_{-\infty}^{+\infty} dy' \int_{0}^{L_z} dz' \mu_0 \vec{J}(\vec{r}', t) e^{-\Gamma r} e^{i(\omega_0 t - k_{pr} \cdot \hat{r})} \right] \] (12)
This is readily integrated to yield [43]
\[ \vec{A}(\vec{r}, t, \Omega_{pr}, \Omega_{pm}) = \Re \left[ \frac{j}{4\pi} e^{i(\omega_0 t - k_{pr} \cdot \vec{r})} \Theta(t) + \tilde{a}_2(t, \Omega_{pr}, \Omega_{pm}) \Theta(t - \tau) e^{-\Gamma t} e^{i(\omega_0 t - k_{pr} \cdot \hat{r})} \right] \] (13)
where \( k_x \hat{x} + k_y \hat{y} + k_z \hat{z} \) represents the reflected wave vector \( \vec{k}_{ref} \). Proceeding with the integration along \( z \) direction, we have
\[ \vec{A}(\vec{r}, t, \Omega_{pr}, \Omega_{pm}) = \Re \left[ \frac{j}{4\pi} e^{i(\omega_0 t - k_{pr} \cdot \vec{r})} \Theta(t) + \tilde{a}_2(t, \Omega_{pr}, \Omega_{pm}) \Theta(t - \tau) e^{-\Gamma t} e^{i(\omega_0 t - k_{pr} \cdot \hat{r})} \right] \]
(14)
Note that \( \lim_{L_z \to 0} \left[ e^{i(k_x - k'_x)z - 1} \right] / i(k_z - k'_z) \) simply gives a factor of \( L_z \).

Calculation of the reflected field in the probe direction is now straightforward [43, 44] using the relation \( \vec{E}_{rad} = -\frac{\partial}{\partial t} - \nabla \Phi \).
As there are no free charges in the medium, the charge density \( \rho = 0 \) and the term containing the scalar potential \( \Phi \) is zero. Thus the radiated electric field in the probe reflection direction is
where $k_z$ is the $z$-component of the wavevector. Again (due to the separation of time scales) we have only considered the most important term containing optical frequency $\omega_0$ while taking the time derivative of $\vec{A}$. The phase $\phi(\vec{r}) = (\pi/2 - k_{\text{ref}} \cdot \vec{r})$.

Note that the polarization in our calculation follows the conventional definition as being the induced dipole moment per unit volume. This is why the sample width $L_z$ explicitly appears in the above expression. One may alternatively define a sheet polarization density without explicitly displaying $L_z$ as has been done, e.g. in [45] in the context of sum frequency generation using dipole radiation formula [46]. Note that the above calculation is essentially an illustration of the idea behind the celebrated Ewald–Oseen extinction theorem [47–49] in the modern context of free-induction-decay at optical frequencies.

Since the radiated electric field in the probe reflection direction is passed through a monochromator which selects out one particular Fourier component (frequency) of the electric field, we express the reflected field (equation (15)) as an integral over its Fourier modes:

$$\bar{E}_{\text{rad}}(\omega, \tau, \Omega_\tau, \Omega_{\omega_\tau}) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \bar{E}_{\text{rad}}(t, \tau, \Omega_\tau, \Omega_{\omega_\tau}) e^{-i\omega t} dt.$$  (16)

Writing the cosine in the reflected field as a sum of exponentials, we perform the integration and obtain

$$\bar{E}_{\text{rad}}(\omega, \tau, \Omega_\tau, \Omega_{\omega_\tau}) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \bar{E}_{\text{rad}}(t, \tau, \Omega_\tau, \Omega_{\omega_\tau}) e^{-i\omega t} dt.$$  (17)

We may now neglect the terms having $\Gamma + i(\omega_0 + \omega)$ in their denominator with respect to the terms having $\Gamma - i(\omega_0 - \omega)$ in their denominator. Such an approximation can be appreciated when one considers that the first denominator is about three orders of magnitude larger than the second one for the case $\omega \equiv \omega_0$. Then we have

$$\bar{E}_{\text{rad}}(\omega, \tau, \Omega_\tau, \Omega_{\omega_\tau}) = \frac{\omega_0^2 L_c \mu_0}{16\pi \sqrt{2\pi} k_z} \left[ \hat{a}_1(\Omega_{\omega_\tau}) + \hat{a}_2(\Omega_{\omega_\tau}) e^{-i\tau \omega_0} \right] \frac{e^{-\Gamma t} e^{i(\omega_0 - \omega)t}}{\Gamma - i(\omega_0 - \omega)}.$$  (18)

The action of the monochromator may be approximated by inserting a $\delta$-function frequency filter around the selected frequency $\omega_m$ while taking the inverse Fourier transform, i.e.

$$\bar{E}_{\text{rad}}(\omega, \tau, \omega_\tau, \Omega_\tau, \Omega_{\omega_\tau}) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \bar{E}_{\text{rad}}(\omega, \tau, \Omega_\tau, \Omega_{\omega_\tau}) e^{i\omega t} \delta(\omega - \omega_m) d\omega.$$  (19)

This gives

$$\bar{E}_{\text{rad}}(t, \tau, \Omega_\tau, \Omega_{\omega_\tau}) = \frac{\omega_0^2 L_c \mu_0}{32\pi^2 k_z} \left[ \hat{a}_1(\Omega_{\omega_\tau}) + \hat{a}_2(\Omega_{\omega_\tau}) e^{-i\tau \omega_0} \right] \frac{e^{-\Gamma t} e^{i(\omega_0 - \omega_m)t}}{\Gamma - i(\omega_0 - \omega_m)}.$$  (20)

The detector measures the intensity integrating over a period of time (in the nanosecond to microsecond range) that is much larger than the time period of oscillation of the electric field and much less than the chopping timescale (which is akin to a coarse graining). So for a detection time scale $1/\omega \ll T \ll 1/\Omega_{\omega_\tau}$ the time integrated signal can be calculated as

$$S(t, \tau, \omega_\tau, \Omega_\tau, \Omega_{\omega_\tau}) = \frac{1}{T} \int_{0}^{T} \bar{E}_{\text{rad}}^2(t, \tau, \omega_\tau, \Omega_\tau, \Omega_{\omega_\tau}) dt.$$  (21)

which contains the products of equations (6) and (7) as well as their individual squares which will have sine and cosine terms containing various combinations of the chopping frequencies $\Omega_\tau$ and $\Omega_{\omega_\tau}$. Note that these are low-frequency modulations created by the opto-mechanical chopper, over and above the high optical frequency oscillation of the electric field. For phase-sensitive detection, a lock-in amplifier multiplies the signal received from the detector with a reference signal given to the lock-in amplifier (for double modulation the multiplicative term is $\cos[(\Omega_\tau + \Omega_{\omega_\tau})t]$) [40]. After passing through a low pass filter in the lock-in amplifier only the components having $(\Omega_\tau + \Omega_{\omega_\tau})$ frequency will survive and all other frequency terms will be rejected. Finally, we have the expression (up to a scale factor denoting the detector efficiency) for the dc voltage $V_{\text{lockin}}$ displayed by the lock-in amplifier as the measured signal for a given $\tau$ and $\omega_m$:

$$V_{\text{lockin}} = -\frac{\omega_0^2 T c^2}{256 \pi^2 k_z^2 \mu_0} \left[ \Gamma^2 + (\omega_0 - \omega_m)^2 \right] |\hat{a}_m|^2 \left[ \bar{E}_{\text{rad}}(t, \tau, \omega_\tau, \Omega_\tau, \Omega_{\omega_\tau}) e^{-\Gamma t} e^{i(\omega_0 - \omega_m)t} \right] \frac{e^{-\Gamma t} e^{i(\omega_0 - \omega_m)t}}{\Gamma - i(\omega_0 - \omega_m)}.$$  (22)

Here, the contribution coming from the cross term of the kind $\hat{a}_1(\Omega_{\omega_\tau}) \hat{a}_2(\Omega_{\omega_\tau}, \Omega_{\omega_\tau})$ or its complex conjugate is only retained while a higher order weak contribution coming from $|\hat{a}_2(\Omega_{\omega_\tau}, \Omega_{\omega_\tau})|^2$ term is neglected.

The theoretically calculated signal (equation (22)) has the following important features: (i) the signal is nonzero at negative delay and it is exponentially decaying with $\tau$ with a time constant $\Gamma = T_c^{-1}$ when monochromator is tuned at the transition frequency, i.e. $\omega_m = \omega_0$. (ii) if the signal is detected at a frequency other than $\omega_0$, an oscillatory feature is superimposed on the exponentially decaying part of the signal as a function of delay, where the oscillation period depends on the detuning $\omega_0 - \omega_m$; (iii) for a fixed $\tau$, the signal oscillates as a function of $\omega_m$, the detection frequency set at the monochromator i.e. coherent spectral oscillations are predicted, and (iv) $\int S(\tau, \omega_\tau) d\omega_\tau \approx 0$ due to the oscillatory cosine term in the signal. This implies that without the monochromator the signal is zero which has been reported earlier [12, 38]. It is
worth noting that while the inverse Lorentzian shape of the signal and coherent oscillations have been reported for negative delay for differential absorption [3], our form for probe reflected signal consists of a single term and is quite different. For zero delay the coherent oscillations vanish and we get a purely negative bleaching.

4. Experimental results

Let us now compare this theory with the experiment performed at low temperature (4 K) on a canonical sample, high quality GaAs QWs. The experimental arrangement is already described in figure 1. The Fourier-transform-broadened (≈10 meV) degenerate pump and probe pulsed-laser-beams (≈100 fs) were frequency tuned to the heavy-hole exciton (hh-x) resonance (≈1.5275 eV) in this multi-quantum well sample having the well-width of 17.5 nm. Figure 3 shows the delay dependence of the PPDR signal measured after it was passed through the monochromator with the bandpass of the monochromator set at the hh-x resonance. The PPDR signal measured at the hh-x peak in the negative delay region (where the probe precedes the pump) survives up to about 6 ps. Note the logarithmic scale along y-axis in figure 3 represents the magnitude of the signal measured by the lock-in amplifier. The straight line behaviour on the semilogarithmic scale is indicative of the exponential decay, as predicted by equation (22). This exponentially decaying signal is the signature of the free-induction-decay. To extract the dephasing time \( T_2 \), the PPDR signal in the negative delay is fitted with a single exponential function, giving \( T_2 = 1.5 \) ps. Note that for the convenience of calculation, the arrival times of the pump and probe pulses are set in theory in such a way that \( \tau \) is positive for negative delay (probe preceding the pump). The experimental results depicts data for both the negative and positive delays and here \( \tau \) is negative (positive) for negative (positive) delays.

Figure 3. Delay dependence of the PPDR signal at the hh-x peak for 17.5 nm QW sample measured at 4 K. Solid line is an exponential fit to the data at negative delay region giving a dephasing time \( T_2 = 1.5 \) ps. The decay of the signal at the positive delay is governed by the radiative lifetime \( T_1 \). Note that identical scales are set along the x- and y-axes for the plots of the experimental and theoretical spectra at different delays. The signal is multiplied by a suitable multiplicative factor to fill the real estate of the plot. While the experimental spectra suggest the presence of a weaker (defect related) second resonance at a slightly lower energy, the theoretical fits (equation (22)) used only a single resonance to minimize the number of free adjustable parameters.

Figure 4. Continuous wave PLE spectrum for the 17.5 nm QW sample is plotted around the hh-x peak. The solid line is a Lorentzian fit which gives the line width of the spectrum corresponding to the dephasing time \( T_2 \) of 1.68 ps which is in excellent agreement with the value estimated in figure 3.

Figure 5. (Left column) Spectrally-resolved pump–probe reflectivity signal for different negative delays for the 17.5 nm QW sample at 4 K. The pump and the probe powers were 10 mW and 0.5 mW respectively. (Right column) Theoretically calculated spectra using equation (22) for \( \text{fs} \) were frequency tuned to the heavy-hole exciton (hh-x) resonance (≈1.5275 eV) in this multi-quantum well sample having the well-width of 17.5 nm. Figure 3 shows the delay dependence of the PPDR signal measured after it was passed through the monochromator with the bandpass of the monochromator set at the hh-x resonance. The PPDR signal measured at the hh-x peak in the negative delay region (where the probe precedes the pump) survives up to about 6 ps. Note the logarithmic scale along y-axis in figure 3 represents the magnitude of the signal measured by the lock-in amplifier. The straight line behaviour on the semilogarithmic scale is indicative of the exponential decay, as predicted by equation (22). This exponentially decaying signal is the signature of the free-induction-decay. To extract the dephasing time \( T_2 = 1/\Gamma \), the PPDR signal in the negative delay is fitted with a single exponential function, giving \( T_2 = 1.5 \) ps. Note
that the radiative decay time $T_1 \gg T_2$ in equation (22) and hence the effect of $T_1$ is safely ignored.

Figure 4 shows the photoluminescence excitation (PLE) spectrum (which is equivalent to measuring the absorption spectrum [39]) around the hh-x peak. The Lorentzian fit to the PLE spectrum gives the full-width-at-half-maximum (FWHM) equivalent to the dephasing time $T_2 (= 2\hbar /\text{FWHM})$ of 1.68 ps which closely matches with the dephasing time estimated from the exponential fit in figure 3. This supports the validity of our PPDR measurements.

Finally, coherent spectral oscillations [3, 14] can be seen in figure 5 where the spectrally-resolved PPDR signal around the hh-x resonance is plotted for the negative delay values fixed at 0, 2, 4, and 6 ps. The theoretically calculated spectra using equation (22) for $\hbar \omega_0 = 1.5275 \text{eV}$ and $\hbar \Gamma = 0.4 \text{meV}$ are shown in the accompanying figures at corresponding delays. They qualitatively match the experimental spectra as they reproduce the coherent spectral oscillation and the exponential decrease of the signal near hh-x peak with increasing delay. Deviations on the lower energy side may be explained by the decrease of the signal near hh-x peak with increasing delay. The oscillation frequency increases with increasing negative delay due to the $\cos[(\omega_0 - \omega_m)\tau]$ dependence.

5. Summary and outlook

Given how non-intuitive the interpretation of the negative-delay pump–probe differential reflectivity (PPDR) signal is, we felt that it will be useful to explicitly work out a complete theory of the PPDR experiment giving a closed-form expression to establish the relationship between the measured signal and the perturbed-free-induction-decay of polarization. The analysis clearly brought out the following specific features of the third-order perturbed-free-induction-decay signal: (i) the signal is nearly zero without the monochromator, (ii) it would scale proportional to both the pump and the probe intensities, (iii) the signal measured at resonance energy decays exponentially with the (negative) delay with the value of the decay constant being the dephasing time, (iv) the signal for a fixed value of negative delay shows coherent spectral oscillations as a function of energy. The predictions were explicitly tested in a low-temperature PPDR experiment on GaAs quantum well sample, where coherent oscillations were observed to survive up to a negative delay of 6 ps between the probe and the pump beam. Our experimental data has a reasonable match with the theoretically calculated output signal. The presence of lower energy bound states make the signal slightly deviate from the theoretical one. Perhaps the most noteworthy is the close agreement of the experimentally obtained dephasing time from the perturbed-free-induction-decay with the inverse linewidth of the absorption profile of the damped driven oscillator (inferred from the continuous wave PLE spectrum linewidth). Given the generality and simplicity of our analysis, we hope that the PPDR experiments will become more popular and will be further used to study other systems having plasmonic and other quasiparticle resonances that may arise out of strong electron correlation.

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