

## Theory of Stark shifts in quantum wells consisting of highly anisotropic molecular-crystalline layers

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We introduce a simple model to calculate the Stark shift in multiple quantum wells consisting of highly anisotropic and optically nonlinear molecular-crystalline layers. This model is used to calculate the exciton absorption peak in quantum-well structures consisting of the archetype planar molecular compounds; 3,4,9,10-perylenetetracarboxylic dianhydride, 3,4,7,8-naphthalenetetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole, and copper phthalocyanine. We find that the exciton absorption peak shifts by 60 to 70 meV in an electric field of  $< 10^6$  V/cm. We also find that both redshifts and blueshifts are achieved for asymmetrical quantum-well structures.

The electric-field dependence of optical absorption near the exciton edge in conventional semiconductor multiple quantum wells is a subject which has been thoroughly studied both theoretically and experimentally.<sup>1-5</sup> The range of phenomena and applications of these semiconductor heterostructures is, however, limited to those material combinations with small lattice mismatch such that their growth can be achieved by conventional epitaxy. Heterostructures consisting of crystalline organic semiconductors, on the other hand, can often be layered in nearly defect-free structures due to the weak van der Waals bonding between molecules.<sup>6,7</sup> In addition, crystalline organic films have exhibited enormous anisotropies in both their conductive and dielectric properties,<sup>8,9</sup> and have already been employed in such photonic devices as photodiodes and optical waveguide switches.<sup>8,10</sup> Moreover, the relatively large exciton binding energy results in an exciton absorption peak deep in the band gap which can lead to large Stark shifts useful for optical modulation. Due to the unique electrical and optical properties of this class of materials, it is important to understand how crystalline organic multiple quantum wells (MQWs) behave in an electric field.

In considering the Stark shift in crystalline organic materials, we note that the major differences between organic and conventional inorganic multiple quantum wells are the following: The dielectric permittivity (3-4) of organic material is much smaller than that of conventional semiconductors ( $\sim 10$ ), and the organic charge-transfer exciton radius is small ( $\sim 10$  Å) compared with 50-100 Å for inorganic semiconductors. The small exciton radius is a result of the large binding energy of the electron-hole pair ( $\sim 1$  eV), and in some cases has been shown to be Wannier-like.<sup>11</sup> In addition, the dielectric and conductive properties of the organic material are highly anisotropic as a result of crystalline structure. Finally, the organic material can be dielectrically nonlinear under an electric field.

In this paper, we study the Stark shift of highly anisotropic organic MQW structures consisting of the archetype compounds: 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 3,4,7,8-naphthalenetetracarboxylic di-

anhydride (NTCDA), 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI), and copper phthalocyanine (CuPc). These compounds are of interest since heterojunctions consisting of pairs of these materials have been extensively studied. Furthermore, with the exception of CuPc, the molecular bonding is purely by van der Waals forces, thereby simplifying the analysis of the electric fields at the heterointerface. We calculate the exciton ground-state energy shift under an applied electric field for quantum-well structures consisting of PTCDA/NTCDA and PTCDA/PTCBI symmetrical wells and PTCDA/CuPc/PTCBI asymmetrical wells. We find an  $\sim 70$ -meV redshift for symmetrical wells in an applied field of  $1.2 \times 10^6$  V/cm, and both redshifts and blueshifts for asymmetric MQW structures.

The Hamiltonian for excitons in organic MQW structures can be written as

$$H = KE_e + KE_h + V_e(z_e) + V_h(z_h) + V_{\text{col}}(\mathbf{r}) + V_{\text{field}}(\mathbf{r}). \quad (1)$$

Subscripts  $e$  and  $h$  are for the electron and hole, respectively,  $\mathbf{r}$  is the position vector where  $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$ , the  $z$  direction is defined as the direction normal to the quantum well stacks,  $KE$  is the kinetic energy,  $V(z)$  is the quantum-well potential,  $V_{\text{col}}(\mathbf{r})$  is the Coulomb interaction between the electron and hole, and  $V_{\text{field}}(\mathbf{r})$  is the potential due to the applied electric field. For the electric field along the  $z$  direction, we have  $V_{\text{field}}(\mathbf{r}) = qFz$ , where  $q$  is the charge,  $F$  is the electric field, and  $z = z_e - z_h$ .

In center-of-mass coordinates, we can rewrite the Hamiltonian as

$$H = H_r(\mathbf{r}) + H_z(Z), \quad (2)$$

where  $Z$  is the position of center of mass in the  $z$  direction, and

$$H_r(\mathbf{r}) = \left[ -\frac{\hbar^2}{2\mu} \nabla^2 \right] - \frac{q^2}{\sqrt{\mathbf{r}^T \boldsymbol{\epsilon}^T \mathbf{r}}} + qFz \quad (3a)$$

and

$$H_z(Z) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial Z^2} + V_e \left[ Z + \frac{m_h}{M} z \right] + V_h \left[ Z - \frac{m_e}{M} z \right]. \quad (3b)$$

Here,  $m_e$  and  $m_h$  are the effective masses of the electron and hole, respectively,  $M = m_e + m_h$ ,  $\mu$  is the reduced mass,  $\hbar$  is the Planck constant divided by  $2\pi$ , and  $r^T \epsilon^T \epsilon r$  is the scalar product of the permittivity tensor and the position vector which reduces to  $(\epsilon r)^2$  for isotropic materials. The term  $H_z(Z)$  describes the center-of-mass motion perpendicular to the quantum-well stacks under a potential which is controlled both by the relative positions of the electron and hole, and by the one-dimensional well potential. Using Eq. (3), we can find eigenstate solutions to Schrödinger's equation  $\xi_z(Z)$ , such that

$$H_z(Z)\xi_z(Z) = \Sigma(z)\xi_z(Z). \quad (4)$$

The eigenvalues of  $H_z(Z)$  are  $\Sigma(z)$ , which are functions of  $z$ , the relative position of the electron and hole perpendicular to the plane of the layers. Using the trial wave function  $\Psi(\mathbf{r}, Z) = \Phi(\mathbf{r})\xi_z(Z)$ , the total energy is then found using

$$E \leq \int \int d\mathbf{r} dZ \Phi(x, y, z) H_r \Phi(x, y, z) \xi_z(Z) \xi_z(Z) + \int \int d\mathbf{r} dZ \Phi(x, y, z) \Phi(x, y, z) \xi_z(Z) H_z \xi_z(Z) + \int \int d\mathbf{r} dZ \left[ -\frac{\hbar^2}{2\mu} \right] \Phi(x, y, z) \xi_z(Z) \frac{\partial \Phi}{\partial z} \frac{\partial \xi_z}{\partial z}. \quad (5)$$

Combining Eqs. (4) and (5), and recognizing that the third term is proportional to  $\partial/\partial z \int dZ \xi_z(Z) \xi_z(Z) = 0$  then gives

$$E \leq \langle \Phi \xi | H_r + \Sigma(z) | \Phi \xi \rangle = \langle \Phi | H_r + \Sigma(z) | \Phi \rangle. \quad (6)$$

From Eq. (6), we see that the problem reduces to finding the eigenstates of Schrödinger's equation for the new Hamiltonian,  $H_{\text{new}} = H_r + \Sigma(z)$ . Separating terms in  $H_r$  leads to

$$H_{\text{new}} = H_0 + H_1, \quad (7a)$$

where

$$H_0 = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{q^2}{\epsilon_{\text{av}} r} \quad (7b)$$

and

$$H_1 = \frac{q^2}{\epsilon_{\text{av}} r} - \frac{q^2}{\sqrt{\mathbf{r}^T \epsilon^T \epsilon \mathbf{r}}} + qFz + \Sigma(z). \quad (7c)$$

To use the hydrogenlike solution to Eq. (7), we include the average effect of the anisotropic Coulomb attraction in  $H_0$  expressed by  $\epsilon_{\text{av}}$ , while leaving the remaining anisotropy as a perturbation. The simplest way of achieving this is to take the algebraic average of the diagonal terms of  $\epsilon$  in  $H_0$ . Thus  $H_0$  is the hydrogenlike Hamiltonian, where we replace the dielectric constant with  $\epsilon_{\text{av}} = \epsilon_{\text{av}0}$  plus the induced nonlinear term, and  $\epsilon_{\text{av}0}$  is the

dielectric constant in zero field. Note that vacuum-deposited organic materials typically have a large third-order nonlinear susceptibility,<sup>10</sup> where the inversion symmetry of the molecule eliminates second-order effects. Near the exciton absorption peak, the resonant nonlinear effect is very strong, and  $\chi^{(3)}(-\omega; 0, 0, \omega)$  due to electroabsorption is usually positive.<sup>10,12</sup> The large exciton binding energy makes it possible for the material to sustain a large field. Under these conditions, therefore,  $\chi^{(3)}(-\omega; 0, 0, \omega): F(0)F(0)$  cannot be neglected. Thus  $P^{(3)}(\omega) = \chi^{(3)}(-\omega; 0, 0, \omega): F(0)F(0)F(\omega)$  is the induced third-order electric polarization, and the induced nonlinear permittivity is  $\chi^{(3)}(-\omega; 0, 0, \omega): F(0)F(0)$ . In the following calculations, we allow  $\chi^{(3)}$  to range from 0 to  $5 \times 10^{-9}$  esu to determine how this nonlinear phenomenon affects the exciton ground-state energy.

When the basis eigenstates to  $H_0$  are known, and as long as  $H_1$  is a small correction to  $H_0$ , we can find the eigenstates and energies for  $H_{\text{new}}$  to first and second orders using perturbation theory. The first two terms in  $H_1$  reflect the anisotropy of the material. For the ground state, their contribution to the total energy is small, whereas the  $\Sigma(z)$  term can be significant. However,  $\Sigma(z)$  is reasonably constant in the region where the exciton probability amplitude is largest. Therefore, it too can be considered as a small perturbation in most cases. Finally, the electric-field term is a perturbation for  $qFz$  small compared to the ground-state energy of the exciton.

We applied this method to calculate Stark shifts in multiple quantum wells consisting of PTCDA or PTCBI as well as bounded by barriers consisting of similar crystalline organic compounds. The barrier materials considered are NTCDA, CuPc, and PTCDA depending on which well materials are used. The energy-band offsets for different combinations of these materials have been measured previously,<sup>13</sup> and are shown in the insets of Figs. 1–3.

It has been shown for PTCDA that the hole mass ( $m_h = 0.18m_0$ , where  $m_0$  is the free-electron mass) is

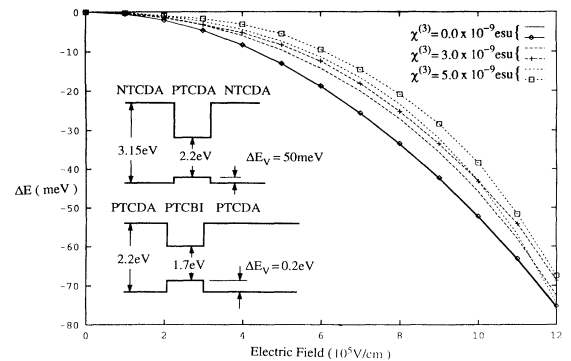


FIG. 1. Exciton ground-state energy shift for bulk PTCDA and symmetrical quantum wells. Lines: Stark shift for bulk PTCDA and 10-Å PTCDA/NTCDA quantum wells. Lines with points: Stark shift for 10-Å PTCDA/PTCBI quantum wells. Inset: Band diagram for PTCDA/NTCDA and PTCDA/PTCBI heterostructures.

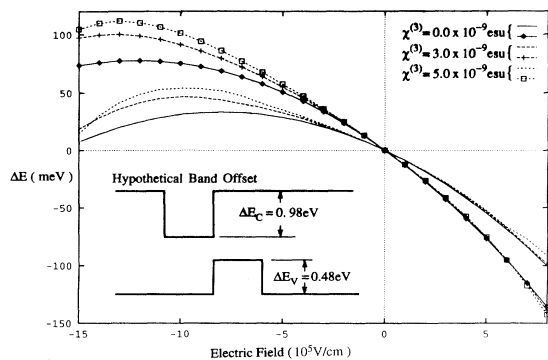


FIG. 2. Exciton ground-state energy shift for a hypothetical band offset. Lines: Well widths for both materials are 10 Å. Lines with points: Well widths are 20 Å. Inset: Hypothetical band diagram.

much lighter than for electrons ( $m_e > 10m_0$ ), and hence the hole is nearly a free particle bound to a heavy electron.<sup>11</sup> The dielectric permittivity tensor of PTCDA relative to the thin-film axes has also been measured previously,<sup>8,9</sup> and the terms are  $\epsilon_{zz} = 1.9$ ,  $\epsilon_{xx} = \epsilon_{yy} = 4.5$ , and  $\epsilon_{xz} = \epsilon_{zx} \approx -1.0$  with all other terms vanishing, where we assume that the PTCDA molecules form stacks tilted at an angle of 11° with respect to the substrate normal.<sup>6,7</sup> Thus in the coordinates constructed by the directions normal and along the macroscopic quantum-well stacks, nonzero off-diagonal terms for the permittivity exist, which can be calculated assuming the permittivity tensor is diagonalized in the PTCDA molecular coordinates. Furthermore, NTCDA is isotropic with a diagonal permittivity tensor given by  $\epsilon_{xx} \approx \epsilon_{yy} \approx \epsilon_{zz} \approx 1.6$ . Also, measurements have been done to determine the dielectric properties of CuPc. It is found that the permittivity is isotropic with  $\epsilon = 4.4$ , and the effective mass of the hole is taken approximately equal to the free-electron mass.<sup>14</sup> Finally, although the permittivity tensors and effective masses have not been reliably determined for PTCBI, its

molecular structure is similar to that of PTCDA. Hence, to good approximation, we assume similar values for the effective mass and permittivity of both materials. Note that because the radius of the exciton is small, the differences of the permittivities in the different materials is a relatively small effect. In addition, the effective hole masses in all materials except PTCDA and PTCBI are of the order of the free-electron mass. Hence the wave function should decay rapidly in the barrier. Thus the exact determination of the permittivity and effective mass in the barrier is not as important as in the well.

We first calculate the exciton energy shift in bulk PTCDA. The ground-state energy of the exciton peak shifts toward red by 40–50 meV in an electric field of  $\sim 10^6$  V/cm (see Fig. 1). We find that a positive  $\chi^{(3)}$  tends to reduce the redshift since it results in a large  $\epsilon_{av} = \epsilon_{av0} + \chi^{(3)}FF$  which screens the Coulomb interaction between the electron and hole. This increases the ground-state energy from the value where  $\chi^{(3)}$  is zero. The reduction is more obvious in high electric field since  $\chi^{(3)}FF$  increases quadratically with field.

Next we examine PTCDA/NTCDA quantum-well structures, where NTCDA is the barrier both for electrons and holes<sup>13</sup> (900 meV for electrons and 50 meV for holes) as shown in the inset of Fig. 1. Such a shallow well should not strongly modify the motion of the hole from the free space case, and thus the situation is similar to a free exciton, as shown in Fig. 1.

The PTCDA/PTCBI quantum-well structure has a deeper potential well for holes<sup>13</sup> (with a 300-meV electron well, and a 200-meV hole well) while PTCDA is the barrier material. The deeper hole well causes a slightly smaller shift under the same dc electric field as a result of a larger binding force for excitons provided by the well barriers (see also Fig. 1). That is, as field is applied, the electron moves toward one heterointerface and the hole moves toward the other. This tendency is reduced by the comparatively deeper PTCDA/PTCBI wells, thus reducing the total-energy shift.

Next we consider asymmetrical heterostructures where hole and electron wells are not in the same material, in which case the quantum well plays a much more significant role than in the symmetrical structures. To illustrate how the asymmetry can cause a blueshift, consider a hypothetical band structure show in the inset of Fig. 2. The shift has a different sign for the electric field directed along the positive or negative  $z$  directions. The reason is that the quantum well, and thus  $\Sigma(z)$ , is asymmetrical, resulting in a binding potential which tends to push the hole in one direction decided by the quantum-well geometry, while the electric field also pushes the hole along the field direction. When these two forces combine constructively, they cause a redshift. For example, a 50-meV shift can be achieved when the electric field is only  $4 \times 10^5$  V/cm. When the two forces are along different directions, they add destructively, which induces a blueshift over intermediate electric-field values, after which the redshift returns since the well potential is insufficiently large to compensate for the electric-field perturbation. A maximum of 30–40-meV blueshift can be found for a field of  $\sim 10^6$  V/cm. Calculation shows

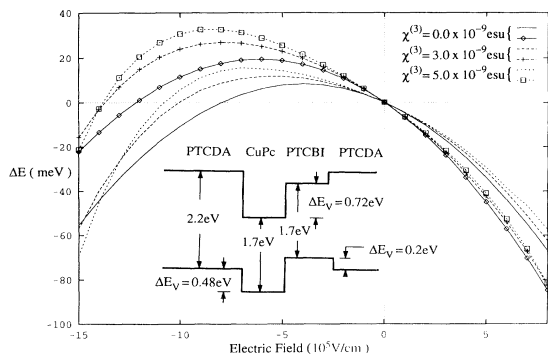


FIG. 3. Exciton ground-state energy shift for PTCDA/CuPc/PTCBI asymmetrical quantum wells with different well widths. Lines: Widths for both well materials are 10 Å. Lines with points: Well widths are 20 Å. Inset: Band diagram of PTCDA/CuPc/PTCBI heterojunctions.

that larger well widths result in larger shifts in both field directions, since a smaller quantum well induces a larger confinement force on the electron and hole, and thus reduces the Stark shift. The energy shift will increase with well width until the well is larger than several exciton radii, at which point the confinement effect tends to vanish although asymmetry still plays a role.

In a "real" quantum-well structure, asymmetry such as shown in Fig. 2 can only partially be achieved by using three different organic materials to form well structures shown in the inset of Fig. 3. Several calculations for different well widths in this geometry have been made, showing that the larger well width results in a larger blueshift. For electric fields of  $\sim 5 \times 10^5$  V/cm, a 10 meV blueshift results for a well width of 10 Å, while a 20-meV blueshift can be found for a slightly higher electric field and a well width of 20 Å. The energy shift becomes independent of well width when the width exceeds several exciton radii, as expected.

If the  $\chi^{(3)}$  effect is included, we find that a large, positive  $\chi^{(3)}$  tends to reduce the redshift. In the blueshift region, the large value of  $\epsilon_{av} = \epsilon_{av0} + \chi^{(3)}FF$  increases the blueshift, thereby extending the field region over which the blueshift occurs, as shown in both Figs. 2 and 3.

In summary, we have calculated the Stark shift of the exciton absorption line for multiple quantum wells consisting of highly anisotropic crystalline molecular layers. Our treatment includes the effects of anisotropy, dielec-

tric nonlinearity, quantum confinement and the strong Coulomb attraction between the electron and hole. The strength of the Coulomb binding makes it possible for the exciton to sustain strong electric fields without dissociation, hence making the nonlinear  $\chi^{(3)}$  term significant as well. Indeed, such  $\chi^{(3)}$ -induced shifts have already been observed in some organic materials.<sup>12</sup> We have also shown that for asymmetrical quantum-well structures, blueshifts can be achieved by applying a dc electric field to the structure, which further increases the Stark shift of the exciton peak.

Finally, it is useful to estimate the linewidth-to-line shift (lw/l<sub>s</sub>) ratio which can be achieved for organic quantum-well structures. The ratio can be thought of as a figure of merit for optical modulators. From previous work,<sup>11</sup> the  $S_0$  exciton of PTCDA has a half-width of approximately 250 meV, centered at approximately 2.2 eV. A total Stark shift of  $\sim 100$  meV therefore results in a lw/l<sub>s</sub>=0.4. While this is somewhat smaller than what can be achieved with inorganic quantum wells where the ratio can be as high as 2 due to the very narrow exciton lines characteristic of covalent/ionic solids,<sup>1</sup> it nevertheless is sufficiently large to be of interest in many practical modulator applications.

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