Binding energies of hydrogen-like impurities in a semiconductor in intense terahertz laser fields

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We present a detailed theoretical study of the influence of linearly polarised intense terahertz (THz) laser radiation on energy states of hydrogen-like impurities in semiconductors. The dependence of the binding energy for ground (1s) and first excited (2s) states, $E_{1s}$ and $E_{2s}$, on intensity and frequency of the THz radiation has been examined for a GaAs-based system. It is found that $E_{1s}$, $E_{2s}$ and $E_{2s} - E_{1s}$ decrease with increasing radiation intensity or with decreasing radiation frequency, which implies that an intense THz field can enhance ionisation of dopants in semiconductors. Our analytical and numerical results show that one of the most important results obtained by A.L.A. Fonseca \textit{et al} [phys. stat. sol. (b) \textbf{186}, K57 (1994)] is incorrect.
1. Introduction

The ionisation of dopants (i.e., donor and acceptor impurities) provides the major source of carriers (i.e., electrons and holes) in semiconductors. The ionised dopants are also the major sources of electron-impurity scattering in semiconductor devices, which determine the transport and optical properties of the device systems at low-temperatures. Hence, the investigation of ionisation of dopants (such as binding energies of donors and acceptors, transition energies and probabilities among different impurity states, etc.) is fundamental in understanding almost all physically measurable properties in semiconductors. In the absence of an intense electro-magnetic (EM) radiation field, the binding energies of dopants and the transition energies among different impurity states in popularly used semiconductor materials are known [1] and the theoretical approaches to calculate these impurity states are well-documented [2].

It should be noted that in semiconductor materials such as GaAs, Ge and Si, the binding energies of donor and acceptor impurities are of the order of terahertz ($10^{12}$ Hz or THz) photon energies [3] so that an intense THz radiation can affect strongly the impurity states. With development and application of coherent, high-power, long-wavelength, frequency-tunable and linearly polarised radiation sources such as THz or far-infrared (FIR) free-electron lasers (FELs) [4], it has now become possible to measure the effect of an intense laser radiation on ionisation and perturbation of dopants (especially shallow impurities) in different semiconductor systems. In recent years, using THz FELs [such as Free Electron Laser for Infrared eXperiments (FELIX) in The Netherlands and CW FELs at UCSB] as intense radiation sources, THz-photon-induced impact ionisation in InAs heterostructures [5], time-resolved shallow donor spectrum in Si-doped GaAs [6] and Lyman transitions in Be-doped GaAs [7] have been investigated through, e.g., transport and/or photoconduction measurements. The results obtained experimentally indicate that in the presence of intense laser radiation such as FEL fields, i) impurity states in different semiconductor systems are perturbed by the intensity and frequency of the THz laser fields [5-7]; ii) photoconduction experiments are more sensitive than optical measurements for detecting transition energies of impurity states in semiconductors [6,7]; and iii) some interesting intense radiation phenomena, such as impact ionisation of dopants [5] and splitting and broadening of the impurity spectrum [7], can be observed. In order to understand these fundamentally new experimental findings and to predicate new radiation phenomena, it is essential to know theoretically how an intense laser field affects the binding energies of impurities in semiconductors and is the prime motivation of the present study.

In this paper, we study binding energy of hydrogen-like impurities in bulk semiconductors in the presence of intense THz laser fields. For semiconductor materials such as GaAs, there is an absolute conduction band minimum at $\mathbf{K} = 0$ with $\Gamma_6$ symmetry and the electron-effective-
mass and dielectric constant can be considered to be isotropic. Therefore, the impurity states in materials such as GaAs are strictly scaled-down versions of those in the hydrogen atom. The small electron-effective-mass coupled with the large static dielectric constant result in small binding energy for donors in these materials [3]. It has been noticed by atomic physicists in their early work that intense UV radiation can affect strongly the structure of atomic hydrogen [8]. Using theoretical approaches proposed and developed in Ref. [8], Nunes and co-workers have investigated the influence of intense laser radiation on hydrogen-like impurity states in bulk semiconductors [9] and in semiconductor quantum well structures [10]. However, in Ref. [9], only the ground-state energy at high-intensity radiation was presented analytically. We find that it is hard to understand the result given by Eq. (13) in Ref. [9], because it shows that at high-intensity radiation limit (ie, $\alpha_0 \to \infty$) the ground-state binding energy $E_0 \to -R_y^*$ (binding energy in the absence of the radiation) with $R_y^*$ being the effective Rydberg constant. In order to see how impurity states in a semiconductor are perturbed within the frequency and intensity range of the current generation of the THz FELs, we think it is necessary to re-examine the dependence of the impurity binding energy in a semiconductor on frequency and intensity of the THz fields. Moreover, since most of the experimental work in this area has been carried out using photoconduction experiments [6,7] which measure the transition energies among different impurity states, it is also necessary to know how an intense THz radiation affects the excited impurity states in a semiconductor. In Section 2, we will first briefly introduce the theoretical approaches used for the calculations then present analytical results of the binding energies for ground and first excited impurity states. The numerical results will be presented and discussed in Section 3 and the conclusions drew from this study will be summarised in Section 4.

2. Analytical results

In this work, we consider the situation where a laser field with a vector potential $A(t)$ is applied along the x-direction of a semiconductor and the radiation field is polarized linearly along the z-direction. Under the effective mass approximation, the time-dependent Hamiltonian to describe the electron-impurity system is given as

$$H(t) = \frac{1}{2m^*}[p_x^2 + p_y^2 + (p_z - eA(t))^2] - \frac{e^2}{\kappa R}.$$  \hspace{1cm} (1)

Here, $m^*$ is the electron-effective-mass, $p_x = -\hbar \partial / \partial x$ is the momentum-operator along the x-direction, under the dipole approximation $A(t) = (F_0/\omega)\sin(\omega t)$ is the vector potential induced by the radiation field with $\omega$ being the radiation frequency and $F_0$ the electric field strength of the radiation field, $R = (r, z) = (x, y, z)$, and $e^2/\kappa R$ is the Coulomb potential induced by electron-impurity interaction with $\kappa$ being the dielectric constant. It can be seen that due to time-dependent nature of the radiation field, in principle, we have to solve time-dependent Schrödinger equation: $[i\hbar \partial / \partial t - H(t)]\Psi(R, t) = 0$ to obtain the electronically...
bounded impurity states. However, at present, there is no simple analytical solution to this problem [11]. Here we employ a tractable theoretical approach proposed and developed by atomic physicists [8] to study the binding energy of the impurity states. The key issue of this approach is to find laser-dressed potential energy. It is found that if the coordinate along the z-axis is shifted by 

\[ z' = z + z_0(t) \]

with \( z_0(t) = -\left(\frac{eF_0}{m^*\omega^2}\right)\cos(\omega t) \), the Schrödinger equation becomes

\[
i\hbar \frac{\partial \Psi(R', t)}{\partial t} = \left[ \frac{p_x^2 + p_y^2 + p_z'^2}{2m^*} + V(R', t) \right] \Psi(R', t),
\]

(2a)

where \( R' = (r, z') \) and

\[
V(R', t) = -\frac{e^2}{\kappa \sqrt{r^2 + [z' - z_0(t)]^2}} + \frac{[eA(t)]^2}{2m^*}.
\]

(2b)

After averaging \( V(R', t) \) over a period of the radiation field, we obtain laser-dressed potential as

\[
V(R') = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} dt \, V(R', t) = E_{em} - \frac{e^2}{2\kappa}[|R' + R_0|^{-1} + |R' - R_0|^{-1}].
\]

(3)

Here \( E_{em} = (eF_0)^2/4m^*\omega^2 \) is the energy shift induced by the radiation field due to dynamical Franz-Keldysh effect [12] and \( R_0 = (0, 0, eF_0/m^*\omega^2) \). It should be noted that in atomic physics, \( E_{em} \) is also called ponderomotive energy [13]. If we replace \( V(R', t) \) in Eq. (2a) by \( V(R') \) given by Eq. (3), the time-dependent problem becomes approximately a time-independent one and the solution is \( \Psi(R', t) = e^{-i(E_N + E_{em})t/\hbar}\Psi_N(R') \), where the wavefunction \( \Psi_N(R') \) and the energy spectrum \( E_N \) are determined by \( (H_0 - E_N)\Psi_N(R') = 0 \) with

\[
H_0 = \frac{p_x^2 + p_y^2 + p_z'^2}{2m^*} - \frac{e^2}{2\kappa}(|R' + R_0|^{-1} + |R' - R_0|^{-1}).
\]

(4)

In contrast to Refs. [8-10], in the derivations shown above we have included the terms associated with \( F_0^2 \) which, as can be seen, only contributes to the energy shift induced by the radiation field alone. The main merit of this approach is that now one can convert a time-dependent problem into a time-independent one and, thus, one can use, e.g., variational method to calculate the energy states and the corresponding wavefunctions. It should be noted that the present theoretical approach is a generalization of those proposed by the atomic physicists. As has been pointed out by Ref. [13], this approach is the lowest order approximation to the atomic problem. Furthermore, the results given by Eqs. (3) and (4) have been documented by Refs. [9,10] for the case of the hydrogen-like impurities in a semiconductor.

In the present work, we employ the wavefunctions for a hydrogen atom as the trial functions for ground state (ie, 1s-state) and first excited state (ie, 2s-state) of the donor impurities, which reads

\[
\Psi_{1s}(R') = ae^{-\beta R'/a_0^*}
\]

(5a)
and

$$\Psi_{2s}(\mathbf{R}') = c(1 + bR'/a_0^*)e^{-\gamma R'/2a_0^*}, \quad (5b)$$

where $\beta$ and $\gamma$ are variational parameters, $a_0^* = h^2\kappa/m^*e^2$ is the effective Bohr radius, $a = (\beta^3/\pi a_0^*3)^{1/2}$ is determined by $< 1s|1s > = 1$, and $b = -(\beta + \gamma/2)/3$ and $c = \gamma^{5/2}/[8\pi a_0^*3(12b^2 + 6b\gamma + \gamma^2)]^{1/2}$ are determined respectively by $< 1s|2s > = 0$ and $< 2s|2s > = 1$. After introducing these trial functions to the variational method, i.e., $E_N = < N|H_0|N >$, the binding energies of the 1s-state and 2s-state are obtained as

$$E_{1s} = -R_y^*(2\alpha_0^* - \beta^2 - \frac{2}{\alpha_0^*}(1 + \alpha_0^*\beta)e^{-2\alpha_0^*\beta}], \quad (6a)$$

and

$$E_{2s} = -\frac{R_y^*(4/\alpha_0^*)}{4}(24b^2 + 12b\gamma + 2\gamma^2 - \mathcal{A}e^{-\alpha_0^*\gamma}) - \gamma^2(4b^2 + 2b\gamma + \gamma^2) \frac{12b^2 + 6b\gamma + \gamma^2}{2b^2 + 6b\gamma + \gamma^2}, \quad (6b)$$

where $\alpha_0^* = eF_0/m^*\omega^2a_0^*$, $R_y^* = m^*e^4/2h^2\kappa^2$ is the effective Rydberg constant, and

$$\mathcal{A} = 24b^2 + 12b\gamma + 2\gamma^2 + \alpha_0^*\gamma(18b^2 + 8b\gamma + \gamma^2) + 2\alpha_0^*b\gamma^2(3b + \gamma) + \alpha_0^*b^2\gamma^3.$$

Furthermore, the variational parameters $\beta$ and $\gamma$ are determined respectively by

$$\beta - (1 + 2\alpha_0^*\beta)e^{-2\alpha_0^*\beta} = 0 \quad \text{and} \quad \partial E_{2s}/\partial \gamma = 0.$$

The results shown above indicate that the effect of the radiation field on binding energy of the impurities is mainly achieved through a dimensionless factor $\alpha_0^* = e^3F_0/h^2\kappa\omega^2 \sim F_0/\omega^2$. For high-frequency and/or low-intensity radiation so that $\alpha_0^* \ll 1$, we have

$$E_{1s} \simeq -R_y^*(1 - \frac{4}{3}\alpha_0^*2) \quad \text{and} \quad E_{2s} \simeq -\frac{R_y^*}{4}(1 - \frac{2}{3}\alpha_0^*2), \quad (7)$$

which suggests that the binding energy decreases quickly with increasing radiation intensity or with decreasing radiation frequency when $\alpha_0^* \sim 1$. When $\alpha_0^* = 0$, $E_{1s} = -R_y^*$ and $E_{2s} = -R_y^*/4$ are well-known results obtained in the absence of the radiation field. For low-frequency and/or high-intensity radiation, entailing $\alpha_0^* \gg 1$, we find that there is no simple analytical expression for both $E_{1s}$ and $E_{2s}$, in contrast to Eq. (13) obtained by Ref. [9]. When $\alpha_0^* \to \infty$, we find $\beta \to 0$ and $\gamma \to 0$ so that $E_{1s} \to 0$ and $E_{2s} \to 0$ (note that a zero binding energy implies that all impurities at this state are ionised). These theoretical results indicate that $E_{1s}$ and $E_{2s}$ are altered from respectively $-R_y^*$ and $-R_y^*/4$ at zero field to zero at high-field limit. One of the most important results obtained by Ref. [9] is that at high-intensity radiation fields, the ground-state binding energy is given by Eq. (13) which shows $E_{1s} \to -R_y^*$ when $\alpha_0 \to \infty$ and $E_{1s} < -R_y^*$. Our results here suggest that Eq. (13) obtained by Ref. [9] is incorrect.
3. Numerical results

Below we present numerical results for semiconductor materials such as GaAs. The material parameters for GaAs taken within the calculations are the effective-electron-mass ratio $m^*/m_e = 0.0665$ with $m_e$ being the electron rest mass and the static dielectric constant $\kappa = 12.9$. The dependence of binding energies $E_{1s}$ and $E_{2s}$ as well as transition energy $E_{2s} - E_{1s}$ on THz laser radiation fields is shown in Figures 1 - 4. From these results, we see that:

a) in the presence of the radiation fields, $E_{1s}$ and $E_{2s}$ are altered from respectively $-R_y^*$ and $-R_y^*/4$ at low-field limit to zero at high-field limit and $E_{2s} - E_{1s}$ is altered from $3R_y^*/4$ at low-field limit to zero at high-field limit. This confirms that Eq. (13) obtained by Ref. [9] is incorrect;

b) with increasing radiation intensity and/or decreasing radiation frequency, $E_{1s}$, $E_{2s}$ and $E_{2s} - E_{1s}$ decrease;

c) $E_{2s}$ depends a bit weakly on the radiation field than $E_{1s}$ does, which can be understood by Eq. (7);

d) the strong effect of the radiation field on binding energy and transition energy can be observed at $\alpha_0^* \sim 1$; and

e) $E_{1s}$, $E_{2s}$ and $E_{2s} - E_{1s}$ depend more strongly on radiation frequency than on radiation intensity because $\alpha_0^* \sim F_0/\omega^2$.

The results discussed above indicate that in the presence of the intense THz laser fields, the binding energies of the impurity states can be reduced and the impurity spectrum in semiconductors can be shifted significantly by the radiation.

It should be noted that the current generation of the FELs can provide intense THz radiation sources in the frequency and intensity range $f \sim 0.1 - 10$ THz and $F_0 \sim 0.1 - 100$ kV/cm [14] so that the condition $\alpha_0^* = e^3F_0/h^2\kappa\omega^2 \sim 1$ can be satisfied by most of the popularly used semiconductor materials. We therefore believe that it has now become possible to investigate the effects of the intense laser radiation on ionisation and perturbation of dopants in semiconductor systems by using current generation of THz or FIR FELs.

4. Further remarks

In the present study, our calculations have been performed for shallow-impurities in semiconductor materials such as GaAs, because these impurities are hydrogen-like. It is well known that in semiconductors, deep-impurities may not be hydrogen-like because their states depend strongly on lattice structure of the material systems, such as the symmetry of the crystal potential, electronic band structure, etc. To examine the effect of intense laser radiation on deep-impurity states in a semiconductor, the above mentioned theoretical approach has to be modified.
To our knowledge, except those theoretical results reported by Refs. [9] and [10] for semiconductor systems, so far very few theoretical and experimental results have been reported regarding the direct effects of the intense laser radiation on binding energies of electrons in atomic systems (two recent reviews are given in Refs. [13] and [15]) or of hydrogen-like impurities in semiconductor systems. The main reason behind this is that when an electronic system (atoms or semiconductors) is subjected to intense laser fields, the investigation of the electronic states (or electronically bounded impurity states) is essentially a time-dependent problem. As a consequence, these states are no longer the eigenstates and transitions among these time-dependent states can occur. Therefore, it is very hard to measure experimentally the binding energy for a certain atomic or impurity state when an intense laser radiation is present. Normally, the results obtained from atomic physics experiments [13,15] are contributions from all possible states and transitions among these states.

The analytical and numerical results shown in this paper are what one can get from the simplest theoretical model. As has been pointed out by Ref. [13], the approach used in the present study is the lowest order approximation to deal with the problem. Under such an approximation, the systems can be described in terms of a set of quasi-eigenstates of atom (or impurity) and laser field and there is no transition among these quasi-eigenstates. Namely, under this approximation, the system is “stable to ionisation”. Thus, the results obtained from this model can be useful in understanding atomic physics phenomena such as free-free transitions and dichotomy of the atomic states [8]. Furthermore, it can be shown [13] that the conditions under which the approach can be applied are \( \hbar \omega \gg E_{em} \) and \( R_0^2 \omega \gg 1 \). Therefore, the very low-frequency and high-intensity results shown in Figs. 1-4 in this paper may not be the case. To examine the effect of these extreme radiation conditions on states of hydrogen-like impurities in a semiconductor, the contributions from higher order terms (see Eq. (28) in Ref. [13]) have to be included. The inclusion of these higher order contributions requires considerably further analytical and numerical calculations and, therefore, we do not attempt it in the present study.

5. Conclusions

In this paper, we have re-examined how a linearly polarised intense laser field affects the binding and transition energies of shallow-donor impurities in a bulk semiconductor. The present study has been conducted on the basis of a theoretical approach proposed by Ref. [8] and documented by Refs. [9,10]. We have obtained results of binding energies for both ground and first excited impurity states and thus we can look into the effects of the radiation field on transition energy between 1s and 2s states, in conjunction with experimental work carried out by photoconductivity measurements [6,7]. The numerical and analytical results obtained from this work show that Eq. (13) in Ref. [9] is incorrect.
We have found that the strong influence of the radiation field on binding and transition energies of the shallow impurity states in bulk semiconductors can be observed when the condition $\alpha_0^* = \frac{e^3 F_0}{\hbar^2 \kappa \omega^2} \sim 1$ is satisfied. For most popularly used semiconductor materials such as GaAs, Si and Ge, these radiation conditions have been realised by the current generation of the THz or FIR FELs. We therefore hope that the phenomena studied and predicated in this paper can be verified experimentally.

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Figure captions

**Fig. 1:** Binding energies, $E_{1s}$ and $E_{2s}$, as a function of THz radiation frequency ($f = \omega/2\pi$) for different radiation intensities. $R_y^*$ is the effective Rydberg constant and for GaAs $R_y^* = 5.44$ meV.

**Fig. 2:** Transition energy between 2s and 1s impurity states, $E_{2s} - E_{1s}$, as a function of radiation frequency for different radiation intensities.

**Fig. 3:** $E_{1s}$ and $E_{2s}$ as a function of radiation intensity for different radiation frequencies.

**Fig. 4:** $E_{2s} - E_{1s}$ as a function of radiation intensity for different radiation frequencies.
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