APPENDIX

The purpose of this Appendix is to give a few mathematical properties of the matrix elements $J_{n'n}(q)$. This quantity is defined by (2.13) and can be put in the form

$$J_{n'n}(q)=\left(\frac{n!}{n'!}\right)^{1/2}\left(\frac{\hbar q^2}{2m\omega_c}\right)^{\frac{1}{2}(n'-n)} \times\exp-\frac{\hbar q^2}{4m\omega_c}L_n^{n'-n}\left(\frac{\hbar q^2}{2m\omega_c}\right), \quad \text{(A1)}$$

by using the properties of the harmonic oscillator functions $\phi(x)$. The formula (A1) is only valid for $n'\geq n$. $L_n^\alpha(x)$ is an associated Laguerre polynomial. An expression similar to (A1) can be found when $n'<n$ by using the relations

$$J_{n'n}(-q)=J_{nn'}(q)=(-1)^{n'-n}J_{n'n}(q). \quad \text{(A2)}$$

Using the properties of the Laguerre polynomials, we are able to derive the relations

$$\frac{\partial J_{n'n}}{\partial q}=\left(\frac{\hbar}{2m\omega_c}\right)^{1/2}[(n+1)^{1/2}J_{n',n+1}-n^{1/2}J_{n',n-1}], \quad \text{(A3)}$$

$$\left(n'-n-\frac{\hbar q^2}{2m\omega_c}\right)J_{n'n}(q) =\left(\frac{\hbar q^2}{2m\omega_c}\right)^{1/2}[(n+1)^{1/2}J_{n',n+1}+n^{1/2}J_{n',n-1}], \quad \text{(A4)}$$

which we have used to simplify the matrix elements (2.12). We can also obtain the useful sum rules

$$\sum_{n'=0}^{\infty} J_{n'n}^2(q)=1, \quad \text{(A5)}$$

$$\sum_{n'=0}^{\infty}(n'-n)J_{n'n}^2(q)=\frac{\hbar q^2}{2m\omega_c}. \quad \text{(A6)}$$

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Effects of an Electric Field on Molecular Excitons

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The influence of an electric field on the second moment $\Delta(t)$ of an exciton wave packet is calculated. The following formula is derived: $\Delta(t)=(2\beta/\hbar^2)[\beta+2\lambda_1(B_1+C_1)]t^2$, where λ_1 is the (uniform) strength of the field along the linear chain molecule and the term B_1+C_1 depends on the parameters of the system. The gradient of the electric field does not contribute to $\Delta(t)$. It is also shown that both the exciton electric dipole moment and B_1+C_1 vanish unless either some states of the units making up the chain (monomers) are parity mixtures (as in molecules), or the coupling potential between monomers is not symmetric with respect to the parity operators of pairs of adjacent monomers. It must also be required that the monomers have zero static dipole moment for the state corresponding to the exciton.

INTRODUCTION

In a previous paper, herein referred to as (A), the author[1] has derived an expression for the acceleration of an exciton wave packet due to an external electric field. The acceleration was shown to be proportional to the gradient of the electric field, the proportionality constant being, therefore, interpretable as the exciton electric dipole moment. In the present paper, we extend the analysis by (a) investigating the effect of the electric field on the rate of spreading of the wave packet, i.e., on the *second* moment of the exciton distribution function, and (b) carrying out a brief evaluation of some of the derived physical constants of the theory, including the exciton dipole moment. All assumptions of the first paper are preserved.

[1] A. Bierman, Phys. Rev. **130**, 2266 (1963).

THE SECOND MOMENT OF THE EXCITON WAVE PACKET

We define the second moment by

$$\Delta(t)=\sum_k \xi_k'^*\xi_k'[k-\langle x\rangle]^2=\sum_k k^2\xi_k'^*\xi_k'-\langle x\rangle^2. \quad (1)$$

The average position $\langle x\rangle$ can be trivially calculated from Eqs. (17) and (71) of (A). Since the wave packet moves with constant acceleration a, and the initial velocity v_0 is given by

$$v_0=\frac{1}{\hbar i}\sum_{k,l} H_{kl}(k-l)\xi_k^*(0)\xi_l(0) =\frac{1}{\hbar i}\sum_{k,l}(k-l)H_{kl}\delta_{k0}\delta_{l0}=0, \quad (2)$$

we find

$$\langle x\rangle=\tfrac{1}{2}at^2.$$

But a is proportional to λ_2, the electric field gradient. To first order in λ, then,

$$\Delta(t)=\langle x^2\rangle=\sum_k k^2\xi_k'^*\xi_k'. \quad (3)$$

But

$$\xi_k'(t)=\xi_k(t)+\lambda\eta_k(t),$$

where $\xi_k(t)$ is the zero-field exciton amplitude; hence,

$$\Delta(t)=\langle x_0^2\rangle+2\lambda\ \mathrm{Re}\sum_k k^2\eta_k\xi_k^*, \quad (4)$$

where

$$\langle x_0^2\rangle=\sum_k k^2\xi_k\xi_k^*. \quad (5)$$

(i) Calculation of $\langle x_0^2\rangle$

We now use an identity given by Magee and Funabashi,[2]

$$\xi_k(t)=e^{-i\alpha t/\hbar}(-i)^{|k|}J_{|k|}(2\beta t/\hbar), \quad (6)$$

for a very long chain where $J_{|k|}$ is a Bessel function of order $|k|$; Eq. (6) can also be proved from Eqs. (11) and (13) of (A) by using the relation,

$$\exp(-i\gamma\cos\varphi)=J_0(\gamma)+2\sum_{m=1}^{\infty}J_m(\gamma)\cos m\varphi(-i)^m. \quad (7)$$

We shall use (6) from here on, *with α set equal to zero*, without loss of generality.

Hence, from (5) and (6),

$$\langle x_0^2\rangle=\sum_{k=-Q}^{Q}k^2J_{|k|}(\gamma)=2\sum_{k=1}^{Q}k^2J_k(\gamma), \quad (8)$$

where $\gamma=2\beta t/\hbar$. Repeated application of

$$\text{(a)}\quad kJ_k(\gamma)=\tfrac{1}{2}\gamma[J_{k-1}+J_{k+1}],$$
$$\text{(b)}\quad \tfrac{1}{2}\gamma^2J_{k-1}J_{k+1}=\tfrac{1}{2}\gamma^2J_k^2-\int_0^\gamma xJ_k^2(x)dx, \quad (9)$$

leads finally to

$$\langle x_0^2\rangle=\tfrac{1}{2}\gamma^2. \quad (10)$$

Equation (10) follows from the assumption that the chain is essentially infinite, i.e., $J_Q(\gamma)\approx 0$ for all finite γ (or t), where Q is the index of the chain ends. This result was also given in Magee and Funabashi. Hence,

$$\Delta(t)=(2\beta^2t^2/\hbar^2)+2\lambda\ \mathrm{Re}\sum_k k^2\eta_k\xi_k^*. \quad (11)$$

(ii) Formula for η_k

To find the differential equation for η_k, we use Eqs. (36) and (41) of (A):

$$\sum_m H_{rm}'(\xi_m+\lambda\eta_m)=\hbar i(\partial/\partial t)(\xi_r+\lambda\eta_r),$$
$$H_{rm}'=H_{rm}+\lambda h_{rm}, \quad (12)$$

with the conclusion that

$$\sum_m H_{rm}\eta_m+\sum_m h_{rm}\xi_m=\hbar i(\partial\eta_r/\partial t) \quad (13)$$

for all r, with $\eta_r(0)=0$. It is easy to show that ξ_r' is properly normalized, since Re $(\sum_r\xi_r^*\eta_r)=0$. The solution of (13) is given by the following:

Theorem:

$$\eta_r(t)=\frac{1}{\hbar i}\sum_{m=-Q}^{Q}\sum_{n=0}^{\infty}\sum_{p=0}^{n}\frac{1}{n!}\left(\frac{-i\beta}{\hbar}\right)^n\binom{n}{p}\times h_{r+n-2p,m}\int_0^t\xi_m(\tau)(t-\tau)^n d\tau. \quad (14)$$

Proof: Define two operators E_r, F_r such that, for any function ϕ_r,

$$E_r\phi_r=\phi_{r+1},$$
$$F_r\phi_r=\phi_{r-1}. \quad (15)$$

Obviously E_r and F_r commute. Using Eq. (12) of (A) in (13) results in

$$\frac{\partial\eta_r}{\partial t}-\frac{\beta}{\hbar i}(E_r+F_r)\eta_r=\frac{1}{\hbar i}\sum_m h_{rm}\xi_m. \quad (16)$$

This first-order, nonhomogeneous differential equation can be solved by the usual methods, treating E_r+F_r as a constant coefficient in (16). The formal solution is

$$\eta_r(t)=\frac{1}{\hbar i}\int_0^t d\tau\sum_m\xi_m(t)\times\exp[(-i/\hbar)\beta(E_r+F_r)(t-\tau)]h_{rm}. \quad (17)$$

Now

$$\exp[-(i/\hbar)\beta(E_r+F_r)(t-\tau)]=\sum_{n=0}^{\infty}\left(\frac{-i\beta}{\hbar}\right)^n\frac{(t-\tau)^n}{n!}(E_r+F_r)^n,$$

where

$$(E_r+F_r)^n=\sum_{p=0}^{n}\binom{n}{p}E_r^{n-p}F_r^p. \quad (18)$$

Since $E_r^{n-p}F_r^ph_{rm}=h_{r-2p+n,m}$, Eq. (14) results immediately.

(iii) Evaluation of the λ_1 part of η_k

To evaluate (14), we turn to Eq. (58) of (A) which gives the h_{sm} in terms of certain coefficients A, B, and C. In particular, the dependence on the λ_1 part of the electric field is given by

$$\lambda_1h_{sm}=\lambda_1\{\delta_{sm}A_1+C_1+(\delta_{sm+1}+\delta_{sm-1})B_1\}. \quad (19)$$

Consider now first the contribution of A_1.

Theorem: The contribution of A_1 to $\Delta(t)$ is zero.

Proof: The A_1 term of (19), when placed into Eq. (14) yields

$$\eta_r^{(1)}(t)=\frac{\lambda_1A_1}{\hbar i}\sum_{n=0}^{\infty}\sum_{p=0}^{n}\frac{1}{n!}(-i)^n\left(\frac{\beta}{\hbar}\right)\binom{n}{p}\int_0^t\xi_{r+n-2p}(t-\tau)^n d\tau. \quad (20)$$

[2] J. L. Magee and K. Funabashi, J. Chem. Phys. 34, 1715 (1961).

Now examine only the dependence of $\eta_r^{(1)}$ on $i=(-1)^{1/2}$. From Eq. (6), ξ_{r+n-2p} goes as $(-i)^{|r+n-2p|}$, so that $\eta_r^{(1)}(t)$ is proportional to $(-i)^{n+1}(-i)^{|r+n-2p|}$ which means $(-i)(-i)^{\pm r}$. Since ξ_r^* goes as $(+i)^{|r|}$, the product $\xi_r^*\eta_r^{(1)}$ is pure imaginary thus yielding no contribution to $\Delta(t)$, as defined by Eq. (11).

Now consider the $\lambda_1 C_1$ term. Its contribution to $\eta_r(t)$, defined here as $\eta_r^{(2)}(t)$ is obviously

$$\eta_r^{(2)}(t)=\frac{\lambda_1 C_1}{\hbar i}\sum_{m=-Q}^{Q}\sum_{n=0}^{\infty}\sum_{p=0}^{n}\left(\frac{-i\beta}{\hbar}\right)^n\frac{1}{n!}\binom{n}{p}\times\int_0^t d\tau(t-\tau)^n\xi_m(\tau). \quad (21)$$

Now use the relation that $\sum_{p=0}^{n}\binom{n}{p}=2^n$; Eq. (21) becomes then

$$\eta_r^{(2)}(t)=\frac{\lambda_1 C_1}{\hbar i}\times\int_0^t \exp[-(2i\beta/\hbar)(t-\tau)]\sum_{m=-Q}^{Q}\xi_m(\tau)d\tau. \quad (22)$$

The sum $\lim_{Q\to\infty}\sum_{m=-Q}^{Q}\xi_m(\tau)$ can be easily evaluated from Eq. (7). Setting $\varphi=0$ and remembering Eq. (6), leads to

$$\lim_{Q\to\infty}\sum_{m=-Q}^{Q}\xi_m(\tau)=\exp(-2i\beta\tau/\hbar). \quad (23)$$

Hence, in (22),

$$\eta_r^{(2)}(t)=(\lambda_1 C_1/\hbar i)t\exp[-(2i\beta/\hbar)t]. \quad (24)$$

Now consider the contribution of $\lambda_1 B_1(\delta_{sm+1}+\delta_{sm-1})$ to η_r, here called $\eta_r^{(3)}(t)$. From (14),

$$\eta_r^{(3)}(t)=\frac{\lambda_1 B_1}{\hbar i}\sum_{n=0}^{\infty}\sum_{p=0}^{n}\frac{1}{n!}\left(\frac{i\beta}{\hbar}\right)^n\binom{n}{p}\times\left\{\int_0^t(\tau-t)^n[\xi_{r+n-2p-1}(t)+\xi_{r+n-2p+1}]\,d\tau\right\}. \quad (25)$$

By virtue of Eqs. (8) and (12) of (A), this becomes

$$\eta_r^{(3)}(t)=\frac{\lambda_1 B_1}{\beta}\sum_{n=0}^{\infty}\sum_{p=0}^{n}\frac{1}{n!}\left(\frac{i\beta}{\hbar}\right)^n\binom{n}{p}\times\int_0^t(\tau-t)^n\frac{\partial\xi_{r+n-2p}}{\partial\tau}d\tau. \quad (26)$$

Now set $s\equiv n-2p$; from the limits of p and n, $-\infty\leq s\leq+\infty$. Consider a given $\dot{\xi}_{r+s}$: What is its coefficient? To determine this, we realize that for any n there must exist a p such that $p=\frac{1}{2}(n-s)$, but p is a nonnegative integer less than n; hence $n\geq|s|$, and furthermore must be summed in steps of two: i.e., $n=|s|$, $|s|+2,\cdots$. This enables us now to rewrite (26) as follows:

$$\eta_r^{(3)}(t)=\frac{\lambda_1 B_1}{\beta}\sum_{s=-\infty}^{\infty}\sum_{n=|s|}^{\infty}{}''\frac{1}{n!}\left(\frac{i\beta}{\hbar}\right)^n\binom{n}{\frac{1}{2}n-\frac{1}{2}s}\times\int_0^t\dot{\xi}_{r+s}(\tau)(\tau-t)^n d\tau, \quad (27)$$

where $\sum''$ means sum in steps of two only. If we write out $\binom{n}{\frac{1}{2}n-\frac{1}{2}s}$, one gets now

$$\eta_r^{(3)}(t)=\frac{\lambda_1 B_1}{\beta}\sum_{s=-\infty}^{\infty}\int_0^t\dot{\xi}_{r+s}(t)\times\sum_{n=|s|}^{\infty}{}''\frac{1}{(\frac{1}{2}n-\frac{1}{2}s)!(\frac{1}{2}n+\frac{1}{2}s)!}\left[-\frac{i\beta}{\hbar}(t-\tau)\right]^n d\tau. \quad (28)$$

Now consider $s>0$, and set $q=\frac{1}{2}n-\frac{1}{2}s$; hence,

$$\sum_{n=s}^{\infty}{}''\frac{1}{(\frac{1}{2}n-\frac{1}{2}s)!(\frac{1}{2}n+\frac{1}{2}s)!}\left[-\frac{i\beta}{\hbar}(t-\tau)\right]^n\equiv(-i)^s\sum_{q=0}^{\infty}\frac{(-1)^q}{q!(q+s)!}\left[\frac{\beta}{\hbar}(t-\tau)\right]^{2q+s}. \quad (29)$$

In this form Eq. (29) can now be recognized to be just equal to $(-i)^s J_s[(\beta/\hbar)(t-\tau)]$.

Similarly consider $s<0$, and let $q=\frac{1}{2}n+\frac{1}{2}s$. Hence,

$$\sum_{n=-s}^{\infty}{}''\frac{1}{(\frac{1}{2}n-\frac{1}{2}s)!(\frac{1}{2}n+\frac{1}{2}s)!}\left[-\frac{i\beta}{\hbar}(t-\tau)\right]^n=(-i)^{|s|}\sum_{q=0}^{\infty}\frac{(-1)^q}{q!(q+|s|)!}\left[\frac{\beta}{\hbar}(t-\tau)\right]^{2q+|s|}=(-i)^{|s|}J_{|s|}[(\beta/\hbar)(t-\tau)]. \quad (30)$$

Inspection shows that for $s=0$, the series is just $J_0[(\beta/\hbar)(t-\tau)]$. Hence,

$$\eta_r^{(3)}(t)=(\lambda_1 B_1/\beta)\sum_{s=-\infty}^{\infty}\int_0^t(-i)^{|r+s|+|s|}J_{|s|}\times[b(t-\tau)]\frac{d}{d\tau}J_{|r+s|}(b\tau)d\tau, \quad (31)$$

where $b\equiv\beta/\hbar$, and we have used Eq. (6).

To simplify further discussion, let $\zeta=bt$, and $Z=b\tau$;

using the well-known relations for $J_k'(z)$, (31) becomes

$$\eta_r^{(3)}(t)=(\lambda_1B_1/2\beta)\sum_{s=-\infty}^{\infty}\int_0^{\zeta}(-i)^{|r+s|+|s|}J_{|s|}\times(\zeta-z)[J_{|r+s|-1}-J_{|r+s|+1}]dz. \quad (32)$$

To evaluate (32), consider separately the terms for which s is less than or equal to $-r$, the terms for which s is between $-r$ and 0, and the terms with $0<s$. It follows immediately that

$$\eta_r^{(3)}(t)=\frac{\lambda_1B_1}{2\beta}(-i)^r\int_0^{\zeta}\{\sum_{s=-\infty}^{\infty}[J_s(\zeta-z)J_{r+s-1}(z)-J_s(\zeta-z)J_{r+s+1}(z)]\}. \quad (33)$$

Now use the Schläfli formula,

$$J_{-\nu}(z+t)=\sum_{m=-\infty}^{\infty}(-1)^mJ_{m-\nu}(t)J_m(z), \quad (34)$$

which results finally in

$$\eta_r^{(3)}(t)=\frac{\lambda_1B_1}{\beta}t\frac{d\xi_r}{dt}. \quad (35)$$

(iv) Evaluation of the λ_2 part of η_k

The λ_2 part of the electric field contributes to h_{sm} the terms

$$\lambda_2h_{sm}=\lambda_2[8mA_2\delta_{sm}+mC_2+sC_2^*+(\delta_{sm+1}+\delta_{sm-1})(mB_2+sB_2^*)]. \quad (36)$$

We can neglect the A_2 contribution because it yields only an imaginary $\eta_r^{(4)}(t)\xi_r^*(t)$ by the same argument as before.

Now consider the contribution of the term $mC_2+sC_2^*$. Its evaluation is greatly simplified by going back to Eq. (18) and noting that one could have written

$$(E_r+F_r)^n=\sum_{p=0}^{n}\binom{n}{p}E_r^pF_r^{n-p}. \quad (37)$$

This enables us now to rewrite (14)

$$\eta_r(t)=(1/2\hbar i)\sum_{m=-Q}^{Q}\sum_{n=0}^{\infty}\sum_{p=0}^{n}(-i\beta/\hbar)^n\frac{1}{n!}\binom{n}{p}\times[h_{r-2p+n,m}+h_{r+2p-n,m}]\times\int_0^t(t-\tau)^n\xi_m(\tau)d\tau, \quad (38)$$

$$\eta_r^{(5)}(t)=\frac{1}{\hbar i}\sum_{m=-Q}^{Q}\sum_{n=0}^{\infty}\sum_{p=0}^{n}(-i\beta/\hbar)^n\frac{1}{n!}\binom{n}{p}(mC_2+rC_2^*)\times\int_0^t(t-\tau)^n\xi_m(\tau)d\tau. \quad (39)$$

The C_2 term vanishes because $\sum_{m=-Q}^{Q}m\xi_m=0$ by symmetry. The contribution of C_2^* vanishes in $\Delta(t)$, because, from (39),

$$\eta_r^{(5)}(t)=rD(t) \quad (40)$$

and therefore,

$$\sum_{r=-Q}^{Q}r^2\eta_r^{(5)}(t)\xi_r^*(t)=0, \quad (41)$$

again by symmetry.

We will now prove that the contribution of the B_2 terms to $\Delta(t)$ is also zero. We start with an $\eta_r^{(6)}(t)$ by introducing the B_2 and B_2^* terms of (36) into (14), with the result,

$$\eta_r^{(6)}(t)=\frac{\lambda_2}{\hbar i}\sum_m\sum_{n,p}\left(\frac{-i\beta}{\hbar}\right)^n\frac{1}{n!}\binom{n}{p}\times[\delta_{r-2p+n,m+1}+\delta_{r-2p+n,m-1}]\times[mB_2+(r-2p+n)B_2^*]\int_0^t d\tau(t-\tau)^n\xi_m. \quad (42)$$

This leads immediately to

$$\eta_r^{(6)}(t)=\frac{\lambda_2}{\hbar i}\sum_{n,p}\left(\frac{-i\beta}{\hbar}\right)^n\frac{1}{n!}\binom{n}{p}\times\left\{(r-2p+n)(B_2+B_2^*)\int_0^t d\tau\times(t-\tau)^n(\xi_{r-2p+n-1}+\xi_{r-2p+n+1})+B_2\int_0^t d\tau(t-\tau)^n(\xi_{r-2p+n+1}-\xi_{r-2p+n-1})\right\} \quad (43)$$

$$=\lambda_2(B_2+B_2^*)\mathrm{I}(t)+\lambda_2B_2\mathrm{II}(t). \quad (44)$$

Consider $\mathrm{I}(t)$. We again replace $\xi_{r-2p+n-1}+\xi_{r-2p+n+1}$ by $(\hbar i/\beta)\dot{\xi}_{r-2p+n}$ and then change variables from (n,p) to (n,s) where $s\equiv n-2p$. The argument is here identical to that in Eqs. (26) to (31). We therefore find

$$\mathrm{I}(t)=\frac{1}{\beta}\sum_{s=-\infty}^{\infty}(r+s)\int_0^t\dot{\xi}_{r+s}\xi_sd\tau. \quad (45)$$

Its contribution to $\Delta(t)$ will, therefore, have the form

$$\Delta_{\mathrm{I}}\sim\sum_{r=-Q}^{Q}{}'\sum_{s=-\infty}^{\infty}r^2(s+r)\xi_r^*\int_0^t\dot{\xi}_{r+s}\xi_sd\tau. \quad (46)$$

It is clear from inspection that Δ_{I} is of the form $\sum_{r,s}F_{rs}$ where $F_{-r-s}=-F_{rs}$; (46) is, therefore, zero.

Now consider $\mathrm{II}(t)$. We rewrite it by using part (a) of

Eq. (9), with $\gamma=2\beta\tau/\hbar$. One can then easily show that

$$\xi_{r-2p+n+1}(\tau)-\xi_{r-2p+n-1}(\tau)=\frac{\hbar}{\beta\tau}(-i)(r+n-2p)\xi_{r+n-2p}(\tau). \quad (47)$$

Hence,

$$\text{II}(t)\sim\sum_{n,p}\left(\frac{-i\beta}{\hbar}\right)^n\frac{1}{n!}\binom{n}{p}(r+n-2p)\times\int_0^t\frac{d\tau}{\tau}(t-\tau)^n\xi_{r+n-2p}. \quad (48)$$

Again change from (n,p) to (n,s), with the result that (48) becomes

$$\text{II}(t)\sim\sum_{s=-\infty}^{\infty}(r+s)\int_0^t\xi_{r+s}\xi_s\frac{d\tau}{\tau}. \quad (49)$$

But, by the same argument as in (46), its contribution to $\Delta(t)$ vanishes.

We, therefore, conclude that the λ_2 part of the electric field does not contribute to $\Delta(t)$.

(v) Calculation of $\Delta(t)$

We now calculate the contributions of (24) and (35) to $\Delta(t)$. We have

$$\Delta(t)=\frac{2\beta^2t^2}{\hbar^2}+2\lambda_1\,\text{Re}\sum_k k^2\xi_k^*\times\left[\frac{C_1}{\hbar i}t\exp-(2i\beta t/\hbar)+\frac{B_1}{\beta}t\frac{d\xi_k}{dt}\right]. \quad (50)$$

The following theorem is helpful:

Theorem:

$$S(t)\equiv\textstyle\sum_k k^2\xi_k^*=i(2\beta t/\hbar)\exp(2i\beta t/\hbar). \quad (51)$$

Proof: Consider Eq. (7) and differentiate twice with respect to φ. The result is

$$i\gamma\exp(-i\gamma\cos\varphi)(\cos\varphi+i\gamma\sin^2\varphi)=-2\sum_{m=1}(-i)^mJ_m(\gamma)m^2\cos m\varphi. \quad (52)$$

Now set $\varphi\equiv0$ and take the complex conjugate of the resulting equation. We find

$$i\gamma e^{i\gamma}=2\textstyle\sum_m(-i)^m m^2J_m(\gamma). \quad (53)$$

This proves the theorem.

Further consider

$$\text{Re}\sum_k\xi_k^*\dot{\xi}_kk^2=\tfrac{1}{2}\sum_k k^2(\xi_k^*\dot{\xi}_k+\xi_k\dot{\xi}_k^*)=\frac{1}{2}\frac{d}{dt}\sum_k k^2\xi_k^*\xi_k, \quad (54)$$

hence,

$$\text{Re}\sum_k\xi_k^*\dot{\xi}_kk^2=\frac{1}{2}\frac{d}{dt}\left(\frac{2\beta^2t^2}{\hbar^2}\right)=\frac{2\beta^2}{\hbar^2}t \quad (55)$$

from (10). Combining now (51) and (55) with (50) leads to

$$\Delta(t)=\frac{2\beta^2t^2}{\hbar^2}+2\lambda_1\,\text{Re}\left(\frac{C_1}{\hbar i}t\exp-(2i\beta t/\hbar)i\frac{2\beta t}{\hbar}\exp(2i\beta t/\hbar)+2\frac{B_1}{\beta}t\frac{\beta^2}{\hbar^2}t\right), \quad (56)$$

$$\Delta(t)=\frac{2t^2\beta}{\hbar^2}[\beta+\lambda_12(B_1+C_1)]. \quad (57)$$

We can then conclude that the λ_1 part of the electric field does modify the second moment of the exciton wave packet. The specific manner in which it does so, depends on the value of B_1+C_1.

We now turn to a partial evaluation of the coefficients, so far derived in the theory.

THE PHYSICAL CONSTANTS OF THE THEORY

In (A) it was shown that the exciton dipole moment is proportional to B_2+C_2; here we have shown that the effect of the electric field on the spreading rate depends on B_1+C_1. These coefficients are defined through Eqs. (47), (49), (55), and (57) of (A). Inspection of these reveals some information about these constants.

From the defining relations, we have

$$\lambda_1(B_1+C_1)=-e\lambda_12\,\text{Re}\{\sum_{\sigma\neq0,1}Z_{\sigma1}\bar{\beta}_\sigma(\epsilon_1-\epsilon_\sigma)^{-1}+Z_{01}V_0(\epsilon_1-\epsilon_0)^{-1}\}, \quad (58)$$

where

$$\bar{\beta}_\sigma=\langle\varphi_1(s)|V|X_\sigma(s+1)\prod_{j\neq s+1}{}'X_0(j)\rangle,$$
$$V_0=\langle\varphi_1(s)|V|X_\sigma(s+1)\prod_{j\neq s+1}{}'X_0(j)\rangle. \quad (59)$$

Hence, $V_0=\bar{\beta}_0$, and (58) can be simplified to read

$$\lambda_1(B_1+C_1)=-2e\lambda_1\,\text{Re}\sum_{\sigma\neq1}Z_{\sigma1}\bar{\beta}_\sigma(\epsilon_1-\epsilon_\sigma)^{-1}. \quad (60)$$

Similarly,

$$\lambda_2(B_2+C_2)=\lambda_2\sum_{\sigma\neq1}\omega_{\sigma1}\bar{\beta}_\sigma=-2e\lambda_2\,\text{Re}\sum_{\sigma\neq1}Z_{\sigma1}\bar{\beta}_\sigma(\epsilon_1-\epsilon_\sigma)^{-1}R, \quad (61)$$

so that B_2+C_2 and B_1+C_1 are proportional to each other by the factor $(\lambda_2/\lambda_1)R$, where R is the distance between successive unit centers.

Now, from Eq. (54),

$$Z_{\sigma1}=\sum_{m=1}^{r}\langle\sigma(s)|Z_m'|1(s)\rangle, \quad (62)$$

where m is the index labeling the r electrons of the atomic or molecular units making up the chain, $\sigma(s)$ refers to the state σ of the sth unit and Z_m' is the Z coordinate of the mth electron relative to its nucleus. Furthermore, from (59) and from Eqs. (3) and (4) of (A)

$$\bar{\beta}_\sigma = \langle X_1(s) \prod_{l\neq s} X_0(l) | V | X_\sigma(s+1) \prod_{j\neq s+1}' X_0(j) \rangle$$
$$= \langle X_1(s) X_0(s+1) | V(s, s+1) | X_0(s+1) X_0(s) \rangle \quad (63)$$

if σ is not zero, and, for $\sigma=0$,

$$\bar{\beta}_0 = 2\langle X_1(s) X_0(s+1) | V(s, s+1) | X_0(s+1) X_0(s) \rangle. \quad (64)$$

The factor 2 in (64) arises because both $V(s, s+1)$ and $V(s, s-1)$ yield a nonzero matrix element. It follows then from (61), (62), and (63) that B_1+C_1 and B_2+C_2 consist of sums of products of the form

$$G_\sigma = \sum_{m=1}^{r} \langle \sigma(s) | Z_m' | 1(s) \rangle \times \langle X_1(s) X_0(s+1) | V(s, s+1) | X_\sigma(s+1) X_0(s) \rangle \times (\epsilon_1 - \epsilon_\sigma)^{-1}. \quad (65)$$

The following theorem can now be easily proved:

Theorem: If (a) all states of a given monomer (atom or molecule making up the chain) are eigenstates of parity about the x, y plane passing through the monomer origin, i.e., $\mathcal{P}_{(s)} | \sigma(s) \rangle = (\pm 1) | \sigma(s) \rangle$, and if (b) the coupling potential $V(s, s+1)$ is a symmetric operator with respect to $\mathcal{P}_{(s)} \mathcal{P}_{s+1}$ [where $\mathcal{P}_{(s)}$ is the parity operator with respect to the origin of the sth monomer and $\mathcal{P}_{s+1}$ with respect to the origin of the $(s+1)$th monomer], i.e., $\mathcal{P}_s^{-1} \mathcal{P}_{s+1}^{-1} V \mathcal{P}_s \mathcal{P}_{s+1} = V$, then $G_\sigma \equiv 0$.

Proof: From the assumptions of the theorem, we have

$$\langle \sigma(s) | Z_m' | 1(s) \rangle = -\langle \sigma(s) | \mathcal{P}_s^{-1} Z_m' \mathcal{P}_s | 1(s) \rangle$$
$$= -\langle \mathcal{P}_s \sigma(s) | Z_m' | \mathcal{P}_s 1(s) \rangle. \quad (66)$$

To be nonzero, $| \sigma(s) \rangle$ and $| 1(s) \rangle$ have opposite parity. Now:

$$\langle X_1(s) X_0(s+1) | V(s, s+1) | X_\sigma(s+1) X_0(s) \rangle$$
$$= \langle X_1(s) X_0(s+1) | \mathcal{P}_s^{-1} \mathcal{P}_{s+1}^{-1} V \mathcal{P}_s \mathcal{P}_{s+1} | X_\sigma(s+1) X_0(s) \rangle$$
$$= \langle \mathcal{P}_s X_1(s) \mathcal{P}_{s+1} X_0(s+1) | V | \mathcal{P}_{s+1} X_\sigma(s+1) \mathcal{P}_s X_0(s) \rangle$$
$$= \langle \mathcal{P}_s X_1(s) X_0(s+1) | V | \mathcal{P}_{s+1} X_\sigma(s+1) X_0(s) \rangle$$
$$= -\langle X_1(s) X_0(s+1) | V | X_\sigma(s+1) X_0(s) \rangle,$$

thus proving the theorem.

Since all isolated atomic states are eigenstates of parity, we can conclude for systems of identical atoms coupled by a parity-symmetric V, that an electric field will not influence exciton wave packets in the manner considered. But, if the units or monomers making up the crystal or giant molecule are molecules with structure, so that their stationary states are not eigenstates of parity, or if V is not the specified symmetry operator, then an effect can be anticipated. If the monomer states are not eigenstates of parity, the static monomer dipole moment may not vanish. On the other hand, as shown in Eq. (33) of (A), the *particular* state for which an exciton arises, say the first excited state, must have a zero, or vanishingly small static dipole moment. Otherwise the coupling of this moment to the gradient of the electric field produces an energy difference between different monomers of the chain, thus destroying the *identity* of the units. In view of the previous paragraph, the absence of this particular static dipole moment now becomes a separate requirement.

These conclusions follow immediately from the consideration that we are looking at an effect which depends both on the electric field and the exciton, but is proportional to λ to the first power only. The exciton property therefore, e.g., the dipole moment, if it is to have a spatially preferred direction, must derive this from an asymmetry inherent in the monomer structure. This requires the monomer state to be a parity mixture, for otherwise such a preferred direction would not exist. More specific information about these coefficients probably depends strongly on the model assumed.

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