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Derivation of Urbach's rule in terms of exciton interband scattering by optical phonons

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The Urbach rule is derived by treating the exciton interband scattering by optical phonons in the dipole approximation in terms of a Green's-function theory. Our results contain in the limit of low phonon fields the quadratic Stark effect, but show that for typical microfields of thermal phonons in polar semiconductors the Urbach rule is caused by the broadening of the exciton level due to tunneling ionization transitions as proposed by Dow and Redfield. Furthermore, an analytic treatment of the electroabsorption model of Dow and Redfield is developed.

I. INTRODUCTION

For ionic semiconductors the excitonic absorption edge has been found[1-3] to vary exponentially according to the Urbach-Martienssen rule $\alpha = \alpha_0 \times \exp[\sigma(\omega - \omega_0)/k_B T^*]$, where α_0, σ, and ω_0 are material constants and T^* is given by $k_B T^* = (\omega_L/2)\coth(\omega_L/2k_BT)$. Here, ω_L is the frequency of the longitudinal optical phonons and $\hbar = 1$ is used. Theoretical explanations of this rule have been given in terms of intraband[4] and interband[5-7] exciton scattering processes by acoustical[4] and optical[5-7] phonons. Because the dominant contributions are due to multiphonon processes, Dexter[6] and Dow and Redfield[7] used the concept of long-wavelength electrical microfields, which ionize the excitons. Recent measurements of the electroabsorption by Mohler and Thomas[8] confirmed that the Urbach tail in pure ionic semiconductors is indeed caused by the ionization of excitons in the microfields of optical phonons. Here, we use a Green's-function technique (similar to that of Sumi and Toyozawa[4]) to treat the exciton ionization by optical phonons in the dipole approximation.

Within this approximation the influence of the phonons on the exciton is that of a homogeneous microfield. For this limit an exact formal solution is found and an analytic treatment of the electroabsorption model of Dow and Redfield is developed. An approximate description of the Urbach tail is obtained by calculating the complex self-energy of the lowest exciton state.

The Hamiltonian of an exciton coupled to optical phonons is given by

$$H = E_g - \frac{\nabla_{\vec{r}}^2}{2m} - \frac{\nabla_{\vec{R}}^2}{2M} + V(r) + \sum_{\vec{q}} \omega_L b_{\vec{q}}^\dagger b_{\vec{q}} + i \sum_{\vec{q}} M_q (b_{-\vec{q}}^\dagger - b_{\vec{q}}) \left[\exp\left(i \frac{m_h}{M} \vec{q}\cdot\vec{r} \right) - \exp\left(-i \frac{m_e}{M} \vec{q}\cdot\vec{r} \right) \right] e^{i\vec{q}\cdot\vec{R}}, \tag{1}$$

where E_g is the band gap, $\vec{r}$ and $\vec{R}$ are the relative and center-of-mass coordinates of the exciton, and m_e and m_h are the effective masses of the electron and hole, respectively. The masses m and M are given by $m = m_e m_h/M$ and $M = m_e + m_h$. $V(r)$ is the electron-hole interaction potential. M_q is the Fröhlich coupling

$$M_q^2 = 2\pi e^2 \omega_L / (V \epsilon^* q^2),$$

where $1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_0$. $b_{\vec{q}}$ and $b_{\vec{q}}^\dagger$ are the optical phonon operators. The center-of-mass motion can be eliminated by a canonical transformation $H' = e^{-iS} H e^{iS}$ with $S = (\vec{K} - \sum_{\vec{q}} \vec{q} b_{\vec{q}}^\dagger b_{\vec{q}})\vec{R}$, where $\vec{K}$ is the total momentum of the system. The resulting transformed Hamiltonian is

$$H' = E_g - \frac{\nabla_{\vec{r}}^2}{2m} + V(r) + \sum_{\vec{q}} \omega_L b_{\vec{q}}^\dagger b_{\vec{q}} + i \sum_{\vec{q}} M_q (b_{-\vec{q}}^\dagger - b_{\vec{q}}) \left[\exp\left(i \frac{m_h}{M} \vec{q}\cdot\vec{r} \right) - \exp\left(-i \frac{m_e}{M} \vec{q}\cdot\vec{r} \right) \right] + \frac{1}{2M} \left(\vec{K} - \sum_{\vec{q}} \vec{q} b_{\vec{q}}^\dagger b_{\vec{q}} \right)^2. \tag{2}$$

The last term does not contribute to the interband scattering and therefore is omitted. Because only long-wavelength phonons can ionize the excitons, the dipole approximation can be used:

$$H' \to E_g - \frac{\nabla_{\vec{r}}^2}{2m} + V(r) + \sum_{\vec{q}} \omega_L b_{\vec{q}}^\dagger b_{\vec{q}} + \sum_{q<q_c} \left(\frac{2\pi e^2 \omega_L}{V \epsilon^*} \right)^{1/2} (b_{\vec{q}} + b_{\vec{q}}^\dagger) \vec{e}_{\vec{q}} \cdot \vec{r}. \tag{3}$$

Here, q_c is a cutoff wave number which has to be determined self-consistently.[7,8] $\vec{e}_{\vec{q}} = \vec{q}/q$ is the unit vector in the direction of $\vec{q}$. In this approximation the influence of the phonons on the exciton is that of a homogeneous electric microfield $\vec{F}$, which is given by

$$\vec{F} = \sum_{q<q_c} \left(\frac{2\pi\omega_L}{V\epsilon^*}\right)^{1/2} (b_{\vec{q}} + b_{\vec{q}}^\dagger)\vec{e}_{\vec{q}} . \tag{4}$$

This microfield can be seen as an interaction mode in the sense of Toyozawa's theory.[4,5] If the microfield $\vec{F}$ is treated classically, the Hamiltonian (3) is equivalent to the Dow-Redfield model.[7]

In the following chapters we calculate the excitonic absorption from the Hamiltonian (3) in two different approaches. For the Dow-Redfield model we develop an analytic expression which is in quantitative agreement with the numerical results of Ref. 7. Furthermore, we show that a good description of the Urbach tail can be obtained by calculating the renormalized Green's function of the lowest exciton state.

II. OPTICAL DIELECTRIC FUNCTION OF AN EXCITONIC COUPLED TO OPTICAL PHONONS

In the framework of the linear response theory the optical dielectric function is given by

$$\epsilon(\omega) = \epsilon_\infty - \frac{4\pi e^2 |M_{cv}|^2}{m_0^2\omega^2} \sum_{n,m} \varphi_n(r=0)\varphi_m^*(r=0)\langle G_{nm}(\omega)\rangle_{\rm ph} + \text{H.c.}(\omega \to -\omega), \tag{5}$$

where M_{cv} is the optical matrix element of the momentum operator. m_0 is the free-electron mass and ϵ_∞ is the background dielectric constant. $\varphi_n(r)$ are the wave functions of the relative motion of the exciton, the quantum number n runs over all bound and continuum states. $G_{nm}(\omega)$ is the Fourier transform of the retarded exciton Green's function

$$G_{nm}(t) = -i\theta(t)\langle a_n(t)a_m^\dagger(0)\rangle . \tag{6}$$

$\langle\ \rangle_{\rm ph}$ denotes the thermal average for the phonons. H.c.$(\omega \to -\omega)$ indicates the nonresonant part which is obtained from the preceding term by taking its Hermitian conjugate and changing the sign of the frequency. This small term is neglected in the further calculations. For the Hamiltonian (3) the retarded exciton Green's functions obey the equation

$$G_{nm}(\omega) = G_{nn}^0(\omega)\left(\delta_{nm} + e\vec{F}\cdot\sum_l \vec{r}_{nl} G_{lm}(\omega)\right). \tag{7}$$

Equation (7) can be diagonalized by the eigenfunctions of its homogeneous part, i.e.,

$$(E_\nu - E_n)U_\nu(n) = e\vec{F}\cdot\sum_l \vec{r}_{nl} U_\nu(l), \tag{8}$$

which yields

$$G_{nm}(\omega) = \sum_\nu \frac{U_\nu(n)U_\nu^*(m)}{\omega - E_\nu + i\epsilon} . \tag{9}$$

Inserting (9) into (5) yields

$$\epsilon(\omega) = \epsilon_\infty - \frac{4\pi e^2|M_{cv}|^2}{m_0^2\omega^2}\left\langle \sum_\nu \frac{|U_\nu(r=0)|^2}{\omega - E_\nu + i\epsilon}\right\rangle_{\rm ph} , \tag{10}$$

where the completeness relation $\sum_n \varphi_n(r=0)U_\nu(n) = U_\nu(r=0)$ has been used. Equations (8) and (10) are the basic equations of the Dow-Redfield theory. Alternatively, one can solve directly the Green's-function equations (7) and use Eq. (5) for calculating the absorption spectrum. Both approaches will be pursued in the following two sections.

III. ANALYTIC TREATMENT OF THE EXCITONIC ELECTROABSORPTION

As has been shown in Sec. II the problem of an exciton in the electric microfields of optical phonons can be reduced in the dipole approximation to the study of an exciton in an effective homogeneous electric field [see Eqs. (8) and (10)]. The resulting absorption coefficient of the exciton in the effective homogeneous field has to be averaged finally over the distribution of the microfields.

The absorption coefficient is obtained from the imaginary part of the dielectric function (10) as

$$\alpha(\omega) = \frac{4\pi^2 e^2|M_{cv}|^2}{m_0^2 n(\omega) c\omega} \frac{2}{E_x a_x^3} \langle |U(0)|^2 S(E)\rangle_{\rm ph}. \tag{11}$$

Here, $n(\omega)$ is the index of refraction and E_x and a_x are the Rydberg energy and Bohr radius of the unperturbed exciton. The factor 2 stems from the spin summation. The dimensionless optical density of states $|U(0)|^2 S(E)$ is defined as

$$|U(0)|^2 S(E) = \frac{a_x^3}{2}\sum_\nu |U_\nu(0)|^2 \delta\left(E - \frac{E_\nu - E_g}{E_x}\right), \tag{12}$$

with $E = (\omega - E_g)/E_x$.

In the coordinate space the Wannier equation (8) for the relative motion of an electron-hole pair in a homogeneous electric field is

$$\left(-\Delta - \frac{2}{r} + fz\right)U_\nu(\vec{r}) = EU_\nu(\vec{r}), \tag{13}$$

where $E = (E_\nu - E_g)/E_x$. The dimensionless field strength is given by $f = eFa_x/E_x$. Equation (13) can be separated[9] in parabolic coordinates $\zeta = r + z$, $\eta = r - z$, and $\varphi = \arctan(y/x)$ with the ansatz

$$U_\nu(\vec{r}) = \chi_1(\zeta)\chi_2(\eta)\exp(im\varphi)/\sqrt{\zeta\eta} , \tag{14}$$

where m is the angular quantum number. The equations for χ_1 and χ_2 are

$$\chi_1'' + \left(\frac{1-m^2}{4\zeta^2} + \frac{\beta_1}{\zeta} + \frac{E}{4} - \frac{f\zeta}{8}\right)\chi_1 = 0 \tag{15a}$$

$$\chi_2'' + \left(\frac{1-m^2}{4\eta^2} + \frac{1-\beta_1}{\eta} + \frac{E}{4} + \frac{f\eta}{8}\right)\chi_2 = 0. \quad (15b)$$

Here, β_1 is the parabolic quantum number. Equation (15a) has bound-state solutions, while the potential of Eq. (15b) has a barrier which separates the Coulomb well for small η and the linear field potential at large values of η. The asymptotic form of the exciton wave function for $r \to 0$ is proportional $(x^2+y^2)^{|m|}$, so that only $m=0$ contributes to $\alpha(\omega)$. The asymptotic form of χ_2 is given by

$$\chi_2 \to \frac{A}{\left(\frac{E}{f} + \frac{\eta}{2}\right)^{1/4}} \sin\left[\tfrac{2}{3} f^{1/2}\left(\frac{E}{f} + \frac{\eta}{2}\right)^{3/2} + \delta\right]. \quad (16)$$

Using the asymptotic behavior of χ_1 and χ_2 one gets for the optical density of states the following expression:

$$|U(0)|^2 S(E) = \sum_{\beta_1} \left(\pi^2 f^{1/2} A^2 \int_0^\infty \frac{d\zeta}{\zeta} \chi_1^2(\zeta)\right)^{-1}. \quad (17)$$

The parabolic quantum numbers β_1 can be obtained by using the ordinary WKB method, which yields the following quantization rule (with $m=0$):

$$\int_0^a d\zeta \left(\frac{1}{4\zeta^2} + \frac{\beta_1}{\zeta} + \frac{E}{4} - \frac{f\zeta}{8}\right)^{1/2} = (n_1 + \tfrac{1}{2})\pi, \quad (18)$$

where a is the classical turning point of Eq. (15a) and n_1 is the number of nodes of χ_1. Evaluating the integral approximately in zeroth order of the centrifugal barrier and taking into account only the first two leading terms of the resulting elliptic integrals, one obtains

$$(n_1 + \tfrac{1}{2})\pi = \frac{\pi}{4y}\left(\tfrac{3}{4}y^4 - \frac{\epsilon^2}{4} + \frac{\epsilon^2}{2}y^2\right), \quad (19)$$

where for simplicity a new scale has been introduced: $\epsilon = E f^{-2/3}$, $\alpha_1 = \beta_1 f^{-1/3}$, and $y = (\epsilon^2 + 8\alpha_1)^{1/4}$. Equation (19) is a fourth-order polynomial in y which has for negative energy ($\epsilon \leq 0$) the following solution:

$$\alpha_1 = (\epsilon^2/8)(4x^4/9 - 1),$$

with

$$x = \frac{z^{1/2}}{2} + \left(\frac{z}{4} - \frac{(z-1)}{2} + \left(\frac{\delta}{2}\right)z^{-1/2}\right)^{1/2}$$

$$z = -\frac{p}{|p|}\frac{4\sqrt{2}}{3}\sinh\left\{\frac{1}{3}\left[\operatorname{arc\,sinh}\left(\frac{27|p|}{16\sqrt{2}}\right)\right]\right\} + \frac{2}{3}$$

$$p = \frac{28}{27} - \frac{\delta^2}{2}$$

and

$$\delta = \sqrt{96}\,(n_1 + \tfrac{1}{2})|\epsilon|^{-3/2}. \quad (20)$$

The eigenvalues α_1 according to Eq. (20) are plotted in Fig. 1 as a function of the reduced energy ϵ for the first three eigenfunctions χ_1 (with $n_1 = 0$, 1, and 2). These analytical results are in good agreement with the numerical values of Ref. 10. For large negative energies the eigenvalues approach those of the unperturbed hydrogen problem, i.e.,

$$\alpha_1 = \sqrt{-\epsilon}\,(n_1 + \tfrac{1}{2}). \quad (21)$$

As a next step we determine the normalization integral

$$J = \int_0^\infty d\zeta\, \frac{\chi_1^2(\zeta)}{\zeta},$$

which appears in the optical density of states [see Eq. (17)].

Because Eq. (15a) has only bound-state solutions which are not strongly influenced by the electric field, we make for the wave function χ_1 an ansatz which has the form of the unperturbed hydrogen ground-state wave function:

$$\chi_1(\zeta) = \sqrt{\zeta}/\exp(\sqrt{-E}\,\zeta/2), \quad (22)$$

where $\sqrt{-E} = \partial\beta_1/\partial n_1$, as can be seen from Eq. (21). Renormalization effects due to the electric field are taken into account by calculating the derivative $\partial\beta_1/\partial n_1$ according to Eq. (20). In this approximation the normalization integral reduces to

$$J = \left(\frac{\partial\alpha_1}{\partial n_1}\right)^{-1} f^{-1/3}. \quad (23)$$

The resulting inverse normalization integral J^{-1} is shown in Fig. 2 as a function of the reduced

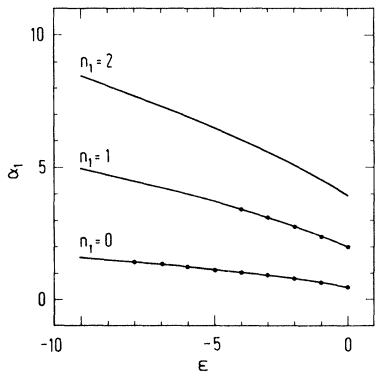

FIG. 1. Parabolic eigenvalue α_1 as a function of the reduced energy $\epsilon = E/f^{2/3}$ for 0, 1, and 2 nodes of the eigenfunction χ_1. The dots are the numerical results of Ref. 10.

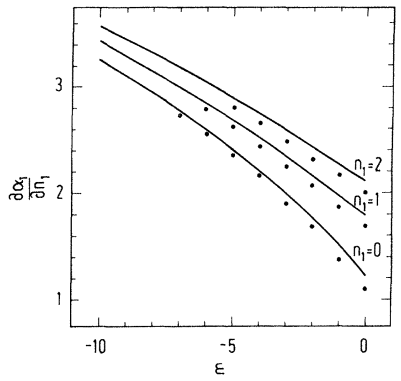

FIG. 2. Inverse normalization constant of χ_1 as a function of the reduced energy $\epsilon = E/f^{2/3}$ for 0, 1, and 2 nodes of the eigenfunction χ_1. The dots are the numerical results of Ref. 10.

energy for $n_1 = 0$, 1, and 2, respectively. Considering the simplicity of the approximation for χ_1 the result compares very favorably with the numerical values of Ref. 10.

Finally, the proportionality constant A in the asymptotic form of χ_2 [see Eq. (16)] has to be evaluated. Because the classical turning points of Eq. (15b) can become complex, one has to use instead of the ordinary WKB method a generalized one, which has been developed by Miller and Good.[11,12] In this method the wave equation

$$\chi_2'' + Q^2\chi_2 = 0 \tag{24}$$

is solved with the ansatz

$$\chi_2(\eta) = \phi(s(\eta))/\sqrt{s'(\eta)}, \tag{25}$$

where $\phi(s)$ fulfills the equation

$$\phi''(s) + P^2(s)\phi(s) = 0. \tag{26}$$

In the lowest order one obtains for the function $s(\eta)$ the implicit relation

$$\int_{s_0}^{s(\eta)} P(\lambda)d\lambda = \int_{\eta_0}^{\eta} Q(\xi)d\xi, \tag{27}$$

which reduces to the ordinary WKB result for the choice $P^2(\lambda) = 1$. The function $Q^2(\eta)$ is divided in three regions: the Coulomb well for small arguments, an intermediate quadratic potential barrier, and a linear decreasing function for large values of η. Using the asymptotic forms of these potential sections, exactly solvable model Hamiltonians for $\phi(s)$ are constructed with the following choices: $P^2(s) = 1/s + 1/4s^2$ in region I, $P^2(s) = H + s^2$ in region II, and $P^2 = s$ in region III, respectively. The resulting eigenfunctions $\phi(s)$ have to be continuous at the classical turning points η_1 and η_2 which divide the different regions. This procedure yields the following value for the coefficient A^2 of Eq. (17):

$$A^2 = \frac{2R^2}{\pi f^{1/2}}, \tag{28}$$

where R^2 is, according to Refs. 11 and 12, given by

$$R^2 = 1 + 2e^{-\pi H} - 2e^{-\pi H}(1+e^{\pi H})^{1/2}\sin(2\varphi - \theta), \tag{29}$$

with

$$H = \frac{2}{\pi} i \int_{\eta_1}^{\eta_2} Q(\eta)d\eta, \tag{30}$$

$$\varphi = \mathrm{Re}\int_0^{\eta_1} Q(\eta)d\eta - \frac{\pi}{4}, \tag{31}$$

and

$$\theta = \arg\Gamma(\tfrac{1}{2} + \tfrac{1}{2}iH) + \frac{H}{2}\left(1 - \ln\frac{|H|}{2}\right), \tag{32}$$

where $\Gamma(z)$ is the gamma function $\Gamma(z) = \int_0^\infty t^{z-1} \times e^{-t}dt$. Combining Eqs. (17), (20), (23), and (28)-(32), the final result for the optical density of states is

$$|U(0)|^2 S(E) = \sum_{\eta_1} \frac{f^{1/3}}{4\pi}\frac{\partial\alpha_1}{\partial n_1} \times \frac{e^{\pi H}}{1 + \frac{1}{2}e^{\pi H} - (1+e^{\pi H})^{1/2}\sin(2\varphi - \theta)}. \tag{33}$$

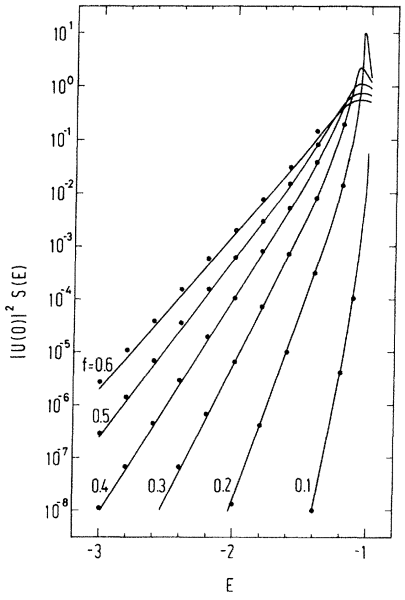

FIG. 3. Absorption edge of the exciton as a function of the energy for various field strengths. The dots are the numerical results of Ref. 7.

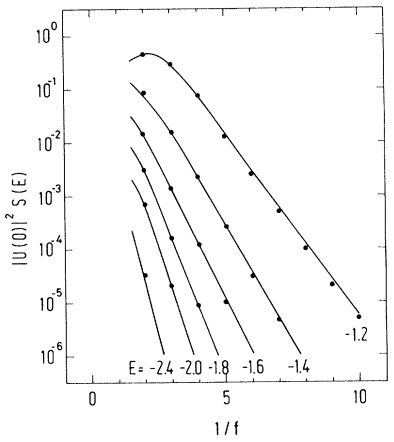

FIG. 4. Absorption edge of the exciton as a function of the inverse field strength for various energies. The dots are the numerical results of Ref. 7.

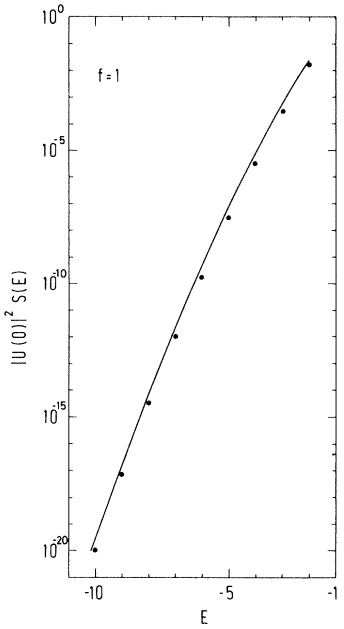

FIG. 5. Absorption edge of the exciton, neglecting the resonance, as a function of the energy for a field strength $f=1$. The dots are the numerical results of Ref. 10.

The phase integrals of Eqs. (30) and (31) are again evaluated in lowest order of the centrifugal barrier. The optical density of states of Eq. (33) consists of the Franz-Keldysh-type function[13] $e^{\pi H}$, which approaches asymptotically for large fields the form $\exp(-\frac{4}{3}|\epsilon|^{3/2})$. The excitonic enhancement factor, which is given by the numerator of Eq. (33), peaks at an energy close to the unperturbed $1s$ exciton level. Therefore, the resulting line shape varies nearly exponentially as a function of $|E|/f$ as can be seen in Figs. 3 and 4, where only the contribution of $n_1=0$ is taken into account. Again our results are compared with the numerical values of Refs. 7 and 10. For very large fields $f \geq 1$ the results approach the Franz-Keldysh line shape (see Fig. 5). The results of Figs. 1–5 demonstrate that the electroabsorption of the exciton can be calculated for *all* field strengths by the generalized WKB methods, i.e., this method is not limited to small fields $f \leq 0.1$, as has been claimed in Ref. 10.

The Urbach tail of the excitonic absorption is, according to Eq. (11), obtained by averaging the optical density of states over the microfield distribution,[7] i.e.,

$$\langle |U(0)|^2 S(E)\rangle_{\rm ph} = (\tfrac{2}{3}\pi\overline{F}^2)^{-3/2} 4\pi \times \int_0^\infty dF\, F^2 \exp\left(-\frac{3F^2}{2\overline{F}^2}\right) |U(0)|^2 S(E)\,, \tag{34}$$

where

$$\overline{F}^2 = \langle F^2\rangle_{\rm ph} = \sum_{q<q_c} \frac{4\pi}{V\epsilon^*} k_B T^* = \frac{2}{3\pi\epsilon^*} q_c^3 k_B T^*. \tag{35}$$

The critical wave number q_c is determined in such a way[7] that the localization energy of an electron in the valley of a sine wave does not yet suppress the tunneling out of the Coulomb potential well. This requirement yields a field-dependent critical wave number

$$q_c^3 \simeq 2me\pi^2\overline{F}\,. \tag{36}$$

Combining Eqs. (35) and (36) finally yields

$$\overline{F} = \frac{4\pi}{3}\frac{me}{e^*} k_B T^*. \tag{37}$$

The results of the thermally averaged optical density (34) are shown in Figs. 6 and 7 as a function of energy and the inverse mean field $\overline{f}^{-1}$ with $\overline{f} = e\overline{F}a_x/E_x$. Again, a nearly exponential energy dependence is obtained. The spectra are in close agreement with the results of Dow and Redfield.[7]

IV. COMPLEX SELF-ENERGY OF THE EXCITON IN THE PHONON FIELD

In this section we develop an approximate description of the excitonic absorption, which demonstrates that the Urbach tail can be obtained by calculating the complex self-energy of the lowest exciton state. It will be shown that the main effect is the broadening of the $1s$ exciton level due to tunneling transitions into the ionization continuum.

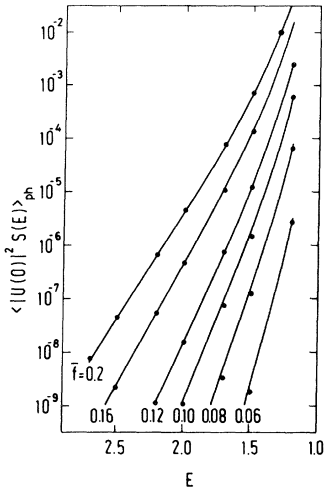

FIG. 6. Averaged absorption of the exciton as a function of the energy for various average field strengths. The dots are the numerical results of Ref. 7.

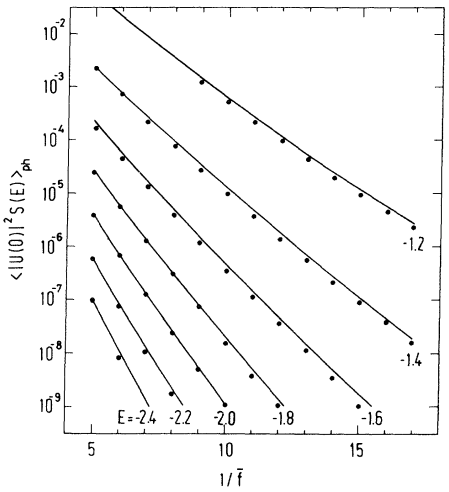

FIG. 7. Averaged absorption of the exciton as a function of the inverse average field strength for various energies. The dots are the numerical results of Ref. 7.

We calculate the dielectric function (5) by solving the Dyson equation (7) directly. First, we note that the nondiagonal elements of G_{nm} are of odd power in the phonon microfields and therefore vanish when the thermal phonon average is taken. As has already been shown in Ref. 7 the main contribution to the Urbach tail stems from the exciton ground state. The contribution of the ionization continuum, e.g., is about three orders of magnitude smaller than that of the exciton ground state.

The Dyson equation for the exciton ground-state Green's function G_{00} is

$$G_{00}(\omega)=G^0_{00}(\omega)\left(1+e\vec{F}\sum_{\vec{k}}\vec{r}_{0\vec{k}}G_{\vec{k}0}(\omega)\right), \tag{38a}$$

$$G_{\vec{k}0}(\omega)=G^0_{\vec{k}\vec{k}}(\omega)e\vec{F}\left(\vec{r}_{\vec{k}0}G_{00}(\omega)+\sum_{\vec{k}'}\vec{r}_{\vec{k}\vec{k}'}G_{\vec{k}'0}(\omega)\right), \tag{38b}$$

where only interband transitions into the ionization continuum (labeled by the wave vector $\vec{k}$) are taken into account. Expanding $G_{\vec{k}0}$ in terms of the Franz-Keldysh-type[9] eigenfunctions of the homogeneous part of Eq. (38b), i.e.,

$$(E_\nu-E_k)U_\nu(\vec{k})=e\vec{F}\sum_{\vec{k}'}\vec{r}_{\vec{k}\vec{k}'}U_\nu(\vec{k}'), \tag{39}$$

we obtain

$$G_{\vec{k}0}(\omega)=G^0_{00}e\vec{F}\cdot\sum_{\nu,\vec{k}'}\vec{r}_{\vec{k}'0}\frac{U_\nu(\vec{k})U^*_\nu(\vec{k}')}{\omega-E_\nu+i\epsilon}, \tag{40}$$

which yields after insertion into Eq. (38a) the exciton ground-state Green's function

$$G_{00}(\omega)=[\omega-E_0-\Sigma(\omega)]^{-1}, \tag{41}$$

where the self-energy is determined by the dynamical complex exciton polarization, i.e.,

$$\Sigma(\omega)=\sum_\nu\frac{e^2|\langle 0|\vec{F}\cdot\vec{r}|\nu\rangle|^2}{(\omega-E_\nu+i\epsilon)}. \tag{42}$$

The self-energy is explicitly proportional to the square of the phonon field $\vec{F}$. A further implicit dependence of $\vec{F}$ stems from the renormalized continuum states $U_\nu(\vec{k})$. These functions are approximately Airy functions due to the acceleration of the electron by the phonon field. Since $\Sigma(\omega)$ contains the matrix element $\langle 0|\vec{F}\cdot\vec{r}|\nu\rangle$ it is related to the probability for finding a continuum electron near the hole (origin of the relative motion).

The optical density of states is given by

$$|U(0)|^2S(E)=-\frac{E_*}{\pi^2}\frac{\mathrm{Im}\Sigma(\omega)}{[\omega-E_0-\mathrm{Re}\Sigma(\omega)]^2+[\mathrm{Im}\Sigma(\omega)]^2}. \tag{43}$$

For very small fields and frequencies below E_0 the imaginary part of the self-energy vanishes and the usual quadratic Stark effect of the exciton is obtained. This result is already contained in Toyozawa's early two-mode model[5] in which he proposed a quadratic exciton-phonon coupling. In the framework of our theory this effective quadratic coupling arises naturally by eliminating the Green's functions $G_{\vec{k}0}$. The same result has been derived phenomenologically by Dexter[6] using the quadratic Stark shift of the exciton in the phonon field.

For larger fields ($f > 0.1$) the exciton broadening becomes dominant. This broadening can be estimated in the following way:

$$\mathrm{Im}\Sigma(\omega) = -e^2F^2\pi \sum_\nu \delta(\omega - E_\nu) \left| \langle 0 | z | \nu \rangle \right|^2 . \quad (44)$$

The renormalized continuum states are approximated by Franz-Kelydsh functions so that the following expression is obtained (see Ref. 13):

$$\mathrm{Im}\Sigma(\omega) = \frac{E_x f^{5/3}}{4\pi} \int_{-\infty}^{\infty} dk_x dk_y \times \left| \int_{-\infty}^{\infty} d^3r\, z\, \mathrm{Ai} \exp(ik_x x + ik_y y - r) \right|^2 , \quad (45)$$

where k_x, k_y, x, y, and z are dimensionless integration variables. The Airy function Ai has the following arguments:

$$\mathrm{Ai} = \mathrm{Ai}(f^{1/3}[z - (E - k_x^2 - k_y^2)/f]) . \quad (46)$$

Expanding the Airy function for small z values and using its asymptotic form for large arguments, one gets for the leading term of the imaginary part of the self-energy

$$\mathrm{Im}\Sigma(\omega) = 32\pi E_x f^3 \exp\left(-\frac{4}{3} \frac{|E|^{3/2}}{f} \right) , \quad (47)$$

where $E = (\omega - E_g)/E_x$. Neglecting the real part of $\Sigma(\omega)$ we plotted the optical density according to Eqs. (47) and (43) in Fig. 8 and compare it again with the numerical results of Ref. 7. One sees that the braodening of the excitonic ground state alone already gives a good description of the excitonic electroabsorption which can be approximated asymptotically by an exponential dependence on $(\omega - \omega_0)/f$.

For the explanation of the changes of $\langle \alpha \rangle_{ph}$ in an external electric field, the exponential shape of $\alpha(\omega)$ even before the thermal average is taken is essential. Recent experiments[8] on TlCl and CuCl showed that the relative change of $\langle \alpha \rangle_{ph}$ due to an external electrical field f_{ext} varies for constant absorption as

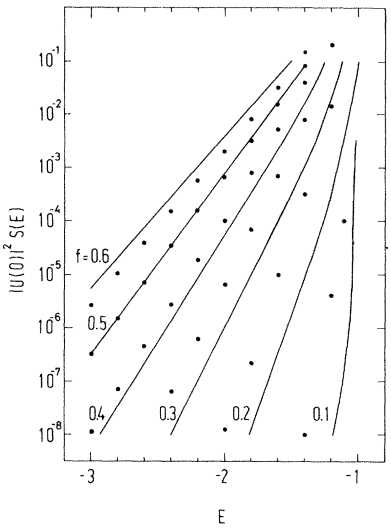

FIG. 8. Absorption edge [Eqs. (43) and (47)] of the exciton as a function of the energy for various field strengths. The dots are the numerical results of Ref. 7.

$$\left. \frac{\Delta \langle \alpha \rangle_{ph}}{\langle \alpha \rangle_{ph} f_{ext}^2} \right|_{\langle \alpha \rangle_{ph} = \mathrm{const}} \propto \left(\frac{\sigma}{k_B T^*} \right)^2 . \quad (48)$$

This result cannot be explained in terms of a simple quadratic Stark-effect theory because it yields a linear dependence of the relative change of $\langle \alpha \rangle_{ph}$ on $(\sigma/k_B T^*)$. This result is easily obtained by superimposing the external field f_{ext} and the microfield f, expanding the resulting absorption coefficient for small f_{ext} and finally averaging it over all possible configurations. However, the experimentally observed quadratic dependence on $\sigma/k_B T^*$ follows directly from the asymptotically exponential absorption spectrum which is obtained as a consequence of the broadening of the exciton ground state.

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