

Acceleration of Molecular Excitons by an Electric Field

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The average location of a molecular exciton wave packet in a long, linear chain molecule in the presence of an electric field directed along the chain is investigated by perturbation theory. Neglecting end effects, and using the Born-Oppenheimer approximation, it is shown that the exciton behaves like an electric dipole—it acquires a constant acceleration along the chain, to first order, due to the gradient of the electric field. The exciton dipole moment is proportional to various atomic dipole moments induced by the applied electric field. It is also shown that the electric field results in long-range atomic coupling even if the coupling Hamiltonian is of the nearest neighbor type only.

INTRODUCTION

BEGINNING with Frenkel's and Peierls' original papers¹⁻³ on molecular excitons, a considerable effort has been devoted to this area with the primary effect of determining stationary states, transition probabilities as well as coupling of excitons to phonons. These investigations, devoted to a study of "stationary" excitons in molecular crystals, are discussed in a recent work by Davydov,⁴ as well as in a review by McClure.⁵ There exists also some experimental evidence⁶ that exciton wave packets may be formed, which transfer energy from one atomic site to a site many atomic distances (1000 Å) away. Aspects of this problem of nonstationary excitons have been studied by a few investigators,^{7,8} but there are still many interesting unanswered questions. One of these questions, examined in this paper, concerns the effect of an external electric field on the motion of a free exciton wave packet (i.e., not coupled to phonons) in a long, linear chain molecule. In particular, we are interested in determining the acceleration (if any) of an exciton by an electric field. We choose the finite model in preference over an infinite (or semi-infinite) crystal because we wish to impose an electric field over the whole physical space. This field is to be treated as a *small* perturbation.

THE EXCITON AMPLITUDE AND THE ACCELERATION MATRIX

We review briefly here the manner whereby stationary and time-dependent exciton amplitudes are constructed. Consider a system of N identical atoms whose nuclei are assumed infinitely heavy; phonons are, therefore, neglected. Let $X_\alpha(k)$ represent the α th state

of the k th atom, obeying

$$H_0(k)X_\alpha(k) = \epsilon_\alpha X_\alpha(k); \quad k=1, 2, \dots, N. \quad (1)$$

Neglecting coupling between the atoms leads to

$$H_0\varphi_0 = E_0\varphi_0, \quad (2)$$

where

$$H_0 = \sum_{k=1}^N H_0(k), \quad E_0 = N\epsilon_0, \quad \text{and} \quad \varphi_0 = \prod_{k=1}^N X_0(k).$$

Equation (2) refers to the molecular ground state. For a situation in which the j th atom is excited, but all others are in the ground state, we get an N -fold degenerate set of wave functions $\varphi_1(j)$, which satisfy

$$H_0\varphi_1(j) = E_1\varphi_1(j), \quad (3)$$

where⁹

$$E_1 = (N-1)\epsilon_0 + \epsilon_1 \quad \text{and} \quad \varphi_1(j) = X_1(j) \prod_{k \neq j} X_0(k).$$

One now adds a coupling term V to H_0 , and we assume in particular that it couples nearest neighbors only; i.e.,

$$V = V(1,2) + V(2,3) + \dots + V(N-1, N). \quad (4)$$

We now seek the eigenfunctions of $H \equiv H_0 + V$; corresponding to the $\varphi_1(j)$, these are given to zeroth order by

$$\Psi_k = \sum_m c_{km} \varphi_1(m) \quad (5)$$

and obey the equation

$$H\Psi_k = \bar{E}_k \Psi_k; \quad k=1, 2, \dots, N. \quad (6)$$

The vector $c_{km} \equiv g_m^{(k)}$, $m=1, 2, \dots, N$ is a representation of a stationary exciton obeying the equation

$$\sum_m H_{km} g_m^{(k)} = \bar{E}_k g_r^{(k)}, \quad r=1, 2, \dots, N; \quad k=1, 2, \dots, N \quad (7)$$

¹ J. I. Frenkel, Phys. Rev. **37**, 17 (1931).

² J. I. Frenkel, Phys. Rev. **37**, 1276 (1931).

³ R. Peierls, Ann. Phys. **13**, 905 (1932).

⁴ A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill Book Company, Inc., New York, 1962).

⁵ D. S. McClure, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 8.

⁶ E. J. Bowen, J. Chem. Phys. **13**, 306 (1945).

⁷ R. E. Merrifield, J. Chem. Phys. **28**, 647 (1955).

⁸ J. L. Magee and K. Funabashi, J. Chem. Phys. **34**, 1715 (1961).

⁹ Although the X 's are assumed properly antisymmetrized with respect to electrons belonging to a given atom, electrons belonging to different atoms are not antisymmetrized in the φ 's. Formation of the Slater determinant, as is done for example in Davydov (reference 4), leads to wave functions which are no longer exact eigenfunctions of H_0 . This problem will be examined in a later paper.

where H_{rm} is just $(\varphi_1(r), H\varphi_1(m))$. Equation (7) can be viewed as a Schrödinger equation for the exciton amplitude $g_r^{(k)}$ defined over a space of N discrete points labeled by r . This is made reasonable by the fact that $|g_r^{(k)}|^2$ is the probability of finding the excitation localized on atom r , if the molecule is in state k .

One can find the corresponding time-dependent Schrödinger equation for an exciton wave packet $\zeta_r(t)$,

$$\hbar i(\partial\zeta_r/\partial t) = \sum_m H_{rm}\zeta_m(t), \quad (8)$$

by starting with a molecular state $\Psi(t)$ obeying the equation

$$H\Psi = \hbar i(\partial\Psi/\partial t) \quad (9)$$

and setting

$$\Psi(t) = \sum_r \zeta_r(t)\varphi_1(r). \quad (10)$$

If, in particular, $\Psi(0) = \varphi_1(j)$, then (8) is supplemented by $\zeta_r(0) = \delta_{rj}$, and has the solution

$$\zeta_r(t) = \sum_k g_r^{*(k)} g_j^{(k)} \exp[-(i/\hbar)\bar{E}_k t] \quad (11)$$

by virtue of the orthonormality of the $g^{(k)}$'s. From (10), $|\zeta_r(t)|^2$ is the probability of finding the excitation localized on the r th atom at time t if it was localized on the j th atom at $t=0$.

Now specialize this theory to a linear chain molecule, consisting of N identical, equally spaced atoms; assuming nearest neighbor coupling, we write:

$$H_{kk} = E_1 + \alpha, \quad H_{k, k\pm 1} = \beta, \quad (12)$$

all other matrix elements being zero. It can be easily shown¹⁰ that

$$g_r^{(k)} = g_k^{(r)} = \left(\frac{2}{N+1}\right)^{1/2} \sin \frac{kr\pi}{N+1}, \quad (13)$$

$$\bar{E}_k = E_1 + \alpha + 2\beta \cos[k\pi/(N+1)].$$

The average position of the exciton packet is obviously given by

$$\langle x \rangle = \sum_{k=1}^N k |\zeta_k(t)|^2. \quad (14)$$

It follows from (8) and (14) that

$$\langle \dot{v} \rangle = \sum_{r,m} \zeta_r^* Y_{rm} \dot{\zeta}_m, \quad (15)$$

$$\langle \dot{v} \rangle = \sum_{r,m} \zeta_r^* Q_{rm} \dot{\zeta}_m, \quad (16)$$

where

$$Y_{rm} = (1/\hbar i) H_{rm}(r-m) \quad (17)$$

and the acceleration matrix Q_{rm} is

$$Q_{rm} = (1/\hbar^2) \sum_n H_{rn} H_{nm} (2n - m - r). \quad (18)$$

If one now uses (12) and (18) one finds that all Q_{rm} are zero except Q_{11} and Q_{NN} which are given by

$$Q_{11} = -Q_{NN} = (2/\hbar^2)\beta^2. \quad (19)$$

These two terms clearly represent the effects of the molecular ends—acceleration due to reflection. This end effect disappears for an exciton wave packet which originates at $t=0$ on the central atom of the chain. By symmetry, $\langle x \rangle$ is a constant in this case.

APPLICATION OF A LONGITUDINAL ELECTRIC FIELD

Now consider the application of a stationary electric field parallel to the molecular chain, which dimension we shall call z and assume that the k th atomic nucleus is located at kR , R being the interatomic distance. Assume the potential can be represented by a power series in z :

$$V = V_0 + \lambda_1 z + \lambda_2 z^2 + \dots \quad (20)$$

Due to the presence of this potential, there are additional terms in the Hamiltonian of the free atom, one such term per electron. Let $z(k, j)$ represent the z coordinate (as measured with respect to the origin of the molecular coordinate system) of the j th electron belonging to the k th atom. We then get a potential energy term

$$U(k, j) = -eV[z(k, j)]. \quad (21)$$

This can be transformed to primed coordinates, defined relative to the k th nucleus:

$$z(k, j) = kR + z'(k, j). \quad (22)$$

This leads to

$$U(k, j) = -e\{V_0 + \lambda_1[kR + z'(k, j)] + \lambda_2[kR + z'(k, j)]^2 + \dots\}. \quad (23)$$

If each atom has r electrons, we find that the new Hamiltonian is

$$H_0'(k) = H_0(k) + \sum_{j=1}^r U(k, j) \\ = H_0(k) + U(k). \quad (24)$$

The new Schrödinger equation becomes

$$H_0'(k)X_\alpha'(k) = \epsilon_\alpha'(k)X_\alpha'(k). \quad (25)$$

To first order in λ_1, λ_2 we get

$$\epsilon_\alpha'(k) = \epsilon_\alpha + (X_\alpha(k), U(k)X_\alpha(k)) \quad (26)$$

and

$$X_\alpha'(k) = X_\alpha(k) + \sum_{\mu \neq \alpha}' \frac{(X_\mu(k), U(k)X_\alpha(k))}{\epsilon_\alpha - \epsilon_\mu} X_\mu(k) \quad (27)$$

$$= X_\alpha(k) + \lambda \sum_{\mu \neq \alpha}' \eta_{\mu\alpha}(k) X_\mu(k), \quad (28)$$

¹⁰ J. L. Magee, in *Comparative Effects of Radiation*, edited by M. Burton, J. S. Kirby-Smith, and J. L. Magee (John Wiley & Sons, Inc., New York, 1960), p. 130.

where λ stands for both λ_1 and λ_2 , and, obviously

$$\lambda\eta_{\mu\alpha}(k) \equiv \frac{(X_\mu(k), U(k)X_\alpha(k))}{\epsilon_\alpha - \epsilon_\mu}. \quad (29)$$

We now use Eq. (28) to construct the various N -particle wave functions φ_μ' , obeying the equation

$$H_0'\varphi_\mu' = E_\mu'\varphi_\mu', \quad (30)$$

where

$$H_0' = \sum_{j=1}^N H_0'(j).$$

In particular, we are interested in the new ground-state function

$$\varphi_0' = \prod_{j=1}^N X_0'(j) \quad (31)$$

and the function

$$\varphi_1'(k) = X_1'(k) \prod_{j \neq k} X_0'(j) \quad (32)$$

representing a state with the k th atom alone being in the first excited state.

It is now of interest to calculate the energy levels $E_1'(k)$ corresponding to the various $\varphi_1'(k)$. To do so, we use Eqs. (23) and (25). This calculation simplifies by virtue of (a) an assumed absence of a static atomic dipole moment, thus leading to $(X_{\alpha, z_k'} X_\alpha) = 0$; and (b) the identity of the N atoms so that $(X_\alpha(j), z'^2 X_\alpha(j))$ is independent of j . It can then be easily shown that

$$E_1'(k) = E_1 + (N-1)\epsilon_0 - e \sum_{j=1}^N \{r(V_0 + \lambda_1 jR + \lambda_2 j^2 R^2) + (N-1)\lambda_2 \sum_{s=1}^r \langle Z_s^2 \rangle_{00} + \lambda_2 \sum_{s=1}^r \langle Z_s^2 \rangle_{11}\}, \quad (33)$$

where

$$\langle Z_s^2 \rangle_{00} = (X_{0, z_s'^2} X_0), \quad \langle Z_s^2 \rangle_{11} = (X_{1, z_s'^2} X_1). \quad (34)$$

Since Eq. (33) is independent of k , we can conclude that the $\varphi_1'(k)$ form an N -fold degenerate set of wave functions with energy E_1' .

At this point we again introduce the coupling potential V from Eq. (4) and proceed to construct exciton wave packets and operators on the basis of Eqs. (30) and (31). This new wave packet $\zeta_r'(t)$ is related to $\zeta_r(t)$, to first order in λ by

$$\zeta_r'(t) = \zeta_r(t) + \lambda\mu_r(t) \quad (35)$$

and obeys the equation

$$\sum_m H_{rm}' \zeta_m' = \hbar i \frac{\partial \zeta_r'}{\partial t}, \quad (36)$$

where

$$H_{rm}' = (\varphi_1'(r), (H_0' + V)\varphi_1'(m)). \quad (37)$$

Similarly, the new acceleration matrix Q_{rm}' is related to Q_{rm} by

$$Q_{rm}' = Q_{rm} + \lambda q_{rm}. \quad (38)$$

The average acceleration of the wave packet in the presence of the electric field is, of course,

$$\langle a \rangle' = \sum_{rm} \zeta_r^{*'}(t) Q_{rm}' \zeta_m'(t). \quad (39)$$

We now use the fact, as shown in Eq. (19), that all elements of Q_{rm} are zero except Q_{11} and Q_{NN} . Since we wish to ignore the end effects and concentrate on the acceleration due to the electric field alone, we now assume that (a) The molecule is very large, $N \gg 1$. (b) The excitation originates at the center, i.e., at $(N+1)/2$.

It follows then that for a sufficiently small time interval t , $\zeta_1(t) \approx 0 \approx \zeta_N(t)$. We can, therefore, neglect Q_{rm} altogether, and the acceleration, to first order in λ becomes

$$\langle a \rangle' = \lambda \sum_{rm} \zeta_r^*(t) q_{rm} \zeta_m(t), \quad (40)$$

where $\zeta_r(t)$ is just the zero-field exciton amplitude constructed out of the $\sin[kr\pi/(N+1)]$ according to Eq. (11). To find (40) we use the fact that the matrix element H_{rm}' can be related to the zero field H_{rm} by

$$H_{rm}' = H_{rm} + \lambda h_{rm}. \quad (41)$$

It follows, by substituting (41) in (18) that, to first order in λ

$$Q_{rm}' = (1/\hbar) \sum_n (2n - m - r) [H_{rn} H_{nm} + \lambda (h_{rn} H_{nm} + H_{rn} h_{nm})]. \quad (42)$$

This means that q_{rm} is shown to be

$$q_{rm} = (1/\hbar) \sum_n (2n - m - r) (h_{rn} H_{nm} + h_{nm} H_{rn}), \quad (43)$$

where, of course, H_{rn} is given by Eq. (12). The use of this equation leads finally to

$$q_{rm} = \beta/\hbar \{ (m+2-r)(h_{r, m+1} - h_{r-1, m}) + (m-2-r)(h_{r, m-1} - h_{r+1, m}) \}. \quad (44)$$

The problem becomes now the determination of h_{rm} . First of all, from Eq. (37).

$$H_{rm}' = \epsilon_1' \delta_{rm} + V_{rm}' = (\epsilon_1 + \lambda b) \delta_{rm} + V_{rm}', \quad (45)$$

where b can be read off from (33).

We now evaluate V_{rm}' to first power in λ , using (28) in (32). It can be readily shown that V_{rm}' consists of the following sum:

$$V_{rm}' = V_{rm} + \lambda \left\{ \sum_{\sigma \neq 1} [\eta_{\sigma 1}(m) W_\sigma(r, m) + \eta_{\sigma 1}^*(r) W_\sigma^*(m, r)] + L_{rm} + L_{rm}^* \right\}, \quad (46)$$

where

$$W_\sigma(r, m) \equiv (\varphi_1(r), V X_\sigma(m) \prod_{j \neq m} X_0(j)) \quad (47)$$

and

$$L_{rm} = \sum'_{\sigma \neq 0} (\varphi_1(r), V X_1(m) \prod_{j \neq m} \eta_{\sigma 0}(j) X(j)). \quad (48)$$

Since σ is not zero in (48), L_{rm} vanishes for all r and m . As for $W_\sigma(r, m)$, the following statements hold:

(1) When $\sigma=0$, $W_0(r, m)$ is nonzero for all r and m because V couples the ground state of the molecule to every state in which any one atom is excited. The applied electric field generates, therefore, a kind of long-range coupling between two states with widely separated excited loci by causing transitions from one of these excited states to the ground state. Furthermore, $W_0(r, m)$ is independent of r and m as long as r is neither 1 nor N . As stated before, we are not concerned with end effects, and, therefore, ignore this latter case. This enables us to set $V_0(r, m) \equiv v_0$ for all r and m .

(2) For $\sigma \neq 0, 1$, $W_\sigma(r, m)$ is nonzero only for $m=r, r \pm 1$; i.e., the nearest neighbor coupling comes into play again. The value of $W_\sigma(r, m)$ depends only on σ and on $|r-m|$; hence,

$$W_\sigma(r, m) = \bar{\alpha}_\sigma \delta_{rm} + \bar{\beta}_\sigma (\delta_{m+1} + \delta_{m-1}). \quad (49)$$

We can now write Eq. (46) as follows:

$$\begin{aligned} V_{rm}' &= V_{rm} + \lambda \{ \eta_{01}(m) v_0 + \eta_{01}^*(r) v_0^* \\ &+ \sum'_{\sigma \neq 0, 1} \eta_{\sigma 1}(m) [\bar{\alpha}_\sigma \delta_{rm} + \bar{\beta}_\sigma (\delta_{m+1} + \delta_{m-1})] \\ &+ \sum'_{\sigma \neq 0, 1} \eta_{\sigma 1}^*(r) [\bar{\alpha}_\sigma^* \delta_{rm} + \bar{\beta}_\sigma^* (\delta_{m+1} + \delta_{m-1})] \}. \end{aligned} \quad (50)$$

Equation (50) combined with (41) and (45) enables us now to express λh_{rm} through the formula

$$\lambda h_{rm} = \lambda \delta_{rm} b + \lambda [F(m) + F(r)^*], \quad (51)$$

where

$$\lambda F(m) = \lambda \sum'_{\sigma \neq 0, 1} \eta_{\sigma 1}(m) [\bar{\alpha}_\sigma \delta_{rm} + \bar{\beta}_\sigma (\delta_{m+1} + \delta_{m-1})] + v_0 \eta_{01}(m). \quad (52)$$

We must now evaluate $\lambda \eta_{\sigma \alpha}$, in particular $(X_\sigma, U X_\alpha)$. It follows from Eq. (23) that, for $\sigma \neq \alpha$,

$$(X_\sigma(k), U(k) X_\alpha(k)) = -e(\lambda_1 + 2kR\lambda_2) Z_{\sigma\alpha} - e\lambda_2 Z_{\sigma\alpha}^2, \quad (53)$$

where

$$Z_{\sigma\alpha} = \sum_{s=1}^r \langle Z_s \rangle_{\sigma\alpha}, \quad Z_{\sigma\alpha}^2 = \sum_{s=1}^r \langle Z_s^2 \rangle_{\sigma\alpha}, \quad (54)$$

using the notation of (34). It is now useful to define two new symbols $\lambda \gamma_{\sigma\alpha}$ and $\omega_{\sigma\alpha}$ by

$$\begin{aligned} \lambda \gamma_{\sigma\alpha} &\equiv -e(\lambda_1 Z_{\sigma\alpha} + \lambda_2 Z_{\sigma\alpha}^2) (\epsilon_\alpha - \epsilon_\sigma)^{-1}, \\ \omega_{\sigma\alpha} &\equiv -2eRZ_{\sigma\alpha} (\epsilon_\alpha - \epsilon_\sigma)^{-1}. \end{aligned} \quad (55)$$

This enables one now to write in Eq. (52)

$$\begin{aligned} \lambda F(m) &= \sum'_{\sigma \neq 0, 1} (\lambda_1 \gamma_{\sigma 1} + \lambda_2 m \omega_{\sigma 1}) [\bar{\alpha}_\sigma \delta_{rm} + \bar{\beta}_\sigma (\delta_{m+1} \\ &+ \delta_{m-1})] + v_0 (\lambda_1 \gamma_{01} + \lambda_2 m \omega_{01}). \end{aligned} \quad (56)$$

Let us now combine terms. Define

$$A_1 \equiv b + \sum'_{\sigma \neq 0, 1} (\bar{\alpha}_\sigma \gamma_{\sigma 1} + \bar{\alpha}_\sigma^* \gamma_{\sigma 1}^*),$$

$$8A_2 \equiv \sum'_{\sigma \neq 0, 1} (\bar{\alpha}_\sigma \omega_{\sigma 1} + \bar{\alpha}_\sigma^* \omega_{\sigma 1}^*),$$

$$B_1 \equiv \sum'_{\sigma \neq 0, 1} (\gamma_{\sigma 1} \bar{\beta}_\sigma + \gamma_{\sigma 1}^* \bar{\beta}_\sigma^*), \quad (57)$$

$$B_2 \equiv \sum'_{\sigma \neq 0, 1} \omega_{\sigma 1} \bar{\beta}_\sigma,$$

$$C_1 \equiv v_0 \gamma_{01} + v_0^* \gamma_{01}^*,$$

$$C_2 \equiv v_0 \omega_{01}.$$

It follows from (51), (56), and (57) that

$$\begin{aligned} \lambda h_{rm} &= \delta_{rm} [\lambda_1 A_1 + \lambda_2 8m A_2] \\ &+ (\delta_{rm+1} + \delta_{rm-1}) [\lambda_1 B_1 + \lambda_2 m B_2 + \lambda_2 r B_2^*] \\ &+ \lambda_1 C_1 + \lambda_2 m C_2 + r C_2^* \lambda_2, \end{aligned} \quad (58)$$

where A_1, A_2, B_1 , and C_1 are real.

We can now evaluate q_{rm} by introducing (58) into (44). It is immediately obvious that only the λ_2 terms survive. In particular:

$$\lambda q_{rr} = \frac{4\beta}{\hbar} \lambda_2 \Re(B_2 + C_2), \quad (59)$$

$$\lambda q_{r+1} = \lambda q_{r+1r} = \frac{8\beta}{\hbar} \lambda_2 \Re(A_2 + C_2).$$

All other $q_{rm} = (8\beta\lambda_2/\hbar) \Re(C_2)$, where neither r nor m take on the values 1 or N . $\Re(y)$ means the real part of y .

We now introduce (59) into (40) and find the following expression for the acceleration:

$$\begin{aligned} \langle a \rangle' &= \frac{4\beta\lambda_2}{\hbar} \Re \{ (B_2 + C_2) \sum_r \zeta_r^* \zeta_r \\ &+ 2(A_2 + C_2) \sum_r \zeta_r^* (\zeta_{r+1} + \zeta_{r-1}) \\ &+ 2C_2 \sum_r \zeta_r^* \sum_{m \neq r, r \pm 1} \zeta_m \}. \end{aligned} \quad (60)$$

We shall now prove two theorems which greatly simplify the above expression.

Theorem 1. $\sum_r \zeta_r^* (\zeta_{r+1} + \zeta_{r-1}) = 0$ for an exciton wave packet which originates at the center of the molecule, i.e., at $(N+1)/2$.

Proof. It follows from Eqs. (8) and (12) that

$$\hbar i (\partial \zeta_r / \partial t) = \alpha' \zeta_r + \beta (\zeta_{r+1} + \zeta_{r-1}), \quad (61)$$

where $\alpha' = \epsilon_1 + \alpha$. Hence,

$$\sum_r \zeta_r^* (\zeta_{r+1} + \zeta_{r-1}) = -\frac{\alpha'}{\beta} + \frac{\hbar i}{\beta} \sum_r \zeta_r^* \frac{\partial \zeta_r}{\partial t}. \quad (62)$$

We now use Eqs. (11) and (13) to evaluate $\partial \zeta_r / \partial t$.

$$\frac{\partial \zeta_r}{\partial t} = -\frac{i\alpha'}{\hbar} \zeta_r - \frac{2i\beta}{\hbar} \sum_k g_r^*(k) g_0^{(k)} \cos \frac{k\pi}{N+1} e^{-(i/\hbar) E_k t} \quad (63)$$

where the subscript zero in $g_0^{(k)}$ indicates $(N+1)/2$, i.e., the molecular center. Equation (62) now becomes

$$\sum_r \zeta_r^* (\zeta_{r+1} + \zeta_{r-1}) = 2 \sum_{rjk} g_r^{*(k)} g_0^{(k)} \cos \frac{k\pi}{N+1} \times g_r^{(j)} g_0^{*(j)} e^{(-i/\hbar)t(E_{k'} - E_{j'})}, \quad (64)$$

which, by virtue of $\sum_r g_r^{*(k)} g_r^{(j)} = \delta_{kj}$, reduces to

$$\sum_r \zeta_r^* (\zeta_{r+1} + \zeta_{r-1}) = 2 \sum_k |g_0^{(k)}|^2 \cos \frac{k\pi}{N+1}. \quad (65)$$

This sum can easily be shown to be zero by replacing $|g_0^{(k)}|^2$ by its value $[2/(N+1)][\sin(k\pi/2)]^2$, thus eliminating all even values of k , and then comparing $\cos[k\pi/(N+1)]$ with its symmetric term $\cos[\pi - k\pi/(N+1)]$.

Theorem 2. Assuming $\zeta_1(t) \approx 0 \approx \zeta_N(t)$, the double sum $\sum_{kj} \zeta_k^*(t) \zeta_j(k)$ is time-independent.

Proof. Consider

$$G \equiv \frac{d}{dt} \sum_{k,j} \zeta_k^*(t) \zeta_j(t). \quad (66)$$

Again we use Eqs. (8) and (12), and find

$$G = \frac{\beta}{\hbar i} \sum_{kj} [\zeta_k^* (\zeta_{j+1} + \zeta_{j-1}) - \zeta_j (\zeta_{k+1}^* + \zeta_{k-1}^*)]. \quad (67)$$

Now

$$\begin{aligned} \sum_k (\zeta_{k+1} + \zeta_{k-1}) &= \sum_{k=2}^N \zeta_k + \sum_{k=2}^{N-1} \zeta_k \\ &= 2 \sum_{k=2}^{N-1} \zeta_k, \end{aligned} \quad (68)$$

where we use the assumption of the theorem. The consequence $G=0$ follows immediately.

Since $G=0$, we can evaluate $\sum_{kj} \zeta_k^*(t) \zeta_j(t)$ at $t=0$. But at $t=0$, $\zeta_m(t) = \delta_{m0}$. Hence,

$$\sum_{kj} \zeta_k^*(t) \zeta_j(t) = 1. \quad (69)$$

It follows from these two theorems that

$$\sum_k \zeta_k^* \sum_{j \neq k, k \pm 1} \zeta_j = 0, \quad (70)$$

since $\sum_k \zeta_k^* \zeta_k = 1$. We then conclude in (60) that

$$\langle a \rangle' = (4\beta\lambda_2/\hbar) \Re(B_2 + C_2), \quad (71)$$

i.e., the exciton acquires a constant acceleration due to the λ_2 part of the electric field. Since $B_2 + C_2$ is a term linear in the various atomic dipole moments $Z_{\sigma\alpha}$, and λ_2 is the (constant) gradient of the electric field, we conclude that the exciton wave packet behaves like a classical electric dipole, with a moment which is a linear combination of the various atomic moments.

CONCLUSIONS

In principle then an electric field can be viewed as a device for guiding an exciton wave packet in a molecule or crystal. On the other hand, since the acceleration depends on the field gradient which should be significant over atomic dimensions, the actual utility of an external field appears dubious. But there still exists the possibility of accomplishing the desired effect by means of intense *local* fields produced by microscopic charge distributions.

There are a number of obvious questions to which answers should be sought: (1) What is the order of magnitude of the electric dipole moment associated with an exciton? (2) How does the electric field affect the width of the wave packet? (3) What is the influence of phonon coupling on the acceleration of excitons? (4) Is there a corresponding effect, due to an external magnetic field?