

## Particle-in-a-box model of one-dimensional excitons in conjugated polymers

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(Received 21 October 1999)

A simple two-particle model of excitons in conjugated polymers is proposed as an alternative to usual highly computationally demanding quantum chemical methods. In the two-particle model, the exciton is described as an electron-hole pair interacting via Coulomb forces and confined to the polymer backbone by rigid walls. Furthermore, by integrating out the transverse part, the two-particle equation is reduced to one-dimensional form. It is demonstrated how essentially exact solutions are obtained in the cases of short and long conjugation length, respectively. From a linear combination of these cases an approximate solution for the general case is obtained. As an application of the model the influence of a static electric field on the electron-hole overlap integral and exciton energy is considered.

### I. INTRODUCTION

The optical properties of conjugated polymers are of considerable interest for basic science as well as applications. Both electroluminescence<sup>1</sup> and optically pumped lasing<sup>2</sup> has been demonstrated in these materials. The conjugated polymers owe their unique optical qualities to the existence of extremely long-ranged electronic excitations extending coherently over several monomer units. The excitation energies of these so-called one-dimensional excitons are typically in the visible range. Moreover, due to their large spatial extent, these excitations can have extremely large oscillator strengths, which lead to efficient coupling to optical fields.

Several experimental techniques are available for studies of conjugated polymers. The spectrum of excitations is typically deduced from various spectroscopic measurements such as absorption,<sup>3</sup> photoluminescence<sup>4</sup> and electro-absorption.<sup>5</sup> In addition, photoconductivity<sup>6</sup> is used as a probe of the dynamic properties of electron-hole pairs. Theoretically, the level structure of conjugated polymers has been calculated using the collective electronic oscillator (CEO) approach<sup>7</sup> or a Green's function technique.<sup>8</sup> The *ab initio* and semiempirical methods that are otherwise frequently applied in quantum chemistry calculations are not suitable for conjugated polymers due to the size of the molecules. In the case of semiempirical methods it is mainly the size of the configuration interaction matrix, which sets an upper limit on the complexity of the molecule. Hence, sufficient accuracy is only retained for relatively small systems. Unfortunately, the CEO and Green's function approaches also suffer from certain restrictions. The CEO model neglects configuration interaction at the expense of introducing a "screening" parameter, which reduces the repulsive electron-electron interaction in order to make calculated energies agree with experiment.<sup>7</sup> Moreover, this method is still rather computationally demanding for large structures. The Green's function technique, on the other hand, is well suited for structures with infinite periodicity, e.g., infinitely long polymer chains. The properties of real polymers, however, may depend on the finite average electron delocalization

length (conjugation length). This has been demonstrated, for instance, in recent photoconductivity experiments.<sup>6,9</sup> In these studies, the minimum electric field needed for exciton dissociation was found to be directly related to the conjugation length (approximately 65 Å). Hence, the infinite chain assumption cannot be made in the interesting case of long but finite conjugation length (approximately 50–100 Å).

In this paper, we present a highly simplified one-dimensional model of excitons in finite-length conjugated polymers. The electron-hole pair is simply assumed to be spatially confined to a box of dimensions  $a \times b \times l$  as illustrated in Fig. 1. The characteristic length scale of the electron-hole Coulomb attraction is given by the effective Bohr radius  $a_B$ , which in the three-dimensional case is given by  $a_B^{3D} = 4\pi\epsilon\epsilon_0\hbar^2/(\mu e^2)$ , where  $\epsilon$  is the relative static dielectric constant and  $\mu$  is the reduced mass. More generally, we can define  $a_B$  as the full  $e^{-1}$  width of the square of the free exciton wavefunction. Hence, the physical meaning of  $a_B$  is clear: When confined to a region of dimension  $l \ll a_B$  the wave function is severely distorted by the boundaries and so Coulomb effects are small perturbations. Conversely, if  $l \gg a_B$  the wavefunction is essentially that of a free exciton and now boundary effects are small perturbations. Hence, assuming  $a_B$  to be significantly larger than the side lengths  $a$  and  $b$  will allow us completely neglect the influence of Coulomb effects on the transverse behavior of the exciton. It follows that we may integrate out the dependence of the exciton wavefunction on the transverse coordinates. The re-

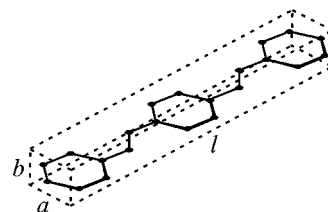


FIG. 1. Geometry of the box potential confining the exciton. The actual molecular potential is replaced by infinite barriers at the walls of a box of dimensions  $a \times b \times l$ .

sulting one-dimensional two-particle equation can be solved exactly in the limit of extremely long conjugation length ( $l \gg a_B$ ) by a separation of relative and center-of-mass motion (quasifree limit). On the other hand, short conjugation length polymers ( $l \leq a_B$ ) can be accurately treated within the Hartree approximation since the effect of confinement dominates over electron-hole interaction. The Hartree approximation applied to the two-particle wave function leads to a simple one-dimensional nonlinear integral Schrödinger equation, which can subsequently be solved numerically. Hence, it is possible to obtain essentially exact solutions in the cases of short and extremely long conjugation length. Finally, in order to bridge the gap between these cases we form a linear superposition between the quasifree and the Hartree solutions. The solution obtained by minimizing the exciton energy then represents a highly accurate approximation for the exciton wave function, which is valid for all values of  $l$ . We apply our theory to study the effects of a static electric field and, as an example, the exciton energy and electron-hole overlap integral are calculated as a function of field strength.

## II. THEORY

Our treatment will be restricted to confinement of excitons in a box of dimensions  $a \times b \times l$  for which the walls are taken to be infinite barriers. This type of model has previously been applied to electrons in smaller conjugated molecules<sup>10</sup> for which Coulomb effects can be neglected. In the present case of large molecules with dimensions comparable to the effective Bohr radius, the Coulomb interaction is, in fact, essential as will be demonstrated below. The exciton wavefunction is denoted  $\Psi(\vec{r}_e, \vec{r}_h)$ , where  $\vec{r}_e$  and  $\vec{r}_h$  are electron and hole positions, respectively. We apply a coordinate system in which the  $x$  and  $y$  axes coincide with the  $a$  and  $b$  sides of the box and the  $z$  axis is directed along  $l$ , i.e., the length of the polymer chain. For the region inside the bounds of the box the Schrödinger equation is identical to that of a free exciton in an infinite medium

$$\left\{ -\frac{\hbar^2}{2m^*}(\nabla_e^2 + \nabla_h^2) + eFz_e - eFz_h - \frac{e^2}{4\pi\epsilon\epsilon_0|\vec{r}_e - \vec{r}_h|} + E_g^{3D} - E_{eh} \right\} \Psi(\vec{r}_e, \vec{r}_h) = 0. \quad (1)$$

In this expression,  $E_{eh}$  is the exciton energy-eigenvalue,  $E_g^{3D}$  is the bare three-dimensional (3D) energy gap,  $\epsilon$  is the relative static dielectric constant and identical effective masses  $m^*$  of electrons and holes have been assumed for simplicity. In addition, a static electric field of magnitude  $F$  directed along the chain axis has been included. In the presence of the confinement the motion of the exciton is restricted to the volume of the box and, hence, the wave function is subject to the boundary condition

$$\Psi(\vec{r}_e, \vec{r}_h) = 0, \quad \text{if } |x_e| \text{ or } |x_h| = a/2, |y_e| \text{ or } |y_h| = b/2, |z_e| \text{ or } |z_h| = l/2. \quad (2)$$

Now, in the case  $a_B \gg a, b$  the Coulomb attraction has a negligible effect on the transverse behavior of the exciton wavefunction. Hence,  $\Psi(\vec{r}_e, \vec{r}_h)$  is approximately given by

$$\Psi(\vec{r}_e, \vec{r}_h) \approx \phi_a(x_e) \phi_a(x_h) \phi_b(y_e) \phi_b(y_h) \psi(z_e, z_h), \quad (3)$$

where  $\phi_a$  and  $\phi_b$  are simple particle-in-a-box wave functions given by

$$\phi_a(x) = \left(\frac{2}{a}\right)^{1/2} \cos\left(\frac{\pi x}{a}\right), \quad \phi_b(y) = \left(\frac{2}{b}\right)^{1/2} \cos\left(\frac{\pi y}{b}\right). \quad (4)$$

The three-dimensional two-particle Schrödinger equation can now be reduced to a relatively simple one-dimensional equation by integrating out the transverse coordinates in analogy to similar calculations carried out for excitons in semiconductor quantum wires.<sup>11</sup> As a result the electron-hole pair interacts via an effective one-dimensional Coulomb potential given by

$$\begin{aligned} V(z_e, z_h) &= \frac{-e^2}{4\pi\epsilon\epsilon_0} \int_{-a/2}^{a/2} \int_{-a/2}^{a/2} \int_{-b/2}^{b/2} \int_{-b/2}^{b/2} \\ &\quad \times \frac{|\phi_a(x_e) \phi_a(x_h) \phi_b(y_e) \phi_b(y_h)|^2}{\sqrt{(x_e - x_h)^2 + (y_e - y_h)^2 + (z_e - z_h)^2}} \\ &\quad \times dy_e dy_h dx_e dx_h \\ &\equiv \frac{-e^2}{4\pi\epsilon\epsilon_0} C(z_e - z_h), \end{aligned} \quad (5)$$

where  $C(z)$  denotes the Coulomb function given by the integral above. By introducing sum and difference coordinates the integral may be reduced to

$$C(z) = \int_0^1 \int_0^1 \frac{f(x)f(y)}{\sqrt{a^2x^2 + b^2y^2 + z^2}} dx dy, \quad (6)$$

with  $f(w)$  given as

$$f(w) = (1-w)[2 + \cos(2\pi w)] + \frac{3}{2\pi} \sin(2\pi w). \quad (7)$$

We have not been able to evaluate the integral Eq. (6) analytically. However, it is found that an excellent approximation is given by the expression

$$C(z) = \frac{1}{|z|} \{1 - \exp(-p|z|)\} - q|z| \exp(-p|z|). \quad (8)$$

In the symmetric case  $a=b$  the values  $p=C(0) = 4.75886/a$  and  $q \approx 2.81/a^2$  (fitted) can be used. A number of examples are shown in Fig. 2. Naturally, the effective potential is considerably softer than the bare one-dimensional Coulomb potential  $\sim 1/|z|$ , which is obtained in the limit  $p \rightarrow \infty$ . It is interesting to note that the bare potential leads to unphysical results such as delta-function localized states and divergent eigenvalues, as shown by Loudon.<sup>12</sup> These problems are eliminated through the use of the softer effective potential. The resulting one-dimensional two-particle Schrödinger equation is now of the form  $(H_{1D} - E_{eh})\psi(z_e, z_h) = 0$ , where the 1D Hamiltonian  $H_{1D}$  reads as

$$\begin{aligned} H_{1D} &= -\frac{\hbar^2}{2m^*} \left( \frac{d^2}{dz_e^2} + \frac{d^2}{dz_h^2} \right) + eFz_e - eFz_h - \frac{e^2}{4\pi\epsilon\epsilon_0} \\ &\quad \times C(z_e - z_h) + E_g. \end{aligned} \quad (9)$$

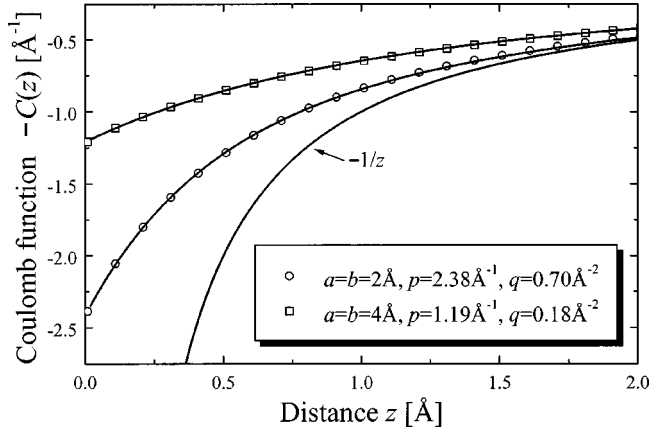


FIG. 2. Coulomb functions for the soft effective potential in comparison to the bare one-dimensional potential  $-1/z$ .

In addition, it is understood that the wavefunction is subject to the boundary conditions

$$\psi(\pm l/2, z_h) = \psi(z_e, \pm l/2) = 0 \quad (10)$$

due to the infinite barriers at the chain ends. The energy gap  $E_g$  is Eq. (9) is the ‘renormalized’ 1D value given by  $E_g = E_g^{3D} + \pi^2 \hbar^2 / 2m^* (1/a^2 + 1/b^2)$ . We will now turn to the two cases for which the above equation can be solved essentially exactly, i.e., the cases of long and short conjugation length, respectively.

### A. Long conjugation length

In the limit  $l \rightarrow \infty$  the two-particle equation can be re-expressed in terms of relative and center-of-mass coordinates and solved separately for each coordinate. Since the center-of-mass motion is simply a plane wave the problem is then reduced to a one-dimensional one-coordinate equation for the relative motion. In the more general case of finite but large  $l$ , the relative and center-of-mass motions are coupled by the boundary conditions Eq. (10). However, for  $l \gg a_B$  the localization of the exciton by the Coulomb forces ensures that the potential barriers at the chain ends are only of minor importance. Hence, the behavior is that of a quasi-free exciton and the wavefunction is taken to be of the form

$$\psi(z_e, z_h) = A \cos\left(\frac{\pi z_e}{l}\right) \cos\left(\frac{\pi z_h}{l}\right) \tilde{\varphi}(z_e - z_h), \quad (11)$$

where the cosines serve as envelope functions satisfying the boundary conditions Eq. (10) and  $\tilde{\varphi}(z)$  is a solution to the relative-motion part of the Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{m^*} \frac{d^2}{dz^2} + eFz - \frac{e^2}{4\pi\epsilon\epsilon_0} C(z) - \tilde{E} \right\} \tilde{\varphi}(z) = 0. \quad (12)$$

The boundary conditions for  $\tilde{\varphi}(z)$  are somewhat arbitrary since the form Eq. (11) already fulfills the boundary conditions for the entire exciton wave function. For the truly free exciton the boundary conditions would be  $\tilde{\varphi}(\pm\infty) = 0$ . However, in the finite  $l$  case the bounds for the relative coordinate is  $|z_e - z_h| \leq l$  and, consequently, we use the more natural choice  $\tilde{\varphi}(\pm l) = 0$ . The normalization constant  $A$  is determined by

$$A = \left\{ \frac{l^2}{8} \int_{-1}^1 f(|w|) |\tilde{\varphi}(lw)|^2 dw \right\}^{-1/2}, \quad (13)$$

where  $f$  is the function given by Eq. (7). Finally, the exciton energy  $E_{eh}$  must be calculated as the expectation value of the 1D Hamiltonian  $\langle \psi(z_e, z_h) | H_{1D} | \psi(z_e, z_h) \rangle$  and, hence,  $E_{eh}$  is related to the eigenvalue  $\tilde{E}$  via the relation

$$E_{eh} = \tilde{E} + \frac{\hbar^2 \pi^2}{m^* l^2} + \frac{\hbar^2 \pi l}{2m^*} |A|^2 \int_{-1}^1 \left\{ (1 - |w|) \cos(\pi w) + \frac{1}{\pi} \sin(\pi |w|) \right\} \sin(\pi w) \tilde{\varphi}'(lw) \tilde{\varphi}(lw) dw + E_g. \quad (14)$$

From left to right the various terms in this expression are the relative motion part, the envelope contribution, a term representing the mixing of relative motion and envelope parts and, finally, the energy gap.

### B. Short conjugation length

In the case  $l \leq a_B$  the Coulomb attraction can be regarded as a perturbation in comparison to the confinement energy. This allows us to simplify the exciton Schrödinger equation considerably by applying the Hartree approximation for the Coulomb interaction. Physically, this approximation amounts to treating the electron as if moving within the Coulomb potential created by the charge density formed by the hole and vice versa. Hence, the two-particle wave function is separable

$$\psi(z_e, z_h) = \varphi_e(z_e) \varphi_h(z_h) \quad (15)$$

and the Coulomb potential acting on the electron is given by

$$V_e(z_e) = \frac{-e^2}{4\pi\epsilon\epsilon_0} \int_{-l/2}^{l/2} C(z_e - z_h) |\varphi_h(z_h)|^2 dz_h. \quad (16)$$

An additional advantage of the Hartree approximation is that it ensures that the error introduced by the separability assumption Eq. (15) is minimized for the lowest exciton state.<sup>10</sup> Moreover, due to the symmetry of the problem the lowest energy electron and hole wave functions are related by a mirror reflection

$$\varphi(z) \equiv \varphi_e(z) = \varphi_h(-z), \quad (17)$$

and the single-particle eigenvalues of electron and hole are identical. This finally allows us to reformulate the wave equation as a one-dimensional single-particle equation

$$\left\{ -\frac{\hbar^2}{2m^*} \frac{d^2}{dz^2} + eFz - \frac{e^2}{4\pi\epsilon\epsilon_0} \int_{-l/2}^{l/2} C(z+z') |\varphi(z')|^2 dz' - E \right\} \varphi(z) = 0. \quad (18)$$

From the solution to the Hartree equation the exciton energy eigenvalue is obtained as

$$E_{eh} = 2E + \frac{e^2}{4\pi\epsilon\epsilon_0} \int_{-l/2}^{l/2} \int_{-l/2}^{l/2} |\varphi(z)|^2 \times C(z+z') |\varphi(z')|^2 dz' dz + E_g. \quad (19)$$

It should be noted that the asymmetry between electron and hole wave functions is only due to the presence of the static electric field and in the case  $F=0$  it is found that  $\varphi_e(z) = \varphi_h(z)$ , i.e., both functions are even.

### C. General case

By means of Eqs. (11) and (15) we have obtained solutions for long and short conjugation lengths, respectively. These two limiting results suggest a general solution of the form

$$\psi(z_e, z_h) = \alpha \varphi(z_e) \varphi(-z_h) + \beta A \cos\left(\frac{\pi z_e}{l}\right) \cos\left(\frac{\pi z_h}{l}\right) \times \tilde{\varphi}(z_e - z_h), \quad (20)$$

where  $\alpha$  and  $\beta$  should be varied in order to minimize the energy while ensuring the normalization of Eq. (20). The normalization condition reads as

$$\alpha^2 + \beta^2 + 2S\alpha\beta = 1, \quad (21)$$

where  $S$  is the inner product between Hartree and quasifree solutions given by

$$S = A \int_{-l/2}^{l/2} \int_{-l/2}^{l/2} \varphi(z_e) \varphi(-z_h) \cos\left(\frac{\pi z_e}{l}\right) \cos\left(\frac{\pi z_h}{l}\right) \times \tilde{\varphi}(z_e - z_h) dz_e dz_h. \quad (22)$$

Similarly, the expectation value for the exciton energy is calculated from

$$E_{eh} = \alpha^2 H_{11} + \beta^2 H_{22} + 2\alpha\beta H_{12}, \quad (23)$$

where  $H_{11}$  and  $H_{22}$  are given by Eqs. (19) and (14), respectively, and  $H_{12}$  is the coupling matrix element that can be written as

$$H_{12} = \left\{ \tilde{E} + \frac{\hbar^2 \pi^2}{m^* l^2} + E_g \right\} S + \frac{\hbar^2 \pi}{m^* l} A \int_{-l/2}^{l/2} \int_{-l/2}^{l/2} \varphi(z_e) \times \varphi(-z_h) \sin\left[\frac{\pi(z_e - z_h)}{l}\right] \tilde{\varphi}'(z_e - z_h) dz_e dz_h. \quad (24)$$

Once the matrix elements  $H_{11}$ ,  $H_{22}$ , and  $H_{12}$  are computed, the final step in our calculation consists in minimizing Eq. (23) under the normalization condition Eq. (21). This provides us with the exciton energy as well as the approximate wave function.

### III. PARAMETERS AND NUMERICAL RESULTS

The main advantage of the present model is its mathematical and physical simplicity. This advantage has been achieved, however, at the expense of limited accuracy and the introduction of additional parameters that should be adjusted to fit the behavior of a particular polymer. These pa-

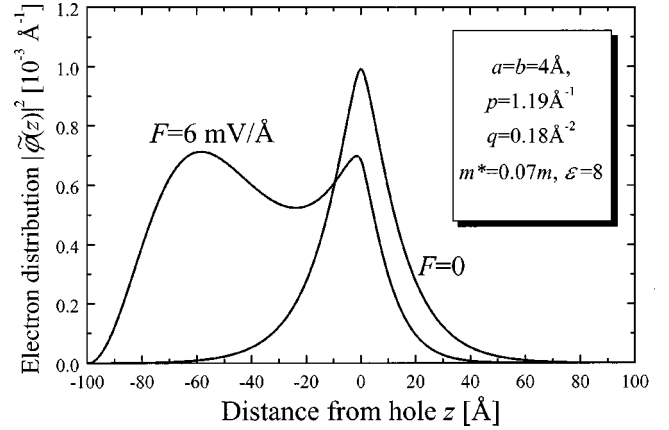


FIG. 3. The electron distribution for a polymer of conjugation length  $l=100$  Å. The symmetric and asymmetric curves are obtained in the absence and presence of a static electric field, respectively.

rameters are the transverse dimensions of the confining box  $a$  and  $b$ , the effective mass  $m^*$  and the dielectric constant  $\epsilon$ . We wish to apply our model to poly(*p*-phenylene vinylene)(PPV) since this is a technologically interesting polymer and reliable calculations exist for infinite chain length.<sup>8</sup> The bulk static dielectric constant of PPV and other conjugated polymers is known to be around 3.5 but this value is an orientational average. In fact, due to the large mobility along the chain axis the appropriate dielectric constant for this direction is considerably larger and we will use the value  $\epsilon=8$  of Ref. 13. The distance between two opposite sites on a phenyl ring in the polymer chain is  $\sim 2.8$  Å. Hence, allowing for a certain delocalization of the  $\pi$  electrons we take the transverse dimensions as  $a=b=4$  Å. This leaves the effective mass as the only undetermined parameter. However, adjusting the spatial extent of the free exciton wavefunction, i.e., the solution in the limit  $l \rightarrow \infty$ , to the value obtained by the Green's function technique<sup>8</sup> allows us to fix this parameter as well. As mentioned in the introduction, the spatial extent of the free exciton is, in fact, the effective Bohr radius, more accurately given as the full  $e^{-1}$  width of the electron distribution. By fitting the results of Ref. 8 to a smooth envelope,  $a_B$  can be estimated as approximately 35 Å and, hence, we will adjust the effective mass in accordance with this value.

In order to obtain the wave function for general values of the conjugation length we must first solve the one-coordinate equations Eqs. (12) and (18) corresponding to the cases of long and short conjugation length, respectively. Among these cases, the former is especially simple since this is an ordinary linear equation. To solve this equation numerically the  $z$  interval  $-l \leq z \leq l$  is divided into a large number of subintervals (typically several hundred) and the smooth potential is replaced by its average within each subinterval. The wavefunction is subsequently propagated from  $z=-l$  to  $z=l$  by matching the function and its derivative at each boundary. The acceptable eigenvalues are finally identified as those for which the boundary condition  $\tilde{\varphi}(\pm l)=0$  is met. The same method is, in fact, applicable to Eq. (18) as well provided an iterative procedure is used. One simply starts from the cosine standing-wave solution for a single particle and through repeated iteration the self-consistent solution is obtained. As mentioned above, the effective mass can be determined by



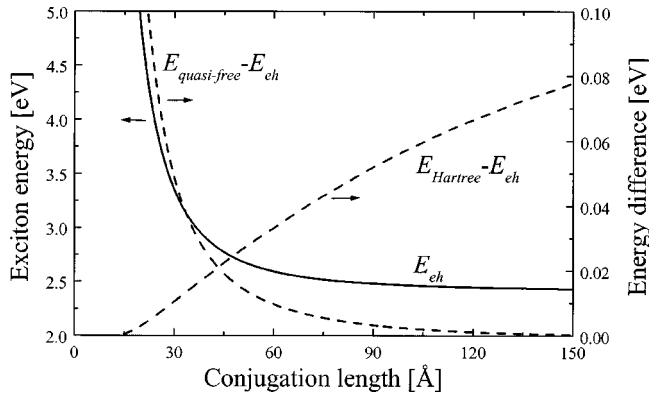


FIG. 4. Exciton energy  $E_{eh}$  (solid line) versus conjugation length. The dashed curves illustrate the “error” introduced by adopting either the quasifree or the Hartree result.

requiring that the width of the electron distribution of the free exciton (in practice  $l=100$  Å) be approximately 35 Å. In this way, a value  $m^*=0.07m$  is found and the resulting electron wave function obtained by solving Eq. (12) numerically using the procedure described above is shown in Fig. 3. Since the exact solution in the limit  $l\rightarrow\infty$  is simply the relative-motion part  $\tilde{\varphi}(z)$  only this function is shown. For comparison, the solution in the presence of a non-zero electric field is shown in the same figure. The field strength  $F=6$  mV/Å is chosen so that the Coulomb attraction is approximately balanced by the field-induced splitting of the exciton. Thus, two maxima are seen in  $\tilde{\varphi}(z)$ . Obviously the finite conjugation length has a dramatic influence on the exciton behavior in the presence of the field. The finite length leads to a finite lowering of the potential equal to  $-eFl$ . Hence, the competition between the field-induced minimum, which tries to dissociate the electron-hole pair, and the Coulomb attraction holding the pair together is strongly dependent on field strength and conjugation length. A simple estimate for the critical field strength  $F_c$ , i.e., the field strength at which Coulomb attraction is balanced by field-induced dissociation, is obtained by equating the corresponding two contributions to the potential<sup>9</sup>

$$e l F_c = \frac{e^2}{4\pi\epsilon\epsilon_0 l} \Rightarrow F_c = \frac{e}{4\pi\epsilon\epsilon_0 l^2}. \quad (25)$$

Thus, the critical field approximately varies as the inverse square of the conjugation length. In the case  $F>F_c$ , a second minimum in the potential appears. The mere presence of this minimum does not necessarily produce any significant splitting of the exciton wavefunction, however. In fact, splitting is only observed when the depths of the two minima are comparable. In the case considered in Fig. 3, i.e.,  $l=100$  Å, one finds  $F_c\approx 0.18$  mV/Å. This value should be contrasted with the value 6 mV/Å, which is actually needed to produce the splitting shown in Fig. 3.

We may now turn to the chain length dependence of the exciton energy. Using the above parameters leads to the curves shown in Fig. 4. The calculations yield an exciton binding energy  $E_g - E_{eh}$  of 0.25 eV in the limit  $l\rightarrow\infty$ . A binding energy of 0.25 eV might seem surprisingly small considering the fact that the Green’s function technique used by Rolfing *et al.*<sup>8</sup> yields a value of 0.9 eV. The origin of

this high value, however, has recently been traced by van der Horst *et al.*<sup>14</sup> who concluded that interchain screening of the Coulomb interaction is essential to describe the properties of bulk polymers. Hence, the value 0.9 eV is only representative of the binding energy for excitons in *isolated* polymer chains. In Ref. 14 the binding energy of excitons in bulk polymers was shown to be dramatically reduced by the inclusion of interchain screening via an appropriate dielectric constant. In addition, it was found that relaxation of the chain geometry (polaronic effects) only produces a small correction. In the present paper, screening is taken into account by the presence of a large dielectric constant ( $\epsilon=8$ ), which is appropriate for bulk PPV (Ref. 13) and, hence, includes contributions from both intra- and interchain screening. This explains the difference between the value obtained by Rolfing *et al.* and the present result. It is noted that the present value compares favorably with the experimental result 0.2 eV for MEH-PPV.<sup>15</sup> The experimental exciton energy for essentially infinite PPV chains is about 2.4 eV (Ref. 16) and, hence, the energy gap is approximately  $E_g = 2.65$  eV. This is the value used in Fig. 4. The differences between the exciton energy, given by Eq. (23), and the quasifree and Hartree results are shown as the dashed curves. As expected, the quasifree and Hartree results approach the variational energy in the case of long and short conjugation lengths, respectively. From the figure it is seen that the “short conjugation length range” is approximately  $l\leq 30$  Å using an energy difference of 0.01 eV as upper limit. Similarly, the “long conjugation length range” is roughly  $l\geq 60$  Å. The crossover point, which marks the transition from confinement dominated to Coulomb dominated behavior, is approximately at 40 Å. This value is close to the effective Bohr radius  $a_B\approx 35$  Å, as was to be expected. In Fig. 5 we have compared the calculated exciton energy to some results for  $n(p$ -phenylene vinylene) oligomers ( $n=1, 2, 3$ , and 4) obtained from PPP (Pariser-Parr-Pople) calculations using single-excited state configuration interaction (CI-PPP). These results are in excellent agreement with experiments.<sup>16</sup> The length of the repeating unit of PPV is approx. 6.4 Å and, hence, the length of the  $n$  oligomer is 6.4 Å ( $n+n_0$ ), where  $n_0$  is added in order to account for electron delocalization at the chain ends. The points in Fig. 5 have been plotted using  $n_0=2.0$ . It is noted that the two calculations are in excellent agreement. This confirms that the present model is, in fact, able to reproduce the chain length dependence of the exciton energy.

The optical absorption by the exciton is proportional to the square of the one-dimensional electron-hole overlap integral  $D$  given by<sup>17</sup>

$$D = \int_{-l/2}^{l/2} \psi(z, z) dz = \alpha \int_{-l/2}^{l/2} \varphi(z) \varphi(-z) dz + \beta A \frac{l}{2} \tilde{\varphi}(0), \quad (26)$$

which expresses the amplitude for the electron and hole to be located in coinciding positions. In Fig. 6, results for the squared overlap integral are shown as a function of field strength along with results for the exciton energy. As expected, the overlap integral decreases upon applying the electric field. Physically, this decrease is due to the spatial separation of electron and hole induced by the applied field.

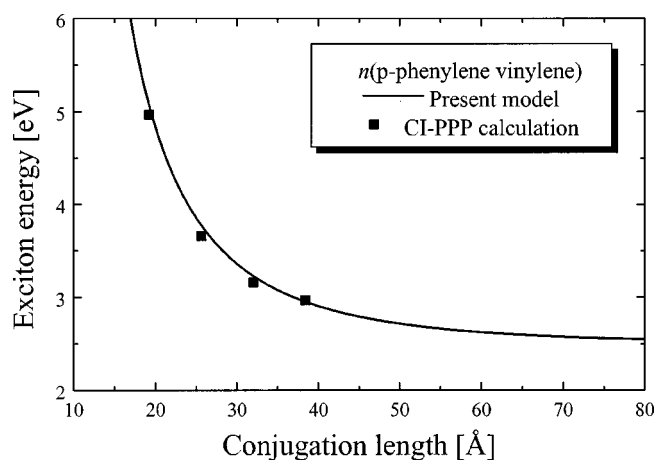


FIG. 5. Comparison between the results of the present model and those of a standard CI-PPP calculation for  $n$ (*p*-phenylene vinylene) ( $n$ PPV) with  $n = 1, 2, 3$ , or  $4$ . For the CI-PPP calculations the conjugation length of the  $n$ -oligomer is taken as  $(n + 2.0) \times 6.4 \text{ \AA}$ .

A comparison of graphs a, b, and c in Fig. 6 shows that the conjugation length is of critical importance for these phenomena. Again, this is explained by the fact that the field needed in order to produce a substantial separation of electrons and holes is strongly dependent on conjugation length, c.f. Eq. (25). It is thus concluded that models in which the conjugation length is taken to be infinite will lead to inaccurate result for the behavior of excitons in electric fields. In the absence of electric fields, however, these models may still be valid due to the localized character of the exciton.

#### IV. SUMMARY

In summary, a highly simplified particle-in-a-box model of excitons in conjugated polymers has been presented. In this model the exciton is treated as an electron-hole pair interacting via Coulomb forces and confined to the polymer backbone by means of infinite barriers defined by the geometry of the polymer chain. In this manner, the original many-body Schrödinger equation is reduced to a one-dimensional two-particle equation. From this relatively simple equation exciton states may be obtained for polymers of arbitrarily long conjugation length in contrast to usual quantum chemistry calculations that are limited by the complexity of large molecular systems. The disadvantage of the particle-in-a-box model is reduced accuracy and the introduction of system-dependent parameters such as dielectric constants and effective masses. The solutions to the two-particle equation are found to be especially simple in the cases of long and short conjugation length. Hence, the approximate translational invariance in the former case and the Hartree approximation in the latter reduce the problem to single-coordinate form for

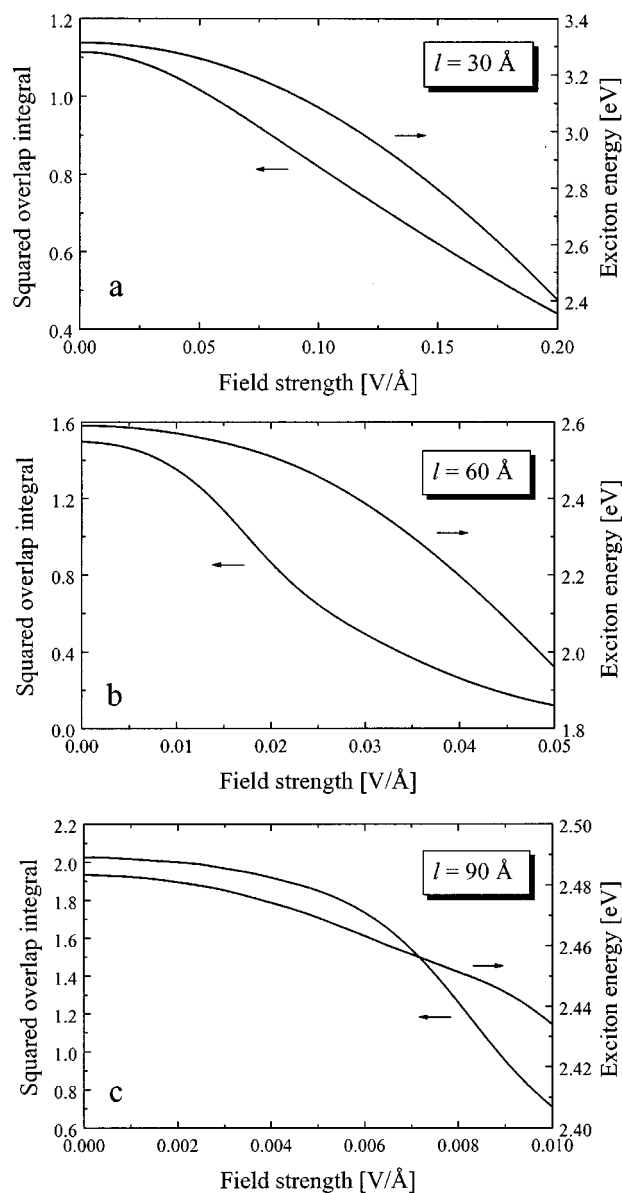


FIG. 6. Illustration of the squared electron-hole overlap integral and exciton energy as a function of field strength for three different values of the conjugation length  $l$ .

which accurate numerical solutions for the exciton wavefunction are easily obtained. By forming a linear combination of these two cases and minimizing the expectation value for the exciton energy, the general case is subsequently treated. As an example of its applicability, the proposed model is used to illustrate the influence of a static electric field on exciton energies and electron-hole overlap integrals for different values of the conjugation length using parameters appropriate for PPV.

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