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ON ELECTRON TRANSFER REACTIONS IN FERRO ELECTRIC POLYMERS

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Abstract Electron transfer reactions in ferro electric polymers are considered. The interaction of the electron transfer system with the polymer is discussed using the Landau-Peker Poluron model. It is found that near T_c (i.e. for large dielectric constant) the electron transfer is inhibited by charge self localization. However if fluctuations are included in the calculation electron transfer is still possible. An expression for the fluctuation driven electron transver mean T_c rate is derived.

Keywords: polaron, ferro electric, Landau-Pekar

The rate of electron transfer reactions depends on two factors:
1) The overlap between relevant orbitals of the donor and acceptor and
2) Changes in the polarization energy associated with the process.

It is the purpose of this note to examine simple models of electron transfer reactions in a ferro electric medium near the transition point and to point out what experiments may be of interest.

For the sake of simplicity we consider a simple model consisting of a ferro electric medium described by an order parameter (polarization) and an electron donor system. Furthermore we assume that a mean field approximation is adequate.

To fix ideas we consider first a model of a hydrogen like atom in a polar medium characterized by a classical continuous polarization field. This method was originally used by Landau[1] to discuss the polaron problem.

Following Landau we assume that the energy of the system can be written in the form

$$-\int \psi^* \frac{\Delta}{2}\psi - \int \frac{\psi^*\psi}{|x|} + \int \frac{divP(x_1)}{|x_1 - x|}\psi^*(x)\psi(x)dx - \int \frac{divP(x_1)d^3x_1}{|x_1|} + \int \alpha \frac{P^2(x_1)d^3x_1}{2} \quad (1)$$

Here the first two terms are the energy of the "hydrogen" atom, the third and fourth term the interaction energy of the H atom with the medium and the last term the polarization energy; α is a suitable constant variation of the energy functional with respect to ψ and P gives two coupled equations from which P can be eliminated giving the non linear equation

$$E\psi = -\frac{\Delta\psi}{2} - \frac{1}{\varepsilon x}\psi - 4\pi\frac{(\varepsilon-1)}{\varepsilon}\int\frac{\psi^*(x_1)\psi(x_1)}{|x-x_1|}d^3x_1\psi x \tag{2}$$

For a free electron this is the Landau equation for the polaron. We note that the medium has two effects:

1) The proton potential is screened

2) A non linear term appears which in the polaron case results in localization of the electron for sufficiently large ε.

From 2) we find

$$E = -\{\int\frac{\psi^*\Delta\psi}{2} + \int\frac{\psi^*\psi}{\varepsilon|x|} + 4\pi\frac{(\varepsilon-1)}{\varepsilon}\int\frac{|\psi(x)|^2|\psi(y)|^2 d^3x d^3y}{|x-y|}}{\int\psi^*\psi d^3x} \tag{3}$$

assuming that $\psi = \frac{\alpha^{3/2}}{\pi^{1/2}}e^{-\alpha r}$

$$E = \frac{\alpha^2}{2} - \frac{\alpha}{\varepsilon} - 2.5\pi\frac{\varepsilon-1}{\varepsilon}\alpha \tag{4}$$

The energy is a minimum for $\alpha = \frac{1}{\varepsilon} + \frac{\pi}{2}(\frac{\varepsilon-1}{\varepsilon})$

as $\varepsilon \to \alpha$ $\alpha \approx 2.5\pi$. Therefore the range of the wave function is about that of the free H atom. We now consider the case of a ferro electric and assume that the order parameter (polarization P) satisfies the equation [2].

$$-\Delta P + a(T - T_c)P + \beta P^3 \tag{5}$$

where α, β are constants T is the temperature and T_C the critical temperature.

In analogy to the Landau theory of the polaron we define a free energy functional given by

$$F = -\int \frac{\psi^* \Delta \psi d^3x}{2} - \int \frac{\psi^* \psi d^3x}{|x|} + \iint div \frac{P(x)}{|x-3|} |\psi(x)|^2 |\psi(y)|^2 d^3x d^3y - \iint div \frac{P(x)}{|x|} d^3x + \int \frac{(\nabla P)^2}{2} + \frac{a}{2}(T - T_c)P^2 + bP^3 \ldots) d^3x \tag{6}$$

Variation of F with respect to ψ and P now gives

$$E\psi = \frac{-\Delta}{2}\psi - \frac{\psi}{|x|} + \int \frac{div P(x_1)}{|x_1 - x|} d^3x_1 \psi - \Delta P + a(T - T_c)P + bP^3 = -grad \int \frac{|\psi|^2 d^3x}{|x-y|} - \frac{1}{|x|} \tag{7}$$

As a first approximation we neglect the term P^3 ..., solve for P and insert into the equation for ψ. We then find

$$E\psi = -\frac{\Delta}{2}\psi - \left(\frac{1}{x} - \frac{e^{-\xi|x|}}{x}\right) - 4\pi \int \frac{e^{-\xi|x-x^1|}}{|x-x_1|} \frac{1}{|x_1 - x_2|} |\psi(x_2)|^2 d^3x_2 d^3x_1 x \psi(x) \tag{8}$$

where $$\xi^{-1} = \frac{1}{(a(T - T_c))^{1/2}}$$

is the correlation length.
As before 8) can be associated to a functional:

$$E = -\left[\frac{\psi^* \Delta \psi}{2}\right] + \int \left[\frac{1}{x} - \frac{1e^{-\xi|x|}}{x}\right] \psi\psi^* d^3x - \iiint \frac{e^{-\xi(x-x_1)} |\psi(x)|^2 |\psi(x_2)|^2}{|x-x_1||x_1 - x_2|} \tag{9}$$

If we again assume that

$$\psi = \frac{\alpha^{3/2}}{\pi^{1/2}} e^{-\alpha|x|}$$

we find that

$$E = \frac{\alpha^2}{2} - \alpha + \frac{4\alpha^3}{(2\alpha + \xi)^2} - \frac{\alpha c}{\xi} \tag{10}$$

where c is a constant and $\xi = a(T - T_c)^{1/2}$

Hence $\alpha \frac{1}{(T-T_c)^{1/2}}$ as $T \rightarrow T_c$ and the proton potential is screened.

Nevertheless the range of the wave function decreases sharply as $T\text{-}T_c$ due to the non linear term. This result is only qualitative since to use linearized mean field theory near T_c is not a good approximation. It is however indicative of the behavior of the system.

It is of interest to consider the coupling integral between two hydrogenic wave functions a distance R apart. This is given by

$$\int \psi(x) \frac{1}{x} \psi(x-R) d^3x = 2\alpha(1+\alpha R) e^{-\alpha R} \tag{11}$$

It follows from the above that the coupling between the two atoms $\rightarrow 0$ as $T \rightarrow T_c$. A consequence of this is that charge separated states can be stabilized in polar media. This can be seen explicitly if we consider the case of an H_2^+ molecule in a polar medium. The "Landau" equation now becomes

$$-\frac{\Delta\psi}{2} - \frac{1}{\varepsilon}\left(\frac{1}{|x-R_1|} + \frac{1}{|x-R_2|}\right) - 4\pi \frac{\varepsilon - 1}{\varepsilon} \int \frac{|\psi(x_1)|^2}{|x-y|} \psi = E\psi \tag{12}$$

if we assume that in this case

$$\psi = a\phi(x-R_1) + b\phi(x-R_2)$$

and

$$-\frac{\Delta}{2}\phi(x-R_1) - \frac{1}{\varepsilon|x-R_1|}\phi(x-R_1) = \varepsilon_0 \phi(x-R_1)$$

a tight binding calculation of the energy E gives

$$E = \frac{\varepsilon_0(a^2+b^2) + 2\Gamma ab + K(a^4+b^4)}{a^2+b^2} \tag{13}$$

It follows that if $\frac{|K|}{2} > |\Gamma|$ the state a = 1, b=0 or a=0, b=1 has lower energy then a = b = $\frac{1}{\sqrt{2}}$. It follows that electron transfer between the two protons is inhibited and the state $H + H^+$ is more stable than the H_2^+ molecule.

The previous calculations suggest that in very polar media electron transfer reaction may be slowed down depending on the relative magnitude of the overlap integrals and Landau non linear term.

However all calculations done so far are time independent and neglect the fluctuations of polarization field. In the following we examine what effect such fluctuations have on the transition rate. To do this we consider a simplified model based on work by Lax and Shugard[3]. We suppose that the electron transfer system in the polar medium can be described by the equation

$$\begin{aligned} i\dot{a} &= (E_a + \varepsilon_1(t))a + \Gamma b \\ i\dot{d} &= (E_d + \varepsilon_2(t))d + \Gamma a \end{aligned} \tag{14}$$

here $E_a \wedge E_d$ are the electronic energies of the acceptor and donor states and ε_1 or (ε 2) are defined by

$$\varepsilon_1(t) = \int \phi_a(x) div \frac{P(x^1 t)}{|x - x_1|} \phi_a(x) d^3x \tag{15}$$

ε_2(t) is given by a similar expression involving the donor wave functions. Following Lax and Shugard we calculate the transition rate from 14) in first order perturbation theory and assume that the fluctuations of the potential at the donor and acceptor are uncorrelated and Gaussian. One then obtains the following expression for the transition rate

$$\int_{-\infty}^{\infty} dt \int d\Omega e^{i\Omega t} \psi(\Omega) e^{-\int_{-\infty}^{+\infty} dw \frac{\phi(w)}{w^2} \sin^2 \frac{wt}{2}} \tag{16}$$

where $$\left\langle \Gamma(t_1)\Gamma(t_2) \right\rangle = \frac{1}{2\pi} \int \psi(\Omega) e^{i\Omega(t - t_1)}$$

and $$\left\langle \varepsilon(t_1)e(t_2) \right\rangle = \frac{1}{2\pi} \int \phi(\Omega) e^{i\Omega(t_1 - t_2)}$$

In the following we ignore the fluctuation of Γ and assume that

$$\phi(w) = \int \frac{d^3 q q_i q_j X_{ij}(qw)}{q^4} \tag{17}$$

For an isotropic medium

$$\phi(w)\int dqX(wq) \tag{18}$$

We finally suppose that the dynamics of the order parameter can be described by a time dependent Landau-Ginsberg equation[4] and that consequently

$$X(q^w)=\frac{1}{iw+q^2+\xi^2} \tag{19}$$

thus the integral in the exponential of 16)

$$\int dq\int dw\frac{c}{w^2+c^2}\frac{\sin wt}{w^2}=I$$

where $c=q^2+\xi^2$

Carrying out the integrations and setting $\xi = 0$

$$I=\iint\frac{k^2}{w^2+k^4}\frac{\sin^2 wt}{w^2}dw=c|t|^{3/2}$$

Therefore the transition rate becomes

$$\text{rate}\quad \Gamma\int_{-\infty}^{2\infty}e^{i\Delta Et-c|t|^{3/2}}dt$$

Consequently the transition rate is finite as $T - T_c$ because of the fluctuations in the medium. The results found here are however only qualitative since the models used are to simple. A better calculation involving and accurate estimate of the $\langle P,P\rangle$ correlation function is needed.

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