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EFFECTS OF ELECTRON-ELECTRON INTERACTIONS ON THE POLARIZATION CHARACTERISTICS OF ELECTROLUMINESCENT POLYMERS*

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Abstract The polarization characteristics of electroluminescent polymers were studied with the theoretical model including the external field, electron-electron and electron-lattice interactions simultaneously. It was discovered that on-site Hubbard energy and the nearest neighbor electron-electron interactions increase the negative polarization of self-trapping bi-excitons in polymers obviously. The physical significance of negative polarization—a new phenomenon, and its possible applications were also explored.

Key words electron-electron interactions, polarization, electroluminescent polymers, external field.

电子-电子相互作用对电致发光高分子极化特性的影响*

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摘要 用同时计入电子-电子相互作用,外电场及电子-晶格相互作用的理论模型研究分析了电致发光高分子的极化特性,发现在位电子相互作用和相邻格点间电子的相互作用明显增加高分子中双激子态的反向极化.本文还探讨了反向极化这个新的物理现象的意义及其可能的应用.

关键词 电子-电子相互作用、极化、电致发光高分子、外电场.

Electroluminescent polymers are new-generation opto-electronic functional materials with wide application prospects. Nowadays, the study on polymers has become a new growing point in the fascinating field of opto-electronics. Electroluminescent frequencies of polymers are in the range of visible light, and have various colors. In addition, polymers are cheap in price, and not heavy in weight. Using polymers we can construct completely flexible and colorful visual displays with large area. Besides, we can also use polymers to make portable and foldaway electronic newspapers. All these mean that polymers will open a new channel for the technology of display and opto-electronics. Therefore, the study of polymeric

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electroluminescence has attracted much interest[1~2] of international academic circles, and become one of the front subjects since 1990's. In recent years, the development of electroluminescent devices has made great progress, and electroluminescent devices are nearing practical application. Because the electroluminescence of polymers is due to the external field, the authors of the article and their cooperators studied the electric-field behavior of polymers, and found that the applied electric fields polarize the self-trapping excitons of polymers, and put forward firstly a new physics idea of negative polarization[3~4]. However, the references [3~4] have not considered the electron-electron interactions. But for polymers, the electron-electron interactions can not be neglected[5]. Hence, this presentation is devoted to study the joint effects of electron-electron interactions, applied fields and electron-lattice interactions on the polarization of polymers. We discover that on-site Hubbard energy and the nearest neighbor electron-electron interactions increase the negative polarization of self-trapping bi-excitons in polymers obviously. The physical significance of negative polarization and its possible applications are also explored.

1 Methodology

Regarding an electroluminescent polymer as a finite chain of N CH groups with nondegenerate ground states, the electron-electron interactions in an electroluminescent polymer can be described by the extended Hubbard model

$$H_{e-e} = \frac{U}{2}\sum_{n}(C^{+}_{n,s}C_{n,s} - \frac{1}{2})(C^{+}_{n,-s}C_{n,-s} - \frac{1}{2}) + V\sum_{n,s,s'}(C^{+}_{n,s}C_{n,s} - \frac{1}{2})(C^{+}_{n+1,s'}C_{n+1,s'} - \frac{1}{2}), \quad (I)$$

Where U is the usual on-site Hubbard energy, and V represents the nearest neighbor electron-electron interaction.

Assuming that a uniform electric field E is along the chain direction, the additional potentical energy due to the field is then

$$H_E = \sum_{n} eEnaC^{+}_{n,s}C_{n,s}. \quad (2)$$

Thus, the Hamiltonican in an electroluminescent polymer can be written as:

$$\hat{H}_{e-p} + \hat{H}_{e-e} + \hat{H}_E + H_{elastic} = \hat{H}_e(\{u_n\}) + H_{elastic}, \quad (3)$$

where H_{e-p} is the electron—lattice interactions,

$$\hat{H}_{e-p} = -\sum_{n,s}[t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e](\hat{C}^{+}_{n+1,s}\hat{C}_{n+1,s} + HC), \quad (4)$$

$H_{elastic}$ is the elastic energy of the lattice.

$$H_{elastic} = \frac{1}{2}K\sum_{n}(u_{n+1} - u_n)^2 + \sum_{n}K'(u_{n+1} - u_n), \quad (5)$$

From the electronic eigenequation

$$H_e\sum_{n}Z_{n,\mu}|n> = \varepsilon_\mu\sum_{n}Z_{n,\mu}|n>. \quad (6)$$

We can get the energies ε_μ and the wave function $Z_{n,\mu}$ of electrons.

It should be pointed out that electroluminescent polymers are different from conventional inorganic semiconductors, for electroluminescent polymers are quasi one-dimensional systems. Low-dimensional lattice has instability. So it is easy to be distorted[5,7]. Extra electron(s) and hole(s) will make a low-dimensional lattice deformed[7,8]. So will the applied electric field. Therefore for polymers, we should consider electron-excitation, lattice relaxation and applied field simultaneously. As a result, the Hamiltonian of electrons depends on atomic configurations. i. e. atomic configurations determine the electronic states. Meanwhile, the eigenvalues of the occupied electronic states as the additional potential of the lattice affects the atomic configurations conversely. Hence we have to use self-consistent method to solve the problem. First we must find out the self-consistent equation. Let the variations of the bond-length $u_{n+1}-u_n$ be $(-1)^{n+1}(\varphi_n+\varphi_{n+1})$, where $\{\varphi_n\}$ represents the static equilibrium configuration of the system. Unfold the total energy of the system around the static equilibrium configuration. Since the lowest energy state is the state which is reasonable in physics and existent in nature, let the coefficient of one-order term be zero, then we obtained the self-consistent equation.

$$(-1)^n(\varphi_n + \varphi_{n+1}) = \frac{2\alpha}{K}\sum_{\mu}^{occ.}Z_{n,\mu}Z_{n-1,\mu} + \frac{K'}{K}, \quad (7)$$

Besides, since the electron-electron interactions are considered, the electronic eigen equation should also be solved self-consistently. In the approximation of Hartree-Fock,

$$\sum_{n,s} C^+_{n,s} C_{n,s} C^+_{n,-s} C_{n,-s} \to \sum_{n,s} (X_{n,s} C^+_{n,s} C_{n,s} + X_{n,-s} C^+_{n,-s} C_{n,-s}) - \sum_{n,s} X_{n,s} X_{n,-s},$$

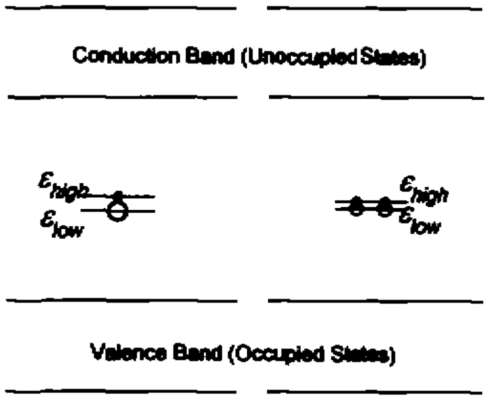
where $X_{n,s} = <\Phi | C^+_{n,-s} C_{n,-s} | \Phi>$. State Φ, which is used to calculate the average value, is the ground state of self-consistent field, and it should also be determined self-consistently. It means that the Schrodinger equation should be also self-consistently solved. In order to arrive at these two self-consistency, we have to solve Eq. (1) to Eq. (7) simultaneously. In this way, we can self-consistently obtain the solutions of atomic configurations and electronic wave functions at the lowest energy states of the system in the presence of any external field.

In the calcuation, the electron-electron interactions U and V are regarded as parameters. U ranges from 0 to 4eV, and $V \leqslant U/2$.

2 The Polarization Characterisitics of a Polymer Chain

Due to the instability of low-dimension[5,7], extra electron(s) and hole(s) will induce a local deformantion in the lattice of polymers, thus leading to the change of electronic energy band structure. Figure 1 shows that the main variation of energy band structure of polymers with extra electron(s) and hole(s) is that the top level of the original valence band and the bottom level of the original conduction band separate from the original continuative band, and enter the original energy gap. Thus these two levels become the localized deep levels ε_{low} and ε_{high} close to the mid-gap. The low level ε_{low} originates from the top level of the original valence band. When there exist no extra electron(s) and hole(s), there should be two electrons at the low level ε_{low}, The high level ε_{high} originates from the bottom level of the original conduction band. When there exist no extra electron(s) and hole(s), there should be no electrons at the high level ε_{high}. Figure 1 (a) represents that there is an extra electron at the ε_{high} level and an extra hole at the ε_{low} levle. Figure 1 (b) denotes there are two extra electrons at the ε_{high} level and two extra holes at the ε_{low} level. It has been pointed out that extra electron(s) and hole(s) will induce a local deformation in the lattice of polymers, leading to a strained field. In the meantime, the extra electron(s) and hole(s) themselves are trapped by the strain field, and the self-trapping bound state of electron(s)-hole(s) is formed[8]. Since the bound state of the electron(s) and hole(s) is known as the exciton, Fig. 1 (a) is single-exciton and Fig. 1 (b) is bi-exciton.

Figure 2 and Figure 3 are the charge density distribution of the single-exciton and bi-exciton, respectively. The charge density is a sum of squares for the absolute values of the wave functions of all the occupied states, i. e. $\rho_n = \sum_{\mu,s}^{occ} |Z^s_{n,\mu}|^2$. In these figures, an electric field is along the chain direction, and the unit of the ordinate is the value of an electron charge e. From the charge density distribution in the figures, we can see that the electric field transfer part of the lattice-point charges in a polymer chain. So the polarization occurs. Figure 2 shows that, in a single-exciton, the positive charges move along the electric field and the negative charges drift in the opposite direction. This is normal polarization. Figure 2 also shows that a single-exciton displays weak normal polarization. Figure 3 depicts that, in a bi-exciton, the positive charges move in the opposite direction of the field and the negative charges along the field. It is negative polarization. Figure 3 exhibits that a bi-ex-



(a) (b)

Fig. 1 The schematic diagram of the energy levels for the polymers with extra electrons and holes

图 1 具有额外电子-空穴的高分子的电子能级分布示意图

(a) 具有 1 个额外的电子-空穴(简称单激子态)

(b) 具有 2 个额外的电子-空穴(间称双激子态)

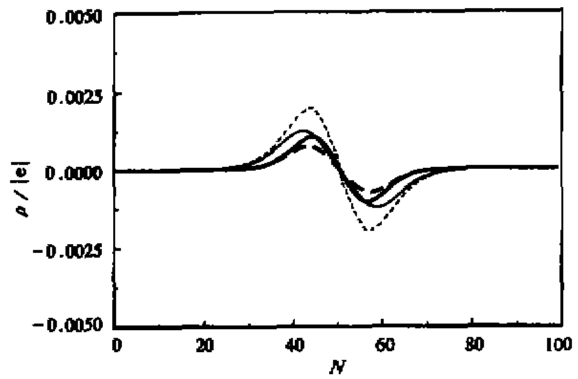


Fig. 2 The charge density distribution of the single exciton under an electric field (the thin solid line: $U=0$ and $V=0$, the thin dashed line: $U=4\text{eV}$ and $V=0$, the thick solid line: $U=4.0\text{eV}$ and $V=0.6\text{eV}$, the thick dashed line: $U=2\text{eV}$ and $V=0.6\text{eV}$. E is along the chain direction)

图2 高分子的单激子态在电场下格点电荷密度分布
细实线：$U=0,V=0$，细虚线：$U=4\text{eV},V=0$，粗实线：$U=4\text{eV},V=0.6\text{eV}$，粗虚线：$U=2\text{eV},V=0.6\text{eV}$，电场沿链方向

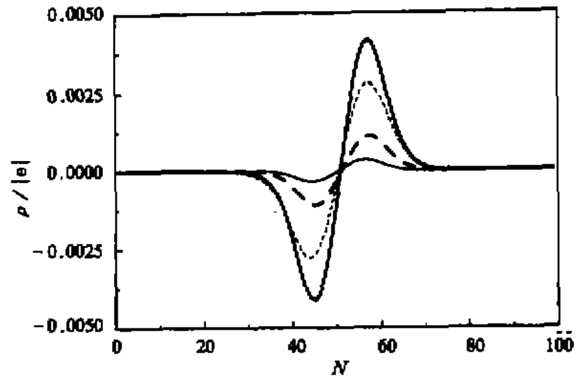


Fig. 3 The charge density distribution of the bi-exciton under an electric field (the thin solid line: $U=0$ and $V=0$, the thin dashed line: $U=4\text{eV}$ and $V=0$, the thick solid line: $U=4.0\text{eV}$ and $V=0.6\text{eV}$, the thick dashed line: $U=2\text{eV}$ and $V=0.6\text{eV}$. E is along the chain direction)

图3 高分子的双激子态在电场下格点电荷密度分布
细实线：$U=0,V=0$，细虚线：$U=4\text{eV},V=0$，粗实线：$U=4\text{eV},V=0.6\text{eV}$，粗虚线：$U=2\text{eV},V=0.6\text{eV}$
电场沿链方向

citon displays obvious negative polarization. The ordinate of Fig. 3 is ten times as large as that of Fig. 2.

In Fig. 2 and Fig. 3, the thin solid line represents $U=0$ and $V=0$, i.e. without considering electron-electron interactions; the thin dashed line is $U=4\text{eV}$ and $V=0$. By comparing the thin solid and dashed lines in Fig. 2 or Fig. 3, respectively, it is clear that the on-site Hubbard energy U obviously increases the polarization of a polymer chain. In these two figures, the thick dashed line denotes $U=2\text{eV}$ and $V=0.6$ eV; the thick solid line is $U=4.0\text{eV}$ and $V=0.6\text{eV}$. Comparing the thick solid and dashed lines in Fig. 2 or Fig. 3, respectively, we can see that the nearest neighbor electron-electron interaction V obviously increases the negative polarization of a bi-exciton, however, the interaction V restrains slightly the normal polarization of a single exciton.

3 The Physical Origin on the Negative Polarization of a Bi-Exciton

Considering that the charge density of a polymer is equal to a sum of squares for the absolute values of the wave functions of all the occupied states, we should analyze what characteristics the wave functions of the electronic levels have, so that we can disclose the physical origin of the negative polarization. We noted that the wave functions of a single-exciton are very similar to those of a bi-exciton, and their variations with the electric field are very similar, too. In addition, we consider that the difference between a single-exciton and a bi-exciton in polymers is the different occupations of electrons on the two localized levels close to the mid-gap, as depicted in Fig. 1. For the single-exciton, there is an electron in both ε_{low} and ε_{high} levels, besides, the levels corresponding to the valence band are fully occupied; whereas, for the bi-exciton, there is no electron in ε_{low} level and there are two electrons in ε_{high} level, besides, the levels corresponding to the valence band are fully occupied, too. Hence, we should study the effects of the electric field on the wave functions corresponding to the two localized states (ε_{low} and ε_{high} states) colse to the mid-gap.

Figures 4 and 5 depict the variation of the wavefunction corresponding to ε_{low} and ε_{high} levels with the electric field, respectively. In the two figures, (a) is obtained with $E=0$, two wave packets in the figures express that two electrons can be accommodated in one level. (b) and (c) in Fig. 4 express electrons moving in the opposite direction of the electric field.

It is normal polarization. Figures 5 (b) and 5(c) display electrons transfer along the electric field. This is negative polariztion.

The quantum-mechanics-theory of polarization can illustrate qualitatively why the wave function of the low level (ε_{low}) corresponds to normal polarization, whereas the wavefuction of the high level (ε_{high}) to negative polarization. Please refer to Appendix A.

It is due to the above-mentioned two reasons ((1). two different polarization characteristics for the two localized electronic states close to the midgap in the polymers with extra electrons and holes. (2). two different occupations of electrons on the two localized electronic states for the single-exciton and bi-exciton in polymers.) that lead to existing two different macroscopic polarization characteristics as follows in a conjugated polymer with extra electron(s) and hole(s).

(1) For a single-exciton, there is only one electron on both the ε_{low} and ε_{high} levels, besides, the quasi-continuative valence band is fully occupied. The negative polarization of ε_{high} level is offset by the normal polarization of ε_{low} level. Therefore, the normal polarization of the single-exciton originates from the fully occupied quasi-continuative valence band. This also means that the fully occupied quasi-continuative valence band displays the characteristic of small normal polarization (as shown in Fig. 2).

(2) For a bi-exciton, there are two electrons on the ε_{high} level and there is no electron on the ε_{low} level, besides, the quasi-continuative valence band is also fully occupied. So the polarization of a bi-exciton should be equal to the difference between the negative polarization of the occupied ε_{high} level and the normal polarization of the fully occupied quasi-continuative valence band. As a result, the bi-exciton shows

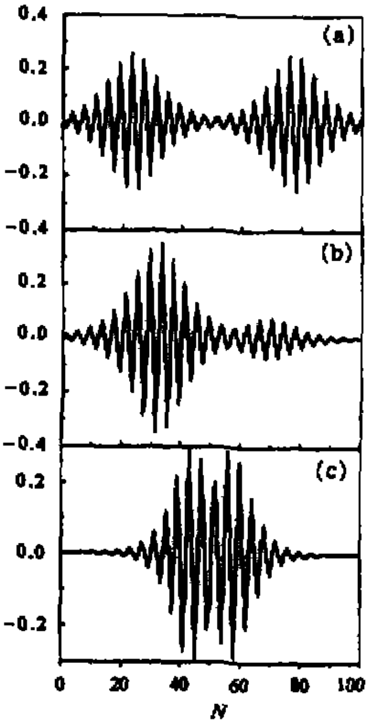


Fig. 4 Wavefunction corresponding to the lower localized level ε_{low}, (a) $t_e=0$, $E=0$, (b) $t_e=0$, $E=10^5$ V/cm. The electric field is along the chain direction. (c) $t_e=0.05$eV, $E=10^5$V/cm. The field is along the chain direction

图4　禁带中央附近,下定域能级 ε_{low} 对应的波函数 (a) $t_e=0$,$E=0$,(b) $t_e=0$,$E=10^5$V/cm　外电场沿链方向,(c) $t_e=0.05$eV,$E=10^5$V/cm,外电场沿链方向

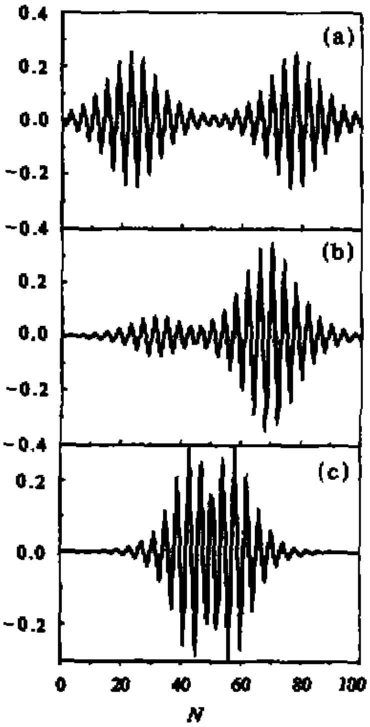


Fig. 5 Wavefunction corresponding to the higher localized level ε_{high}, (a) $t_e=0$, $E=0$, (b) $t_e=0$, $E=10^5$ V/cm. The electric, field is along the chain direction, (c) $t_e=0.05$eV, $E=10^5$V/cm. The field is along the chain direction

图5　禁带中央附近,上定域能级 ε_{high} 对应的波函数 (a) $t_e=0$,$E=0$,(b) $t_e=0$,$E=10^5$V/cm 外电场沿链方向,(c) $t_e=0.05$eV,$E=10^5$V/cm 外电场沿链方向

obvious negative polarization (as depicted in Fig. 3) due to the large negative polarization of the ε_{high} level and small normal polarization of quasi-continuative valence band. In addition, the charge transfer quantity of the localized electronic states increases quickly as the electron-electron interactions U and V increase. Whereas, the total charge transfer quantity of the occupied quasi-continuative valence band is affected slightly by U and V. As a result, the electron-electron interactions increase the negative polarization of a bi-exciton obviously, as shown in Fig. 3.

4 The Significance and Possible Applications of Negative Polarization

With the quantum-mechanics perturbation theory, the appendix A demonstrates that a microscopic electronic state can exhibit, in certain condition, negative polarization. The negative polarization of microscopic electronic states originates from the reason that microscopic states demand orthogonality. Therefore, the polarization of microscopic states depends not only on the applied field but also on an extra restricted condition-the orthogonality of wave functions. The orthogonality of the wave functions implies that it is impossible that all the electronic states correspond to normal polarization in the persence of an electric field. The joint action of an applied field and the orthogonality of wave functions will compel some microscopic electronic states having negative polarization. For example, this presentation illustrates that the wave functions of the high level ε_{high} correspond to negative polarization. Negative polarization of microscopic electronic states will lead to, in some circumstances, the macroscopic negative polarization. For example, the negative polarization of the bi-exciton in polymers originates from the negative polarization of the microscopic states.

The negative polarization is also due to that the bi-exciton in polymers is an excited state. From the viewpoint of energy, the electronic state which has negative polarization is to have higher energy, whereas, the electronic state with normal polarization is to have lower energy. Hence, if the occupied states are quasi-continuative (here "quasi-continuative" means there is no unoccupied state under the highest occupied state), there exists no negative polarization. Only when there is unoccupied state under the highest occupied state, could there be macroscopic negative polarization in certain condition (the condition is the negative polarization of the occupied state, which is above the unoccupied state, is larger than the normal polarization of the quasi-continuative occupied states, which are under the unoccupied state). Such as the bi-exciton in polymers.

By using the polarization characteristics of polymers that a single-exciton corresponds to normal polarization and a bi-exciton exhibits negative polarization, absorbing a photon can make a single-exciton become a bi-exciton in polymers. The process makes the inversion of the polarization. Therefore there could exist a new photoinduced phenomenon-photoinduced polarization inversion. Dynamical study[9] shows that the relaxation time of an exciton is usually very short. Hence, the phenomenon might be used to make photo-induced ultrafast quantum switch devices or molecular switch devices.

Appendix A

The Hamiltonian in an electric field is

$$H = H_0 + H' \tag{8}$$

H', the perturbation induced by the electric field, can be written as

$$H' = -PE, \tag{9}$$

where P is the polarized vector of the system and $P = -e\int \rho(x) x \mathrm{d}x$. Since

$$H_0 \psi^0_\mu = \varepsilon^0_\mu \psi^0_\mu, \qquad H\psi_\mu = \varepsilon_\mu \psi_\mu, \tag{10}$$

the wave function including the first-order in H' is

$$\psi_\mu = \psi^0_\mu + \sum_\upsilon{}' \frac{H'_{\mu\upsilon}}{\varepsilon_\mu - \varepsilon_\upsilon} \psi^0_\mu, \tag{11}$$

where the summation $\sum_\upsilon{}'$ excludes $\mu = \upsilon$. Since $H'_{\mu\upsilon} = -P_{\mu\upsilon}E$,

$$\psi_\mu = \psi^0_\mu - \sum_\upsilon{}' \frac{P_{\mu\upsilon}E}{\varepsilon_\mu - \varepsilon_\upsilon} \psi^0_\upsilon. \tag{12}$$

The polarization of the μth level can be expressed as

$$P_\mu = <\psi_\mu | P | \psi_\mu> \tag{13}$$

$$=<\psi_\mu^0|P|\psi_\mu^0>-E\sum_v{}'\frac{2|P_{\mu v}|}{\varepsilon_\mu-\varepsilon_v}+ \text{higher-order term.} \qquad (14)$$

where the first term corresponds to zero field, and the second term is due to the polarization induced by the electric field. Since $\Delta P=\chi E$, the polarizability of the μth level is

$$\chi_\mu=\sum_v{}'\frac{2|P_{\mu v}|^2}{\varepsilon_\mu-\varepsilon_v}. \qquad (15)$$

The two localized levels ε_{low} and ε_{high} are energetically close to each other, and far from the other levels. According to the distribution of energy, the ε_{high} level dominates the contributions to χ_{low}, and so does the ε_{low} level to χ_{high}, and the contribution of the other levels to χ_{low} or χ_{high} can be neglected. Furthermore, the wavefunction of ε_{low} level has odd parity and the wavefunction of ε_{high} level has even parity. Since the two (odd and even) wavefunctions "match" each other completely, their dipole transition matrix element is large and makes dominant contributions to P, while the wavefunctions of the other levels don't match one another, the dipole matrix element of the other levels is thus small and contributes little to P. Because of these reasons, χ_{low} and χ_{high} can be written approximately as

$$\chi_{low}\simeq\frac{2|P|^2}{\varepsilon_{low}-\varepsilon_{high}}, \qquad (16)$$

$$\chi_{high}\simeq\frac{2|P|^2}{\varepsilon_{high}-\varepsilon_{low}}, \qquad (17)$$

Since $\varepsilon_{low}<\varepsilon_{high}$, $\chi_{low}<0$, i.e. the electron on the low level (ε_{low}) moves in the opposite direction of the electric field (normal polarization). However, $\chi_{high}>0$, i.e. the electron on the high level (χ_{high}) drifts along the the electric field (negative polarization). Hence, the direction of the polarization of these two localized electronic states is opposite.

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