Electron–phonon relaxation and excited electron distribution in zinc oxide and anatase

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Received 13 June 2012, in final form 8 August 2012
Published 12 September 2012
Online at stacks.iop.org/JPhysCM/24/405802

Abstract

We propose a first-principles method for evaluations of the time-dependent electron distribution function of excited electrons in the conduction band of semiconductors. The method takes into account the excitations of electrons by an external source and the relaxation to the bottom of the conduction band via electron–phonon coupling. The methods permit calculations of the non-equilibrium electron distribution function, the quasi-stationary distribution function with a steady-in-time source of light, the time of setting of the quasi-stationary distribution and the time of energy loss via relaxation to the bottom of the conduction band. The actual calculations have been performed for titanium dioxide in the anatase structure and zinc oxide in the wurtzite structure. We find that the quasi-stationary electron distribution function has a peak near the bottom of the conduction band and a tail whose maximum energy rises linearly with increasing energy of excitation. The calculations demonstrate that the relaxation of excited electrons and the setting of the quasi-stationary distribution occur within a time of no more than 500 fs for ZnO and 100 fs for anatase. We also discuss the applicability of the effective phonon model to energy-independent electron–phonon transition probability. We find that the model only reproduces the trends in the change of the characteristic times whereas the precision of such calculations is not high. The rate of energy transfer to phonons at the quasi-stationary electron distribution also have been evaluated and the effect of this transfer on the photocatalysis has been discussed. We found that for ZnO this rate is about five times less than in anatase.

1. Introduction

Zinc oxide in the wurtzite structure and titanium dioxide in the anatase structure are semiconductors of great interest from many viewpoints. Both demonstrate photocatalytic activity in the UV region of the sun’s spectra, and they are widely used as basic compounds in attempts to create photocatalysts active in visible sunlight that can be used to clean the environment of organic pollutants and pathogenic bacteria [1–5]. They are also prospective materials for applications in solar energetics and random access memory devices [6–8]. The photocatalytic activity, magnetic properties and charge transport in these oxides to a great extent depend on the dynamics of the excited states, therefore in many works the characteristics of fast electron and hole dynamics have been studied. In [9–12] the relaxation rates of excited electrons in ZnO via electron–phonon coupling have been estimated, while in [13–16] the characteristics of relaxation rates for anatase have been evaluated.

Understanding the results obtained in the experimental works requires an application of some theoretical models that should incorporate both the conditions of the experiments.
and the characteristics of electron dynamics determined by the properties of the solids under study. Such models have been successfully developed and widely applied for excited electron relaxation in metals [17–19]. In the case of semiconductors, this aim is, however, far from being achieved, partly because only recently have the rigorous methods for evaluations of the characteristics of electron dynamics been developed. The main phenomenon responsible for the relaxation of the low-energy excited electrons in semiconductors (whose energy with respect to the bottom of the conduction band is no more than the band gap) is the electron–phonon coupling. A number of first-principles methods for the calculations of the parameters of this coupling have been developed that permit one to perform subsequent calculations for the temporal characteristics of electron relaxation. Possibly the most promising of these is provided by the density-functional perturbation theory [20, 21] implemented in the pseudo-potential Quantum Espresso (QE) computer code. Recently this approach has been applied to the evaluations of the characteristics of electron relaxation in ZnO [22], anatase and rutile [23], and germanium [24]. The calculations have demonstrated a reasonable correspondence to experimental data and helped in understanding some fine relations between the band structure and electron dynamics in the compounds.

The shortfall of the evaluations of [22, 23] was that they had been performed for a case of a single excited electron in the conduction band that falls down to the bottom of the band, losing energy via the electron–phonon coupling. More rigorous estimations of the electron dynamics should include also the emergence of new electrons excited by the external light source and also the effect of filling the energy level under consideration with the electrons falling from the higher levels. The method of such evaluations is proposed in the current paper. Although the concrete results are obtained for ZnO and TiO$_2$, the proposed method does not have any features preventing its application to different kinds of semiconductor. The method is based on fully first-principles calculations of the electron–phonon coupling constants. So it does not have simplifying assumptions on the energy dependence of the rate of electron–phonon relaxation. It is worth noting that the neglect of the energy dependence of the electron–phonon interaction is a conventional approximation, as it is, for example, with Fröhlich’s Hamiltonian [25–28]. So, together with the characteristics of electron relaxation in ZnO and TiO$_2$, we discuss also the applicability of the energy-independent electron–phonon coupling and find that in the current case it is of very limited accuracy.

2. Method of calculations

2.1. Quasi-stationary electron distribution

We start with the following Boltzmann equation for the time-dependent distribution function $f(t, \epsilon)$ of excited electrons (hereafter EDF) at an energy $\epsilon$ above the bottom of the conduction band of a semiconductor (hereafter excess energy)

$$\frac{df(t, \epsilon)}{dt} = \left[ (1 - n(t, \epsilon)) \int_{0}^{\omega_{e}} n(t, \epsilon + \hbar \omega) F(\epsilon + \hbar \omega, \omega) d\omega - n(t, \epsilon) \int_{0}^{\omega_{e}} F(\epsilon, \omega)(1 - n(t, \epsilon - \hbar \omega)) d\omega \right] + \frac{\partial f_{\text{inel}}(t, \epsilon)}{dt}. $$

(1)

In this equation $n(t, \epsilon) = f(t, \epsilon)/N(\epsilon)$, with $N(\epsilon)$ being the density of electronic states, is the population of a single band state at the $\epsilon$ level. The first integral describes, in a momentum-averaged manner, the process of electrons going to the level $\epsilon$ from all the electronic states higher in energy by $\hbar \omega$, a process accompanied by the emission of phonons whose maximum frequency is $\omega_{e}$. $F(\epsilon + \hbar \omega, \omega)$, the spectral function of electron–phonon interaction, is the probability for electrons to fall from all the band states with energy $\epsilon + \hbar \omega$ to the states at energy $\epsilon$, emitting phonons with energy $\hbar \omega$ satisfying the conditions of energy and momentum conservation. Similarly, the second integral describes the process of electron transitions from the $\epsilon$ level to the levels lower in phonon energy by $\hbar \omega$. We discuss only the case of low intensity irradiation, so we assume that the $n(t, \epsilon)$ values are small and omit the factors $1 - n(t, \epsilon)$. The spectral function $F(\epsilon, \omega)$, satisfying energy and momentum conservation, has the form

$$F(\epsilon, \omega) = \sum_{nkk'} \sum_{\sigma \sigma'} P(nk, n'k', \sigma \sigma') \delta(\epsilon - e_{nk}) \delta(\omega - \omega_{q} - \hbar \omega_{q}) \delta(\epsilon - e_{n'k'}) $$

(2)

where $P(nk, n'k', \sigma \sigma')$ is the probability of a single electron transition between the electronic band states $|nk\rangle$ and $|n'k'\rangle$ accompanied by the emission or absorption of a photon with frequency $\omega_{q}$. The calculations of such a spectral function, which for the Fermi level in metals is proportional to the well-known Eliashberg function, have been extensively discussed in the literature [29, 30]. In accordance to the ‘golden Fermi rule’, this probability, per unit of time, is determined as

$$P(nk, n'k', \sigma \sigma') = \frac{2(2\pi/\hbar)^{2}}{\langle |nk| \Delta V_{q} |n'k'\rangle^{2}} \delta(e_{nk} - e_{n'k'}). $$

(3)

Here the value $\Delta V_{q}$ is the variation of the self-consistent potential in the crystal caused by the displacement mode of the phonon, and the value $\langle |nk| \Delta V_{q} |n'k'\rangle$ is the matrix element of the electron–phonon interaction. The energy of the phonon, small in comparison with the energy of electronic states, is neglected here. The ways of calculating this matrix element also have been discussed [21].

Notice that in such an approach electron scattering accompanied by the emission of both optical and acoustic phonons with all kinds of polarization is incorporated. This is an advantage of the approach in comparison with methods that consider the emission of only optical phonons, such as the dielectric constant approach for bulk phonons [29], hybrid phonons approach for multilayers [31] or quantum-kinetic approach for quantum dots [32]. In our approach we neglect
polaronic effects, since they are essential for slow electrons in the states very close to the bottom of the conduction band and that is outside the region of our interest. This is confirmed by the theoretical evaluations of Persson et al [33], demonstrating that for rutile the polaronic effects essentially modify the dielectric function only at 0.05 eV. On the other hand, the experimental cyclotron mass of electrons in ZnO, 0.23, is very close to the calculated band mass, 0.24, see Imanaka et al [34]. Since the experimental mass is influenced by polaronic effects, such a comparison demonstrates the weakness of these effects.

The term \( \frac{\partial f_{\text{inst}}(t, \epsilon)}{\partial t} \) in equation (1) describes the instantaneous electron distribution in the conduction band produced by the external source of excited electrons. One can take for this term the approximation

\[
\frac{\partial f_{\text{inst}}(t, \epsilon)}{\partial t} = S_0(t)S(\epsilon)
\]  

where the factor \( S_0(t) \), which in general can be time-dependent, is the concentration of the excited electrons determined by the power of the light radiation, and \( S(\epsilon) \) is the instantaneous spectral function (hereafter IEDF) which describes the probability for an excited electron to have an excess energy \( \epsilon \). Naturally, IEDF should be normalized to unity:

\[
\int_0^\infty S(\omega) \, d\omega = 1.
\]

If one linearizes the energy dependence of the \( F(\epsilon + h\omega_0, \omega) \) with \( \omega \) as a small parameter then equation (1) is written in the form

\[
\frac{\partial f(t, \epsilon)}{\partial t} = \frac{\partial}{\partial \epsilon} \left[ N^{-1}(\epsilon)f(t, \epsilon)B(\epsilon) \right] + \frac{\partial f_{\text{inst}}(t, \epsilon)}{\partial t}.
\]  

Here the function

\[
B(\epsilon) = \int_0^{\omega_{\text{exc}}} \hbar \omega F(\epsilon, \omega) \, d\omega
\]

is the energy lost by the electrons at the level \( \epsilon \) via phonon emission. So the value which we define as \( \Delta \epsilon = B(\epsilon)/N^2(\epsilon) \) is the averaged energy lost by one electron in the process of phonon emission; a first-principles approach to the calculations of this value has been demonstrated in [23, 22].

Equation (5) describes the time evolution of the \( f(t, \epsilon) \) EDF when the light source produces an instantaneous distribution of excited electrons in the conduction band. We discuss here the quasi-stationary case, when the temporal evolution of the external pulse is slow and \( \frac{dS_0(t)}{dt} \ll S_0(t)B(\epsilon) \). Taking \( \frac{\partial f(t, \epsilon)}{\partial t} \approx 0 \) one has the solution of the equation (5) in the form

\[
f(t, \epsilon) = S_0(t) \frac{1}{\Delta \epsilon N(\epsilon)} \int_{\epsilon}^{\epsilon_{\text{exc}}} S(\epsilon') \, d\epsilon'
\]

where \( \epsilon_{\text{exc}} \) is the highest excess energy of the excited electrons.

The IEDF, \( S(\omega) \), can be obtained from the electronic band structure calculations. Namely, if the energy of the quantum of optical excitation is \( E_{\text{exc}} \), then for the excess energy \( \epsilon \) one has to sum the probabilities of all direct excitations from the electronic states at energy \( \epsilon - E_{\text{exc}} \) to the states at energy \( \epsilon \). Hence, the un-normalized IEDF is

\[
S(\epsilon) = \sum_{k n' k'} \delta(\epsilon - \epsilon_{n k})T(n k, n' k') \delta(\epsilon - E_{\text{exc}} - \epsilon_{n' k'})
\]

where \( T(n k, n' k') \) is the probability of the transition between the states \( |n k\rangle \) and \( |n' k'\rangle \). (In practical calculations we replace the \( \delta \)-functions with the normalized Gaussians whose width at the half-maximum is 0.01 eV). The transition probability also can be evaluated on the basis of first-order perturbation theory. In order to calculate the matrix elements of equation (8) we take advantage of the atomic sphere approximation [35]. In this approximation integration over the space of a crystal is replaced with an integration over atomic spheres. In every atomic sphere we take for the perturbation the dipole approximation [36]. With this approximation the Hamiltonian of the interaction of an atom with the electric field of the light \( \mathbf{E}(\omega) \) has the form

\[
H_S = e\mathbf{D}_S \mathbf{E}(\omega).
\]

Here \( \mathbf{e} \mathbf{D}_S = e\sum \mathbf{r}_j^2 \), where \( \mathbf{r}_j^2 \) is the radius with respect to the center of the given atom, is the operator of the dipole moment of the atom. Hence, the interaction of an electron with the field is

\[
H(\omega) = e \sum_S \mathbf{r}_j^2 \epsilon_{\mathbf{k}} \mathbf{E}(\omega).
\]

We consider the case of interaction of light with a polycrystal, so we have for the angle-averaged transition rate

\[
T(n k, n' k') = \frac{2\pi}{\hbar} e^2 (E(\omega))^{\frac{3}{2}} \delta(e_{n k} - \epsilon_{n' k} - \omega)
\]

\[
\times \frac{1}{3} \left| \sum_S \langle k, j | \mathbf{r}_j^2 | k', j \rangle \right|^2.
\]

Here the overlap of atomic spheres is neglected, and the coefficient 1/3 emerges because of the averaging over the angle between the vector \( \mathbf{r}_j^2 \) and the directional vector of the field \( \epsilon_{\mathbf{k}} \), see details in [36].

2.2. Electron–phonon energy loss time and the time of EDF setting

The value \( F(\epsilon + h\omega_0, \omega) \) in equation (1), according to the definition (2), is the probability of transitions from all the electronic states at energy \( \epsilon + h\omega_0 \) to all the states at energy \( \epsilon \). So we apply to this value the approximation

\[
F(\epsilon + h\omega_0, \omega) = N(\epsilon + h\omega_0)P(\epsilon)N(\epsilon)\delta(\omega - \omega_0)
\]

where \( P(\epsilon) \) is the momentum-averaged probability of a single transition at electron energy \( \epsilon \) and phonon energy \( h\omega_0 \). The energy dependence of \( P(\epsilon) \) is often neglected, as it takes place in numerous works with Fröhlich’s electron–phonon interaction, see e.g. [25, 27, 28]. We will show in section 3 that the energy dependence of \( P(\epsilon) \) can be omitted only for the aim of interpretation. In fact this dependence is not negligible. Employing approximation (12) and introducing for the external source definition

\[
\frac{\partial n_{\text{inst}}(t, \epsilon)}{\partial t} = \frac{\partial f_{\text{inst}}(t, \epsilon)}{\partial t} / N(\epsilon)
\]

we can rewrite equation (1) in the form

\[
\frac{\partial f(t, \epsilon)}{\partial t} = \frac{\partial}{\partial \epsilon} \left[ N^{-1}(\epsilon)f(t, \epsilon)B(\epsilon) \right] + \frac{\partial f_{\text{inst}}(t, \epsilon)}{\partial t}.
\]
\[
\frac{\partial n(t, \epsilon)}{\partial t} = [n(t, \epsilon + \hbar \omega_0)P(\epsilon)N(\epsilon + \hbar \omega_0) - n(t, \epsilon)P(\epsilon)N(\epsilon - \hbar \omega_0)] + \frac{\partial n_{inst}(t, \epsilon)}{\partial t}.
\]  \tag{14}

After linearization near energy \(\epsilon\) the equation becomes
\[
\frac{\partial n(t, \epsilon)}{\partial t} = P(\epsilon)\hbar \omega_0 \frac{1}{N(\epsilon)} \frac{\partial}{\partial \epsilon} [N^2(\epsilon)n(t, \epsilon)] + \frac{\partial n_{inst}(t, \epsilon)}{\partial t}.
\]  \tag{15}

The \(B(\epsilon)\)-value takes in the effective phonon approximation of the form \(B(\epsilon) = \hbar \omega_0 N(\epsilon)P(\epsilon)N(\epsilon)\). Then it follows that \(\Delta \epsilon(\epsilon) = \hbar \omega_0 P(\epsilon)\). So the relation between the \(\Delta \epsilon\) and \(\hbar \omega_0\) values is quite sensible; the loss of electron energy is simply the product of the averaged emitted phonon energy and the averaged probability of emission (all per unit of time).

We introduce a new variable
\[
q(t, \epsilon) = N^2(\epsilon)n(t, \epsilon)
\]  \tag{16}

and get for this value the equation
\[
\frac{\partial q(t, \epsilon)}{\partial t} = \hbar \omega_0 N(\epsilon) \frac{\partial q(t, \epsilon)}{\partial \epsilon} + \frac{\partial n_{inst}(t, \epsilon)}{\partial t} N^2(\epsilon).
\]  \tag{17}

One can show that in the absence of light the formal solution of equation (17) at energy \(E\) can be written as
\[
q(t, E) = \Phi \left\{ t + [\hbar \omega_0]^{-1} \int_{E_i}^{E} d\epsilon (P(\epsilon)N(\epsilon))^{-1} \right\}
\]  \tag{18}

where \(\Phi\) is an arbitrary function; this function and the energy \(E_i\) have to be chosen in order to satisfy the initial conditions. We assume for the initial conditions that at \(t = 0\) the electron is excited by the external source to the level \(E_i\), and afterwards the source is switched off. It is easy to check that these conditions are satisfied if \(\Phi\) is a \(\delta\)-like function, so
\[
n(t, E) = N^{-2} \delta \left\{ t + [\hbar \omega_0]^{-1} \int_{E_i}^{E} d\epsilon (P(\epsilon)N(\epsilon))^{-1} \right\}.
\]  \tag{19}

The equation
\[
t + [\hbar \omega_0]^{-1} \int_{E_i}^{E} d\epsilon (P(\epsilon)N(\epsilon))^{-1} = 0
\]  \tag{20}

is then that of relaxation of the excited electron. Hence for the rate of energy relaxation we have
\[
\frac{dE}{dt} = -\hbar \omega_0 P(E)N(E)
\]  \tag{21}

and the energy loss time, that is the time necessary for the electron to fall from the level \(E_i\) to the bottom of the conduction band, is
\[
\tau_l(E_i) = (\hbar \omega_0)^{-1} \int_0^{E_i} (P(\epsilon)N(\epsilon))^{-1} d\epsilon.
\]  \tag{22}

In real calculations the lower limit of integration has to be replaced with the maximum energy of phonons \(\hbar \omega_m\), since at lower energy the distribution function is determined by different mechanisms, mainly by electron–hole recombination.

Equation (22) demonstrates the relation between the time of energy loss and the density of states. One can reveal also the relation between the energy loss time in the current paper and that in the previous works [23, 22]. In the cited papers the rate \(\Gamma(\epsilon)\) of the electron–phonon relaxation has been defined via
\[
\Gamma(\epsilon) = P(\epsilon)N(\epsilon).
\]  \tag{23}

So the \(\Gamma\) value is the transition probability from the electronic state at energy \(\epsilon\) to all the states inside the energy interval from \(\epsilon - \hbar \omega_m\) to \(\epsilon\), and the equation for the energy loss time is
\[
\tau_l(E_i) = (\hbar \omega_0)^{-1} \int_0^{E_i} \Gamma^{-1}(\epsilon) d\epsilon.
\]  \tag{24}

Since the value \(\Delta \epsilon\) is almost independent of energy [23, 22], this equation is similar to the equation for the energy loss time proposed in [23, 22].

One more function of interest is also the time of setting of the quasi-stationary electron distribution. Now we assume that the source of light is switched on at \(t = 0\) and slowly changes afterwards, satisfying the condition \(dS_0(t)/dt \ll S_0(t)B(\epsilon)\). The time of setting is determined as the time necessary for transient processes to extinguish after the light is switched on. Employing definitions (13) and (23) and neglecting the energy dependence of \(P\) we can rewrite equation (14) as
\[
\frac{\partial n(t, \epsilon)}{\partial t} = n(t, \epsilon + \hbar \omega_0)\Gamma(\epsilon + \hbar \omega_0) - n(t, \epsilon)\Gamma(\epsilon - \hbar \omega_0) + \frac{\partial n_{inst}(t, \epsilon)}{\partial t}.
\]  \tag{26}

We solve this equation supporting on a set of excess electron energies \(\epsilon_p = \hbar \omega_m + p\hbar \omega_0\), \(p = 0–m\), that is from \(\hbar \omega_m\) to the maximum excess energy \(\epsilon_m\). Introducing the notation \(\Gamma_p = P(\epsilon_p)N(\epsilon_p)\) we transform equation (28) to the set of equations near the \(\epsilon_p\) levels:
\[
\frac{\partial n(t, \epsilon_m)}{\partial t} = -n(t, \epsilon_m)\Gamma_m - \frac{\partial n_{inst}(t, \epsilon_m)}{\partial t} + \frac{\partial n_{inst}(t, \epsilon_{m-1})}{\partial t}.
\]  \tag{27}

\[
\frac{\partial n(t, \epsilon_{m-1})}{\partial t} = -n(t, \epsilon_{m-1})\Gamma_{m-1} - \frac{\partial n_{inst}(t, \epsilon_{m-1})}{\partial t} + \frac{\partial n_{inst}(t, \epsilon_{m-2})}{\partial t}.
\]  \tag{27}

\[
\frac{\partial n(t, \epsilon_{m-p})}{\partial t} = -n(t, \epsilon_{m-p})\Gamma_{m-p} - \frac{\partial n_{inst}(t, \epsilon_{m-p})}{\partial t} + \frac{\partial n_{inst}(t, \epsilon_{m-p+1})}{\partial t}.
\]  \tag{27}

For the highest energy level the solution is
\[
n(t, \epsilon_m) = \int_0^t \frac{\partial n_{inst}(t', \epsilon_m)}{\partial t} \Gamma_{m-1} + n(0, \epsilon_m) e^{-\Gamma_{m-1}t'} dt'.
\]  \tag{28}
For the lower energy levels, except of the zeroth, the solution obtained by recursion is
\[ n(t, \epsilon_m) = \left[ \int_{0}^{t} \frac{\partial n_{\text{inst}}(t', \epsilon_{m-p})}{\partial t'} e^{-\Gamma_{m-p} t'} + n(0, \epsilon_{m-p}) \right] \times e^{-\Gamma_{m-p} t}. \tag{29} \]

Here we defined the modified source function
\[ \frac{\partial \tilde{n}(t, \epsilon_{m-p})}{\partial t} = \frac{\partial n_{\text{inst}}(t, \epsilon_{m-p})}{\partial t} + n(t, \epsilon_{m-p+1}) \Gamma_{m-p+1}. \tag{30} \]

The solution for the \( m \)th level has terms proportional to \( e^{-\Gamma_{m} t} \), so omitting these terms decaying with characteristic time \( \tau_m = 1/\Gamma_{m-1} \) one obtains the static solution
\[ n(t, \epsilon_m) = \frac{\partial n_{\text{inst}}(t, \epsilon_m)}{\partial t} / \Gamma_{m-1}. \tag{31} \]

The solution for the level \( \epsilon_{m-1} \) becomes static after the time
\[ \tau_{m-1} = \tau_m + 1/\Gamma_{m-2} \tag{32} \]
and it has the form
\[ n(t, \epsilon_{m-1}) = \frac{1}{\Gamma_{m-1} \Gamma_{m-2}} \times \left[ \frac{\partial n_{\text{inst}}(t, \epsilon_m)}{\partial t} + \frac{\partial n_{\text{inst}}(t, \epsilon_{m-1})}{\partial t} \right] \Gamma_{m-1}. \tag{33} \]

It follows from further recursion that for an arbitrary level \( \epsilon_p \) the static solution is realized after the time
\[ \tau_p = \sum_{k=p}^{m-1} 1/\Gamma_k \tag{34} \]
and it is
\[ n(t, \epsilon_p) = \frac{1}{\Gamma_p \Gamma_{p-1} \cdots \Gamma_1} \frac{\partial n_{\text{inst}}(t, \epsilon_p)}{\partial t} \prod_{s=p}^{m-1} \Gamma_s. \tag{35} \]

Taking into account the smallness of the \( \hbar \omega_0 \) value and the definition (23) we can replace these sums with integrals
\[ \tau_s(E_i) = (\hbar \omega_0)^{-1} \int_{E_{i-1}}^{E_i} \Gamma(\epsilon)^{-1} \, d\epsilon \tag{36} \]
and
\[ n(t, E_i) = \frac{1}{\hbar \omega_0 (P(E_i) N(E_i))^2} \times \int_{E_{i-1}}^{E_i} P(\epsilon) N(\epsilon) \frac{\partial n_{\text{inst}}(t, \epsilon)}{\partial t} \, d\epsilon. \tag{37} \]

Equation (36) is similar to equation (22), but contrary to the time of energy loss the time of EDF setting is determined by the time of the transitions to \( E_i \) from all the higher states. It is easy to show that if the source function is defined via equation (4) then equation (37) becomes, as it has to be, equivalent to equation (7).

3. Technical details

We apply the described approach to the cases of ZnO in the wurtzite structure and TiO2 in the anatase structure. Pure ZnO is a semiconductor with a direct band gap of 3.4 eV, whereas anatase has a band gap 3.2 eV. The energy band structure of pure anatase and zinc oxide has been extensively studied, mainly by the methods of density-functional theory. Normally such methods produce a value of band gap much less than the experimental data. The present study is based on the band structure calculations [37, 23, 22] for the pure and doped anatase modified by applying single-site Coulomb correlation corrections within the LSDA + U approach based on the LMTO band structure method. Such an approach produces, for the pure and doped anatase, values of the band gap and energies of impurity states close to experimental data. However, this method of the band gap correction is not sufficient for zinc oxide. So in this case we apply to the conduction band states of zinc oxide the ‘scissor operator’, hence we perform a rigid shift of all the conduction band states to a higher energy until a good value of the band gap is achieved. Such an approach is justified by the comparison with the results of the band structure calculations of ZnO corrected by the application of the GW many-body theory [38]. They demonstrate that the application of the many-body GW corrections produces almost uniform shifts of the conduction band states to a higher energy.

4. Results and discussions

In figures 1 and 2 the main data on the band states, IEDF and EDF are given for zinc oxide. The bands of ZnO between −6.2 and −4 eV are those composed of the Zn 3d-states, the states between −4 eV and the Fermi level consist of the O 2p valence states, whereas the conduction band states, composed of the Zn 4s-states, are separated by the direct band gap 3.4 eV wide.

In figure 2 instead of the \( f(\epsilon) \) EDF function for zinc oxide the function \( \phi(\epsilon) \) is given which is associated with \( f(\epsilon) \) as \( \phi(\epsilon) = f(\epsilon) N(\epsilon)/\epsilon S(\epsilon) \). It reflects fine details of the relation between the IEDF and EDF functions and does not depend on time. The EDF \( f(\epsilon) \)-function itself is smooth and it hardly depends on the excitation energy \( E_{\text{exc}} \). An example of this function is given in the conclusions.

It follows from figure 2 that in the case of zinc oxide the main feature of the \( S(\omega) \) IEDF function is a Gaussian peak whose maximum energy increases linearly with a rise in excitation energy. This peak corresponds to the vertical transitions from the highest valence band states to the lowest conduction band states for the points located in the \( \Gamma\text{–}K \) direction of the Brillouin zone and in the vicinity of this direction. With an increase of the excitation energy the wavevector of the transition shifts from the \( \Gamma \) to the \( K \) point. The transition matrix elements of such excitations are much higher than the TME for excitations from all the lower valence band states, so the excitations from the lower states manifest themselves as low satellites of the main peak. In correspondence with this IEDF function, the quasi-stationary...
function $\phi(\omega)$ demonstrates a Fermi-like distribution of the excited electrons in the conduction band, with an almost constant number of electrons at energy levels from the bottom of the conduction band to the energy $E_{exc} \approx 3.4$ eV.

In figures 3 and 4 the data concerning electron dynamics in ZnO anatase are given. Figure 3 also characterizes the applicability of the 'effective phonon' approximation with energy-independent transition probability $P$. The change of the total probability $\Gamma(\epsilon)$ (taken from [22, 23]) with energy is almost linear beginning from the lowest excess energy $\epsilon = \hbar \omega_{m}$, whereas the density of states $N(\epsilon)$ also changes almost linearly, but reduces to very small values at the low limit. Therefore the value $P(\epsilon) = \Gamma(\epsilon)/N(\epsilon)$ diverges near the bottom of the conduction band, but at an energy above 0.3 eV the change of $P(\epsilon)$ with energy is slow.

The calculated data on the energy loss time $\tau_l$ and EDF setting time $\tau_s$ are shown in figure 4. They demonstrate that the relaxation of the electrons to the bottom of the conduction band occurs within a time less than 500 fs. The setting of the quasi-stationary electron distribution in the presence of the steady-in-time light source also occurs within a time of no more than 500 fs. These data are in reasonable correspondence with the experimental data [9, 12, 10, 11]. An analysis of the problems of comparing the experimental and theoretical data can be found in [22].

In figure 4 also the data on $\tau_l$, $\tau_s$ are given, calculated with a constant value of the transition probability $P$. In order to obtain the best results the integration interval from 0 to 0.3 eV has been excluded from the calculations. The calculations demonstrate that the approximation of the energy-independent $P$ produces sufficiently good results only at an excess energy more than 0.7 eV. Variation of the $P$-value does not help to improve the correspondence with the results of the calculations with the energy-dependent probability.
Figure 3. Dependence of the relaxation rate $P$ on the excess energy $\epsilon$ for zinc oxide. In the inset also the energy dependences of the total relaxation rate $\Gamma$ and density of states $N$ are given.

In figure 5 the density of states and dispersion curves for anatase are given. The conduction band states at energies from 3.2 to 7.8 eV above the Fermi level are composed mainly of 3d Ti states. The corresponding density of states changes sharply with energy, evoking the essential variation of $\Gamma$-probability [22]. Opposite to the case of ZnO, the calculations demonstrate that the band gap of anatase is not direct. The highest valence band states, with almost equal energy, are observed at the Z- and M-point whereas the lowest conduction band state is at the $\Gamma$-point. The decrease of energy of the highest valence states in the direction from the M to $\Gamma$ point has been confirmed recently in ARPES experiments [39].

In figure 6, at excitation energies from 3.5 to 3.8 eV the $S(\omega)$ dependences for anatase also are Gaussian peaks accompanied by low-energy satellites. Similarly to the case of zinc oxide they correspond to the transitions from the highest occupied valence band states to the lowest conduction band states. The wavevectors of these excitations are located in the $\Gamma$–Z direction or in the vicinity of it. For example, the excitations at 3.5 eV occur from the states near the middle point of the $\Gamma$–Z direction, the excitations at 3.6 eV occur from the states near the Z point, and the excitations at 3.8 eV occur from the states near the $\Gamma$ point. However, contrary to the case of zinc oxide, the TME for excitations from some lower band states are higher than those for the excitations from the highest valence band states. Such are the band states that belong to the 13th and 14, 15th degenerate dispersion curves on figure 4 and the states of general symmetry in the vicinity of these curves. So, when the excitation energy increases to a value sufficient for the excitations from these lower bands, and this energy is 3.9 eV, a shift of the $S(\omega)$ peaks to the lower $\omega$ occurs. At energies above this threshold the

Figure 4. Dependence of the EDF setting time $\tau_s$ (thick solid line) and energy loss time $\tau_l$ (thick dashed line) on the excess energy $\epsilon$ for ZnO. Also the values of the $\tau_s$ (thin solid line) and $\tau_l$ (thin dashed line) are given calculated with the constant transition probability $P = 1$ eV fs$^{-1}$.

Figure 5. Left panel: the density of states of anatase; right panel: energy band structure of anatase near the band gap. Both kinds of data are given with respect to the Fermi level.
excitations from the highest valence band states to the lowest conduction band states contribute only to low satellites of the $S(\omega)$ functions. In comparison with ZnO, this modification of $S(\omega)$ provokes an essential change in the corresponding $\phi(\omega)$ EDF function. At energies above 3.9 eV it is no longer a Fermi-like regularity, but is composed of the main peak at $\epsilon \leq 0.6$ eV and a low shoulder extending up to an excess energy equal to $E_{\text{exc}} - 3.2$ eV. So at any $E_{\text{exc}}$ and $\epsilon$ the number of excited electrons in anatase is markedly less than in ZnO.

The characteristics of electron dynamics are given for anatase in figures 7 and 8. As in the case of ZnO, the transition probability $P$ shows divergence near the bottom of the conduction band. The interval of rapid change of $P$ with energy extends from zero to about 0.7 eV. At higher energy, $P$ varies near 0.25 eV fs$^{-1}$, a value much less than in the case of ZnO. Nevertheless, as follows from figure 8, both the energy loss time $\tau_l$ and EDF setting time $\tau_s$ appear to be much less than for ZnO. This is associated with much higher values of density of states that provide higher rates of electron–phonon relaxation. Also the $\tau_l$ and $\tau_s$ values are shown in figure 8, calculated with constant value $P = 0.25$ eV fs$^{-1}$.

5. Conclusions

We have proposed a first-principles method for evaluations of the distribution function of excited electrons in the conduction band of semiconductors. The approach takes into account
the rate of the energy transfer
higher density of states in the conduction band of anatase.

Therefore, the rate of the energy transfer via electron–phonon coupling, the emergence of new electrons excited by an external light source and redistribution of electrons between the energy levels. The method has been applied to the evaluations of the static electron distribution function in anatase and zinc oxide; the time of energy loss and the time of setting of the static distribution also have been calculated.

The method also helps lead to some conclusions that may have a relationship to the photocatalytic activity of the compounds. It is generally accepted that the photocatalytic activity of the oxide semiconductors is to a great extent determined by light absorption because it is proportional to the number of created electron–hole pairs. Therefore the band structure and optical absorption in pure and doped ZnO and TiO$_2$ has been the subject of a great number of calculations, see e.g. [40]. Also a factor important for the photocatalytic activity is the rate of charge transfer between the oxide and molecules absorbed on surface; this rate should be higher than the rate of electron–hole recombination. This factor deserves special attention, but so far it has hardly been touched upon in first-principles approaches. Our calculations permit one to discuss one more characteristic of oxides that also can be important. Namely, one should expect that, irrespectively of the details of the processes on the surface, the less the energy loss of excited electrons in the bulk, the more is the portion of the absorbed energy of light that can be used to produce a photochemical reaction. So it is worthwhile introducing the value

$$
epsilon_{ph}(\epsilon) = \hbar \omega_{\gamma}(\epsilon) \Gamma(\epsilon)$$  \hspace{1cm} (38)$$

as the measure of the energy transfer to the phonon system. In figure 9 we compare these values for ZnO and anatase (the factor $\hbar \omega_{\gamma}$ is omitted). They are given for an excess energy of 0.3 eV, that is, the energy midway between the band gap and the edge of the solar light, 4 eV. The EDF for different $E_{exc}$ are similar to the given EDF and differ only in the presence of a low tail that extends up to the excess energy $\epsilon = E_{exc} - E_G$. The $\Gamma$ value for anatase is about five times higher than for ZnO, but the $f(\epsilon)$ value for anatase is much less in this energy region than for ZnO because of much higher density of states in the conduction band of anatase.

Therefore, the rate of the energy transfer $\epsilon_{ph}(\epsilon)$ appears to be much higher for ZnO than for anatase. This can be a factor in favor of the higher photocatalytic activity of anatase. Since this factor depends only on the states of conduction band and on the electron–phonon coupling for only these states, one can expect that such a conclusion is also valid for ZnO and anatase doped with any element producing states inside the band gap. So, based only on these data, we may expect that the doped anatase is a more promising material for photocatalytic applications in visible light than the doped ZnO.

There is, however, a factor that acts in the opposite direction, namely, the value of the $f(\epsilon)$ EDF-function itself. It is generally accepted that the chemical transformation of a molecule absorbed on the surface of an oxide semiconductor is a consequence of the electron transfer from the bulk of the semiconductor to the empty anti-bonding state of the molecule. So, one should expect that the higher the value of the EDF, the more intensive the electron transfer and the more pronounced the photocatalytic activity of the semiconductor. Since the EDF of ZnO is much higher in the whole discussed energy region, based on the $f(\epsilon)$ value one may expect that the ZnO should be the more active photocatalyst. The photocatalytic properties of doped ZnO have been studied much less than those of doped TiO$_2$. Nevertheless, there are a few papers containing the comparison of activity of ZnO and anatase in the reactions of photo-bleaching of red dye [41, 42]. It has been shown in [41] that a ZnO catalyst composed of nano-particles has an activity equal to that of the analogous anatase catalyst, in spite of the surface area of the anatase catalyst being more extensive. The comparison of the effectiveness of ZnO- and TiO$_2$-based photocatalysts in degradation of dyes made by the authors of the [42] demonstrated a 20–30% superiority of the ZnO-based catalysts. There are also examples of doped ZnO-based catalysts that have high activity in visible light [43, 44].

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