The impact of molecular polarization on the electronic properties of molecular semiconductors

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Abstract. – In a molecular semiconductor, the carrier is dressed with a polarization cloud that we treat as a quantum field of Frenkel excitons coupled to it. The consequences of the existence of this electronic polaron on the dynamics of an extra charge in a material like pentacene can thus be evaluated.

Molecular organic semiconductors in general and oligoacenes in particular are seriously being considered today as materials for application in optoelectronic devices. Pentacene, for example, has already been used with success in organic field effect transistors [1–3]. Critical to their eventual use as electronic materials, therefore, is a proper understanding of the charge transport mechanisms in these molecular solids. Currently, the paradigm in force describing the electronic properties of oligoacenes views carrier transport in terms of lattice polaron theories applied to narrow-band crystals [4–8]. However, we believe, as other authors [9,10] have also pointed out, that this approach omits an important effect specific to organic materials composed of large polarizable molecules, \textit{i.e.}, adding a carrier onto a molecule in such a crystal creates a polarization cloud around the carrier, also called electronic polaron or Coulomb polaron [11], which accompanies the itinerant charge as it moves about in the solid. This effect has actually been confirmed by photoemission experiments [12,13] wherein the spectra of individual molecules in the gas phase are compared to the corresponding spectra in the solid phase [12] or within a molecular cluster [13].

In these crystals, the time scale for establishing molecular polarization is related to the energetic distance $\varepsilon$ between the ground state and the first-excited state of the neutral molecule, generally on the order of one electronvolt. The characteristic time, given by $\tau_{\varepsilon} = h/\varepsilon$ (where $h$ is the Planck constant), is thus on the order of $2 \cdot 10^{-15}$ s. This is a very fast process, about ten times faster than the characteristic time for carrier motion from molecule to molecule $\tau_J = h/J$, where $J \sim 0.1 \text{ eV}$ is the bare transfer integral between two adjacent molecular

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sites along the easiest direction of propagation in the crystal [8]. On this basis, one would thus expect the Coulomb polaron to readily follow the extra charge in its motion through the crystal without any significant scattering or friction. The general feeling among physicists therefore is that polarization effects are minor and that electron-phonon processes probably explain the bulk of transport phenomena in these materials.

We will show, however, that the electronic polaron does actually play an important role in the dynamics of an extra carrier, in particular, by i) significantly renormalizing the transfer integrals in the perfect crystal, ii) enhancing the effect of any type of disorder including thermal disorder, and iii) creating correlations between diagonal (on-site) disorder and non-diagonal (transfer integral) disorder. In contrast to early calculations (reviewed by Silinsh and Čapěk [14]), as well as more recent ones [10], which use a self-consistent approach in the limit of vanishing molecular overlap to compute the polarization energies, we will present here a theoretical approach which accounts for the finite-bandwidth effects by treating the entire solid quantum-mechanically. This is essential for studying the transfer of the itinerant carrier through the solid. The treatment of polarization here is applicable to all types of organic solids composed of large conjugated molecules, disordered or not, and provides good insight into the possible roles of polarization in charge transport.

To demonstrate our points, we start from a model Hamiltonian, inspired by the pioneering work of Čapěk on the polarization of a molecular trimer [15]. We will consider both the tight-binding charge propagation from site $n$ to the neighboring sites $n + h$ and the consequent polarization of the molecular sites $\ell$ coupled electrostatically to the extra charge. Thus, the annihilation and creation operators $\hat{a}$ and $\hat{a}^\dagger$ describe the narrow-band $J$ excitations while the operators $\hat{b}$ and $\hat{b}^\dagger$ take into account the internal electronic degrees of freedom in the neutral molecules responsible for polarization.

When the molecule is anisotropic, like pentacene, the polarization excitations are direction dependent. It is convenient then to describe each molecule $\ell$ located at position $r_\ell$ in the frame of the principal axes of its polarizability tensor $\bar{\bar{\alpha}}_\ell$. In this orthonormal frame where the unit vectors can be called $(e^1_\ell, e^2_\ell, e^3_\ell)$, the dipolar transition tensor $\bar{\bar{\mu}}_\ell$ is also diagonal and can be represented by the three components $\mu_{\ell i}$:

$$\mu_{\ell i} = e \langle \phi_H | r_\ell | \phi^1_L \rangle,$$

where $\phi_H$ is the non-degenerate HOMO state and $\phi^1_L$ the particular LUMO state excited by a dipolar transition in the direction $i$. In the spirit of a tight-binding model, the $\phi^1_L$ are three different linear combinations of the $\pi$ orbitals selected when the particular direction $i$ of the dipolar transition is considered. For the sake of simplicity, we assume that these states have essentially the same energy $\varepsilon$ with respect to the HOMO level [14]. In this approach, the polarization of the molecules $\ell$ results from a small depopulation of the HOMO in favor of the LUMO. This excitation process, internal to the molecules, is represented by the operator pairs $\hat{b}_\ell$ and $\hat{b}^\dagger_\ell$.

The quantum operator representing the dipolar moment on each site $\ell$ is the vector

$$\hat{d}_\ell = \sum_{i=1}^{3} \hat{d}_{\ell i} e^i_\ell \quad \text{with} \quad \hat{d}_{\ell i} = \mu_{\ell i} (\hat{b}_\ell + \hat{b}^\dagger_\ell)_i.$$

The diagonal polarization tensor $\bar{\bar{\alpha}}_\ell$ is then written as $(\bar{\bar{\alpha}}_\ell)_{ii} = 2 \mu_{\ell i}^2 / \varepsilon$.

With this notation, the Hamiltonian for the extra charge, in the presence of the polarization
cloud, can then be written in the dipolar approximation as

\[ \hat{H} = \sum_{n} \hat{a}_{n}^{\dagger} \hat{a}_{n} \left\{ \sum_{\ell \neq n} \sum_{i=1}^{3} \varepsilon (\hat{b}_{\ell}^{\dagger} \hat{b}_{\ell})_{i} - \frac{q}{4 \pi \varepsilon_{0}} \frac{\langle \mu_{\ell}, \mu_{n} \rangle}{|\mathbf{r}_{\ell} - \mathbf{r}_{n}|^{3}} \right\} + \sum_{\ell \neq m} \sum_{i,j=1}^{3} (W_{\ell,m})_{i,j} (\hat{b}_{\ell}^{\dagger} + \hat{b}_{\ell})_{i} (\hat{b}_{m}^{\dagger} + \hat{b}_{m})_{j} - \sum_{n} \sum_{n+h} J_{n,n+h} \hat{a}_{n+h}^{\dagger} \hat{a}_{n} , \tag{3} \]

where \( J_{n,n+h} \) are the transfer integrals between sites \( n \) and \( n+h \) and

\[ (W_{\ell,m})_{i,j} = \frac{\mu_{\ell}, \mu_{m}, \varepsilon}{4 \pi \varepsilon_{0} |\mathbf{r}_{\ell} - \mathbf{r}_{m}|^{3}} \left[ (\mathbf{e}_{\ell} \cdot \mathbf{e}_{m}) - 3 \frac{(\mathbf{r}_{\ell} - \mathbf{r}_{m}) \cdot \mathbf{e}_{\ell} \cdot (\mathbf{r}_{\ell} - \mathbf{r}_{m}) \cdot \mathbf{e}_{m}}{|\mathbf{r}_{\ell} - \mathbf{r}_{m}|^{2}} \right] \tag{4} \]

are the dipolar interactions between pairs of molecules in the structure, responsible for the van der Waals contribution to the cohesive energy.

In fact this Hamiltonian describes a simplified version of the motion of a charge carrier interacting with a quantum field of Frenkel excitons of energy \( \varepsilon \) [11].

In molecular crystals like acenes, the motion of the excess charge is slow compared to the relaxation time necessary for the polarization of the electronic orbitals of the molecules surrounding the charge carrier, i.e. \( J \ll \varepsilon \). To approximate the ground state of the Hamiltonian (3), we have thus used a variational method with a dressed carrier trial function. This method is an electronic version of the Lang-Firsov calculation [16] used in molecular crystals by Munn, Silbey [17] and Kenkre [18]. A perturbation theory would also give such solution when \( \tau_{\varepsilon} \ll \tau_{J} \).

The eigenstates of the Hamiltonian are represented as a superposition of local states, taken to be the product of a local electronic state \( |n\rangle \) and the “polarization” state \( |\chi(n)\rangle \) of the surroundings, associated with the carrier’s occupation of site \( n \):

\[ |\psi\rangle = \sum_{n} u_{n} |n\rangle \otimes |\chi(n)\rangle. \tag{5} \]

The local polarization states which constitute \( |\chi(n)\rangle \) can be expressed in terms of the unitary translation operators \( \hat{U}_{\ell} \), where \( |0_{\ell}\rangle \) is the ground state of the \( \ell \)-th molecule and

\[ |\chi(n)\rangle = \otimes \prod_{\ell} \hat{U}_{\ell}(n) |0_{\ell}\rangle, \tag{6} \]

\[ \hat{U}_{\ell}(n) = \exp \left[ \sum_{i=1}^{3} X^{*}_{\ell,1}(n) \hat{b}_{\ell}^{\dagger} - X_{\ell,1}(n) \hat{b}_{\ell} \right] . \]

The unitary operator \( \hat{U}_{\ell}(n) \) represents a translation of the molecular state due to the electric field of the charge placed on site \( n \):

\[ \hat{U}_{\ell}^{-1}(n) \hat{b}_{\ell} \hat{U}_{\ell}(n) = \hat{b}_{\ell} - X_{\ell,1}(n) \hat{I}_{\ell} , \]

\[ \hat{U}_{\ell}^{-1}(n) \hat{b}_{\ell}^{\dagger} \hat{U}_{\ell}(n) = \hat{b}_{\ell}^{\dagger} - X^{*}_{\ell,1}(n) \hat{I}_{\ell} , \tag{7} \]

where \( \hat{I}_{\ell} \) is the identity operator.
The functions $X_{\ell,i}(n)$ are determined by minimizing the expectation value of the Hamiltonian (3) with the variational wave functions (5) and (6) above:

$$
\langle \psi | \hat{H} | \psi \rangle = \sum_n |u_n|^2 \left\{ \sum_{\ell \neq n} \sum_{i=1}^{3} \left( \varepsilon |X_{\ell,i}(n)|^2 + \frac{q}{4\pi\varepsilon_0} \mu_{\ell,i} \frac{(r_\ell - r_n) \cdot e^i_\ell}{|r_\ell - r_n|^3} (X_{\ell,i}(n) + X_{\ell,i}^*(n)) \right) + \frac{1}{2} \sum_{\ell \neq m} \sum_{m} \sum_{i,j=1}^{3} (W_{\ell,m})_{i,j} (X_{\ell,i}(n) + X_{\ell,i}^*(n)) (X_{m,j}(n) + X_{m,j}^*(n)) \right\} - \sum_n \sum_{h} J n_{n+h} u_n \exp \left[ -\frac{1}{2} \sum_{\ell} \sum_{i=1}^{3} \left( |X_{\ell,i}(n)|^2 + |X_{\ell,i}(n + h)|^2 - 2X_{\ell,i}(n)X_{\ell,i}^*(n + h) \right) \right],
$$

where we have used the Weyl identity

$$
\langle 0_\ell | \exp \left[ \delta b_\ell^\dagger - \delta b_\ell \right] \exp \left[ \gamma b_\ell^\dagger - \gamma b_\ell \right] | 0_\ell \rangle = \exp \left[ \delta^\dagger \gamma - \frac{(|\delta|^2 + |\gamma|^2)}{2} \right].
$$

We now minimize the energy of eq. (8) with respect to the variational functions, the $X_{\ell,i}(n)$’s. Since we are concerned with the stability of a slow carrier, we need only minimize the potential-like energy. Thus, to the lowest order in $J/\varepsilon$, we get

$$
\varepsilon X_{\ell,i}(n) + \frac{q}{4\pi\varepsilon_0} \mu_{\ell,i} \frac{(r_\ell - r_n) \cdot e^i_\ell}{|r_\ell - r_n|^3} + \sum_m \sum_{j=1}^{3} (W_{\ell,m})_{i,j} (X_{m,j}(n) + X_{m,j}^*(n)) = 0.
$$

Substituting (10) in (8), the local polarization energy becomes

$$
E_p(n) = \sum_{\ell \neq n} \frac{q}{4\pi\varepsilon_0} \sum_{i=1}^{3} \mu_{\ell,i} \frac{(r_\ell - r_n) \cdot e^i_\ell}{|r_\ell - r_n|^3} X_{\ell,i}(n).
$$

Within the subspace of states $| \psi \rangle$ representing the dressed electrons defined by relation (6), the total energy minimum (8) can thus be written as

$$
E = \sum_n E_p(n) |u_n|^2 - \sum_{n,n+h} J_{n,n+h} u_{n+h}^* u_n.
$$

Then, the Hamiltonian (3) describes a dressed carrier (or a quasi-particle) at site $n$ having a potential energy $E_p(n)$ and an effective transfer integral

$$
\tilde{J}_{n,n+h} = J_{n,n+h} e^{-S_0(h)}
$$

with

$$
S_0(h) = \frac{1}{2} \sum_{\ell} \sum_{i=1}^{3} (X_{\ell,i}(n) - X_{\ell,i}^*(n + h))^2.
$$

The effective quasi-particle Hamiltonian $\hat{H}$ with parameters renormalized by the Frenkel exciton field is just the tight-binding Hamiltonian

$$
\hat{H} = \sum_n E_p(n) |n\rangle \langle n| - \sum_{n,n+h} \tilde{J}_{n,n+h} |n\rangle \langle n + h|,
$$
Table I – Polarization energy $E_p$ and renormalized transfer integral $\tilde{J}/J$ in the perfect crystals of naphtalene, anthracene, tetracene and pentacene for an angular disorder of $3^\circ$.

|                  | Nph | Ac  | Tc  | Pc  |
|------------------|-----|-----|-----|-----|
| Polarization tensor $\bar{\alpha}$ (Å$^3$) | 21.5 | 33.9 | 48.2 | 91  |
|                 | 17.6 | 29.2 | 34.7 | 38  |
|                 | 10.1 | 12.9 | 15.6 | 17.7|
| Polarization energy(a) $E_p$ (eV) | $-0.99$ | $-1.19$ | $-1.39$ | $-1.55$ |
| Bare transfer integral(b) $J$ (meV) | 41.5 | 47.9 | 68.8 | 97.8 |
| Renormalized transfer $\tilde{J}/J$ | 0.86 | 0.83 | 0.74 | 0.64 |
| Diagonal disorder $\delta$ (meV) | 6.2  | 9.7  | 11.3 | 15.8 |
| Correlation factor $\delta'$ (eV) | 5.3  | 3.4  | 1.0  | 0.4  |

(a) The values for Nph, Ac and Tc are from [14]; the values for Pc are from [19].
(b) The values are from [8], along the easiest propagation direction.

where $E_p(n)$ and $\tilde{J}_{n,n+h}$ are defined by relations (11) and (13).

In the case of a perfect crystal, the polarization energy $E_p$ is uniform and shifts the ground state everywhere by about 1 eV as observed in acenes [12,13]. Correlatively, the bare bandwidth is significantly narrowed (independently of the temperature). Values of $E_p$ (from [12]) and $\tilde{J}/J$ have been reported in table I. We can conclude therefore that at low temperatures in a perfect molecular crystal, a band model with an appropriate renormalized bandwidth describes the extended ground state properly [14] (claim i) above).

The situation changes greatly when disorder, however small, enters the system. The local changes of polarization energy $E_p$ due to disorder are greater than any other electronic parameter change, transfer integral, HOMO and LUMO positions, etc. In particular, thermal disorder arising from librations or low-energy intermolecular phonons is interpreted as being static on the time scale $\tau_J$ and induces non-negligible polarization energy variations.

Indeed, consider any kind of static (or thermal) disorder which can be described by a random variable in the lattice. The polarization energy $E_p$ is in turn also random. We denote $\delta_n$ the fluctuation of $E_p$ from site to site. Then $\tilde{J}_{n,n+h}$ also becomes random through the fluctuations of $X_{\ell,i}(n)$. Thus the motion of the quasi-particle representing an extra-charge in the disordered crystal is controlled by an Anderson Hamiltonian with correlated diagonal and non-diagonal disorder that we shall now study in more detail.

For this purpose, we have developed a numerical method for calculating $E_p$ and $\tilde{J}$ in disordered situations. Still working within the dipolar approximation, we solve the linear equations in relation (10) numerically. This calculation is precise enough to determine the characteristics of the electronic polaron in naphtalene and anthracene. In tetracene and pentacene, where the molecular polarizability is higher, corrections beyond the dipolar approximation are important. In this case, the linear calculation would give values of $X_{\ell,i}(n)$ exceeding 1/2 on certain sites, which would correspond to values of the dipole components exceeding the corresponding dipolar transition component $\mu_{\ell,i}$ of relation (1). In order to limit this artefact and to take into account the hyperpolarizability, the terms $\varepsilon |X_{\ell,i}(n)|^2$ in eq. (8) are replaced by $\varepsilon \left(1 - \sqrt{1 - 4|X_{\ell,i}(n)|^2}\right)$. The system of equations in (10) then becomes non-linear and must be solved by using an iterative numerical procedure. Figure 1 represents the dipole distribution induced by a charge in a perfect crystal of pentacene.

We have also introduced an orientational disorder which is known to be important in acenes. Pope and Swenberg give typical thermal disorder values for rotation angles of $\pm 3$
degrees at room temperature [20]. Other sources of rotational disorder with angles even larger than 3° are also likely in actual acene materials, for example, metastable polymorph domains, stacking faults, zones close to grain boundaries, dislocation cores, etc. [21]. The simplest disorder distribution that is worth investigating is an angular Gaussian distribution with mean-square value $\Delta \theta$. By averaging over 4000 samples for each $\Delta \theta$, the mean-square fluctuations $\delta$ and $\delta'$ can be deduced as functions of $\Delta \theta$. Table I summarizes the results of our calculations. Polarization energy $E_p$ and renormalized transfer integral $\tilde{J}/J$ in the perfect crystal are calculated from eqs. (11) and (13), respectively. The diagonal energy disorder $\delta$ is calculated for an angular disorder of 3° while $\delta'$ represents the correlations between diagonal and non-diagonal disorder (see eq. (15)). The polarization tensors and the bare transfer integrals are from the literature (see footnotes to table I).

On the basis of this result, a good approximation for the related Anderson Hamiltonian, would be

$$\hat{H} = \sum_n (\langle E_p \rangle + \delta_n) |n\rangle \langle n| - \sum_{n,n+h} \tilde{J} \exp \left[ \frac{\delta_n + \delta_{n+h}}{\delta'} \right] |n\rangle \langle n+h|, \quad (15)$$

where the distribution of $\delta_n$ is characterized by the mean-square value $\delta$ and the correlations by the value $\delta'$. In the two-dimensional channel of an organic field effect transistor these disorder energies, reported in table I, are non-negligible fractions of the renormalized transfer integral $\tilde{J}$.

It is important to note that, from the point of view of the extra-charge travelling into the molecular semiconductor, any thermal or static disorder which modulates the bare tight-binding parameters is amplified by molecular polarization. These “solvation” effects yield much larger disorder energies than the corresponding single-electron quantities. The amplification factor is of the order $E_p/J \sim 10$ (claim ii) above). Moreover, the electronic polaron effect introduces long-range correlations which are very efficient in terms of localization (claim iii) above). Work on the spectrum of Hamiltonian (15) is presently in progress to examine in detail the consequences of these correlations. At the present stage, we believe that the possibility to map the many-body Hamiltonian (3) on the single-electron Hamiltonian (14), in the subspace of the class of pertinent wave functions, will be useful for further theoretical developments in the field.
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