Free-carrier and exciton Franz-Keldysh theory for one-dimensional semiconductors

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The optical properties of a one-dimensional semiconductor in the presence of a static electric field applied along the long axis are calculated. An analytic, nonperturbative expression for the complex free-carrier dielectric constant is obtained in terms of Airy functions. In addition, broadening of the dielectric constant is included analytically. Analytic expressions for the numerical results of Hughes and Citrin [Phys. Rev. Lett. **84**, 4228 (2000)] are presented. The characteristics of the Franz-Keldysh effect, i.e., oscillatory modulation of the spectra and below-gap absorption, are clearly observed. It is demonstrated that these signatures of the electric field may be much more pronounced than the corresponding effects in bulk materials. The influence of electron-hole interaction is subsequently analyzed and exciton eigenstates of an effective Hamiltonian including the one-dimensional Coulomb interaction and the electric field are obtained from an expansion in the free-carrier basis. The exciton Franz-Keldysh effect is compared to the free-carrier result. It is concluded that field-induced changes in the spectral region below the band gap are greatly suppressed in comparison to the free-carrier case as a result of the large exciton binding energy. The oscillatory modulation of the spectra above the band gap is found to be essentially intact, however. In agreement with experiments, the shift of absorption resonances with electric field is found to behave very differently for discrete resonances below the gap and continuum resonances.

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I. INTRODUCTION

Several decades ago, Franz[1] and Keldysh[2] independently derived analytic, nonperturbative expressions for the influence of electrostatic fields on the optical properties of bulk semiconductors. In these early papers, the field-induced change in the absorption coefficient of a simple semiconductor near the band edge was considered. Following this work, Callaway[3] and Tharmalingam[4] obtained closed-form expressions valid at arbitrary optical frequencies in terms of Airy functions. Aspnes[5–7] extended the earlier work in order to treat anisotropic effective-mass tensors, nonparabolicity, and broadening. In addition, he obtained an analytic expression for the real part of the dielectric constant using Kramers-Kronig relations.[6] Experimentally, extensive use of electroabsorption and electroreflectance techniques on conjugated polymer systems (see, e.g., Refs. 8, 9) has recently led to renewed interest in the influence of electric fields on the optical properties of materials. It has been demonstrated that electroabsorption spectroscopy is particularly sensitive in these quasi-one-dimensional materials. In addition, the techniques have been successfully applied to inorganic one-dimensional structures such as metal complexes[10] and porous silicon quantum wires.[11]

Despite these experimental advances there exists no full theoretical analysis of the Franz-Keldysh effect in one-dimensional organic and inorganic semiconductors. A few papers (see, e.g., Refs. 12, 13) have treated related cases in which the electric field is applied perpendicular to the long axis. However, a theory for the Franz-Keldysh regime requires a nonperturbative inclusion of an electric field applied along the long axis. In a recent paper describing the Franz-Keldysh regime, Hughes and Citrin[14] have calculated the induced polarization from a numerical solution of the semiconductor Bloch equations. Both free-carrier and exciton spectra were presented. This highly elegant procedure provides a clear physical picture based on the temporal dynamics of electron-hole wave packets, which are excited by the optical field and subsequently propagate in an asymmetric fashion due to the electrostatic field. Being a numerical procedure, however, this method does not provide analytic expressions for the optical spectra and, hence, cannot easily be used for comparison with various experimental data. In addition, the detailed dependence on the different parameters of the model is hard to extract. A semianalytic expression for the field dependence of the imaginary part of the dielectric constant was given by Yamamoto *et al.*[10] in the form of a definite integral. No closed-form expression was obtained, however, and the real part of the dielectric constant was not considered. Weiser and Horvath[15] have presented analytic expressions for the field-induced changes of the optical spectra. While their free-carrier expressions yield the resonant part of spectra, these authors omitted the nonresonant contributions and, more seriously, exciton effects were neglected.

The purpose of the present paper is twofold: First, we wish to provide analytic expressions for the free-carrier Franz-Keldysh effect including both real and imaginary parts of the spectrum as well as broadening and nonresonant contributions. To this end, we consider a one-dimensional semiconductor in the presence of a strong electrostatic field directed along the long axis. A two-band model and the effective-mass approximation are assumed to provide a reasonably accurate description of the semiconductor. In particular, our framework will apply to simple conjugated polymers such as *trans*-polyacetylene with well-separated bands. Second, we wish to apply our analytic framework derived for the free-carrier case to the exciton problem. In this manner, excitonic effects are incorporated by solving a simple matrix equation using the free-carrier solutions as a basis set. The exciton binding energy in one-dimensional semiconductors is

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greatly enhanced over the bulk value due to quantum confinement of electrons and holes. This effect is already seen in two-dimensional quantum wells where the binding energy reaches four times the bulk value in the limit of perfect confinement.[16] In one-dimensional semiconductors, however, the exciton binding energy diverges logarithmically in this limit, as shown already several decades ago by Loudon.[17] In this sense there is no theoretical upper limit for the binding energy, but obviously the finite barriers and finite wire width of any real material will limit the maximum obtainable value. Still, the binding energy may be enhanced by an order of magnitude over the bulk material value. Hence, exciton effects are indispensable in any qualitatively and quantitatively correct theory of the optical properties of one-dimensional semiconductors. We apply our quasianalytic technique to calculate both real and imaginary part of the excitonic optical susceptibility. In addition, the shift of absorption maxima with increased field strength is analyzed and important differences between the discrete and continuum part of the spectrum are demonstrated.

The outline of the paper is as follows: In the following section, the free-carrier Franz-Keldysh effect for unbroadened transitions is analyzed. In Sec. III, these results are generalized by the inclusion of broadening via the convolution technique. Then, in Sec. IV, Coulomb effects are introduced and the one-dimensional Hamiltonian for electron-hole pairs in the presence of an electric field is constructed. Also, the properties of the lowest exciton state are derived from a variational procedure. In Sec. V, we then present our calculations for the excitonic optical susceptibility including the effect of the static electric field. Numerical calculations for moderate and strong fields are presented and the spectra with and without electron-hole interaction are compared. From the spectra, the shift of absorption maxima with field strength are extracted and the differences between discrete and continuum resonances are discussed. Finally, a summary is given in Sec. VI.

II. FREE-CARRIER FRANZ-KELDYSH THEORY

The description of charge carriers in the presence of an infinitely extended uniform electrostatic field is a complicated task because the accompanying potential is unbounded. In order to handle this problem we follow Ref. 18. In this approach the separation of the electron-hole pair $z=z_e-z_h$ is restricted to an interval $-L<z<L$. The potential due to an electric field F is given by eFz, $e>0$ being the charge unit, and by restricting the range of z the potential becomes bounded by the values $\pm eFL$. L is assumed to be sufficiently large that the electron-hole wave function vanishes at the repulsive potential end $z=L$ (we assume $F>0$ throughout). In this manner, the allowed eigenstates are determined solely from the boundary condition at $z=-L$ and the final expressions will be shown to be independent of L. In the electron-hole pair picture the relative-motion wave function satisfies the Schrödinger equation

$$\left\{-\frac{h^2}{2\mu}\frac{d^2}{dz^2}+eFz+E_g\right\}\varphi_n(z)=E_n\varphi_n(z) \tag{1}$$

provided $-L<z<L$. Outside this interval the wave function vanishes. Here, μ and E_g are the reduced mass and band gap, respectively. If we introduce the scaled quantities $f=2\mu eF/\hbar^2$ and $\varepsilon_n=2\mu(E_n-E_g)/\hbar^2$ the normalized eigenstates can be expressed as[18]

$$\varphi_n(z)=a_nAi(f^{1/3}z-\varepsilon_n f^{-2/3}),\quad a_n=\left(\frac{2\pi^2 f}{3(n-1/4)}\right)^{1/6}, \tag{2}$$

where Ai is the first Airy function and the corresponding eigenvalues are

$$\varepsilon_n=\left(\frac{3\pi f(n-1/4)}{2}\right)^{2/3}-fL. \tag{3}$$

Note that there is an error in the normalization constants used in Ref. 18. We choose the following strategy for the calculation of optical constants: As the primary step, the imaginary part of the dielectric constant $\varepsilon''(\omega)$ is calculated in the limit of vanishing broadening, i.e., as a sum of delta function terms. Then, the complex dielectric constant including broadening is obtained via the convolution technique. Hence, the first step consists in evaluating the unbroadened expression for $\varepsilon''(\omega)$

$$\varepsilon''(\omega)=\frac{2\pi e^2}{\varepsilon_0 m_0^2\omega^2 A}|p_{vc}|^2\sum_n |\varphi_n(0)|^2\delta(E_n-\hbar\omega), \tag{4}$$

where ε_0 is the vacuum permittivity, m_0 is the free electron mass, A is the cross-sectional area of the one-dimensional semiconductor, and p_{vc} is the effective interband momentum matrix element, which includes the overlap integral of the transverse part of electron and hole wave functions. Throughout, transverse excitations are neglected, i.e., only the lowest eigenstates for the transverse directions are considered. For later use in the convolution calculation it should be noted that the above expression is valid for positive frequencies only. If negative frequencies are allowed as well, the combination $\varepsilon''(\omega)-\varepsilon''(-\omega)$, where $\varepsilon''(\omega)$ is given by Eq. (4), should be used. To proceed, we insert Eqs. (2) and (3) into the above expression and convert the summation into an integral. This conversion requires that the separation between adjacent levels $\varepsilon_{n+1}-\varepsilon_n$ is small. However, as seen from Eq. (3), the values of n at which a transition is at resonance with $\hbar\omega$ are necessarily very large due to the subtracted amount fL. Hence, the inverse density of states at large n values is given by

$$\varepsilon_{n+1}-\varepsilon_n\approx\frac{\partial\varepsilon_n}{\partial n}=\left(\frac{2\pi^2 f^2}{3(n-1/4)}\right)^{1/3}=a_n^2 f^{1/3}, \tag{5}$$

which decreases as $n^{-1/3}$ and, hence, justifies the conversion into an integral when n is sufficiently large. In this manner

$$\varepsilon''(\omega)=\frac{2\pi e^2}{\varepsilon_0 m_0^2\omega^2 A}|p_{vc}|^2 \times\sum_n a_n^2 Ai^2(-\varepsilon_n f^{-2/3})\frac{2u}{\hbar^2}\delta\left(\varepsilon_n-\frac{2\mu}{\hbar^2}(\hbar\omega-E_g)\right) = \frac{2\pi e^2}{\varepsilon_0 m_0^2\omega^2 A f^{1/3}}|p_{vc}|^2 \times\int Ai^2(-\varepsilon f^{-2/3})\frac{2\mu}{\hbar^2}\delta\left(\varepsilon-\frac{2\mu}{\hbar^2}(\hbar\omega-E_g)\right)d\varepsilon, \tag{6}$$

where the cancellation between $a_n^2 f^{1/3}$ and $(\partial\varepsilon_n/\partial n)^{-1}$ has been utilized. Because of the delta function, the integral is readily evaluated yielding the result

$$\varepsilon''(\omega)=\frac{2^{3/2}\pi e^2\mu^{1/2}}{\varepsilon_0 m_0^2\hbar\omega^2 E_f^{1/2}A}|p_{vc}|^2 Ai^2\left(\frac{E_g-\hbar\omega}{E_f}\right), \tag{7}$$

where we have introduced the *field energy* E_f given by $E_f=\hbar^2 f^{2/3}/(2\mu)$. This formula constitutes our simple, closed-form expression for the imaginary part of the dielectric constant of a one-dimensional semiconductor in the presence of a static longitudinal field. From this result, the absorption coefficient $\alpha(\omega)$ measured in experimental electroabsorption studies is readily obtained via the relation $\alpha(\omega)=\omega\varepsilon''(\omega)/(nc)$, where n is the refractive index. In passing it is noted that, in fact, the integral expression used in Ref. 10 can be shown to coincide with the above result using certain relations derived by Aspnes in Ref. 5.

It is well known[18] that the optical properties of one-dimensional (1D) semiconductors are characterized by the square-root singularity at the band edge. In the present case, this fact is easily demonstrated in the limit $f\to 0$ since

$$\lim_{f\to 0}\frac{1}{E_f^{1/2}}Ai^2\left(\frac{E_g-\hbar\omega}{E_f}\right) = \frac{\theta(\hbar\omega-E_g)}{\pi\sqrt{\hbar\omega-E_g}}\sin^2\left[\frac{2}{3}\left(\frac{\hbar\omega-E_g}{E_f}\right)^{3/2}+\frac{\pi}{4}\right], \tag{8}$$

where $\theta(x)$ is the step function. Thus, the square-root singularity emerges as the envelope of the spectrum. However, a rapidly oscillating term with a period proportional to the applied field modulates the spectrum. Hence, strictly speaking the limit $f\to 0$ does not exist. This unphysical result is due to our neglect of broadening, however. Naturally, if broadening is included, the rapid oscillations will be smeared out once the period is much less than the broadening. Hence, we now turn to the influence of broadening on the spectrum.

III. BROADENING OF THE FREE-CARRIER SPECTRUM

The complex dielectric constant $\varepsilon_\Gamma(\omega)$ including broadening can be obtained from the convolution between the unbroadened quantity $\varepsilon(\omega)$ and a Lorentzian of width Γ,

$$L(\nu-\omega)=\frac{\Gamma/\pi}{(\nu-\omega)^2+\Gamma^2}. \tag{9}$$

The numerator Γ/π ensures that the limiting behavior of the line-shape function as $\Gamma\to 0$ is a delta function $\delta(\nu-\omega)$. The imaginary part of $\varepsilon(\omega)$ is already given in Eq. (7) and a Kramers-Kronig transformation provides us with the real part $\varepsilon'(\omega)$. Since an integral over both positive and negative frequencies is involved, care should be taken that the expression $\varepsilon''(\omega)-\varepsilon''(-\omega)$ is used for the imaginary part. Hence, two contributions to the result are obtained. By a simple sign change in the second term, however, the final expression for the transformation reads as

$$\varepsilon'(\omega)=1+\frac{2}{\pi}P\int_{-\infty}^{\infty}\varepsilon''(\nu)\frac{\nu}{\nu^2-\omega^2}d\nu, \tag{10}$$

where ε'' is given by Eq. (7) and P denotes taking the principle value. The combined actions of the Lorentzian convolution and the Kramers-Kronig transformation can be shown to lead to the following simple transformation.

$$\varepsilon_\Gamma(\omega)=1+\frac{2}{\pi}\int_{-\infty}^{\infty}\varepsilon''(\nu)\frac{\nu}{\nu^2-(\omega+i\Gamma)^2}d\nu, \tag{11}$$

which provides both real and imaginary parts of the broadened dielectric constant. In order to evaluate the integral, we expand in partial fractions and utilize the relation (derived from results in Ref. 5)

$$\int_{-\infty}^{\infty}\frac{Ai^2(-x)}{x-z+i\gamma}dx = -i\pi\,\mathrm{sgn}(\gamma)Ai^2(-z+i\gamma)+\pi AiBi(-z+i\gamma), \tag{12}$$

with the shorthand notation $AiBi(x)\equiv Ai(x)Bi(x)$, Bi being the second Airy function. By summing the various pole contributions, we consequently obtain the result

$$\varepsilon_\Gamma(\omega)=1+CF\left(\frac{\hbar(\omega+i\Gamma)}{E_g},\frac{E_f}{E_g}\right), \tag{13}$$

where C is a material-dependent constant given by

$$C=\frac{2^{3/2}\pi e^2\hbar\mu^{1/2}}{\varepsilon_0 m_0^2 E_g^{5/2}A}|p_{vc}|^2, \tag{14}$$

and F is a complex *susceptibility function* given by

$$F(x,y)=\frac{1}{y^{1/2}x^2}\left\{AiBi\left(\frac{1-x}{y}\right)+iAi^2\left(\frac{1-x}{y}\right) +AiBi\left(\frac{1+x}{y}\right)-iAi^2\left(\frac{1+x}{y}\right)-2AiBi\left(\frac{1}{y}\right)\right\}. \tag{15}$$

The real and imaginary parts of the susceptibility function in the unbroadened limit $x\approx\hbar\omega/E_g$ are illustrated in Fig. 1. In this figure, a rather large field energy $\sim 0.1E_g$ is used and as a consequence the square-root singularity is severely distorted. The oscillatory component, which is a hallmark of the

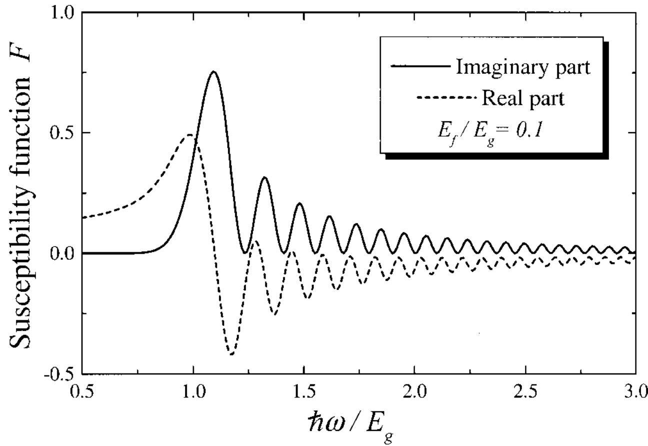

FIG. 1. Imaginary and real parts of the complex susceptibility function F_0 for a one-dimensional semiconductor in the presence of an electric field. The ratio of field energy E_f to band gap E_g is taken as 0.1.

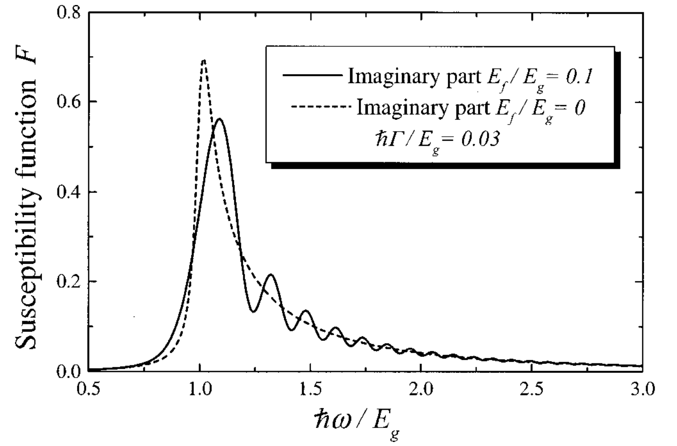

FIG. 2. Imaginary part of the broadened susceptibility function F_Γ for a field energy of $E_f = 0.1 E_g$ and a broadening of $\hbar\Gamma = 0.03 E_g$. For comparison the usual zero-field result is shown as the dashed line.

Franz-Keldysh effect, is clearly visible. In contrast to the bulk Franz-Keldysh effect,[18] the modulation of the spectrum due to the oscillations is 100% in the sense that the imaginary part goes to zero at the valleys. As discussed above, this result should be interpreted with care since it requires the field energy to be much larger than the broadening. Otherwise, broadening will smear out the oscillations and thereby reduce the modulations. Another hallmark is the appearance of absorption below the band gap, which can be interpreted as a result of field-induced tunneling across the band gap. This effect is also clearly visible in Fig. 1 and from an analysis of the asymptotic behavior of the Airy function it can be shown to decay approximately exponentially as

$$\varepsilon''(\omega) \propto \exp\left(-\frac{4}{3} \left(\frac{E_g - \hbar\omega}{E_f} \right)^{3/2} \right), \quad \hbar\omega \ll E_g. \tag{16}$$

This result is perfectly analogous to the bulk case.[1,2] At this point we pause to notice that the expressions proposed in Ref. 15 contain only the first and second of the five terms in Eq. (15). This amounts to retaining only the resonant part of the expression whereas our result includes the nonresonant part as well. While the imaginary part of the spectrum at and above the band gap may be approximated by the resonant contribution alone, a considerable error is found for the real part, as the nonresonant terms are comparable to the resonant ones. If only the field-induced *change* of the spectrum is considered, however, the error is approximately canceled. Hence, the full expression should be used for the dielectric constant itself, but the field-induced change may be approximated by the resonant contribution alone.

In Figs. 2 and 3, we have plotted imaginary and real parts of this susceptibility function for a broadening of $\hbar\Gamma = 0.03 E_g$. For comparison, the results of the zero-field expression for the dielectric constant

$$\varepsilon_{\Gamma,F=0}(\omega) = 1 + \frac{C}{2\pi x^2} \left\{ \frac{1}{\sqrt{1-x}} + \frac{1}{\sqrt{1+x}} - 2 \right\} \tag{17}$$

have been included in the plots. The dielectric spectra in the presence of an electric field are seen to oscillate around the zero-field value for optical frequencies above the band gap. Below the band gap, field-induced absorption is clearly visible even in the presence of broadening. Numerically, the general expression Eq. (15) is found to agree perfectly with Eq. (17) if $E_f \ll \hbar\Gamma$, i.e., when the effects of the field are completely dominated by spectral broadening. When E_f and $\hbar\Gamma$ are comparable, as in Figs. 2 and 3, the characteristic oscillations are still visible. However, as a consequence of broadening the modulation is somewhat reduced. Assuming material parameters given by $E_g = 2$ eV and $\mu = 0.1 m_0$ (see below), the parameters used in Figs. 2 and 3 correspond to a broadening of $\hbar\Gamma = 60$ meV and an applied field of $F \approx 15$ mV/Å. It is noted that our results in Fig. 2 are in good agreement with the numerical results shown in Fig. 2 of Ref. 14 for the case of vanishing excitonic effects. This confirms the correctness of the present analytic theory.

Before ending the free-carrier analysis, we wish to compare our results for the broadened spectra to the usual bulk expressions for the Franz-Keldysh effect. When broadening is included, the results of Aspnes[6] read

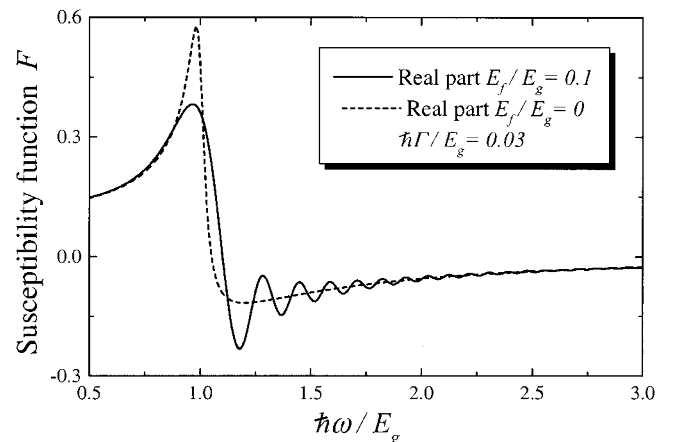

FIG. 3. Same as Fig. 2 but for the real part.

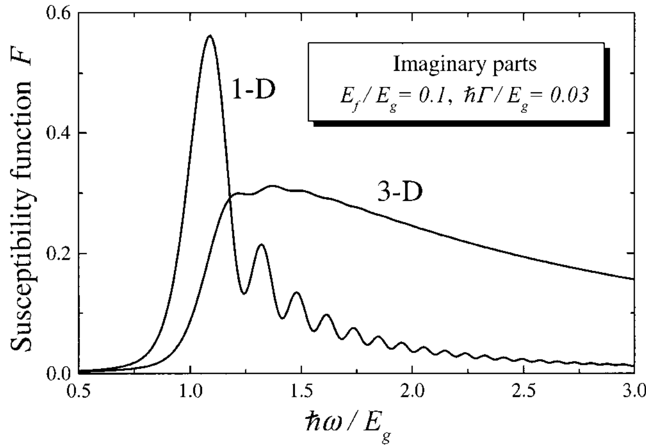

FIG. 4. Comparison between the Franz-Keldysh effect in one-dimensional and three-dimensional semiconductors. Notice the increased contrast of the oscillations in the one-dimensional case.

$$\varepsilon_{\Gamma}^{(3\mathrm{D})}(\omega)=1+\frac{2^{1/2}e^2\mu^{3/2}}{\pi\varepsilon_0 m_0^2\hbar E_g^{3/2}}|p_{\nu c}|^2F^{(3\mathrm{D})}\left(\frac{\hbar(\omega+i\Gamma)}{E_g},\frac{E_f}{E_g}\right) \tag{18}$$

with

$$\begin{aligned}F^{(3\mathrm{D})}(x,y)=\frac{\pi y^{1/2}}{x^2}\Bigg\{&\frac{x-1}{y}\left[AiBi\left(\frac{1-x}{y}\right)+iAi^2\left(\frac{1-x}{y}\right)\right]\\&+Ai'Bi'\left(\frac{1-x}{y}\right)+iAi'^2\left(\frac{1-x}{y}\right)\\&-\frac{x+1}{y}\left[AiBi\left(\frac{1+x}{y}\right)-iAi^2\left(\frac{1+x}{y}\right)\right]\\&+Ai'Bi'\left(\frac{1+x}{y}\right)-iAi'^2\left(\frac{1+x}{y}\right)\\&+\frac{2}{y}AiBi\left(\frac{1}{y}\right)-2Ai'Bi'\left(\frac{1}{y}\right)\Bigg\}.\end{aligned} \tag{19}$$

Here, a prime denotes the derivative with respect to the argument. A direct comparison between susceptibility functions for the three- and one-dimensional cases is shown in Fig. 4 using identical parameters. The characteristic square-root and inverse square-root behaviors are clearly distinguished. It is noted, however, that the modification of the spectrum is much more pronounced in the one-dimensional case. This, obviously, is a consequence of the larger oscillatory modulation in the one-dimensional case. The comparison demonstrates that an increased contrast is observed even in the presence of broadening. Thus, in agreement with experiments, one-dimensional systems are found to be highly sensitive to the perturbing field. Physically, the increased sensitivity of electrons in one-dimensional systems to the presence of long-axis fields is a result of the reduced degrees of freedom. Hence, in a one-dimensional system the electrons are forced to move along the field and the motion is severely affected. In contrast, the motion of electrons in bulk materials is less perturbed as only one out of three degrees of freedom is affected. This physical picture and the entire analysis so far ignores the role of the Coulomb interaction, however. Obviously, the attractive electron-hole interaction will counteract the field-induced charge separation and thereby increases the overlap. This effect is expected to be particularly pronounced in one-dimensional materials as a result of the increased exciton binding energy. Thus, a competition between field-induced exciton dissociation and attractive Coulomb forces determines the properties. The analysis of this competition is the subject of the remaining part of this paper.

IV. ONE-DIMENSIONAL COULOMB EFFECT

We now include the Coulomb interaction and present the effective one-dimensional Hamiltonian from which electron-hole states are derived. For three- and two-dimensional materials the role of electron-hole interactions in the Franz-Keldysh effect was studied several decades ago.[19,20] The one-dimensional case requires extra care, however, due to the singular behavior of the one-dimensional Coulomb interaction.[17] Since we only consider long-axis fields the electric field does not influence the transverse part of the wave function. The Coulomb interaction, however, couples the transverse and longitudinal motion. To circumvent this complication, we apply the technique used previously in the particle-in-a-box model of one-dimensional excitons[21] as well as by Hughes and Citrin.[14] In this approach, the confinement is assumed to be sufficiently strong that the transverse part of the wave function is unaffected by the Coulomb interaction potential. Accordingly, the longitudinal part of the wave function is calculated from an effective one-dimensional Coulomb potential obtained by averaging the bare three-dimensional potential over the transverse dimensions weighted by the transverse electron-hole probability density. An additional complication arises from the fact that Coulomb screening in one-dimensional semiconductors is generally anisotropic, in particular in conjugated polymers. In the particle-in-a-box model[21] this fact was taken into account by simply using the long-axis dielectric constant rather than the three-dimensional average. This *ad hoc* procedure is not correct, however. In fact, if the long axis is taken as the z axis so that the dielectric tensor is of the form $\overleftrightarrow{\varepsilon}=\mathrm{diag}(\varepsilon_x,\varepsilon_x,\varepsilon_z)$ the appropriate dielectric constant for the long-range tail of the interaction is ε_x. This follows from the solution of Poisson's equation in a uniaxial anisotropic material,[22] which yields a Coulomb interaction between two point charges of magnitude $+e$ and $-e$

$$V_{3\mathrm{D}}(x,y,z)=-\frac{e^2}{4\pi\varepsilon_0\sqrt{\varepsilon_x\varepsilon_z x^2+\varepsilon_x\varepsilon_z y^2+\varepsilon_x^2 z^2}}. \tag{20}$$

Thus, whenever the long-axis separation $|z|$ is much larger than the transverse separation $\sqrt{x^2+y^2}$ the screening is determined by ε_x rather than ε_z. On the other hand, the lowest excitons are sharply localized near $z=0$ and, hence, the effective screening for these states is a combination of ε_x and ε_z. From a weighted transverse average of the bare three-

dimensional potential above we now obtain the effective one-dimensional Coulomb interaction as

$$V_{1\mathrm{D}}(z)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}V_{3\mathrm{D}}(x_e-x_h,y_e-y_h,z)\times|\varphi_e(x_e,y_e)|^2|\varphi_h(x_h,y_h)|^2dx_edy_edx_hdy_h, \tag{21}$$

where $\varphi_e(x_e,y_e)$ and $\varphi_h(x_h,y_h)$ are the transverse electron and hole wave functions, respectively. In order to simplify the notation, we introduce the Coulomb function $C(z)$ via

$$C(z)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{|\varphi_e(x_e,y_e)|^2|\varphi_h(x_h,y_h)|^2}{\sqrt{(x_e-x_h)^2+(y_e-y_h)^2+z^2}}\times dx_edy_edx_hdy_h. \tag{22}$$

In this manner, the one-dimensional interaction reads as

$$V_{1\mathrm{D}}(z)=-V_0C(z\sqrt{\varepsilon_x/\varepsilon_z}), \tag{23}$$

where

$$V_0=\frac{e^2}{4\pi\varepsilon_0\sqrt{\varepsilon_x\varepsilon_z}}. \tag{24}$$

It is seen that the anisotropic screening leads to a scaling of the z dependence in Eq. (23). For simplicity, however, we will ignore this scaling and set $\varepsilon_x=\varepsilon_z\equiv\varepsilon$. The expression for the Coulomb function obviously depends on the model used for the transverse confinement. Following Ref. 21, we assume infinite barrier confinement for which

$$C(z)\approx\frac{1-\exp(-|z|/\eta)}{|z|}, \tag{25}$$

where $\eta\approx a/4.758\,86$, a being the width of the potential well. It may be noticed that, if Gaussian wave functions of the form $\varphi(x)=(2/\pi)^{1/4}\exp(-x^2/\eta^2)/\eta^{1/2}$ are assumed as in Ref. 14, the Coulomb function becomes

$$C(z)=\pi^{1/2}\exp(z^2/\eta^2)\frac{1-\Phi(|z|/\eta)]}{\eta}, \tag{26}$$

where Φ is the error function. The behavior of the two Coulomb functions Eqs. (25) and (26) is qualitatively similar in that both choices are finite at the origin $z=0$ and approach $1/|z|$ as $|z|\to\infty$ or $\eta\to 0$.

We now turn to the calculation of eigenstates for the exciton Hamiltonian. Before analyzing the influence of the electric field we briefly discuss the eigenstates for the unperturbed electron-hole pair. For an infinite one-dimensional semiconductor the appropriate Schrödinger equation reads as

$$\left\{-\frac{\hbar^2}{2\mu}\frac{d^2}{dz^2}-V_0C(z)+E_g-E_{\mathrm{ex}}\right\}\phi_{\mathrm{ex}}(z)=0. \tag{27}$$

The eigenvalues E_{ex} and eigenfunctions ϕ_{ex} cannot be found analytically but an excellent approximation to the ground state, which is by far the most important one for the optical properties, is provided by the ansatz

$$\phi_{\mathrm{ex}}(z)=\frac{1}{\sqrt{\lambda}}\exp(-|z|/\lambda), \tag{28}$$

where λ is a variational parameter. This simple form may appear surprising as the asymptotic solutions to Eq. (27) behave as $|z|\exp(-|z|/\lambda)$ for large $|z|$. However, the ground-state solution is sufficiently localized that the behavior at large $|z|$ is of minor importance. Using Eq. (28) and choosing Eq. (25) for the Coulomb function, we obtain the following expression for the energy

$$E_{\mathrm{ex}}=E_g+\frac{\hbar^2}{2\mu\lambda^2}-\frac{2V_0}{\lambda}\ln\left(1+\frac{\lambda}{2\eta}\right). \tag{29}$$

Denoting the λ value, which minimizes the energy, by λ_0, the ground-state energy is given by the expression

$$E_{\mathrm{ex}}=E_g-\frac{\hbar^2}{2\mu\lambda_0^2}-\frac{2V_0}{2\eta+\lambda_0}. \tag{30}$$

With the parameters $V_0=1\ \mathrm{eV\,Å}$, $\eta=1.0\ \mathrm{Å}$, and $\mu=0.1m_0$, which will be used as a typical parameters in the following section, the binding energy $E_b=E_{\mathrm{ex}}-E_g$ and decay length are -0.15 eV and 23 Å, respectively. Experimentally, the binding energy in conjugated polymers has been a matter of controversy. For the well-characterized material poly(*para*-phenylene vinylene) values of $|E_b|$ ranging from <0.1 eV (Ref. 23) to 0.2 eV (Ref. 24) and even higher have been reported. Hence, the value 0.15 eV taken here is assumed to be roughly representative of this class of materials. Also, the band gap of these materials typically lies in the range $E_g=2-3$ eV and we will take $E_g=2$ eV throughout. The reduced mass is probably a conservative estimate and may be lower in some materials. Note that a lower reduced mass leads to a larger influence of the electric field due to the scaling of the field energy $E_f=(\hbar eF)^{2/3}/(2\mu)^{1/3}$. The $\mu^{-1/3}$ dependence is rather weak, however.

We now include the electric field applied along the positive z direction. The field couples to the electron-hole dipole and leads to a modified Schrödinger equation given by

$$\left\{-\frac{\hbar^2}{2\mu}\frac{d^2}{dz^2}+eFz-V_0C(z)+E_g-E_{\mathrm{ex}}\right\}\phi_{\mathrm{ex}}(z)=0. \tag{31}$$

No analytic solutions to this equation have been found. Hence, an alternative strategy has to be followed. The procedure is based on an expansion of the exciton states in a basis formed by the solutions to the free-carrier Schrödinger equation including the electric field given by Eq. (1). In the φ_n basis, the matrix elements of the full Hamiltonian are given by

$$H_{nm}=E_n\delta_{nm}-V_0\langle\varphi_n|C(z)|\varphi_m\rangle. \tag{32}$$

Unfortunately, the matrix elements of the Coulomb function cannot be evaluated analytically except in the case of extremely strongly binding potentials where

$$\langle\varphi_n|C(z)|\varphi_m\rangle=-2[\gamma+\ln(f^{1/3}\eta)]\varphi_n(0)\varphi_m(0), \tag{33}$$

where $\gamma=0.5772...$ is Euler's constant. In the general case, we evaluate the matrix elements numerically using Gaussian quadrature with at least 1000 points in the interval $-L<z<L$. Note that an extremely accurate numerical procedure is required since the integrand is highly oscillatory and the region around $z=0$ must be adequately sampled. The Hamiltonian matrix is diagonalized numerically and from the eigenvectors exciton states of the form

$$\phi_{\rm ex}(z)=\sum_n c_n\varphi_n(z) \tag{34}$$

are formed. In turn, these states and the corresponding eigenvalues provide the information needed to calculate the exciton Franz-Keldysh effect in the following section.

V. EXCITON FRANZ-KELDYSH EFFECT

In the present section, the optical properties of the one-dimensional semiconductor including electron-hole interactions are calculated. No analytic expression for the spectrum can be derived in this case. Thus, we calculate directly the normalized complex susceptibility function $F(\omega)$ including broadening from the expression

$$F(\omega)=\frac{\hbar E_g^{5/2}}{(2\mu)^{1/2}}\sum_{\rm ex}\frac{|\phi_{\rm ex}(0)|^2}{E_{\rm ex}[E_{\rm ex}^2-\hbar^2(\omega+i\Gamma)^2]}. \tag{35}$$

As described in the preceding section, the exciton states are derived under the restriction that the electron-hole separation is limited to the interval $-L<z<L$. For a particular value of L, the free-carrier energy spectrum is given by Eq. (3). For the optical properties in the neighborhood of the band edge only a small part of the spectrum is needed, however. The dominant contributions are those for which $\varepsilon_n\approx 0$ corresponding to excitation energies close to E_g. Thus, for a given L the relevant part of the spectrum is located around the quantum number N for which

$$\varepsilon_N=0\ \Rightarrow\ N\approx \mathrm{int}\left[\frac{2}{3\pi}(fL^3)^{1/2}\right]. \tag{36}$$

Hence, upon restricting the size of the basis set to 100 elements we have found that by retaining the range $n\in[N-20,N+79]$ the relevant exciton states are adequately described. The separation between energy levels ΔE decreases approximately as $n^{-1/3}$ for large values of L as shown by Eq. (5). The magnitude of L should thus be large enough that the level separation is much less than the level broadening, i.e., $\Delta E \ll \hbar\Gamma$. On the other hand, the range of levels, which form the basis set, becomes increasingly narrow as L is increased. Consequently, for very large values of L only excitons very close to the band edge are correctly described. It follows that a compromise should be used and in practice values around $L=3500$ Å are found to be satisfactory.

Before examining the effect of the electric field, we look at the influence of electron-hole interaction on the zero-field optical properties of the semiconductor. As explained above, the band gap is taken as $E_g=2$ eV, the reduced mass as $\mu=0.1m_0$ and the broadening as $\hbar\Gamma=0.02E_g$. A broadening of this magnitude is reasonable for well-ordered samples at relatively low temperatures. The quantities describing the Coulomb interaction are taken as $V_0/\eta=1$ eV and $\eta=1.0$ Å. For a vanishingly small electric field, the imaginary part of Eq. (35) yields the spectra shown in Fig. 5 for the cases with and without electron-hole interaction. The free-carrier spectrum is characterized by the broadened square-root singularity at the band edge. In comparison, the exciton spectrum is clearly red shifted and the fundamental peak is much more intense. The maximum of this spectrum is located at $\hbar\omega\approx 0.93E_g$ in accordance with the exciton binding energy of -0.15 eV. In addition, the exciton line shape is much more symmetric than the free-carrier curve. Thus, the inclusion of electron-hole interaction leads to a complete rearrangement of the spectrum and the role of excitons certainly cannot be ignored.

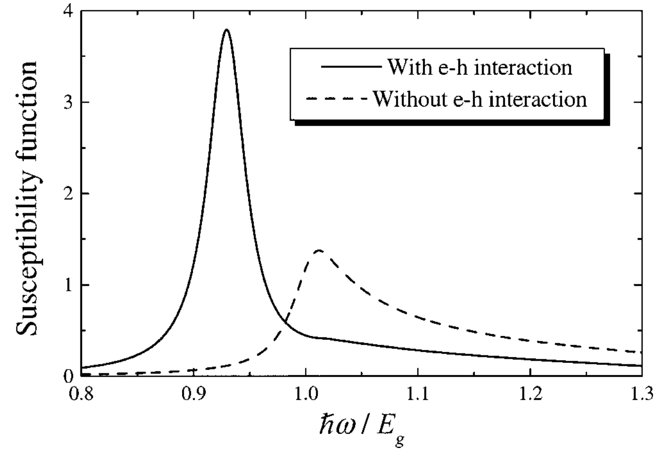

FIG. 5. Illustration of the influence of electron-hole interaction on the zero-field optical properties. The parameter values $V_0=1$ eV Å, $\eta=1.0$ Å, and $\mu=0.1\,m_0$ are applied and correspond to an exciton binding energy of approximately $-0.075E_g$.

We now include the presence of an electric field and investigate the role of electron-hole interaction on the optical properties in this case. The results shown in Figs. 6 and 7 are obtained using field energies of $E_f=0.05E_g$ and $E_f=0.1E$, respectively. Note that the exciton binding energy $E_{\rm ex}-E_g$ is approximately $-0.075E_g$. Therefore, the results shown in the figures correspond to cases with $E_f<|E_{\rm ex}-E_g|$ and $E_f>|E_{\rm ex}-E_g|$, respectively. The upper and lower panels in these figures illustrate the imaginary and real parts of the normalized susceptibility. It is clearly seen that the trends in the zero-field case (Fig. 5) survive in the case of a finite field. In fact, the red shift and magnification of the fundamental peak is practically as pronounced in the case with $E_f=0.05\,E_g$ (Fig. 6) as in the $E_f=0$ case. For the larger field in Fig. 7, only the red shift remains intact and the magnification is somewhat reduced. The influence of electron-hole interactions on the hallmarks of the Franz-Keldysh effect can be deduced from a comparison of free carrier and exciton spectra in Figs. 6 and 7. As demonstrated in the first part of this paper, two significant effects of the electric field are noticed in the free-carrier case, viz., the presence of increased absorption below the band gap and the appearance of an oscillatory modulation of the spectra above the gap. When

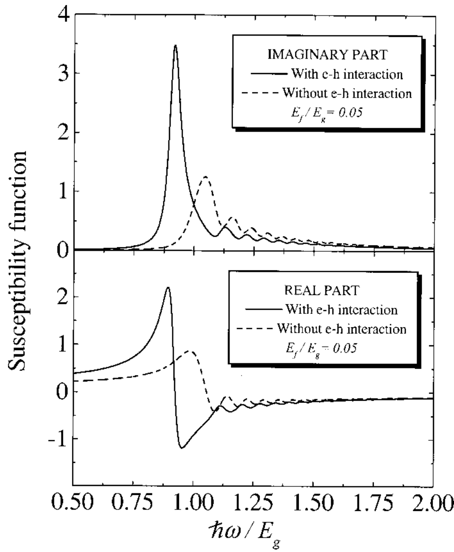

FIG. 6. Real and imaginary parts of the susceptibility function calculated with (solid lines) and without (dashed lines) electron-hole interaction. The value of the field energy is $E_f = 0.05E$ and the remaining parameters are identical to those in Fig. 5.

electron- hole interaction is taken into account, these features are clearly less pronounced. In particular, the spectral region below the fundamental exciton transition remains practically unchanged by the electric field. The main effect is a small Stark shift, which will be discussed below. From a comparison of Figs. 5–7 it is seen that the intensity of the fundamental exciton peak is slightly reduced at $E_f = 0.05\,E_g$ and approximately reduced by 50% at $E_f = 0.1\,E_g$. This is a consequence of the reduced electron-hole overlap in the electric field, which acts to increase to electron-hole separation. On the other hand, if the electric field is too weak to overcome the strong Coulomb attraction of the electron-hole pair, the field only weakly perturbs the exciton. This demonstrates that whenever the field energy E_f is much less than the exciton binding energy, the field-induced modification of the spectral region below the band gap will be greatly suppressed compared to the free-carrier result. The characteristic oscillations in the continuum above the band gap are clearly visible both with and without electron-hole interaction. Their amplitude in the former case is slightly reduced, however. In addition, the oscillations are stretched compared to the free-carrier case. This is because the Coulomb interaction tends to red shift the lower transitions and thereby enlarges the oscillation period. These features are observed in both real and imaginary parts of the spectra.

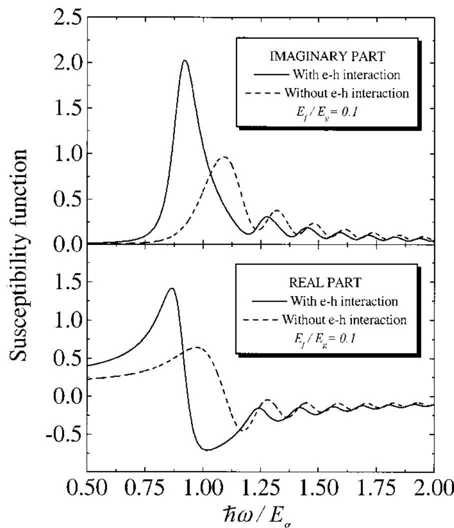

FIG. 7. Same as Fig. 6 but for a field energy of $E_f = 0.1E$.

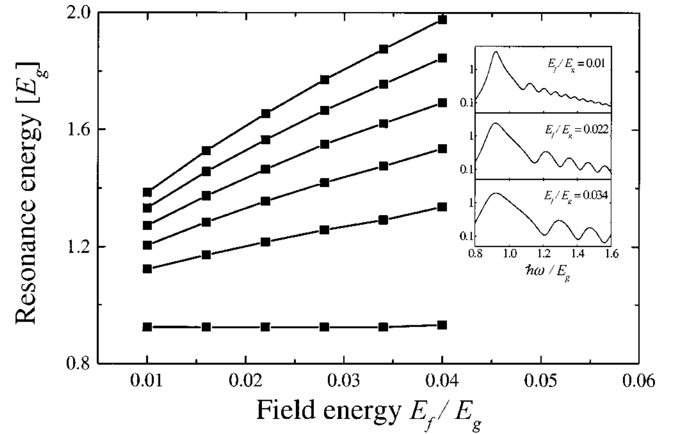

FIG. 8. Shift of absorption resonances with field energy $E_f \propto (\text{field strength})^{2/3}$ using parameters identical to those in Fig. 5. Notice the different behavior below and above the band gap. The inset shows the frequency dependence of the imaginary part of the susceptibility (on a log scale) for three different values of the field energy.

Experimentally, the excitonic Franz-Keldysh effect in a one-dimensional semiconductor has been observed most clearly in polydiacetylene polymers[25] by Horvath *et al.* The trends of the measured electroabsorption spectra are qualitatively very similar to the present theoretical results. Thus, below the band gap the experimental spectrum displays discrete exciton lines and their vibronic replicas. In the presence of the electric field, the only discernable modification of these transitions is a small Stark red shift, which simply displaces the exciton line by a small amount. Above the band gap, however, the Franz-Keldysh effect is clearly visible. Hence, in the continuum part of the spectrum a number of distinct oscillations appear and, furthermore, the oscillatory modulation shifts with the magnitude of the electric field. In order to compare with the Franz-Keldysh effect, Horvath *et al.* have plotted the shift of the oscillatory modulation with the electric field, confirming the predicted $F^{2/3}$ dependence. In Fig. 8, we have used the present theory to plot the calculated shift of the absorption maxima as a function of the field energy $E_f = \hbar^2 f^{2/3}/(2\mu)$ normalized by the band-gap energy. It is readily seen that the field dependence is in qualitative agreement with the experimental results. The lowest curve corresponding to the fundamental exciton transition shows practically no variation with the electric field. In fact, there is a small negative shift due to the Stark effect, which is hardly noticeable in the figure. For the resonances in the continuum, on the other hand, there is a distinct dependence on the field energy. The slope is slightly sublinear due to the Coulomb

interaction, which adds a small red shift to the lower part of the continuum transitions. To a high degree of accuracy, however, the shift is seen to vary linearly with $F^{2/3}$. The inset shows the calculated spectra (on a log scale) for three values of the field energy. Again, the distinctly different behavior of discrete and continuum resonances is noticed. We conclude from the agreement between experiment and theory that the present model is able to account for several aspects of the exciton Franz-Keldysh effect in one-dimensional semiconductors.

VI. SUMMARY

In the present paper, a detailed analysis of the free carrier and exciton Franz-Keldysh effect in one-dimensional semiconductors has been presented. A two-band effective-mass model is assumed for the electronic system. In the free-carrier case, we have derived an analytic, nonperturbative expression for the influence of a static electric field on the optical properties. Hence, our result constitutes the one-dimensional analog of the classic bulk Franz-Keldysh effect. A simple closed-form formula for the complex dielectric constant including broadening has been obtained in terms of Airy functions. It is found that the electric field severely distorts the characteristic square-root singularity at the band edge. In addition, the hallmarks of the Franz-Keldysh effect, i.e., an oscillatory modulation of the spectra and the appearance of absorption below the band gap, are clearly visible. It is predicted that the field-induced modulations may be much more pronounced for a one-dimensional semiconductor than for a bulk material. As an example, a comparison shows that the oscillatory modulation of the one-dimensional spectrum has a much larger contrast than the corresponding three-dimensional spectrum, even in the presence of broadening.

The exciton Franz-Keldysh effect is tackled by expanding exciton states in the free-carrier basis. Real and imaginary parts of the optical susceptibility are calculated and results with and without electron-hole interaction are compared. When electron-hole interaction is included the fundamental exciton line below the gap completely rearranges the spectrum. Due to the large exciton binding energy this spectral region is only weakly susceptible to any external perturbation. Thus, at low or moderate field strength the dominant effect of the electric field is the Stark Shift, which simply red shifts the exciton line rigidly. In the continuum above the gap, however, the characteristic oscillatory modulation prevails. The amplitude of the oscillations is comparable to the free-carrier case and a slight stretching of the period is observed. By plotting the shift of absorption maxima with field energy the distinctly different behavior of discrete exciton lines and continuum resonances is highlighted. In agreement with experimental electroabsorption spectra, the small Stark red shift of the discrete lines is contrasted by a blue shift varying approximately as $(\text{field strength})^{2/3}$ of the continuum resonances.

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