Modeling of Quantized Electron and Hole States in GaAs Cylindrical Nanowires

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Recently, it has become possible to grow gallium arsenide nanowires of different crystal structures, zincblende and wurtzite, or alternating sections of these in a single nanowire. In order to understand the optical properties of such semiconducting nanowires, we apply an envelope function approximation to GaAs cylindrical nanowires. The wavefunction is described in terms of a cylindrical envelope function and perfect crystal Bloch states at the conduction band minimum (CBM) and valence band maximum (VBM). Degeneracies resulting from the VBM are described by the Kohn-Luttinger Hamiltonian in the case of zincblende and a modified version including a crystal field splitting in the case of wurtzite. As only the total angular momentum of the system is conserved, coupling of different angular momentum Bloch functions in the Hamiltonian leads to unusual coupling effects of the quantized states. The admixture of the crystal wave function in these quantized states has a significant effect on the polarization of emitted light, caused by a recombination of electron and hole states at the CBM and VBM, respectively. Energy eigenvalues for each structure are described in terms of the relevant quantum numbers and their dependence on nanowire radius, with appropriate visualizations to represent these findings. The polarization ratio of emitted light is understood as a function of temperature, as a result of the admixture of states.
Background

Nanowires are extremely thin but comparatively long crystals, roughly on the order of ~5-100 nm in radial size and several microns long. They are most often grown in the laboratory under extremely controlled conditions[1]. While the types of nanowires range from organic to semiconducting to metallic[1], the scope of this paper is limited to a discussion of semiconductor nanowires, currently a developing field. With the potential for electronic, ionic, and phonon transport, photoconductivity, and magnetic effects[2,3], there are a vast number of possible applications for semiconductor nanowires, and so there is a rapidly increasing interest in them.

Figure 1: Transmission electron micrograph from different segments of a single GaAs nanowire[4].

Due to the size restriction of nanowires, however, there is almost certainly a quantized effect on the wavefunctions of electrons in the nanowire. This requires a more detailed understanding of the electronic states of a semiconducting nanowire. Any differences from that of a bulk crystal model would then lead to different results, such as transport and optical properties. Many of the differences are derived from the lower dimensionality of the model: nanowires are effectively one-dimensional based on the length-to-radius ratio, and so the motion
is restricted to the transverse directions. Potentially, by determining these new properties, the capacity to begin creating semiconducting devices out of nanowires will exist: sensors, LEDs, and transistors on the nanometer scale[2,3].

Specifically, the focus of the paper is to determine and discuss these wavefunctions for gallium arsenide (GaAs) nanowires. Recent studies have reported on two structures found in GaAs nanowires, zincblende and wurtzite, whereas the bulk case of GaAs only exists in the zincblende structure[]. It appears possible to control the type of crystal structure by the growth rate, and nanowires in which the sections of both crystallographic types alternate can be grown by varying the growth conditions during the growth run. These separate crystal structures may significantly affect the electronic states of the nanowire.

Figure 2: Changes in symmetries as a result of zincblende and wurtzite mixing. Blue/red zincblende crystals form a cubic lattice, while green/red zincblende and wurtzite crystals form a hexagonal lattice[4].

In particular, changes in the polarization of light emitted by GaAs nanowires in photoluminescent spectra have been observed, but these findings are not yet understood.

Zincblende nanowires are observed to emit light that is polarized along the long axis of the nanowire, while wurtzite nanowires are observed to emit transversely polarized light, but could change to parallel polarization as a result of slightly increased temperature. It is not yet understood why this occurs for some nanowire samples and not others.
We will seek to understand the energy levels occurring in zincblende nanowires, taking into account added complications in valence band degeneracies at the quantized level. From there, we will generalize the case for wurtzite nanowires. The different crystallographic types are theoretically similar, and in our model the only difference is between the two is the inclusion of a crystal field splitting which separates the light and heavy holes in the valence band. This splitting results from a lower symmetry: zincblende has cubic, but wurtzite is hexagonal. If we take the valence band maximum (VBM) states by their X, Y, and Z-like components, a cubic crystal matches these components exactly while a hexagonal crystal’s Z-like component differs from its X and Y. (The terminology of heavy and light holes and their components will be discussed in more detail later.) Finally, by using the energy levels and wave functions derived in the previous cases, we will determine their consequences on the photoluminescence, focusing only on the lowest level in the electron and hole states. At low temperatures, these states appear at the ground level after excitation, with possible small splittings of order meV.

**Envelope function approximation**

A full description of a semiconducting nanowire, on a quantum mechanical level, requires the inclusion of confinement effects brought on by the overarching cylindrical shape of the wire as well as the effect of the underlying crystal structure with its periodically varying potential on electrons. In the bulk crystal case of a semiconductor, we need only concern ourselves with a single unit cell by assuming that the crystal itself is periodic. In the case of the nanowire, we require the additional constraint that the structure must take the shape of a cylinder, with the periodic behavior occurring dominantly along the axis of the cylinder, with any changes in transverse directions being truncated or only slightly perturbed near the surface. For even a small nanowire (~10nm), taking into account each individual unit cell, roughly 1nm
in diameter, across the whole cross section would require a model of 1000 atoms. As this is not an easy model to solve directly, we instead prefer to use an approximate method: the envelope function approximation (EFA)[5].

By assuming that the wavefunctions inside the nanowire only vary slightly from cell to cell, we can make a continuum approximation to describe the changes based on the cylindrical confinement. Furthermore, the effect of the crystal potential on the electrons can be included through effective mass parameters.

Although it is assumed that the reader is familiar with band theory of electrons, we recall that, in a periodic potential, the energy levels are given by energy bands: for each wavevector \( k \) there are several bands \( E_n(k) \). Near the band edges, either minima or maxima of the wavevector, the bands have approximately a parabolic dependence on \( k \) (acting as a quasi-momentum) and thusly behave as particles with an effective mass. If some bands reach a degenerate or nearly-degenerate state for some point of \( k \), as is the case for the valence band maximum of most semiconductors (such as GaAs), we require a generalization of this concept: an effective Hamiltonian with each matrix element of order \( k^2 \), whose eigenvalues determine the energy bands.

In the EFA, the total wave function in the nanowire is written as a product of a slowly-varying envelope function and the crystal Bloch functions at the band edges. This requires us to assume, within the scope of the approximation, that the variation inside each unit cell is independent of the variation from cell to cell. By using this wavefunction in the Schrödinger equation of the nanowire, it can be shown[6,7] that the envelope functions must obey a slightly different Schrödinger equation: the effective Hamiltonian becomes the operator acting on the envelope function by substituting the quasi-momentum, \( \hbar k \), with a more standard operator,
with the envelope function obeying appropriate boundary conditions. By assuming the potential to be infinite outside the nanowire and constant inside (excepting the established periodic potential), the envelope function must go to zero at the boundary of the nanowire. Upon solving the Schrödinger equation, there will be quantized values of \( k \) and therefore the energy levels are discrete.

![Figure 3: Example of a periodic function with a slowly-varying envelope confinement. Produced with Mathematica.](image)

For a cylindrical nanowire, the envelope function is just a cylindrical function, which is given generally by the following:

\[
\psi_{m,n,k_z}(\rho, \phi, z) = C_m J_m(k \rho) e^{i m \phi} e^{i k_z z} \tag{1}
\]

The radial coordinate is determined by the Bessel function, with appropriate coefficient; the angular coordinate is expressed as a periodic function, as \( \phi \) ranges from 0 to \( 2\pi \); the longitudinal coordinate is expressed in terms of a plane wave. Of particular significance is the interdependency of the radial and angular functions. This form of the envelope function results from solving the modified Schrödinger equation in cylindrical coordinates using the separation of variables method, which will be discussed in following sections with greater detail.

The effect of the crystal lattice is incorporated in our theory through the Bloch functions and the assumed \( E_n(k) \) or \( H_{ij}(k) \). As previously established, these correspond to bands near the
band edges: thus we have already restricted our attention to the states in the nanowires that result only from these bulk crystalline states. For GaAs, these band edges occur at \( k = 0 \), so the Bloch functions used, generally described as the product \( e^{ik\vec{r}}u_{k,\mu}(\vec{r}) \), are simply periodic functions. The full details of this Bloch function no longer matter: their effect is already incorporated into the \( E_n(k) \) or \( H_{ij}(k) \). The only consideration from the Bloch states, in fact, is their symmetry with regards to the nanowire. For the non-degenerate conduction band maximum (CBM), there is only one such function, separated by spin that is unnoticed in the band structure. For the VBM, there is a 3-fold degeneracy and thus there are several Bloch functions corresponding to the same energy.

The full wavefunction is expressed in the following terms:

\[
\psi_F(\rho, \phi) = \sum_{\mu} u_{\mu} \chi_{\mu}^F(\rho) e^{i(F-\mu)\phi} e^{ikz} \tag{2}
\]

where \( \mu \) is Bloch angular momentum component and \( F \) is the total angular momentum component. \( F \) will be conserved if we assume that the Hamiltonian used for the VBM maintains axial symmetry: the details of this Hamiltonian are discussed later in the paper.

At this point, we can restrict our view to the desired area: near the conduction band minimum (CBM) and valence band maximum (VBM) states. The wavefunctions in this region correspond to Bloch states in at the wavevector \( k = 0 \) where the CBM/VBM occur. Each band will now be determined separately.

**Conduction Band**

The energy of the electron at the CBM in a semiconductor like GaAs is similar to that of the free electron case, except that the electron carries an effective mass due to the properties of the semiconductor:
\[ E = \frac{\hbar^2}{2m^*} \mathbf{k}^2 \]  

where \( m^* \) is the effective mass of the electron. The wavefunction for a unit cell is given by a Bloch function, though due to the condition of \( \mathbf{k} = 0 \) only the periodic function remains. The envelope function is treated using three-dimensional cylindrical coordinates. It has been shown that the envelope function can be determined by replacing \( \hbar \mathbf{k} \) with \( -i\hbar \nabla \), the momentum operator acting on the envelope function. In this case, we obtain the Schrödinger equation

\[-\left( \frac{\hbar^2}{2m^*} \right)^2 \nabla^2 = E \] for a constant potential but with mass \( m^* \).

By taking our second-order differential in cylindrical coordinates and applying the separation of variables method, the solution is based on cylindrical harmonics. Namely, there is an independent plane wave along the axis of the cylinder and a periodic function dependent on the angular coordinate: the remainder of the differential equation is what is known as the Bessel function, \( J_m(k_\perp \rho) \), which depends both on the angular and radial coordinates. We find the wavefunction to be exactly the same form as (1): \( m \) can be understood here as the quantum number \( L_z \), providing a different angular form for a given \( m \).

At this point boundary conditions can be added in the following way: \( J_m(k_\perp a) = 0 \), where \( a \) is the radius of the nanowire. This restricts \( k_\perp \) to discrete values, thereby determining discrete energy values of the form \( E_{m,n} \), for a given \( m \) and the \( n \)th zero of \( k_\perp \). In the \( k_z \) direction we still have a plane wave, and so there is a continuous distribution of energy levels. That is, there is still an energy band \( \frac{\hbar^2}{2m_z} k_z^2 \), with \( m_z \) as the effective mass for motion in the \( z \)-direction, equal to \( m^* \) for the isotropic case but may change in other cases.

**Valence Band**
Unlike the conduction band, which consists of s-type atomic states, the valence band in GaAs corresponds to p-type atomic states. This causes a 3-fold degeneracy in the energy band at \( k = 0 \), resulting in three separate bands come together at this point that cannot be quantized separately, as they are mixtures of the same Bloch functions. These three bands are now derived from a 3x3 Hamiltonian matrix, leading to a three-component envelope function whose components interact with each other. The Hamiltonian used to describe this case is called the Kohn-Luttinger (KL) Hamiltonian[6]. The KL Hamiltonian is written explicitly as

\[
H_{ij} = \sum_{a,b} D_{ij} k_a k_b,
\]

where the matrix element \( D_{ij} \) corresponds to a particular Bloch function, which we define in terms of \( X, Y, \) and \( Z \) vectors, and \( a \) and \( b \) are the constituent coordinates of \( k \). It contains only quadratic terms but produces off-diagonal elements, implying that there are interactions between \( X, Y, \) and \( Z \) states, and that the effective mass of the electron will depend on direction. We will refer to these bands as holes rather than electrons, because they normally are filled and it is only the missing electrons or holes that matter for our purposes.

In full, the Hamiltonian takes the following general form:

\[
H = \begin{pmatrix}
Ak_x^2 + B(k_y^2 + k_z^2) & Ck_yk_x & Ck_zk_x \\
Ck_yk_x & Ak_y^2 + B(k_x^2 + k_z^2) & Ck_xk_y \\
Ck_zk_x & Ck_xk_y & Ak_z^2 + B(k_x^2 + k_y^2)
\end{pmatrix}
\]  

(4)

using Cartesian coordinates \( x, y, \) and \( z \). \( A, B, \) and \( C \) are Luttinger parameters that collectively determine the effective mass in a particular hole state. The form of this matrix can be deduced from symmetry considerations, and it should be noted that there are only three mass parameters. In addition to the 3-fold degenerate states based on direction of motion, there is also spin degeneracy: this leads to a 6-fold degeneracy in total.
Figure 4: Basic layout of band structure in GaAs. The band gap between CBM and VBM is ~1.5 eV.

By including the factor of spin-orbit coupling, the degeneracy splits into a 4-fold state and a 2-fold state, similar to the well-known atomic problem: the orbital angular momentum for p-states is \( L = 1 \) and the total angular momentum magnitude is given by \( J = L \pm 1/2 \). The 4-fold state corresponds to \( J = 3/2 \) and the 2-fold state corresponds to \( J = 1/2 \). The bands resulting from diagonalization of this matrix can be separated into the light hole, heavy hole, and split-off holes, each containing a 2-fold spin degeneracy. The light hole band curves most strongly, as it has the lowest mass, and starts out at the 4-fold level at \( \mathbf{k} = 0 \); the heavy hole band also starts at the 4-fold state but has a higher mass, indicating less curvature; the split-off holes exist at an energy level higher than the light and heavy holes, as a result of spin-orbit coupling. If we assume the energy levels found in the light and heavy holes to be much less than the spin-orbit coupling energy, we can ignore the split-off holes, altogether, leaving a 4-fold degeneracy among the light and heavy hole states.
The four Bloch states corresponding to the 4-fold degeneracy can be written in terms of their total angular momentum along the z-axis, \( J_z \): this produces \( m_j \) values of \( 3/2, 1/2, -1/2, \) and \(-3/2\), hereafter defined as Bloch angular momentum \( \mu \). From here, we can write out the KL Hamiltonian in terms of \( \mu \) and \( k \to -i\hbar \nabla \). As a final assumption, based on experimental results, we make a simplification of the Luttinger parameters in order to produce a more symmetric Hamiltonian. This is important for later simplifications because, together with the cylindrical symmetry of the boundary condition, it means that the total angular momentum of the wavefunction, \( F \), must be conserved. The result is a Hamiltonian of the following form:

\[
\begin{pmatrix}
\frac{\gamma_1}{2m_0} \nabla_z^2 + \frac{\gamma}{2m_0} (\nabla_x^2 - 2\nabla_y^2) & -i\sqrt{3}\gamma \frac{\nabla_x \nabla_y}{m_0} & \sqrt{3}\gamma \frac{\nabla_z^2}{m_0} & 0 \\
-i\sqrt{3}\gamma \frac{\nabla_x \nabla_y}{m_0} & \frac{\gamma_1}{2m_0} \nabla_z^2 - \frac{\gamma}{2m_0} (\nabla_x^2 - 2\nabla_y^2) & 0 & \sqrt{3}\gamma \frac{\nabla_z^2}{m_0} \\
\sqrt{3}\gamma \frac{\nabla_x \nabla_y}{m_0} & 0 & \frac{\gamma_1}{2m_0} \nabla_z^2 - \frac{\gamma}{2m_0} (\nabla_x^2 - 2\nabla_y^2) & i\sqrt{3}\gamma \frac{\nabla_x \nabla_y}{m_0} \\
0 & \sqrt{3}\gamma \frac{\nabla_x \nabla_y}{m_0} & -i\sqrt{3}\gamma \frac{\nabla_x \nabla_y}{m_0} & \frac{\gamma_1}{2m_0} \nabla_z^2 + \frac{\gamma}{2m_0} (\nabla_x^2 - 2\nabla_y^2)
\end{pmatrix}
\]

(5)

For convenience, the gradients are written such that \( \nabla^2 = \nabla_x^2 + \nabla_y^2 + \nabla_z^2 \), \( \nabla^2 = \nabla_x^2 + \nabla_y^2 \), and \( \nabla = \nabla_x \pm i\nabla_y \). In addition, the original Luttinger parameters are now in terms of \( m \) and \( \gamma_1, \gamma_2, \) and \( \gamma_3 \), and as a result of the simplification earlier, we write \( \gamma_2 \approx \gamma_3 \equiv \gamma \): the effective masses of the light and heavy hole are defined as \( m_\ell = m/(\gamma_1 + 2\gamma) \) and \( m_h = m/(\gamma_1 - 2\gamma) \), respectively.

Because the \( z \)-dependent part of these functions is in terms of a plane wave and separate from the rest of the problem, any \( \nabla_z \) will add a factor \( i\hbar k_z \). In our treatment of GaAs nanowires, we set \( k_z = 0 \), allowing for the kinetic energy related to motion along the \( z \)-axis to be added separately. With this simplification, several matrix elements disappear and the 4x4 Hamiltonian
breaks into two separate 2x2 matrices: this leads to two sets of two-component envelope functions and a 2x2 coupled different equation for each set. One couples the $\mu = 3/2$ and $\mu = -1/2$ states, the other couples $\mu = 1/2$ and $\mu = -3/2$. This leads to two Hamiltonians written as:

$$H_3^{3/2} = \frac{1}{2} \begin{bmatrix} \frac{\gamma + \gamma}{2m} & \frac{\sqrt{3}\gamma}{m} \\ \frac{\sqrt{3}\gamma}{m} & \frac{\gamma - \gamma}{2m} \end{bmatrix}$$

(6)

$$H_3^{3/2} = \frac{3}{2} \begin{bmatrix} \frac{\gamma - \gamma}{2m} & \frac{\sqrt{3}\gamma}{m} \\ \frac{\sqrt{3}\gamma}{m} & \frac{\gamma + \gamma}{2m} \end{bmatrix}$$

(7)

as well as a pair of two-component radial envelope functions written as:

$$\begin{pmatrix} \chi_{3/2}^F(\rho) \\ \chi_{-1/2}^F(\rho) \end{pmatrix} = \begin{pmatrix} c_{3/2}^F J_{F-3/2}\left(k\rho\right) \\ c_{-1/2}^F J_{F+1/2}\left(k\rho\right) \end{pmatrix}$$

(8)

$$\begin{pmatrix} \chi_{1/2}^F(\rho) \\ \chi_{-3/2}^F(\rho) \end{pmatrix} = \begin{pmatrix} c_{1/2}^F J_{F+1/2}\left(k\rho\right) \\ c_{-3/2}^F J_{F+3/2}\left(k\rho\right) \end{pmatrix}$$

(9)

By plugging (8) and (9) into (6) and (7), respectively, one can obtain the coefficients of the envelope function components, which describe the admixture of Bloch states at $\mathbf{k} = 0$ in the bands.

When understanding the states occurring at the VBM, it is of significant importance to remember that $\mu = \pm 3/2$ corresponds to heavy hole states and $\mu = \pm 1/2$ corresponds to light hole states. Thus, to say that the $\mu = 3/2$ and $\mu = -1/2$ states are coupled leads to the conclusion that the light and heavy hole states themselves are coupled, unlike the case for a bulk semiconductor. Furthermore, applying boundary conditions to each coupled envelope function
means that each component must go to zero simultaneously, and so the boundary condition must be written in terms of a linear combination of the components.

Zincblende Solutions

The quasi-momentum $\hbar k$ found by substituting (3) into the Schrödinger equation that uses (2) as the wavefunction and (5) as the Hamiltonian describe its relation to the energy of the holes, E:

$$ (\hbar k_{l,h})^2 = 2E \frac{m}{(\gamma_1 \pm 2\gamma)} $$

(10)
This relation corresponds to the light and heavy hole effective masses, and describe the
dispersion of the light and heavy exciton motion. The coefficients, $C_{\mu}^E$, for each Bloch state, are,
in the light hole states:

$$C_{3/2}^E = \frac{\sqrt{3}}{2}, C_{-1/2}^E = \frac{1}{2} \quad (11, 12)$$

$$C_{1/2}^E = \frac{1}{2}, C_{-3/2}^E = \frac{\sqrt{3}}{2} \quad (13, 14)$$

and for the heavy hole states:

$$C_{3/2}^E = \frac{1}{2}, C_{-1/2}^E = -\frac{\sqrt{3}}{2} \quad (15, 16)$$

$$C_{1/2}^E = -\frac{\sqrt{3}}{2}, C_{-3/2}^E = \frac{1}{2} \quad (17, 18)$$

We can now solve the boundary condition equation in terms of the envelope functions by
writing out $C_{\mu}^E J_{F-\mu}(k_{LH} a)$ for each component (where radius $a$ is the boundary of the nanowire),
then defining the linear combination of these components to be equal to zero. This expression is
what accurately describes the admixture of light and heavy hole states. We use the following
substitution $\equiv E/(h^2/2m a^2)$, to give the energy in dimensionless units: as a further
simplification, we introduce the variables $\eta = \sqrt{\varepsilon/(\gamma_1 - 2\gamma)}$ and $\beta = \sqrt{(\gamma_1 - 2\gamma)/(\gamma_1 + 2\gamma)}$,
such that the Bessel functions in the expression can now be written as $J_{F-\mu}(\eta)$ and $J_{F-\mu}(\eta\beta)$ for
the light and heavy hole excitons, respectively. This allows us to write the boundary condition
equation in the following way:

$$a \left( \frac{\sqrt{3}}{2} J_{F-3/2}(\eta\beta) \right) + b \left( \frac{1}{2} J_{F-3/2}(\eta) \right) = (0) \quad (19)$$
for the cases of $\mu = 3/2$ and $\mu = -1/2$ states and $\mu = 1/2$ and $\mu = -3/2$ states, respectively.

Finding the energy values of this system of equations is the same as finding its eigenvalues, in terms of $\eta$, given by the determinant of each system:

$$3J_{F-3/2}(\eta \beta)J_{F+1/2}(\eta) + J_{F+1/2}(\eta \beta)J_{F-3/2}(\eta) = 0$$  \hspace{1cm} (21)$$

$$J_{F-1/2}(\eta \beta)J_{F+3/2}(\eta) + 3J_{F+3/2}(\eta \beta)J_{F-1/2}(\eta) = 0$$  \hspace{1cm} (22)$$

The values of the coefficients corresponding to the linear combination factors in each system of equations ($a$ and $b$ for the $\mu = 3/2$ and $\mu = -1/2$ states, $c$ and $d$ for the $\mu = 1/2$ and $\mu = -3/2$ states) relate to the dominance of the light or heavy hole state. In particular, $a$ and $d$ represent the heavy hole component and $b$ and $c$ represent the light hole component for their respective system of equations. If we write these coefficients as ratios $b/a$ and $c/d$, the admixture can now be understood in terms of the light hole or heavy hole dominance using, for instance, $|b/a|/(1 + [b/a]^2)$: values greater than one indicate light hole dominance, and values less than one indicate heavy hole dominance.

The coefficient ratios are given by the following expressions:

$$\frac{b_F}{a_F} = \frac{\sqrt{3}J_{F-3/2}(\eta_i \beta)}{J_{F-3/2}(\eta_i)}$$  \hspace{1cm} (23)$$

$$\frac{c_F}{d_F} = \frac{\sqrt{3}J_{F-1/2}(\eta_i)}{J_{F-1/2}(\eta_i \beta)}$$  \hspace{1cm} (24)$$

where $\eta_i$ is the $i$th solution of the boundary condition equation, for a given value of $F$. 
The total wavefunction of each mixture of light and heavy hole states can be written in terms of the envelope and periodic functions. This gives us, for each coupled state:

\[
\psi_{\frac{F-1}{2}}(\rho, \phi) = \frac{a_F}{2} \left\{ \left( \sqrt{3} J_{F-3/2} \left( \eta \frac{\rho}{a} \right) - \sqrt{3} J_{F-1/2} \left( \eta \frac{\rho}{a} \right) \right) \right\} \\
\left\{ J_{F+1/2} \left( \eta \frac{\rho}{a} \right) + 3 \frac{J_{F-3/2} \left( \eta \frac{\rho}{a} \right)}{J_{F-3/2} \left( \eta \right)} J_{F+1/2} \left( \frac{\rho}{a} \right) \right\} (e^{i2\phi})
\]

(25)

\[
\psi_{\frac{F-3}{2}}(\rho, \phi) = \frac{d_F}{2} \left\{ \left( \sqrt{3} J_{F-1/2} \left( \eta \frac{\rho}{a} \right) - \sqrt{3} J_{F-1/2} \left( \eta \frac{\rho}{a} \right) \right) \right\} \\
\left\{ J_{F+3/2} \left( \eta \frac{\rho}{a} \right) + 3 \frac{J_{F-1/2} \left( \eta \frac{\rho}{a} \right)}{J_{F+1/2} \left( \eta \right)} J_{F+3/2} \left( \frac{\rho}{a} \right) \right\} (e^{i2\phi})
\]

(26)

where \(b_F\) has been written in terms of \(a_F\) and \(c_F\) has been written in terms of \(d_F\). Normalization of this wavefunction depends on the values of \(a_F\) and \(d_F\), and by setting \(|\psi|^2 = 1\), we are given the following normalized coefficients:

\[
a_F^{-2} = \frac{3}{4} a^2 \int_0^1 x dx \left( J_{F-3/2} \left( \eta \beta x \right) - \frac{J_{F-3/2} \left( \eta x \right)}{J_{F-3/2} \left( \eta \right)} J_{F-3/2} \left( \eta x \right) \right)^2
\]

\[
+ \frac{1}{4} a^2 \int_0^1 x dx \left( J_{F+1/2} \left( \eta \beta x \right) + \frac{J_{F-3/2} \left( \eta x \right)}{J_{F-3/2} \left( \eta \right)} J_{F+1/2} \left( \eta x \right) \right)^2
\]

\[
d_F^{-2} = \frac{3}{4} a^2 \int_0^1 x dx \left( J_{F-1/2} \left( \eta \beta x \right) - \frac{J_{F-1/2} \left( \eta x \right)}{J_{F-1/2} \left( \eta \right)} J_{F-1/2} \left( \eta x \right) \right)^2
\]

\[
+ \frac{1}{4} a^2 \int_0^1 x dx \left( J_{F+3/2} \left( \eta \beta x \right) + \frac{J_{F-1/2} \left( \eta x \right)}{J_{F+1/2} \left( \eta \right)} J_{F+3/2} \left( \eta x \right) \right)^2
\]

(27)

(28)

which can be plugged into our original wavefunction to satisfy the normalization condition.

Our original wavefunction, Eq. (2), expresses the angular component in terms of \(m\).

However, in the wavefunctions (25) and (26) there are two separate values of \(m\), as a result of the admixture of light and heavy hole states which required two values of \(\mu\) for a given value of \(F\).

This means that there are two wavefunctions, one from each coupled state, that have a
component with the same value of m: for instance, \( m = 0 \) exists both in the \( \mu = 1/2 \) component for \( F = 1/2 \) and in the \( \mu = 3/2 \) component for \( F = 3/2 \). Thus we can say that the energy levels for a given m are not only a result of the admixture between light and heavy hole states, but also of different total angular momentums.

**Wurtzite Solutions**

The setup for wurtzite nanowires is similar to that of zincblende, except that we now must introduce a crystal field splitting term to the Bloch states. The effect of the field splitting is that the light and heavy holes are separated by some energy level \( \Delta \), similar to the separation of light and heavy holes from the split-off holes. In the Hamiltonian, we express this field splitting by shifting the heavy holes by \(-\Delta/2\) and the light holes by \(+\Delta/2\): thus the new Hamiltonian for each coupled state is written as:

\[
H_{3/2}^{-1/2} = \begin{bmatrix}
\gamma_1 + \gamma & \sqrt{3} \gamma \\
2m & m
\end{bmatrix}
\begin{bmatrix}
\frac{\Delta}{2} & \frac{\Delta}{2} \\
\frac{\Delta}{2} & \frac{\Delta}{2}
\end{bmatrix}
\begin{bmatrix}
\gamma_1 - \gamma \\
2m
\end{bmatrix}
\]

\[
H_{3/2}^{3/2} = \begin{bmatrix}
\gamma_1 - \gamma & \sqrt{3} \gamma \\
2m & m
\end{bmatrix}
\begin{bmatrix}
\frac{\Delta}{2} & \frac{\Delta}{2} \\
\frac{\Delta}{2} & \frac{\Delta}{2}
\end{bmatrix}
\begin{bmatrix}
\gamma_1 + \gamma \\
2m
\end{bmatrix}
\]

The form of the envelope function remains unchanged, so the quasi-momentum relation to the energy levels, written as \( k_E = (h^2/2m)k^2 \), is expressed as:

\[
k_E^{\pm}(E) = \frac{\gamma_1 E - \gamma(\Delta/2) \pm \sqrt{4\gamma^2 E - \gamma_1 \gamma \Delta E + (\gamma_1^2 - 3\gamma^2)(\Delta/2)^2}}{\gamma_1^2 - 4\gamma^2}
\]

which, in the units given, describes the relation of the square of the momentum to the energy of the holes \( E \). By taking \( \Delta = 0 \), we find that the values of \( k_E \) are given as \( E/(\gamma_1 - 2\gamma) \) and
$E/(\gamma_1 + 2\gamma)$, similar in form to $\eta$ and $\eta \beta$ used in the case of zincblende. Notice that the quasi-momentum is given as a function of the energy.

The coefficients for the radial envelope function are determined by the following relation, for each coupled state:

$$c_{3/2}^{F,\pm} = \frac{\sqrt{3} \gamma k_E^\pm}{k_E^\pm (y_1 + \gamma) - \Delta/2 - E} c_{-1/2}^{F,\pm}$$ (32)

$$c_{1/2}^{F,\pm} = \frac{\sqrt{3} \gamma k_E^\pm}{k_E^\pm (y_1 - \gamma) + \Delta/2 - E} c_{-3/2}^{F,\pm}$$ (33)

Substituting $k_E^\pm$ into Eq. () gives us the values for each coefficient. These are also a function of the energy:

$$c_{3/2}^{F,\pm}(E) = \frac{\text{sign}[k_E^\pm (y_1 + \gamma) - \Delta/2 - E] \sqrt{3} \gamma k_E^\pm}{\sqrt{(k_E^\pm (y_1 + \gamma) - \Delta/2 - E)^2 + 3(\gamma k_E^\pm)^2}}$$ (34)

$$c_{1/2}^{F,\pm}(E) = \frac{|k_E^\pm (y_1 + \gamma) - \Delta/2 - E|}{\sqrt{(k_E^\pm (y_1 + \gamma) - \Delta/2 - E)^2 + 3(\gamma k_E^\pm)^2}}$$ (35)

$$c_{1/2}^{F,\pm}(E) = -\frac{\text{sign}[k_E^\pm (y_1 - \gamma) + \Delta/2 - E] \sqrt{3} \gamma k_E^\pm}{\sqrt{(k_E^\pm (y_1 - \gamma) + \Delta/2 - E)^2 + 3(\gamma k_E^\pm)^2}}$$ (36)

$$c_{-3/2}^{F,\pm}(E) = \frac{|k_E^\pm (y_1 - \gamma) + \Delta/2 - E|}{\sqrt{(k_E^\pm (y_1 - \gamma) + \Delta/2 - E)^2 + 3(\gamma k_E^\pm)^2}}$$ (37)

where $\text{sign}[]$ is a function that returns +1 if the formula inside is greater than zero and -1 if the formula inside is less than zero.

As in the case of zincblende, we can now write the boundary condition equation in terms of the envelope functions by writing out $C_{\mu}^{F}\mu F_{-\mu}(\kappa_\pm a)$ for each component (where $\kappa_\pm(E, a) =$
\[ k_F^\pm(E) / (\hbar^2 / 2m a^2) \] is the dimensionless function for radius \( a \), then defining the linear combination of these components to be equal to zero. This gives us the following expressions, for each coupled state:

\[
\begin{align*}
a \left( C_{F,3/2}^+(E_i) J_{F-3/2}(\kappa_+(E_i, a)) \right) + b \left( C_{F,3/2}^-(E_i) J_{F-3/2}(\kappa_-(E_i, a)) \right) &= (0) \\
c \left( C_{F,1/2}^+(E_i) J_{F-1/2}(\kappa_+(E_i, a)) \right) + d \left( C_{F,1/2}^-(E_i) J_{F-1/2}(\kappa_-(E_i, a)) \right) &= (0)
\end{align*}
\] (38) (39)

The coefficient ratios (\( a \) and \( b \) for the \( \mu = 3/2 \) and \( \mu = -1/2 \) states, \( c \) and \( d \) for the \( \mu = 1/2 \) and \( \mu = -3/2 \) states) are given by the following expressions:

\[
\begin{align*}
b_F &= - \frac{C_{F,3/2}^+(E_i) J_{F-3/2}(\kappa_+(E_i, a))}{C_{F,3/2}^-(E_i) J_{F-3/2}(\kappa_-(E_i, a))} \\
c_F &= - \frac{C_{F,1/2}^+(E_i) J_{F-1/2}(\kappa_+(E_i, a))}{C_{F,1/2}^-(E_i) J_{F-1/2}(\kappa_-(E_i, a))}
\end{align*}
\] (40) (41)

where \( E_i \) is the \( i \)th solution of the boundary condition equation, for a given value of \( F \).

Determining the wavefunction is just as in the case of zincblende, combining the envelope and periodic functions, where each wavefunction contains two separate components corresponding to different values of \( \mu \). The wavefunctions for each coupled state are:

\[
\begin{align*}
\psi_{F,3/2}^{\pm}(\rho, \phi) &= a_F \left\{ \left( \frac{C_{F,3/2}^+(E_i)}{J_{F-3/2}(\kappa_+(E_i, a) \frac{\rho}{a})} - \frac{J_{F-3/2}(\kappa_+(E_i, a))}{J_{F-3/2}(\kappa_-(E_i, a))} \frac{1}{J_{F-3/2}(\kappa_-(E_i, a) \frac{\rho}{a})} \right) \right\} \\
&= a_F \left\{ \left( \frac{C_{F,1/2}^+(E_i)}{J_{F-1/2}(\kappa_+(E_i, a) \frac{\rho}{a})} - \frac{J_{F-1/2}(\kappa_+(E_i, a))}{J_{F-1/2}(\kappa_-(E_i, a))} \frac{1}{J_{F-1/2}(\kappa_-(E_i, a) \frac{\rho}{a})} \right) e^{i2\phi} \right\}
\end{align*}
\] (42)
\[ \psi_{F}^{\frac{1}{2} + \frac{1}{2}}(\rho, \phi) = d_{F} \left\{ \left( c_{1/2}^{F, +}(E) \left[ I_{F-1/2}(\kappa_{+}(E, a) \rho \phi_{a}) - I_{F-1/2}(\kappa_{-}(E, a) \rho \phi_{a}) \right] \right) \right\} (e^{i\phi}) \]

and the normalization constants for each wavefunction are:

\[ a_{F}^{-2} = (c_{1/2}^{F, +}(E) a)^{2} \int_{0}^{1} dx \left( I_{F-3/2}(\kappa_{+}(E, a) x) \right) \]

\[ - \frac{I_{F-3/2}(\kappa_{+}(E, a))}{I_{F-3/2}(\kappa_{-}(E, a))} I_{F-3/2}(\kappa_{-}(E, a) x) \right) \]

\[ + (c_{-1/2}^{F, +}(E) a)^{2} \int_{0}^{1} dx \left( I_{F+1/2}(\kappa_{+}(E, a) x) \right) \]

\[ - \frac{I_{F-1/2}(\kappa_{+}(E, a))}{I_{F-1/2}(\kappa_{-}(E, a))} I_{F+3/2}(\kappa_{-}(E, a) x) \right) \]

\[ d_{F}^{-2} = (c_{1/2}^{F, +}(E) a)^{2} \int_{0}^{1} dx \left( I_{F-1/2}(\kappa_{+}(E, a) x) \right) \]

\[ - \frac{I_{F-1/2}(\kappa_{+}(E, a))}{I_{F-1/2}(\kappa_{-}(E, a))} I_{F-1/2}(\kappa_{-}(E, a) x) \right) \]

\[ + (c_{-3/2}^{F, +}(E) a)^{2} \int_{0}^{1} dx \left( I_{F+3/2}(\kappa_{+}(E, a) x) \right) \]

\[ - \frac{I_{F+3/2}(\kappa_{+}(E, a))}{I_{F+3/2}(\kappa_{-}(E, a))} I_{F+3/2}(\kappa_{-}(E, a) x) \right) \]

There is, however, a small modification necessary under certain conditions. In the range

\(-\Delta/2 < E < \Delta/2\), the value of \(k_{F}(E)\) becomes negative, and hence the energy would be
imaginary. To rectify this, the Bessel function used for $k_F^-$ is replaced with a modified Bessel function, $I_m(k\rho)$, using the relationship $J_m(i\kappa_-) = i^m I_m(\kappa_-)$. For instance, the boundary condition equations in this specific range will be written as follows:

\[
\begin{align*}
a \left( \frac{c_{3/2}^F(E) I_{F-3/2}(\kappa_+ (E, a))}{c_{-1/2}^F(E) I_{F+1/2}(\kappa_+ (E, a))} \right) + b \left( \frac{c_{3/2}^F(E) I_{F-3/2}(\kappa_- (E, a))}{c_{-1/2}^F(E) I_{F+1/2}(\kappa_- (E, a))} \right) &= (0) \\
&\quad (46) \\
\end{align*}
\]

\[
\begin{align*}
c \left( \frac{c_{1/2}^F(E) I_{F-1/2}(\kappa_+ (E, a))}{c_{-3/2}^F(E) I_{F+3/2}(\kappa_+ (E, a))} \right) + d \left( \frac{c_{1/2}^F(E) I_{F-1/2}(\kappa_- (E, a))}{c_{-3/2}^F(E) I_{F+3/2}(\kappa_- (E, a))} \right) &= (0) \\
&\quad (47) \\
\end{align*}
\]

**Photoluminescence of Nanowire**

Optical transitions occurring in the nanowire are fundamentally understood by a process known as photoluminescence. The nanowire is bombarded with photons, some of which are directly absorbed into the nanowire and enter a state of higher energy. After bombardment, the nanowire will seek to reach ground state and so will emit photons: the most noticeable of these photons will have energies equal to the difference in the ground energy CBM and VBM. The photoluminescence during this photon emission can be studied with reasonable accuracy.

The equation needed to express this energy difference can be derived from Fermi’s golden rule, which uses a time-dependent relation to find the transition rate, in the form of the square of the matrix elements of the interaction perturbation, between initial and final states. In the case of a semiconductor, we examine the effect of the vector potential on the wavevector momentum of the electron as it moves from the conduction band to the valence band, and the matrix elements can be found using the following expression:

\[
\mathcal{M} = -\frac{e}{m_0 c} \left< \Psi_e^{\mu} , (\hat{A} \cdot \hat{p}) | \Psi_e \right> \\
\]

\[
(48) \\
\]

Many of the details regarding optical transport, fortunately, can be disregarded: as shown later, many terms will cancel in the formula that measures the degree of polarization. The important detail remaining is that the matrix element breaks out into an integral overlap on the
envelope functions and a matrix element of the momentum operator between only the Bloch states. The Bloch states carry information regarding selection rules intrinsic to the material, while the overlap of the envelope functions describes the due to the nanowire confinement. The effect of the electric field inside the nanowire, where $\vec{E} = (i/c)\vec{A}$, is different for parallel and transverse components: this will strongly influence the relative strength of parallel and transverse transitions.

The envelope function overlap is expressed as the inner product of the initial and final states, in this case the envelope functions corresponding to the conduction and valence bands, respectively. By restricting our attention to the lowest energy transitions, only the ground state of the electrons and holes is necessary: in the case of the conduction band, this specifies $m = 0$ as the envelope angular momentum. Therefore, only the $m = 0$ components of the valence band envelope function are allowed. Since, for a given $m$, there are two possible values of $F$, we must take into account both cases in the equations.

The overlap corresponding to $F = 3/2$ also has $\mu = 3/2$, and so uses the coupled envelope function with states $\mu = 3/2$ and $\mu = -1/2$. This equates to the “heavy hole component” of the optical transition. The overlap corresponding to $F = 1/2$ has $\mu = 1/2$, and so uses the coupled envelope function with states $\mu = 1/2$ and $\mu = -3/2$. This equates to the “light hole component”. A combination of these two components with respect to the conduction band is necessary, since these are the two candidates for lowest and next lowest energy levels. In particular, the inner product takes the following form:

$$\langle \psi_\mu | \psi_e \rangle = \int_0^a \rho d\rho \left( \chi_\mu^e \left[ \eta_0 \left[ \frac{p}{a} \right] \right] \right) \left( f_0 \left[ k_0 \left[ \frac{p}{a} \right] \right] \right)$$

(49)
where $\Psi_e$ is the envelope function of the conduction band and $\Psi_{\mu}^F$ is the envelope function of the valence band: $k_0$ and $\eta_0$ are the first-term solutions of the CBM and VBM boundary condition equations, respectively.

With regards to the material properties of the nanowire, there are two significant effects: the effect of dielectric constants on the electric field and the effect of Bloch states on the photon polarization in the Kane matrix elements. The electric field in the nanowire is unaffected along the z-axis, but changes in the transverse direction are based on the following formula:

$$
\varepsilon_\perp = \frac{\varepsilon_{\perp 0}}{1 + \frac{\varepsilon_1 - \varepsilon_2}{2\varepsilon_2}}
$$

Thus, in general, parallel polarization will be favored over transverse polarization. In the case of GaAs, where $\varepsilon_1 = 12.9$ compared to air, the electric field is roughly ten times less in the transverse direction than along the z-axis. In addition, the Bloch states are valued such that:

These adjustments result in proportional changes to the polarization. If we recall that the heavy holes are defined in the $\mu = \pm 3/2$ states and the light holes in the $\mu = \pm 1/2$ states, then we can express the proportions as:

$$
|W^{(hh)}(k_\perp)|^2 \propto \frac{1}{(1 + (\varepsilon_1 - \varepsilon_2)/2\varepsilon_2)^2} \frac{p^2}{2}
$$

$$
|W^{(lh)}(k_\perp)|^2 \propto \frac{1}{(1 + (\varepsilon_1 - \varepsilon_2)/2\varepsilon_2)^2} \frac{p^2}{6}
$$

$$
|W^{(th)}(k_\perp)|^2 = \propto \frac{2p^2}{3}
$$

where $P$ contains the Kane matrix elements. This is all that is necessary to understand the basics of the photoluminescence effect.
Degree of polarization is given by the following formula:

\[ \rho_{pol} = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \]  \hspace{1cm} (54)

where \( I_\parallel \) is the light intensity in the parallel direction and \( I_\perp \) is the light intensity in the transverse direction. As shown in the previous proportions, \( I_\parallel \) has one term for the \( \mu = 3/2 \) state, while \( I_\perp \) has two terms, one for the \( \mu = 3/2 \) state and another for the \( \mu = 1/2 \) state. A final consideration due to temperature must be added for the more energetic of the two states by a factor of \( e^{\Delta E/kT} \), where \( \Delta E \) is the energy difference between the two states, \( T \) is the temperature, and \( k \) is the Boltzmann constant. For an ideal system where \( T = 0 \), there are only vacant electrons and holes at the very lowest energy state: as \( T \) increases, there becomes an increasing possibility for vacancies in higher energy states. If \( kT \) becomes comparable to \( \Delta E \), then a noticeable effect can occur.

**Results**

The following sections show different results, both for zincblende and wurzite crystals.

**Energy Values**

The eigenvalues for the conduction band are based on the boundary condition equation, \( J_m(k_\perp a) = 0 \), such that for a given value of \( m \) one can find a series of \( k_\parallel \) values that correspond to energy values. By using Eq. (3), one can then determine the energy values.
Graph 1: Solution to the boundary condition of the conduction band of GaAs, with m=0. It is equivalent to the plot of a zero-order Bessel function; the \( i \)th \( k \) value will produce \( i-1 \) nodes in the corresponding wavefunction.

<table>
<thead>
<tr>
<th>( i )</th>
<th>( k_i )</th>
<th>( r = 10\text{nm} )</th>
<th>( r = 20\text{nm} )</th>
<th>( r = 50\text{nm} )</th>
<th>( r = 100\text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.40483</td>
<td>7.05416</td>
<td>1.76354</td>
<td>0.282166</td>
<td>0.0705416</td>
</tr>
<tr>
<td>2</td>
<td>5.52008</td>
<td>37.1680</td>
<td>9.29199</td>
<td>1.48672</td>
<td>0.371680</td>
</tr>
<tr>
<td>3</td>
<td>8.65373</td>
<td>91.3450</td>
<td>22.8362</td>
<td>3.65380</td>
<td>0.913450</td>
</tr>
<tr>
<td>4</td>
<td>11.7915</td>
<td>169.597</td>
<td>42.3993</td>
<td>6.78389</td>
<td>1.69597</td>
</tr>
<tr>
<td>5</td>
<td>14.9309</td>
<td>271.926</td>
<td>67.9816</td>
<td>10.8771</td>
<td>2.71926</td>
</tr>
<tr>
<td>6</td>
<td>18.0711</td>
<td>398.332</td>
<td>99.5831</td>
<td>15.9333</td>
<td>3.98332</td>
</tr>
</tbody>
</table>

Table 1: Values of \( k_i \) and \( E_i \) in the conduction, with m=0, for various radii.

Since zincblende and wurtzite are only different by way of the valence band structure, these values are the same regardless of the crystallographic type. The radius is noted to be inversely proportional to the energy level, as expected by the boundary condition equation.

The eigenvalues for the valence band are more complicated to determine, as they require a different Hamiltonian, but nonetheless take a similar form to that of the conduction band in the case of the zincblende structure. As explained previously, \( \eta \) is given written as a function of dimensionless energy: this allows the graphical result to be compared reasonably well to the conduction band.
Graph 2: One solution to the boundary condition of the valence band in zincblende GaAs, derived from the coupled equation involving $\mu = 3/2$ and $\mu = -1/2$. It takes the form of a product of zero-order and second-order Bessel functions.

Graph 3: The other solution to the boundary condition of the valence band in zincblende GaAs, derived from the coupled equation involving $\mu = 1/2$ and $\mu = -3/2$.

Unlike the conduction band, which only requires one set of $k_i$ in order to determine each energy level, two sets in the valence band can have the same value of $m$, and both must be accounted for in the determination of the energy levels. For instance, in the case shown on Graphs 2 and 3 for $m = 0$, the lowest energy level exists in the coupled state of $\mu = 3/2$ and $\mu = -1/2$, the next lowest exists in the coupled state of $\mu = 1/2$ and $\mu = -3/2$, etc. In other terms, this also means that the lowest energy level exists in a light hole component, given that $F = \mu = 1/2$ in order to satisfy our angular momentum condition, and that the next lowest energy level exists in
a heavy hole component, for similar reasons. A more detailed list of energy levels with relation to η is shown on Table 2.

<table>
<thead>
<tr>
<th>η</th>
<th>F</th>
<th>m</th>
<th>coeff. ratio</th>
<th>Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r = 10nm</td>
<td>r = 20nm</td>
<td>r = 50nm</td>
<td>r = 100nm</td>
</tr>
<tr>
<td>3.05450</td>
<td>1/2</td>
<td>0</td>
<td>2</td>
<td>-1.08</td>
</tr>
<tr>
<td>3.83171</td>
<td>1/2</td>
<td>-1</td>
<td>1</td>
<td>∞</td>
</tr>
<tr>
<td>4.05057</td>
<td>3/2</td>
<td>0</td>
<td>2</td>
<td>0.629</td>
</tr>
<tr>
<td>4.77662</td>
<td>3/2</td>
<td>1</td>
<td>3</td>
<td>-1.04</td>
</tr>
<tr>
<td>5.31486</td>
<td>3/2</td>
<td>0</td>
<td>2</td>
<td>-4.64</td>
</tr>
<tr>
<td>5.47140</td>
<td>1/2</td>
<td>0</td>
<td>2</td>
<td>0.130</td>
</tr>
<tr>
<td>7.01559</td>
<td>1/2</td>
<td>-1</td>
<td>1</td>
<td>∞</td>
</tr>
<tr>
<td>7.03715</td>
<td>3/2</td>
<td>1</td>
<td>3</td>
<td>0.247</td>
</tr>
</tbody>
</table>

Table 2: List of first eight energy levels for varying values of F and m. Each coupled state corresponds to two coupled values of m, and so both are shown here.

In total, each coupled state was tested for both $F = \frac{3}{2}$ and $F = \frac{1}{2}$, allowing for four possible pairs of envelope function angular momentums. The coefficient ratio here is given in terms of $b/a$ and $c/d$ for the $\mu = \frac{3}{2}$ and $\mu = -\frac{1}{2}$ states and $\mu = \frac{1}{2}$ and $\mu = -\frac{3}{2}$ state, respectively. The only unusual phenomenon in these ratios is the appearance of an infinity for the $m = \pm 1$ state. If we examine the boundary condition equation of this state, we find that the product appears as $J_{-1}(ka)J_{1}(ka) = -J_{1}(ka)^2$: naturally, as the components of the equation are identical, a linear combination of the two is perfectly synchronized.

Of particular note is are the energy values in the $m = 0$ states, as these match up with the energy values determined earlier in the conduction band. In addition, the energy levels themselves fall within the spin-orbit coupling energy approximation used in the model: as this energy of GaAs is $\sim 400\text{meV}$, we can see that even in the very small nanowire radii the energy levels do not come close. Since experiments are currently confined to the $\sim 100\text{nm}$ region, the split-off holes can be safely ignored.

The energy levels for the valence band in the wurtzite structure are even more difficult to analyze, since the momentum and coefficients depend on the energy values themselves:
attempting to substitute for dimensionless energies or \( \eta \) proved more arduous than meticulously rearranging the solutions of the boundary conditions to be in energy levels of meV. Thus, the graphical representation of the solution appears different from that of the zincblende: this is mostly due to the fact that \( E \) is proportional to the square of \( k \).

In addition to the difference in units, the crystal field splitting has a significant effect on the determination of the energy levels. As the heavy hole is placed \(-\Delta/2\) from the zero-point and the light hole \(\Delta/2\) from the zero point, the beginning energy level also depends on the value of the field splitting. In GaAs it has been shown\(^7\) that \( \Delta \) is roughly 100meV. With this in mind:

Graph 4: Solution to the boundary condition of the valence band in wurtzite GaAs, derived from the coupled equation involving \( \mu = 3/2 \) and \( \mu = -1/2 \): radius of the nanowire is 10nm. There is a discontinuity at \( E = \Delta/2 \) arising from the equation change, as noted in Eq. ( ).
Graph 5: Solution to the boundary condition of the valence band in wurtzite GaAs, derived from the coupled equation involving \(\mu = 1/2\) and \(\mu = -3/2\): radius of the nanowire is 10nm.

As in the case of the zincblende solutions, both solutions where \(m = 0\) must be accounted for in the determination of energy levels: in this case, we see that the lowest energy level comes from the \(F = 3/2\) state, corresponding to the heavy hole component, and the next lowest energy level comes from the \(F = 1/2\) state, corresponding to the light hole component. Given that the heavy hole begins at a lower energy level, this is within expectations.

Graph 6: Solution to the boundary condition of the valence band in wurtzite GaAs, derived from the coupled equation involving \(\mu = 3/2\) and \(\mu = -1/2\): radius of the nanowire is 100nm.

As the radius is increased, the energy levels shrink accordingly. Interestingly, there exist energy levels at the light hole state, even though the state doesn’t “exist” on this level, as a result of the admixture of light and heavy hole states.

Graph 7: Solution to the boundary condition of the valence band in wurtzite GaAs, derived from the coupled equation involving \(\mu = 1/2\) and \(\mu = -3/2\): radius of the nanowire is 100nm.
### Table 3: Energy levels and coefficient ratios of the valence band in wurtzite GaAs, for $\Delta = 100\text{meV}$.

<table>
<thead>
<tr>
<th>F</th>
<th>soln. #</th>
<th>coeff. ratio</th>
<th>Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$r = 10\text{nm}$</td>
</tr>
<tr>
<td>3/2</td>
<td>1</td>
<td>1.89</td>
<td>-29.4049</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.89</td>
<td>104.580</td>
</tr>
<tr>
<td>1/2</td>
<td>1</td>
<td>0.186</td>
<td>27.0454</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.390</td>
<td>102.398</td>
</tr>
</tbody>
</table>

The energy levels, after taking off 50meV to account for the field splitting, are on the order of 0.1-1meV in the 100nm region, similar to the conduction and zincblende valence bands. As the radius shrinks, the energy levels grow much faster than that of previous cases, possibly as a result of the change in equations after $+50\text{meV}$. As a comparison, a similar table for $\Delta = 50\text{meV}$ has also been recorded:

### Table 4: Energy levels and coefficient ratios of the valence band in wurtzite GaAs, for $\Delta = 50\text{meV}$.

<table>
<thead>
<tr>
<th>F</th>
<th>soln. #</th>
<th>coeff. Ratio</th>
<th>Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$r = 10\text{nm}$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.89</td>
<td>43.1312</td>
</tr>
<tr>
<td>1/2</td>
<td>1</td>
<td>0.186</td>
<td>37.8670</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.387</td>
<td>40.5986</td>
</tr>
</tbody>
</table>

As it turns out, the coefficient ratios are virtually identical: at least on this scale, the mixing between light and heavy holes does not appear to change, even if the energy levels decrease accordingly.

**Wavefunctions**

Some examples of wavefunctions for the zincblende are given here. Mostly the graphical forms are used to verify that the wavefunctions are properly normalized and have the correct number of nodes, so that the integral overlap equations are confirmed to be correct.
The $m = 0$ wavefunction is radially symmetric, as it should be, and the boundaries smoothly reach the zero-point (indicated at the color surrounding the circle). The $m = 2$ wavefunction has two nodes, based on the $e^{i2\phi}$ angular component factored into the envelope function.

While not as smooth as the $F = 3/2$ state, each wavefunction in this case still goes to zero, and has the same properties as the first two wavefunctions.

**Degree of Polarization**

The degree of polarization for zincblende, based on (54), can be written as follows
\[
\rho_{pot} = \frac{(2/3)I_{3/2}^2 - \left[ (1/6)I_{1/2}^2 + (1/2)e^{-\Delta E/kT}I_{3/2}^2 \right] [2\epsilon_2/(\epsilon_2 + \epsilon_1)]^2}{(2/3)I_{1/2}^2 + \left[ (1/6)I_{1/2}^2 + (1/2)e^{-\Delta E/kT}I_{3/2}^2 \right] [2\epsilon_2/(\epsilon_2 + \epsilon_1)]^2}
\]

where \(I_{3/2}^2\) and \(I_{1/2}^2\) are the integral overlap (understood here as the square of the light transition intensity) between conduction and valence bands of the heavy hole component and light hole component, respectively. These are calculated using (25) and (26) with values taken from Table 2. The degree of polarization as a function of temperature is shown on Graph 12:

Graph 12: Degree of polarization as a function of temperature. Zincblende nanowires heavily favor parallel polarization, with only a slight change due to the next energy level in the heavy hole state.

\(\epsilon_1 = 12.9\) and \(\epsilon_2 = 1\) are the dielectric constants for GaAs and air, respectively. Since only the heavy hole component carries any transverse polarization in the equation, and as it is already greatly dampened by the electric field effect in the transverse direction, it is the light hole component that dominates the photoluminescence effect in zincblende.

**Conclusion**

Great progress has been made in modeling both zincblende and wurtzite valence bands in GaAs, and applications such as degree of polarization can be shown to produce expected results for
zincblende. Further work should be done to calculate the wavefunctions for wurtzite so that the degree of polarization can be understood in its unique structure.

References


