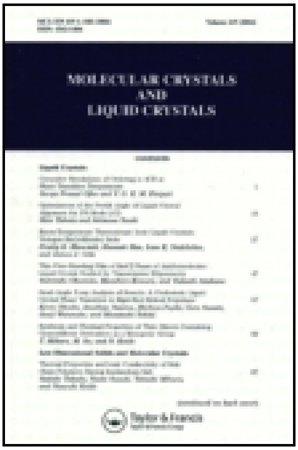

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Localization of Electrons in Extended Systems

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Localization of Electrons in Extended Systems

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The problem of localization of electrons in extended systems is treated. The solution of the electronic Schrödinger equation is simulated using an iterative procedure. The method predicts whether electrons or excitons are localized or delocalized at T=0 in organic or inorganic crystals. The important parameters are reorganization energy and electronic coupling between sites, which are calculated for the smaller single and double site systems, respectively. The occupation of each site, which is fractional, determines bond orders, which in their turn determine bond lengths and reorganization energy. 'Sharp' metal-insulator transitions follow from our model. Applications are given to organic crystals, graphite, and linear polyenes.

Keywords: Organic crystals; metal-insulator transitions; electron localization; reorganization energy; coupling

1. INTRODUCTION

Localization of electrons is an intriguing problem of decisive importance for the understanding of conductivity and mobility properties of extended systems. For example transition metal oxides are considered to have more localized electrons (in some sense) than corresponding sulfides since oxides are less apt to be black and conducting. A good explanation of this difference in atomic terms is difficult to find. In text-books on inorganic chemistry one refers to higher polarizability of sulfur than of oxygen. However, there is no direct connection between polarizability of the component atomic ions and conductivity and absorption properties. According to the standard description of repetitive systems (the Bloch model), NiO and NiS would be metals due to the absence of a gap at the Fermi level [1].

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Why is NiO a 'Mott insulator' while NiS has metal-like properties? Mott has explained this with reference to the electronic repulsion that has to be overcome to transfer an electron from one site to another. However, since his model assumes a localized 3d orbital, the problem of predicting localization from first principles is not solved.

In the case of organic molecular crystals [2] a related problem may be stated as follows. Will an additional electron or hole be localized on a single molecule or completely delocalized over the whole crystal, or something in between? Trapping is directly connected to nuclear distortions. If the electron belongs mainly to one of the molecules in an organic crystal, this molecule has different bond lengths, due to the different number of electrons. The same type of problem is important in infinite π systems, such as graphite, where a small region with modified bond lengths could appear, at least hypothetically.

In Mott insulators, for example NiO doped by Li_2O, Ni^{3+} sites are formed [1,3,4]. The conductivity which is much increased compared to pure NiO, is activated in spite of zero band gap. The simple explanation is probably that a state with a localized 3d hole has a lower energy than a state with a delocalized 3d hole. The conditions for application of the Bloch model are not at hand. In the localized model the activation energy is obtained by the Marcus model and is non-zero. But even pure NiO cannot be sufficiently well described by the band model since the latter cannot properly describe the antiferromagnetic state or the absorption spectrum.

In some classes of compounds the electron mobility shows a great variation which may be connected to the localization properties of electrons [5]. Localization in its turn depends on the quotient between reorganization energy and coupling [5–10]. This not universally accepted idea is our point of departure in the present paper.

At elevated temperatures thermal fluctuations in diagonal and off-diagonal matrix elements break translational (or other) symmetry and lead to localization [1,10]. In the present paper we primarily discuss the case T=0 and first try to solve, in principle, the static, 'quantum chemical' problem by geometry optimization. Since most interesting systems are too large to be approached directly by quantum chemical methods of the usual type, we will here introduce a methodology to study large systems which only uses data from calculations on the subsystems. An early example of a localization problem in quantum chemistry is the O_2 molecule, photoionized in the 1s shell. Bagus and Schaefer found that the symmetry broken, unrestricted Hartree-Fock method gives 1s ionization energies which much better agree with the experimental ones than those of restricted Hartree-Fock [11]. A fact which at first appears puzzling is that the symmetry may be restored by symmetry projection or configuration interaction between the non-symmetric solutions, with retained agreement with the experimental ionization energies. However, the explanation is simple. Symmetry breaking in this case is not a physical effect but an expedient way to obtain a good wave function at low cost. Good results can also be obtained by using only symmetry adapted states in a CI calculation [12].

In organic crystals the situation is different since localization is directly connected to nuclear displacements of the site molecule in question [2]. There are local minima in the potential energy curve, each corresponding to an electron being localized on one or many particular sites. The global minimum may or may not correspond to a localized electron. Below we will show that in some extended systems, the question of a localized or delocalized electron can be determined by the electronic coupling between the sites, J, and the reorganization energy for a single site, λ. In the case of anthracene, J and λ are available from ab initio calculations[13]. When the latter parameters are known, a simulation of the ground state of a lattice of N anthracene molecules and an extra electron may be performed which tells whether the ground state is localized or delocalized.

In the case of mixed valence systems the localization-delocalization problem is well understood [7,9,14–16]. Very often a darkening of a spectrum of a metal oxide or salt is due to metal ions in different, localized oxidation states [17]. An accepted classification based on localization for mixed valence systems has been given by Robin and Day [14]. This explanation cannot be used for pure NiO, however, which has a unique valence. We may perhaps consider delocalization of excitations rather than electrons, as in the Davydov model for organic crystals [18]. The reorganization energy for an excitation within the 3d sub-shell is known to be large. At the same time the coupling between two sites is small, since the transition moment for excitation within the 3d sub-shell is almost zero, leading to almost vanishing Förster coupling between the sites. Hence, since the ratio J/λ is small or zero, the excited states for NiO should be localized and the crystal have the single site absorption spectrum, close to that of a Ni^{2+}ion in water solution. The charge transfer transitions are in this case in the UV region. Thus in spite of the fact that the Fermi level is in a continuous band of orbital energies, there is mainly local absorption and we may conclude that the band model cannot be used in the calculation of the absorption spectrum of NiO.

2. INTRAMOLECULAR REORGANIZATION ENERGY

If the dependence of the equilibrium geometry on number of electrons is moderately small, the parabolic approximation of the energy surface, the Marcus model [19], is a sufficient description. The important parameter in this model is the reorganization energy when an electron is accepted (λ_1) or removed (λ_2). Transfer of an electron includes two processes, donation and acceptance, and hence the total reorganization energy is $\lambda=\lambda_1+\lambda_2$. λ_1 and λ_2 refer to a single molecule and may hence be obtained more easily than quantities, which refer to the full system. If the energy surfaces are parabolas with the same force constants for different oxidation states, λ_1 is equal to λ_2. We found in an earlier paper on organic π-systems that the Hartree-Fock method often overestimates λ by a factor of two[13] and that the wave function must be of at least (U)MP2 quality [20].

If the force constant is known, a reorganization energy ($\lambda_1$and λ_2) may be obtained in a method by Siebrand [21]from the bond length changes as

$$\lambda = \frac{1}{2}k \sum_{\text{bonds}} \delta R_{\mu\nu}^2 \qquad (1)$$

$\delta R_{\mu\nu}$ were obtained from bond orders of the Hückel model:

$$P_{\mu\nu} = \sum_{i} c_{\mu i} c_{\nu i} n_i \qquad (2)$$

where n_i is the occupation number of the orbital.

$$R_{\mu\nu} = -0.2 \times P_{\mu\nu} + 1.534(\text{Å}); \qquad (3)$$

Eq. (3) reflects the fact that a typical double bond is 1.334 Å (P=1) and the typical single bond 1.534 Å (P=0). Almost all reorganization energy is due to CC bond length changes [20]. From the fact that the fractional bond order is the determining factor for bond-length in organic π-systems, we deduce that the fractional occupation number, C^2, [C (different from $c_{\mu i}$) is defined below in section 5] for the whole molecule in an organic crystal also determines the bond lengths for that molecule. The reorganization energy, being proportional to the square of the bond length change, is thus proportional to the fourth power of the fractional occupation number of LUMO. For example if the wave function is delocalized over two molecules, the bond length change is only half of what it is when a full electron or hole is on a single molecule. λ_1 (or λ_2) depend on the bond length change squared and is hence only 25% of the value when the electron is localized to a single molecule. The sum of reorganization energy for the two molecules, $2\lambda_1$, is thus 50 % of the localized value.

3. ELECTRONIC COUPLING BETWEEN SITES

In the past many attempts have been made to calculate the band width for anthracene [13,22–25] and naphthalene [23–25]. The large span of values obtained (≈factor of five) emphasizes the need for accurate calculation.

The hopping integral (coupling) J is an important concept in simple, parametrized models such as the Mott-Hubbard model[11]. A question arises as to the correct definition of this parameter. It is reasonable to define it by comparison to the equivalent electron transfer problem, where an electron is exchanged between two anthracene molecules. In the latter energy surface crossing problem, the energy difference at the avoided crossing is equal to 2J. Hence we define J as half of this difference [26]. The avoided crossing is defined as the point where the wave functions for the system of two anthracene molecules and one excess electron have the latter electron equally localized over the two molecules. We may use Koopmans' theorem to obtain the splitting between the energy surfaces, corresponding to a symmetric and an unsymmetric wave function [26]. Hence we take molecular orbital energy splitting between $\varphi_+=(\varphi_a+\varphi_b)/\sqrt{2}$ and $\varphi_-=(\varphi_a-\varphi_b)/\sqrt{2}$, where φ_a and φ_b are the LUMO's of the single molecules, as 2J in the symmetric case of electron transfer. The transition state with 50–50% distribution of the charges, is attained with the help of small external charges using a well tested method [26].

4. POTENTIAL SURFACE FOR ELECTRON EXCHANGE BETWEEN TWO MOLECULES

Two adjacent sites A and B in an organic crystal with identical structure are assumed to have interacting HOMO (or LUMO), φ_a and φ_b, respectively. At a given moment the new delocalized MO is $\phi=\cos\theta\ \varphi_a + \sin\theta\ \varphi_b$. The eigenvalue problem for the one electron – two site problem may be written as

$$\begin{bmatrix} H_{aa}-\varepsilon & J \\ J & H_{bb}-\varepsilon \end{bmatrix} \begin{bmatrix} \cos\vartheta \\ \sin\vartheta \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{4}$$

where:

$$\mathrm{tg}2\vartheta = \frac{2J}{H_{aa}-H_{bb}} \tag{5}$$

($\vartheta=\pi/4$ for $H_{aa}=H_{bb}$). If J is large compared to $|H_{aa}-H_{bb}|$, ϑ is close to $\pi/4$, which means that the coefficients $\cos\vartheta$ and $\sin\vartheta$ have about the same magnitude and that the localization at either site is weak. If J is small, localization occurs already for a small $|H_{aa}-H_{bb}|$. H_{aa} and H_{bb} are energies in the absence of interactions between the sites, which in the harmonic approximation are written as functions of distortions from the equilibrium geometries of A and B:

$$H_{aa} = \sum_i \frac{1}{2}k_i(x_i + x_{i0})^2; \quad H_{bb} = \sum_i \frac{1}{2}k_i(x_i - x_{i0})^2 \tag{6}$$

H_{aa} is the total energy for the two sites when the electron is at A and H_{bb} the total energy when the electron is at B. The vertical energy difference H_{bb}-H_{aa} at x_i=-$x_{i0}$is equal the reorganization energy needed to move the electron without bond or solvent readjustments:

$$\lambda = \sum_i 2k_i x_{i0}^2 \tag{7}$$

λ consists of bond length changes when electrons are added to a neutral anthracene or removed from the negative anthracene ion.

If we assume that a single bond coordinate in each of A (x_1=q_a) and B (x_2=q_b) is responsible for the bond reorganization energy, eq. (6) may be written:

$$H_{aa} = \frac{k}{2}(q_a - q_{a0})^2 + \frac{k}{2}(q_b + q_{b0})^2 \quad \text{and}$$
$$H_{bb} = \frac{k}{2}(q_a + q_{a0})^2 + \frac{k}{2}(q_b - q_{b0})^2 \tag{8}$$

Due to the symmetry $q_{a0} = q_{b0} = q_0$the minimum energy path satisfies $q = q_a = -q_b$ to a good approximation and hence:

$$H_{aa} = k(q - q_0)^2, \quad H_{bb} = k(q + q_0)^2, \quad \text{and} \quad \lambda = 4kq_0{}^2 \tag{9}$$

If J is small the activation energy is simply $\lambda/4 = kq_0{}^2$ [q=0 in eq.(9)].

The solution to the secular equation of eq. (4) is given by

$$E_\pm = \frac{H_{aa} + H_{bb}}{2} \pm \left[\left(\frac{H_{aa} - H_{bb}}{2}\right)^2 + J^2\right]^{1/2} \tag{10}$$

It follows that for H_{aa}=H_{bb}, E_+-E_-=2J. If we set the derivative with respect to q for the lower energy solution of the secular equation of eq. (4), we find that energy minima are obtained for:

$$q = \pm q_0 \left[1 - \frac{J^2}{4k^2q_0^4}\right]^{1/2} = \pm q_0 \left[1 - \frac{(2J)^2}{\lambda^2}\right]^{1/2} \tag{11}$$

There are two minima for:

$$4kq_0^2 = \lambda > 2J \tag{12}$$

and otherwise just one (for q=0). In the latter case the electrons are transferred without activation energy. Eq. (12) is the condition for activated transfer in the cluster model and hence directly related to the metal-semiconductor transition.

From the equations above follows that the larger the coupling the smaller the activation energy. We obtain [8].

$$E_a = (J - 2kq_0{}^2)^2/4kq_0{}^2, \quad \text{for} \quad \lambda \geq 2|J| \tag{13}$$

For λ < 2J, the activation energy disappears.

Notice that we have estimated the nature of the energy surface for a well-defined electron transfer with the help of two quantities where J is of a purely electronic origin: while λ is related to the coupling between electronic and nuclear motion. If we had carried out an ab initio calculation of the reaction path we would find approximately the same energy surface. The trapping is partly electronic and partly due to how the nuclei respond to the motion of the electrons. Escape from a trap, deep or shallow, is only possible by interaction with nuclear modes. If there is no trap the electrons may be considered as essentially free, even if it is still possible to create localized wave packets. Depending on velocity, moving electron wave packets may interact with and be trapped by different types of nuclear modes. Trapping by bond stretch modes is much faster than trapping by modes where the molecules move as entities [2].

5. ORGANIC CRYSTALS

To test whether the additional electron is localized or delocalized, to determine the size of the localization area, we simulate the solution of the Schrödinger equation for a single electron in a cluster of m anthracene molecules (corresponding to ten shells outside a central one) using the parameters determined in the calculations described above. We assume that the total wave function for m sites may be written as

$$\Psi = \sum_{i=1}^{m} C_i A_{mN+1}[\Phi_1^N \cdot \Phi_2^N \cdot \ldots \Phi_i^{N+1} \cdot \ldots \Phi_m^N] \quad \sum_{i=1}^{m} C_i^2 = 1 \qquad (14)$$

where A_{mN+1} is an antisymmetrization operator for mN + 1 electrons. N is the total number of electrons at a site. The site diagonal element is set equal to zero, corresponding to a completely delocalized electron. The bond length changes at a site i are proportional to C_i^2, since the bond length changes in the molecule, according to eqs (2,3), are scaled by the total number of electrons on the molecule. The reorganization energy is thus proportional to C_i^4. The diagonal matrix elements are hence given by

$$H_{ii} = -C_i^4 \cdot \lambda; \qquad (15)$$

where λ is the reorganization energy for adding an electron to a single molecule. There are a number of polarization terms as well as vertical electron affinity which are a part of the binding energy of the electron, but these terms are of pure electronic origin and therefore show up in the localized as well as the delocalized case. We may compare to the case of O_2mentioned above. There is a large polarization energy associated with ionization from the 1s shell; nevertheless the final wave function is symmetric and thus completely delocalized in tis electronic distribution. In the O_2 case there is no reorganization of nuclear coordinates of importance for the localization problem and hence $\lambda=0$.

If the electron is localized at a single molecule the polarization energy may be calculated from the Born approximation. The polarization energy is proportional to C_i^4. The electronic polarization may contribute slightly to the energy lowering in the localized case as compared to the delocalized case, since restoration of the symmetry may cancel part of the polarization. For anthracene we have $\lambda = 0.070$ eV [13]. The previously calculated [27] values of the coupling are J_{xy}=-0.094 and J_y =0.0595 eV for the xy and x directions, respectively. Ten shells of molecules (331 molecules) are included in the calculation in an iterative procedure. The results are given in Fig. 1.

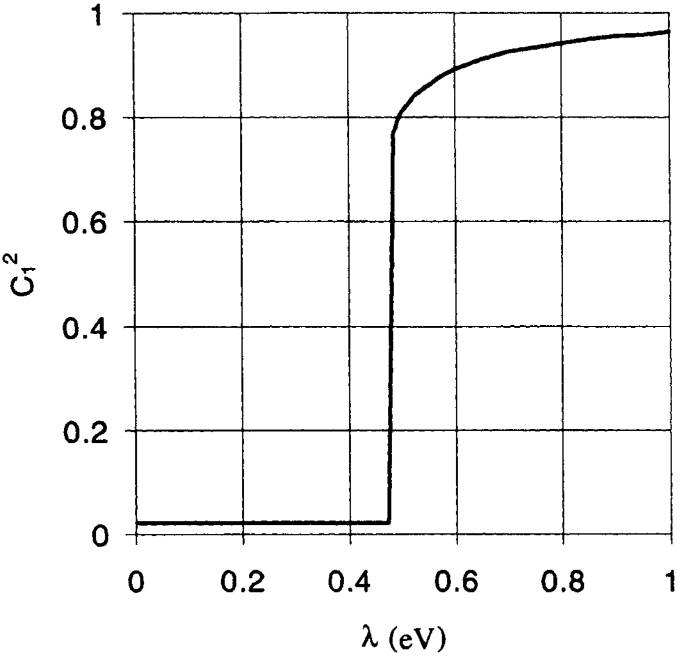

FIGURE 1 Square of coefficient C_1 for central anthracene molecule as a function of reorganization energy λ, surrounded by ten shells of anthracene molecules (331 molecules) in the *ab*-plane. The coupling parameters are those calculated in ref. [27]

If $|H_{ii}-H_{jj}|$ is much larger than |J| for the neighbors i and j, the electron will remain localized on a single molecule. On the other hand if $|H_{ii}-H_{jj}|$ decreases, the delocalization increases and the system becomes delocalized. In the localized case there is an energy lowering due to reorganization, in the delocalized case an energy of delocalization. Since the reorganization energy is decreased proportional to the occupation C_i^4, one expects that if localization takes place it will occur mainly on a single site.

At T=0 the electron is either localized or completely delocalized. In the case of anthracene *ab*-plane, a single additional electron is delocalized, since the reorganization energy is considerably less than 0.5 eV seen to be the transition point in Fig. 1. At T=0 we expect a wave packet to move freely without activation energy, essentially as in a metal.

When the temperature is raised, there are disorder effects, particularly due to rotations [28], which temporarily decrease the coupling between two molecules. The probability of localization increases. In k-space this is described as scattering. At elevated temperatures the mobility therefore have contributions from both delocalized and localized electrons and the mobility decreases as the temperature is raised. The CC vibrations determine to an increasing extent the motion of the electronic wave packet. This happens in spite of the fact that the activation barrier is equal to zero [29].

If we hypothetically assume that the CC-vibrations play a slightly greater role than they actually do, there is activation energy. The mobility then increases with temperature since modes are excited which help the system overcome the small activation energy. Eventually the up-going, hypothetical mobility curve will reach the actual down-going one. Since the actual mobility cannot be less than the former, there may be a mobility minimum at a certain temperature (experimentally for naphthalene 150K).

6. POLYACETYLENE AND GRAPHITE

Polyacetylene C_nH_{n+2} consists of chains with alternating short and long bonds between -CH= units. The coupling is strong between the atomic sites but weak between chains. The theory of Peierls [30] explains the alternation in bond length and the gap at the Fermi level, and the bond lengths may be simulated by the same methods (and the same parameters) as used for anthracene above. The coupling strength β relative to the coupling β_0 at 1.4Å is given by an exponential:

$$\beta = \beta_0 \exp[-(R_{\mu\nu} - 1.40)/a] \qquad (16)$$

where a=0.3106Å [31]. The bond length $R_{\mu\nu}$ is obtained from the bond order $P_{\mu\nu}$ [eq.(2,3)] and the Hückel problem is solved iteratively. In a cyclic system the bond lengths depend on whether the number of carbon atoms n is odd or even. For a large chain and even n, there is bond alternation with a difference of 0.08 Å between long bonds and short bonds, which agrees with experimental data [32,33] and accurate calculations. In general the iterative Hückel method has proven to give very good results for CC bond lengths for all aromatic molecules, except those where there is some type of strain which is not accounted for in the simple method.

In the case of odd n, spin is localized in a soliton over about 20 carbon atoms in the middle of the chain. In this region the bond alternation is small. A single added (or removed) electron localizes in the soliton and cancels the spin with zero reorganization energy [32]. In the positive or negative ions of even-n system there is also localization of the charge (and spin) over about 20 carbon atoms. The reorganization energy is about 0.23eV [32] in agreement with accurate calculations [20]. The iterative, bond order based procedure gives excellent results. The non-iterative procedure on the other hand, gives delocalized spin and charge and zero reorganization energy.

At alkali doping the donated electrons go to the odd chains, initially canceling the spin in agreement with the experiments [35,36]. At low doping levels there is activation energy for conductivity, which beyond doubt can be associated with the localization behaviour mentioned in the previous paragraph. However, at high doping the conductivity is large and increasing at T=0. The alkali ions are localized in tubes [35], so densely that the distance between them is shorter than the electron delocalization length. The activation energy disappears since the trapping becomes ineffective. Some remaining trapping is evident by the fact that the conductivity increases at increased T. The insulator to metal transition is very distinct as a function of doping level [35]. This may be connected to the amplifying effect due to the C^4 dependence of the reorganization energy on wave function coefficient C, which leads to a sudden insulator-metal transition as a function of some external parameter.

In graphite there is no Peierls distortion and all CC bond lengths are the same. To test if soliton or polaron formation is possible we drop an additional electron and apply the same Hückel-SCF model to a plane of graphite. A central benzene molecule is extended with ten shells of hexagons, converging to a graphite layer as the number of layers tends to infinity. One or two electrons are added on the central C_6-ring. The initially applied CC bond length difference between single and double bonds disappears after a few iterations. The added electron is delocalized over the whole system, which leads to infinitesimal change of bond length and zero reorganization energy. In addition the band gap is zero which is consistent with metallic behaviour. We may compare to diamond. In a semi-empirical calculation including 27 carbon atoms and saturated with hydrogens, we obtained λ=2.5eV. This is particularly due to a great change in a single CC bond length. The conclusion is that electrons inserted into the conduction band of diamond are very localized and move slowly.

7. DISCUSSION

Many properties of large systems are intimately connected to the electron localization problem. False localization in the sense that it depends on the approximation method in the quantum chemical calculation is often encountered in odd-electron systems, for example symmetry breaking in unrestricted Hartree-Fock. The K-shell ionized O_2 molecule, was cited above as an example [11]. The reason for the localization at the unrestricted Hartree-Fock level of approximation is simply that more variational energy is gained by localization than lost due to loss of symmetry. If the symmetry is restored by further improvement of the wave function, the delocalization energy energy is regained. The improvements in the wave function due to symmetry breaking remain, but in a less explicit way than before symmetrization.

True localization requires that the wave function responds to a nuclear displacement sufficiently strongly to give a self-supporting new geometry. The localization-delocalization phenomenon has been discussed from different points of view during many decades. Most inorganic mixed valence systems are localized since the equilibrium geometry corresponding to different oxidation states is sufficiently different to compete with gains by delocalization. One exception is the mixed valence Creutz-Taube ion which was shown by experimental methods to have delocalized electrons [16] which also may be predicted if accurate calculations are carried out [37]. Aromatic systems connected by saturated spacers may be localized if the chain is sufficiently long[38].

We have here tried to forward a treatment where the insulator → metal transition is studied on the basis of cluster models where only the trapping energy, the reorganization energy λ and the coupling J are known. The coupling J has to be defined with respect to electron transfer properties since it is unrelated to other forms of coupling, for example magnetic coupling. By using accurate ab initio calculations we find that an additional electron in an anthracene crystal is delocalized in the *ab*-plane (but may localize at elevated temperatures). In the *c* direction the coupling is almost zero and the charge localized to a single *ab* plane.

8. CONCLUSION

An important conclusion in the present paper is that the borderline between localized and delocalized is sharp since the reorganization energy depends on the population quadratically. If an electron due to delocalization spreads to other molecules, the bond length modification due to the presence of the electron is decreased proportional to the population. Since the reorganization energy is proportional to the square of the distortions, it decreases quadratically with the electron or hole population.

We have given some examples where the sharpness of the metal-insulator transition is seen experimentally. If the temperature is raised, the fluctuations in the diagonal and off-diagonal matrix elements of the hamiltonian lead to disorder[10] which is 'ignored' by the wave function if the disorder is small but finally sets in as a second order phase transition. Other examples may be giant magnetoresistance where the transition occurs in a small temperature interval [39] and possibly the transition from superconducting to nearly insulating behaviour as found in high-T_c superconductors.

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