Binding energy of the Wannier exciton on an organic quantum wire

François Dubin and Michel Schott

_Institut des Nanosciences de Paris, UMR 7588 of CNRS,
Université Pierre et Marie Curie et Université Denis Diderot,
Campus Boucicaut, 140 rue de Lourmel 75015 Paris_

The exciton on a single polydiacetylene chain is considered in a Wannier approach, taking into account the surrounding polarizable medium. The electron-hole Coulomb interaction potential is explicitly obtained for a quantum wire of circular cross-section, and numerically calculated for a rectangular one. The predicted binding energy and Bohr radius, starting from the chain conformation, are in good agreement with experimental values. This shows the importance of considering the monomer matrix embedding the chain, and the major role of confinement, together with electron correlations, for describing the exciton. The method is general and applicable to any quantum wire.

A large amount of experimental and theoretical works is currently done on excitons in semiconductor quantum wires (QWRs). Excitonic properties of strictly one-dimensional (1D) systems are known to be singular, with an infinite ground state exciton binding energy and a zero Bohr radius. However, any physical wire has finite lateral dimensions; once this is taken into account, the strictly 1D pathological behaviour disappears.

We have developed organic polymeric quantum wires which show the theoretically expected - but up to now rarely observed- behaviour for quasi-one dimensional excitons, i.e., a radiative lifetime increasing as $\sqrt{T}$, and a $1/\sqrt{E}$ energy singularity at the band edge. These wires consist of a polydiacetylene (PDA) chain, made of a linear chain of Carbon atoms linked by alternating single, double, and triple bonds. PDA’s are typical conjugated polymers, and can be very diluted in their single crystal monomer matrix such that interchain interactions are negligible, the inhomogeneous broadening being then minimal, with each chain possibly considered as an isolated QWR. Its lateral dimensions are of the order of the atomic radius of Carbon, i.e. a few Å; This is clearly close to the lowest achievable
The experimentally measured binding energy of PDA ground state exciton is quite large, $E_b = 0.6 \text{ eV}$ [4], and the inferred exciton radius fairly small, $a_{1D} \approx 20 \text{ Å}$ [5]. Nevertheless, the exciton is not localized by disorder since the exciton resonance emission energy is the same at all positions along a $20 \mu\text{m}$ long chain within the experimental resolution of $50 \mu\text{eV}$ [6].

There are indications that such chains are strongly correlated systems [7], so the large $E_b$ may be associated to lateral confinement, or to correlations, or to both. The purpose of this work is to explore the role of lateral confinement alone, by considering the polymeric wire as an ordinary semiconductor QWR (as in [1]).

A straightforward calculation of a QWR having the PDA chain conformation in vacuum leads to a too large $E_b$ and too small $a_{1D}$. Quantum chemical calculations on PDA’s or other conjugated polymers meet the same problem, with predicted $E_b$ of the order of $2 \text{ eV}$ [8]. The reason is obvious: PDA chains in our experiments - and in all similar studies on conjugated polymers- are embedded in a dielectric, polarizable, medium - the monomer single crystal - which influence on the electronic energy levels must be taken into account, as was already done for molecular crystals. This is done in the present paper, the effect being computed within the standard image method [9, 10].

Based on the treatment given in [1], the appropriate electron-hole Coulomb interaction potential for quasi-1D ground state excitons is first recalled in section I, and the associated $E_b$ and $a_{1D}$ are deduced. In section II, the influence of the surrounding medium on the ground state excitonic parameters is introduced. By the mean of appropriate dielectric constants, $\epsilon_w$ and $\epsilon_m$, for the wire and medium respectively, the electron-hole interaction potential is rewritten. Its exact evaluation being somewhat complex, we propose an alternative procedure which is approximate but quite precise. It is based on the image charges of the confined carriers. This treatment yields a much simpler expression for the electron-hole interaction potential. It is used in section III to calculate $E_b$ and $a_{1D}$ for PDA’s. The accuracy of our model is demonstrated in the last section by comparing the obtained values of $E_b$ and $a_{1D}$ to the measured ones. It is of importance to stress that the proposed method is actually quite general and not restricted to organic quantum wires.
I. QUASI-1D ELECTRON-HOLE COULOMB POTENTIAL

We consider a QWR with a rectangular section along (Oxy) and a free axis along (Oz). Let \((x_e, y_e, z_e)\) and \((x_h, y_h, z_h)\) be the coordinates of the electron and hole confined in the wire. As shown in [1], the exact interaction potential between the electron and the hole for the lowest energy singlet exciton, so called ground state exciton in a semiconductor terminology \((X_0)\), can be written in terms of \(z = (z_e - z_h)\) only. It reads

\[
V(z_e - z_h) = \left\langle f_{h,1} \right\vert \sum f_{e,1} \frac{-e^2}{\sqrt{(z_e - z_h)^2 + (x_e - x_h)^2 + (y_e - y_h)^2}} \left\vert f_{e,1} \right\rangle \otimes \left\vert f_{h,1} \right\rangle
\]  

(1)

where \(f_{e,1}\) (\(f_{h,1}\)) is the eigen-function for the first energy level of the 2D confined motion of the free electron (hole) in the (Oxy) plane (see for instance Appendix A of [1]).

In order to find an analytical expression for the \(X_0\) relative motion wave function, Combescot et al. have shown that \(V(z_e - z_h)\) can be approximated by

\[
V_{\text{eff}}(z_e - z_h) = -\frac{e^2}{|z_e - z_h| + b^*}
\]

where \(b^*\) represents the effective width of the wire. It is such that \(V_{\text{eff}}(0) = -\frac{e^2}{b^*}\). By setting \(b^* = \lambda a_x \beta^*_\lambda / 2\), \(a_x\) being the 3D exciton Bohr radius and \(\lambda\) the Landau re-scaling energy parameter, the \(X_0\) relative motion wave function reads

\[
\phi_{\lambda,0}(z > 0) = A e^{-(z + \beta^*_{\lambda})/2} U(-\lambda, 0, z + \beta^*_{\lambda})
\]

(2)

\[
\phi_{\lambda,0}(z < 0) = A e^{-(z - \beta^*_{\lambda})/2} U(-\lambda, 0, -z + \beta^*_{\lambda})
\]

(3)

where \(U\) denotes the Kummer series [11]. The eigenvalues \(\lambda\) are given by the continuities of the wave function and its derivative for \(z = z_e - z_h = 0\).

The effective potential built with this \(b^*\) has to be good over the ground state exciton extension. Therefore, this \(b^*\) parameter needs to be chosen very carefully since \(E_b\) strongly depends on it. At first order, \(b^*\) is selfconsistently obtained from \(\lambda\) through

\[
D(\lambda) = \left\langle \phi_{\lambda,0} \right\vert V_{\text{eff}}(z) + \frac{e^2}{|z| + \lambda a_x \beta^*_\lambda / 2} \left\vert \phi_{\lambda,0} \right\rangle = 0
\]

(4)

Consequently, we have to look for the appropriate energy parameter \(0 < \lambda_0 < 1\) such that \(D(\lambda_0) = 0\), and then, deduce the \(X_0\) binding energy \(E_b = -R_x / \lambda_0^2\), \(R_x\) being the 3D Rydberg. The effective \(X_0\) Bohr radius is obtained through \(a_{1D} = \sqrt{\left\langle \phi_{\lambda_0,0} \right| z^2 \left| \phi_{\lambda_0,0} \right\rangle}\).
II. POLARIZABILITY OF THE QUANTUM WIRE OUTSIDE MEDIUM

The exact electron-hole interaction potential presented above (equation (1)) is obtained assuming that the QWR dielectric constant, \( \varepsilon_w \), is equal to the one of the outside medium, \( \varepsilon_m \). In this case, by construction, the potentials created by the confined carriers are continuous at the boundary between the QWR and its environment. On the contrary, if \( \varepsilon_w \neq \varepsilon_m \) equation (1) is no more valid. The potentials created by the confined electron and hole both need to be rewritten in order to ensure their continuity at the boundary between the QWR and the outside. The latter modifies the electron-hole Coulomb interaction potential. To find its exact expression for the \( X_0, V^{(\varepsilon_w \neq \varepsilon_m)} \), a circular wire has to be studied [10]. Actually, circular and rectangular wires have been shown to give identical \( X_0 \) parameters if their cross sections are the same [1].

A. Exact potential for a circular wire

In order to derive the equivalent of equation (1) for \( \varepsilon_w \neq \varepsilon_m \), we first establish the expression of the potential created by an electron confined within the wire, \( V^{(\varepsilon_w \neq \varepsilon_m), e} \). Let \( R \) be the wire radius, and \( (\rho_e, \theta_e, z_e) \) the electron position in polar coordinates. \( V^{(\varepsilon_w \neq \varepsilon_m), e} \) reads in terms of the Bessel functions \( I_0 \) and \( K_0 \) [10] as

\[
V^{(\varepsilon_w \neq \varepsilon_m), e,\text{in}}(\rho, \theta, z) = -\frac{2e}{\pi} \int_0^\infty [K_0(m\|\rho - \rho_e\|) + A(m, \rho_e)I_0(m\|\rho - \rho_e\|)] \cos(m(z - z_e)) \, dm
\]

\[
V^{(\varepsilon_w \neq \varepsilon_m), e,\text{out}}(\rho, \theta, z) = -\frac{2e}{\pi} \int_0^\infty B(m, \rho_e)K_0(m\|\rho - \rho_e\|) \cos(m(z - z_e)) \, dm
\]

\[
(5)
\]

\( V^{(\varepsilon_w \neq \varepsilon_m), e,\text{in}} \) and \( V^{(\varepsilon_w \neq \varepsilon_m), e,\text{out}} \) being the expression of \( V^{(\varepsilon_w \neq \varepsilon_m), e} \) inside and outside the wire respectively. The functions \( A \) and \( B \) appearing in (5) are deduced from the two boundary conditions

\[
(V^{(\varepsilon_w \neq \varepsilon_m), e,\text{in}} - V^{(\varepsilon_w \neq \varepsilon_m), e,\text{out}})_{\rho=R} = 0, \quad \left( \varepsilon_w \frac{\partial V^{(\varepsilon_w \neq \varepsilon_m), e,\text{in}}}{\partial \rho} - \varepsilon_m \frac{\partial V^{(\varepsilon_w \neq \varepsilon_m), e,\text{out}}}{\partial \rho} \right)_{\rho=R} = 0
\]

\[
(6)
\]

Consequently, from equations (1,5,6), we find that equation (1) transforms into

\[
V^{(\varepsilon_w \neq \varepsilon_m), e,\text{in}}(z_e - z_h) = e < f_{h,1} \otimes < f_{e,1} \mid V^{(\varepsilon_w \neq \varepsilon_m), e,\text{in}}(\rho_h, \theta_h, z_h) \mid f_{e,1} \otimes f_{h,1} > \quad (7)
\]
FIG. 1: Image distribution for a charge $q=-e$ confined in a dielectric medium (I) separated from its environment (II) by two infinite planes, as for a charge in a finite quantum well. The image charges in (II) need to be considered to evaluate the potential created by the confined carrier $q$.

The evaluation of (7) yields a fifth integration of an oscillating product of Bessel functions over an infinite domain. This integral obviously converges, but is technically difficult to compute. To calculate the electron-hole interaction potential we present an alternative procedure, approximate but precise enough, based on the electron-hole charge images [9, 10]. For that purpose, let us first recall the basic results of the charge image representation.

B. Image charges for a rectangular wire

We consider two media, (I) and (II), with dielectric constants $\epsilon_I$ and $\epsilon_{II} \neq \epsilon_I$. Let (I) be embedded in (II) and separated by planar interfaces. The potential created by a charge $q$ confined in (I) is strongly affected by the dielectric mismatch ($\epsilon_I \neq \epsilon_{II}$). This potential can be expressed in terms of the electrostatic images of $q$ in (II). With $S = (\epsilon_I - \epsilon_{II})/(\epsilon_I + \epsilon_{II})$, a charge $q$ located at $(x_q, y_q, z_q)$ in (I) has a double set of $(S^{[n]}q)$ electrostatic images in (II), located at $((-1)^n(x_q - nL), y_q, z_q)$ (see figure 1). The charge $q$ plus its images lead a
potential in the medium (I) which reads

\[ V_q^{(I)}(x, y, z) = \frac{q}{\sqrt{(x - x_q)^2 + (y - y_q)^2 + (z - z_q)^2}} \]

\[ + \sum_{n \neq 0} \frac{S_n^{\mid q \mid}}{\sqrt{(x - (-1)^n(x_q - nL))^2 + (y - y_q)^2 + (z - z_q)^2}} \]  

This electrostatic images representation has been successfully used to calculate the binding energy of an exciton confined in a quantum well close to a metallic mirror as well as for a quasi-2D electron gas confined in a finite quantum well [9]. For carriers in quantum wells the procedure is rather simple since the interfaces between the well and the outside medium are made of two 2D planes (see fig. 1). On the contrary, the case of charges in quantum wires is far more subtle. Besides the fact that the QWR cross section is very small, the inclusion of the dielectric mismatch between the wire and its outside medium in terms of electrostatic images is questionable. We nevertheless apply it in the following, and show in section III that this method leads to relevant results, as many similar ones in which bulk properties are extended to rapidly varying situations.

Let us consider a QWR of dielectric constant \( \epsilon_w \), embedded in a medium of dielectric constant \( \epsilon_m \). The wire section is rectangular with extension \( L_x=a \) along (Ox) and \( L_y=b \) along (Oy). Let \( T = (\epsilon_w - \epsilon_m)/(\epsilon_w + \epsilon_m) \) and \( (x_e, y_e, z_e) \) (with \( |x_e| < a/2 \) and \( |y_e| < b/2 \)) be the electron coordinates in the wire. The carrier has then two infinite sets of \((-T_n^{\mid e \mid})\) electrostatic images, one along (Ox), placed at \((-1)^n(x_e - na), y_e, z_e\), and another set of images along (Oy), having the same \((-T_n^{\mid e \mid})\) charge and placed at \((x_e, -1)^n(y_e - nb), z_e\), \( n \) being a positive or negative integer. From the distribution of the electron images, the potential it creates, \( V_{e,\text{in}}^{(\text{im})} \), inside and outside the wire, \( V_{e,\text{in}}^{(\text{im})} \) and \( V_{e,\text{out}}^{(\text{im})} \) respectively, can be expressed. \( V_{e,\text{out}}^{(\text{im})} \) has a form depending on the region where it is calculated. For instance, on the right side of the wire, i.e., at \((x > a/2, y, z)\), only images on the left side of the wire, i.e., having an abscissa \((x < -a/2)\), have to be included. \( V_{e,\text{out}}^{(\text{im})} \) there reads

\[ V_{e,\text{out}}^{(\text{im})}(x, y, z) = \frac{-Te}{\sqrt{(x - x_e)^2 + (y - y_e)^2 + (z - z_e)^2}} \]

\[ - \sum_{n>0} \frac{-T_n^{\mid e \mid}}{\sqrt{(x - (x_e - na))^2 + (y - y_e)^2 + (z - z_e)^2}}, \text{ for } x > a/2 \]  

The expression of \( V_{e,\text{out}}^{(\text{im})} \) at a random \((x, y, z)\) position is deduced generalizing the previous example [10]. It is not extensively written here since this expression is not essential for the
FIG. 2: Image distribution of an electron-hole pair confined in a rectangular quantum wire. Their interaction potential is evaluated with the sum of the vertical and horizontal images of the electron and hole (see equation (12)).

The problem studied. On the contrary, $V_{e,in}^{(im)}$ is always given by

$$V_{e,in}^{(im)}(x, y, z) = -\frac{e}{\sqrt{(x-x_e)^2 + (y-y_e)^2 + (z-z_e)^2}} + V_{e,in}^{(im)}(x, y, z)$$  \hspace{1cm} (10)

$$V_{e,in}^{(im)}(x, y, z) = \sum_{n\neq 0} -\frac{T^{[n]}e}{\sqrt{(x - (-1)^n(x_e + na))^2 + (y - y_e)^2 + (z - z_e)^2}}\frac{T^{[n]}e}{\sqrt{(x-x_e)^2 + (y - (-1)^n(y_e + nb))^2 + (z-z_e)^2}}$$  \hspace{1cm} (11)

$V_{e}^{(im)}$ scales like $(1/r)$. It is therefore a general solution of Laplace equation, however different from the particular one continuous at the interface between the wire and its outside medium, $V_{e}^{(\epsilon \neq \epsilon_m)}$. Nevertheless, as shown below, the discontinuity of $V_{e}^{(im)}$ at the boundaries is fairly small, $V_{e}^{(\epsilon \neq \epsilon_m)}$ being obtained by continuous prolongation of $V_{e}^{(im)}$.

With the image representation, the evaluation of the electron-hole interaction potential requires the inclusion of three contributions: the direct electron-hole Coulomb interaction, the interaction between the hole and the electron’s images, and the one between the electron
and the hole's images. The electron-hole interaction potential then reads

$$V^{(im)}(z_e - z_h) = \langle f_{h,1} | \bigotimes \left( f_{e,1} | \frac{-e^2}{\sqrt{(x_e - x_h)^2 + (y_e - y_h)^2 + (z_e - z_h)^2}} \right) | f_{e,1} \rangle \bigotimes | f_{h,1} \rangle$$

(12)

$$+ e \langle f_{h,1} | \bigotimes \left( f_{e,1} | V^{(im)}_{\text{eff}}(x_h, y_h, z_h) - V^{(im)}_{\text{eff}}(x_e, y_e, z_e) \right) | f_{e,1} \rangle \bigotimes | f_{h,1} \rangle$$

which is much simpler to evaluate than (7) since it reduces to a fourth integration of a rational fraction over a finite domain. Moreover, as in section I, $V^{(im)}$ is very well approximated by

$$V^{(im)}_{\text{eff}}(z_e - z_h) = -A^{(im)} \frac{e^2}{|z_e - z_h|} + b^{(im)}$$

(13)

The image representation is hereafter applied to evaluate polydiacetylenes $X_0$ binding energy and Bohr radius. As previously mentioned, PDA’s are excellent quantum wires thanks to the very regular confinement potential of the monomer crystal surrounding the chains. In the particular case of poly-3BCMU red chains, single chain spectroscopy has revealed that red chains optical excitation, the so-called red exciton, has a center of mass motion described by a one dimensional band exhibiting the $1/\sqrt{E}$ energy singularity at the band edge \[3\]. This undoubtedly indicates that this excitation is an excellent quasi-1D Wannier exciton, which is furthermore highly bound ($E_b=0.6$ eV), with an inferred small Bohr radius ($a_{1D}=15 \text{ Å}$) \[4, 5\], as expected for quasi-1D $X_0$.

### III. APPLICATION TO POLY-3BCMU CHAINS

The geometrical cross section of the poly-3BCMU chain is about $4 \times 3$ Å$^2$, using the Van der Waals radius of Carbon atoms \[12, 13\]. However, electronic wave functions are not strictly confined within this volume and slightly larger dimensions are probably appropriate, so the calculations are also carried out with a $7 \times 5$ Å$^2$ chain cross section. The chain dielectric constant $\epsilon_w$ has not been measured, but should be around 10 $\epsilon_0$ like polyacetylene \[14\] while the monomer dielectric constant $\epsilon_m=2.5 \epsilon_0$ \[15\]. Poly-3BCMU chains $X_0$ effective mass being $\approx 0.1 m_0$ ($m_0$ denotes the free electron mass) \[2\], the three dimensional binding energy and Bohr radius of this excitation are equal to 25 meV and 36 Å respectively.

Let us quantify the error on the electron-hole interaction potential for the $X_0$ when calculated by the image representation. To do so we first evaluate the discontinuity of $V^{(im)}_{\text{eff}}$ at the boundary between the poly-3BCMU chain and the monomer crystal. In Figure \[3\] the
FIG. 3: Potential $V^{(im)}_e$ created along (Ox) by an electron confined at (0,0,0) within a poly-3BCMU chain. $L_x=4$ Å is the chain extension along (0x). The dashed line materializes the boundary between the chain and its outside medium where the potential discontinuity is 5%.

potential created along (Ox) by an electron confined in the center of the chain is presented. As expected, $V^{(im)}_e$ does not fulfill the boundary conditions, however its discontinuity at the interface between the chain and the monomer is only 5%. In general, $V^{(im)}_e$ discontinuity at the boundary never exceeds 10% for any position of the confined electron. Consequently $V^{(im)}_e$ is a good approximation of $V^{(\epsilon_c \neq \epsilon_m)}_e$. Moreover, to calculate $V^{(im)}$ (equation (12)), the electron-hole interaction potential is integrated on the section of the chain. As shown above, $V^{(im)}_e$ only differs from $V^{(\epsilon_c \neq \epsilon_m)}_e$ at the boundary neighborhood, elsewhere within the chain $V^{(im)}_e = V^{(\epsilon_c \neq \epsilon_m)}_e$. The contribution of the boundary ($0.4 < |x/L_x| < 0.5$ and $0.4 < |y/L_y| < 0.5$) in the integration being 5%, the calculation of the electron-hole interaction potential by the image method is then only a $\approx 1\%$ approximation. This procedure is here preferred to study poly-3BCMU red chains $X_0$ properties within a well controlled computation.

For a poly-3BCMU chain embedded in its single crystal monomer matrix, $V^{(im)}$ and its associated effective potential $V^{(im)}_{eff}$ are presented in Figure 4. For $A_{im}=14$ and $b^*_{im}=4.3$ Å the effective image potential is shown to reproduce accurately $V^{(im)}$. For $b^*_{im}=4.3$ Å, the resolution of equation (11) yields $(\lambda_{im}, \beta^*_{im})=(0.6,0.87)$. The binding energy and Bohr radius of the poly-3BCMU $X_0$ are then deduced equal to $900 \pm 9$ meV and $22 \pm 0.2$ Å respectively, i.e., in close agreement with measured values. The $X_0$ properties are then well reproduced starting from the most probable chain conformation. This geometrical factor
FIG. 4: Open circles: electron-hole interaction potential for the $X_0$ given by the image method (equation (12)) for $R=0.6$, $L_x=4\ \text{Å}$ and $L_y=3\ \text{Å}$. Line: Associated effective potential (equation (13)) for $A_{im}=14$ and $b_{im}^*=4.3\ \text{Å}$.

governs the calculated $E_b$ and $a_{1D}$, the stronger the confinement is, the larger $E_b$ and $a_{1D}$ are. Indeed, starting with a poly-3BCMU chain with a rectangular section of $7\times5\ \text{Å}^2$, the $X_0$ Bohr radius and binding energy are $a_{1D}=17\ \pm\ 2\ \text{Å}$ and $E_b=700\ \pm\ 8\ \text{meV}$, i.e., closer to the measured values. The lateral confinement of PDA chains could thus be slightly wider than the extension of their Carbon atoms, of the order of five Angstrom. For such small lateral confinement the validity of our treatment is questionable; the chain could also be modelled as a linear chain of atoms in order to investigate its optical excitation. Nevertheless, from an experimental point of view, poly-3BCMU red chains $X_0$ has been evidenced as a quasi-1D Wannier exciton [3], the corresponding formalism is then here developed. In regard to our analysis, it seems very likely that the strong confinement of PDA chains plays a crucial role in the understanding of their optical properties, the strong electronic correlations being the other fundamental parameter which influence should be quantitatively studied.

IV. CONCLUSION

The influence of the polarizability of a quantum wire outside medium on quasi-1D excitonic parameters has been investigated. The exact electron-hole Coulomb interaction potential for the ground state exciton is first presented. It is governed by the lateral confinement...
and yields the inferred exciton binding energy and Bohr radius. The exact interaction potential numerical evaluation being complex, we propose an approximation based on the confined carriers image charges representation. When applied to the specific case of PDA chains, our procedure demonstrates its accuracy. The calculation of the electron-hole interaction potential for poly-3BCMU red chains is shown to exhibit a 1% precision. Furthermore, starting with the chain’s most probable conformation, i.e., with a section of $\approx 7 \times 5 \, \text{Å}^2$, the deduced ground state exciton binding energy and Bohr radius are in good agreement with the measured values. The only relevant parameter of our model being the cross-section of the chain, we conclude that the large binding energy and the small Bohr radius of PDA excitons can both be understood in terms of the strong confinement of PDA chains, i.e., deriving from the excellent quasi-one dimensional character of these organic semiconductors.

The authors are very thankful to Monique Combescot for helpful discussions and corrections of the present manuscript.

1: francois.dubin@uibk.ac.at (present adress: Institut für Experimentalphysik, Universität Innsbruck, Technikerstrasse 25, A-6020 Innsbruck)
Guillaume, M. Combescot, O. Betbeder-Matibet, *Solid. Stat. Comm.* **108**, 193 (1998)

[10] E. Durand, *Electrostatique: Tomes II et III* (Editions Masson, Paris, 1966)

[11] Ederlyi et al., "Higher transcendental functions" Vol. 1 (Ed. Mc Graw-Hill, New York, 1953)

[12] V. Enkelmann, *Adv. Poly. Sci.* **63**, 91 (1984)

[13] M. Schott, "Optical Properties of Single Conjugated Polymer Chains" in "Photophysics of Molecular Materials" p49 (Ed. G. Lanzani, Wiley-VCH, Berlin, 2005)

[14] G. Leising, *Phys. Rev. B.* **38**, 10313 (1988)

[15] S. Haacke, J. Berréhar, C. Lapersonne-Meyer and M. Schott, *Chem. Phys. Lett.* **308**, 363 (1999)