Effects of dynamical screening on resonances at inner-shell thresholds in semiconductors

G. Strinati
Università degli Studi di Roma "La Sapienza," Dipartimento di Fisica, I-00185 Roma, Italy
and Institute for Theoretical Physics, University of California, Santa Barbara, California 93106
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A theory of core excitons in semiconductors is formulated, taking into account the frequency dependence of the dielectric matrix which screens the electron-hole attraction. The present approach combines standard many-body techniques (which reduce the Bethe-Salpeter equation for the two-particle Green's function to an effective eigenvalue problem) with elements drawn from Fano's formalism for discrete states interacting with continuum channels. The positions and the widths of core-exciton resonances are affected by dynamical screening, which *increases* the binding energy above its value for static screening and *decreases* its Auger width below its value for a core hole. The latter effect is peculiar to a dynamical theory and has recently been confirmed experimentally.

I. INTRODUCTION

Core excitons in semiconductors can be considered *resonant levels* since the core hole decays by Auger effect. Their spectra width is comparable to their binding energy, being typically of a few tenths of an electron volt. This paper deals with the relationship between width and binding energy that rests on the dynamical screening by the other electrons represented by a frequency-dependent dielectric matrix.[1]

Previous attempts to include dynamical screening effects in the core-exciton problem, either by a Green's-function approach[2] or by a variational approach to the electronic polaron problem,[3] have considered only the increase of the core-exciton binding energy which results from an incomplete screening of the electron-hole attraction at shorter distances of these two quasiparticles. In fact, as this distance decreases, the valence electrons pass from screening two pointlike charges independently (and statically) to screening a dipolar complex in a complicated fashion. This reduction of the screening rests on the localization of the core hole and on the resulting strength of its field within the central cell. Previous work[2,3] considered the large value of the core-hole effective mass, but this effect proved insufficient to account quantitatively for the large increase of the observed binding energy of core excitons with respect to valence excitons.[3,4] Other workers sought the solutions of the core-exciton problem in the inclusion of intervalley mixing among equivalent conduction-band minima[5,6] and central-cell corrections[7] while treating the screening statically.

The present work revives the role of dynamical screening in the core-exciton problem by treating its effects more thoroughly. Specifically, it will be shown that dynamical screening leads not only to an increase of the binding energy but *also* to a decrease of the Auger width of the core exciton. In other words, the electron orbiting at shorter range about the core hole reduces both the induced screening charge and the Auger recombination rate. The latter effect, which has been reported in recent experiments,[8,9] can be considered a fingerprint of dynamical screening since it cannot be obtained within the framework of a static theory. Thus, dynamical screening influences the core-exciton binding energy, provided its effects are included on the same footing as intervalley mixing and central-cell corrections.

Quite generally, to determine the positions and the widths of resonances in complex systems one may resort to an effective non-Hermitian eigenvalue problem which includes the effects of continuum (decay) channels upon the discrete states, along the lines of the effective Hamiltonian method developed for nuclear reactions.[10] In the case of core excitons these channels identify complicated many-electron processes, such as the virtual excitation of secondary electron-hole pairs which screen the primary electron-hole interaction collectively.

The many-body aspect of the bound states of an electron-hole pair can be dealt with more systematically by searching for the poles of the particle-hole Green's function in the complex energy plane, whose positions provide the excitation energies and the associated spectral widths of the N-particle excited states.[11] All possible correlation effects are thus included in principle. A suitable algorithm to locate these poles reduces the Bethe-Salpeter integral equation for the two-particle Green's function to an eigenvalue problem.[11–13] This reduction, however, has so far been attempted only in the case of vanishing spectral widths (i.e., for valence excitons).[2,13] Extension to the case of finite spectral widths (core excitons) would require a nontrivial analytic continuation off the real energy axis across the branch cut originating from the continuum states responsible for the decay. Analytic continuation can, however, be avoided, by combining the reduction of the Bethe-Salpeter equation with elements of Fano's mixing of discrete and continuum states,[14,15] provided the spectral widths of the resonances are small enough for certain approximations to hold. The resultant eigenvalue equation will contain an effective non-Hermitian Hamiltonian which depends on the spectral widths of both the core hole and the core exciton, thereby allowing for the inclusion of lifetime effects in the electron-hole attraction as well as for a comparison of the

two widths.[16]

Since quantitative results have been presented earlier,[1] this paper concentrates on analytical details. Section II contains a detailed derivation of the effective eigenvalue problem for core excitons, Sec. III a discussion of the physical effects which originate from dynamical screening, and Sec. IV gives the conclusions.

II. REDUCTION TO AN EFFECTIVE EIGENVALUE PROBLEM

The derivation of the effective eigenvalue equation, which determines binding energies and lifetimes of core excitons, rests on the reduction of the Bethe-Salpeter equation for the two-particle Green's function to an effective non-Hermitian eigenvalue problem within the ladder approximation with a dynamically screened interaction. It starts from the analysis of the linear combinations of the four time variables in the two-particle Green's function which identifies its particle-hole portion for the relevant types of excited states. It will then proceed by Fourier-transforming a single linear combination to extract the dominant contribution in the neighborhood of a core-exciton resonance. The effects of the decay channels upon the core exciton will be taken into account by representing the approximate bound state as a linear superposition of N-particle exact excited states with a Lorentzian weight. This approach will thus enable us to determine the relevant parameters of the Lorentzian, i.e., its center and its full width at half maximum, while remaining on the real energy axis by performing a suitable average across the range of the resonance with the same Lorentzian weight. The procedure thus restricts the validity of the final equations to narrow resonances, as implied by the very concept of elementary excitations in condensed matter.[17]

A. Particle-hole correlation function

Consider the usual single-particle,[18]

$$G_1(1,2)=-i\langle N\,|\,T[\psi(1)\psi^\dagger(2)]\,|\,N\rangle\ , \tag{2.1}$$

and two-particle,

$$G_2(1,2;1',2')=(-i)^2\langle N\,|\,T[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')]\,|\,N\rangle\ , \tag{2.2}$$

Green's functions, where $|\,N\rangle$ stands for the ground state of the interacting N-electron system, T is Wick's time-ordering operator, the ψ are field operators in the Heisenberg picture, and the labels 1,2,... signify the set of space, spin, and time variables. It is convenient to introduce the two-particle correlation function defined as

$$L(1,2;1',2')=-G_2(1,2;1',2')+G_1(1,1')G_1(2,2')\ . \tag{2.3}$$

This function satisfies the following form of the Bethe-Salpeter integral equation:

$$L(1,2;1',2')=G_1(1,2')G_1(2,1')+\int d3456\,G_1(1,3)G_1(4,1')\Xi(3,5;4,6)L(6,2;5,2')\ , \tag{2.4}$$

where the kernel Ξ is an effective two-particle interaction expressed compactly as the functional derivative of the self-energy operator with respect to the single-particle Green's function:[11,19]

$$\Xi(3,5;4,6)=\frac{\delta\Sigma(3,4)}{\delta G_1(6,5)}\ . \tag{2.5}$$

It has long been known[12,13] that Eq. (2.4) or its equivalents provide information about the excitation energies E_S-E_0 of the N-particle system. These energy differences appear only in the phase factors of the two-particle Green's function (2.2), multiplied by the symmetric combinations of time variables:

$$t^1=\frac{t_1+t_{1'}}{2},\quad \tau_1=t_1-t_{1'}\ ,\quad t^2=\frac{t_2+t_{2'}}{2},\quad \tau_2=t_2-t_{2'}\ .$$

For our purposes it is sufficient to choose infinitesimal values $\tau_1=0^-$ and $\tau_2=0^-$, whereby the spectrum depends only on t_1 and t_2. The 8 (out of 24) terms of the two-particle Green's function which contain the phase factors $\exp[i(E_S-E_0)t^1]$ and $\exp[i(E_S-E_0)t^2]$ are then called the particle-hole Green's function. They are expressed conveniently in terms of the right- and left-hand particle-hole amplitudes

$$\chi_S(\vec{x}_i,\vec{x}_j;t_i-t_j)=\langle N\,|\,T[\psi(i)\psi^\dagger(j)]\,|\,N,S\rangle\exp[i(E_S-E_0)(t_i+t_j)/2]\ , \tag{2.6a}$$

$$\tilde{\chi}_S(\vec{x}_i,\vec{x}_j;t_i-t_j)=\langle N,S\,|\,T[\psi(i)\psi^\dagger(j)]\,|\,N\rangle\exp[-i(E_S-E_0)(t_i+t_j)/2]\ , \tag{2.6b}$$

in the following way:[11]

$$\begin{aligned}G_2^{ph}(1,2;1',2')=&-\sum_S\chi_S(\vec{x}_1,\vec{x}_{1'};\tau_1)\tilde{\chi}_S(\vec{x}_2,\vec{x}_{2'};\tau_2)\exp[i(E_S-E_0)(t^2-t^1)]\Theta(t^1-t^2-\tfrac{1}{2}\,|\,\tau_1\,|-\tfrac{1}{2}\,|\,\tau_2\,|)\\&-\sum_S\chi_S(\vec{x}_2,\vec{x}_{2'};\tau_2)\tilde{\chi}_S(\vec{x}_1,\vec{x}_{1'};\tau_1)\exp[i(E_S-E_0)(t^1-t^2)]\Theta(t^2-t^1-\tfrac{1}{2}\,|\,\tau_1\,|-\tfrac{1}{2}\,|\,\tau_2\,|)\ .\end{aligned} \tag{2.7}$$

In Eqs. (2.6) and (2.7) the $\vec{x}$ signify the set of space $\vec{r}$ and spin variables, the generalized sum extends over the complete set of N-particle excited states $|\,N,S\rangle$, and Θ is the unit step function.

We proceed now to the Fourier transformation whose result will exhibit the poles of the spectrum E_S-E_0. The vari-

able to be transformed is $t^2=(t_2+t_2)/2=t_2-\frac{1}{2}\tau_2\rightarrow t_2$ because it appears in the function L on both sides of Eq. (2.4) (the corresponding variable t^1 will eventually factor out). The symbol $t_2^+=t_2+\frac{1}{2}\delta$, where δ is a positive infinitesimal, will replace $t_{2'}$ to indicate that the proper limit of a step function within L is to be taken before the transform. The particle-hole portion of the left-hand side of Eq. (2.4) yields

$$L^{ph}(\vec{x}_1,\vec{x}_2;\vec{x}_{1'},\vec{x}_{2'}\,|\,t_1,t_{1'};\omega)\equiv-\int_{-\infty}^{+\infty}dt_2 e^{-i\omega t_2}L^{ph}(\vec{x}_1t_1,\vec{x}_2t_2;\vec{x}_{1'}t_{1'},\vec{x}_{2'}t_2^+)$$
$$=-ie^{-i\omega(t^1-|\tau_1|/2)}\sum_S\frac{\chi_S(\vec{x}_1,\vec{x}_{1'};\tau_1)\tilde{\chi}_S(\vec{x}_2,\vec{x}_{2'};-\delta)}{\omega-(E_S-E_0)+i\delta}e^{-i(E_S-E_0)|\tau_1|/2}$$
$$+ie^{-i\omega(t^1+|\tau_1|/2)}\sum_S\frac{\chi_S(\vec{x}_2,\vec{x}_{2'};-\delta)\tilde{\chi}_S(\vec{x}_1,\vec{x}_{1'};\tau_1)}{\omega+(E_S-E_0)-i\delta}e^{-i(E_S-E_0)|\tau_1|/2}\,. \tag{2.8}$$

Notice that the transform of the single-particle factor in Eq. (2.3) vanishes provided ω is nonzero.

B. Relevant approximations

Equation (2.8) is still exact. Our aim, however, is to extract the *dominant contribution* to the Fourier transform of Eq. (2.4) near a core-exciton resonance. To this end, we adopt the following approximations.

(i) The dynamics of the bound electron-hole pair is embodied in the effective two-particle interaction Ξ. Sham and Rice[13] have shown that, in the effective-mass limit, Ξ reduces to a Coulomb potential modified by the macroscopic dielectric constant of the insulating medium. Quite generally, this limit can be recovered from Eq. (2.5) by taking the non-Hartree part M of the self-energy operator Σ within the so-called GW approximation,[20]

$$M(1,2)=iW(1^+,2)G_1(1,2)\,. \tag{2.9}$$

Here W is the dynamically screened interaction defined in terms of the bare Coulomb potential

$$v(1,2)=2\delta(t_1-t_2)/|\vec{r}_1-\vec{r}_2|$$

and of the (time-ordered) inverse dielectric matrix,[21]

$$W(1,2)=\int d3\,\epsilon_T^{-1}(1,3)v(3,2)\,, \tag{2.10}$$

and 1^+ implies that the time variable t_1 is augmented by a positive infinitesimal. By further neglecting the implicit dependence of the screened interaction on G_1 while taking the functional derivative, one obtains, in fact,

$$\Xi(3,5;4,6)=-i\delta(3,4)\delta(5^-,6)v(3,6)$$
$$+i\delta(3,6)\delta(4,5)W(3^+,4)\,. \tag{2.11}$$

The first term originates from the Hartree part of the self-energy and the second from the screened Fock term (2.9). Diagrammatically, the two terms represent the random-phase-approximation (RPA) contribution to the polarizability and its screened exchange counterpart, respectively, the latter giving rise to the so-called ladder approximation.

Here, we extend the form (2.11) for Ξ to the case of core excitons, whose ratio E_B/ϵ_g is of the order of 0.1, even though the form (2.11) is exact only within the effective-mass limit[13] in which the excitonic radius is large compared with lattice spacing, and the exciton binding energy E_B is much smaller than the valence energy gap ϵ_g. In this sense, we limit our goal to the study of the effects of dynamical screening on core-exciton resonances, but our procedure may be supported later by experimental verification of novel effects to be discussed below.

(ii) We represent all single-particle Green's functions entering Eq. (2.4) in the *quasiparticle approximation*:[22]

$$G_1(1,2)=G_1(\vec{x}_1,\vec{x}_2;t_1-t_2)$$
$$=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega(t_1-t_2)}G_1(\vec{x}_1,\vec{x}_2;\omega)\,, \tag{2.12a}$$

$$G_1(\vec{x}_1,\vec{x}_2;\omega)\simeq\sum_K\frac{u_K(\vec{x}_1)u_K^*(\vec{x}_2)}{\omega-\epsilon_K}\,, \tag{2.12b}$$

where the $u_K(\vec{x})$ are (orthonormalized) single-particle wave functions which are assumed to be known by a previous solution of a band eigenvalue problem, and the ϵ_K are the corresponding eigenvalues. Moreover, we set, as usual, $\epsilon_K\rightarrow\epsilon_K-i\delta$ for the conduction bands and $\epsilon_K\rightarrow\epsilon_K+i\delta$ for the valence bands of the semiconductor, retaining for the core band a *finite* imaginary part γ.

(iii) An explicit, albeit approximate, expression for the particle-hole amplitudes can be obtained from their definition (2.6) by expanding the field operators in terms of the single-particle wave functions $u_K(\vec{x})$ introduced above and retaining the same approximation that has led to the energy denominators of Eq. (2.12b). For the states of interest to us we set

$$\chi_S(\vec{x},\vec{x}';\tau)\simeq-e^{i(E_S-E_0)|\tau|/2}\sum_{d,c}u_c(\vec{x})u_d^*(\vec{x}')A_S(d,c)[\Theta(\tau)e^{-i\epsilon_c\tau}+\Theta(-\tau)e^{-i(\epsilon_d+i\gamma)\tau}]\,, \tag{2.13}$$

where d and c stand for deep (core) and conduction-band quantum numbers, respectively. The (yet to be determined) expansion coefficients $A_s(d,c)$ can be expressed as transition matrix elements in terms of creation and destruction operators,

$$A_S(d,c)=\langle N\,|\,a_d^\dagger a_c\,|\,N,S\rangle\,. \tag{2.14}$$

A similar expression holds for $\tilde{\chi}_S(\vec{x},\vec{x}';\tau)$.

(iv) We restrict the range of the frequency ω in the Fourier transform of Eq. (2.4) to a neighborhood of the (yet to be determined) position Ω of a core-exciton resonance; the second term on the right-hand side of Eq. (2.8) whose energy denominators remain large will accordingly be discarded. Physically, ω plays the role of the frequency of the impinging photon which creates the exciton and can thus be regarded as a parameter.

(v) We note that the generalized sum over the complete set of N-particle exact excited states $|N,S\rangle$ in the first term on the right-hand side of Eq. (2.8) includes an integration over the continuous variable E_S-E_0 ranging across Ω. Aiming only at determining the position Ω and the full width at half maximum 2Γ of a core-exciton resonance, we perform the integration approximately as follows. According to Fano's formalism for discrete states interacting with continuum channels[14,15] the integrand contains a density-of-states factor $D(E_S-E_0)$ which describes the dilution of the approximate electron-hole–pair excited states into exact N-particle excited states. If Γ is sufficiently small, one can represent this factor by a Lorentzian of unit weight

$$D(E_S-E_0)=\frac{\Gamma/\pi}{(E_S-E_0-\Omega)^2+\Gamma^2} . \tag{2.15}$$

We also neglect the variation of all other factors in the integrand across the resonance (2.15), taking their values at the resonance frequency Ω. For $\omega\simeq\Omega$ one then obtains

$$L^{ph}(\vec{x}_1,\vec{x}_2;\vec{x}_{1'},\vec{x}_{2'}\,|\,t_1,t_{1'};\omega)\simeq -i\,e^{-i\omega t_1}\frac{1}{\omega-(\Omega-i\Gamma)}\sum_{\{s\}}\bar{X}_s(\vec{x}_1,\vec{x}_{1'};\tau_1)\bar{\bar{X}}_s(\vec{x}_2,\vec{x}_{2'};-\delta) . \tag{2.16}$$

The sum is now restricted to the discrete set $\{s\}$ of (possibly) degenerate core-exciton resonances (thereby disregarding the contribution of a smooth background). The bars over the particle-hole amplitudes signify that the density of states (2.15) has been factored out from the expressions (2.6), and that the excitation energy E_S-E_0 has been replaced by the variable ω. We shall refer to the expression (2.16) as the *quasi bound electron-hole–pair approximation* in analogy with the more familiar quasiparticle approximation for the single-particle Green's function.

C. Effective inverse dielectric matrix

With these approximations, we now proceed to reduce the Bethe-Salpeter equation (2.4) to an effective eigenvalue problem which will determine the core-exciton excitation energy Ω, its spectral width Γ, and the expansion coefficients A. To achieve this reduction, we insert the expressions (2.11)–(2.13) and (2.16) into the Fourier transform of Eq. (2.4) and perform the following steps in the resultant equation.

(i) Project both sides onto $u_c(\vec{x}_1)u_d^*(\vec{x}_{1'})$ and make use of the assumed orthonormality of the single-particle wave functions.

(ii) Take the limit as $\tau_1=0^-$ and drop the common factor $\exp(-i\omega t_1)$.

(iii) Multiply both sides by $\bar{X}_r(\vec{x}_{2'},\vec{x}_2;-\delta)$ where r belongs to the degenerate set $\{s\}$ appearing in the expression (2.16), integrate over $\vec{x}_2$ and $\vec{x}_{2'}$, and utilize the orthonormality of the coefficients $\bar{A}$:

$$\sum_{d,c}\bar{A}_r(d,c)\bar{A}_s^*(d,c)=\delta_{rs} . \tag{2.17}$$

[Recall that the bars over the coefficients A signify that their value is taken at the resonance center after extracting the square root of the density-of-states factor (2.15). The orthonormality (2.17) holds in the present form only in the limit of narrow resonances, assumed throughout the present treatment.]

(iv) Multiply both sides by

$$[\omega-(\Omega-i\Gamma)][\omega-(\epsilon_c-\epsilon_d-i\gamma)] .$$

The result is

$$\begin{aligned}&[\epsilon_c-\epsilon_d-i\gamma-(\Omega-i\Gamma)]\bar{A}_r(d,c)\\&+\sum_{d',c'}\bar{A}_r(d',c')\left\{\int d\vec{x}_1 d\vec{x}_2 u_c^*(\vec{x}_1)u_d(\vec{x}_1)\frac{2}{|\vec{r}_1-\vec{r}_2|}u_{c'}(\vec{x}_2)u_{d'}^*(\vec{x}_2)\right.\\&-\int d\vec{x}_1 d\vec{x}_2 u_c^*(\vec{x}_1)u_{c'}(\vec{x}_1)\int d\vec{r}_3\left[i\int_{-\infty}^{+\infty}\frac{d\omega'}{2\pi}e^{-i\omega'\delta}\epsilon_T^{-1}(\vec{r}_1,\vec{r}_3;\omega')\right.\\&\left.\left.\times\left[\frac{1}{\omega-\omega'-(\epsilon_{c'}-\epsilon_d)+i\gamma}+\frac{1}{\omega+\omega'-(\epsilon_c-\epsilon_d)+i\gamma}\right]\right]\frac{2}{|\vec{r}_3-\vec{r}_2|}u_d(\vec{x}_2)u_{d'}^*(\vec{x}_2)\right\}=0 .\end{aligned} \tag{2.18}$$

This equation should be read as follows. First, suppose that the effective two-particle interaction were switched off. In this case one would obtain, from Eq. (2.18), $\Omega=\epsilon_c-\epsilon_d$ and $\Gamma=\gamma$, as expected for an uncorrelated electron-hole pair. Consider, next, the first term in large curly brackets which does not contain any effect of screening. This term is known to be responsible for the longitudinal-transverse splitting of the excitonic states[23] and is also known to induce a mixing of different spin-orbit eigenstates.[24] This term will be neglected in what follows since, being of short-range character, it does not affect the excitonic energy when the excitonic radius is relatively large. The last term in large curly brackets in

Eq. (2.18) is the only one to depend on the frequency ω. To interpret it physically, we recast it in a more meaningful form by making use of the relation between time-ordered (T) and -retarded (R) inverse dielectric matrices[21] and of the Kramers-Kronig relations obeyed by the latter. This term then reads

$$-\int d\vec{x}_1 d\vec{x}_2 u_c^*(\vec{x}_1) u_{c'}(\vec{x}_1) \int d\vec{r}_3 \epsilon^{-1}_{dc,dc'}(\vec{r}_1,\vec{r}_3;\omega) \frac{2}{|\vec{r}_3-\vec{r}_2|} u_d(\vec{x}_2) u_{d'}^*(\vec{x}_2) ,$$

where we have introduced the following notation:

$$\epsilon^{-1}_{dc,dc'}(\vec{r}_1,\vec{r}_3;\omega)=\delta(\vec{r}_1-\vec{r}_3)-\frac{1}{\pi}\int_0^\infty d\omega' \,\mathrm{Im}[\epsilon_R^{-1}(\vec{r}_1,\vec{r}_3;\omega')] \left[\frac{1}{\omega-\omega'-(\epsilon_{c'}-\epsilon_d)+i\gamma}+\frac{1}{\omega-\omega'-(\epsilon_c-\epsilon_d)+i\gamma}\right] . \quad (2.19)$$

The diagonal elements ($c=c'$) of expression (2.19) can thus be interpreted as defining an *effective inverse dielectric matrix,* whereby an electron excited into a conduction-band state c probes the density response of the system with a hole in the state d. This expression has to be contrasted with the ordinary inverse dielectric matrix of linear response theory, that is,

$$\epsilon_R^{-1}(\vec{r}_1,\vec{r}_3;\omega)=\delta(\vec{r}_1-\vec{r}_3)-\frac{1}{\pi}\int_0^\infty d\omega' \,\mathrm{Im}[\epsilon_R^{-1}(\vec{r}_1,\vec{r}_3;\omega')] \left[\frac{1}{\omega-\omega'+i\delta}-\frac{1}{\omega+\omega'+i\delta}\right] , \quad (2.20)$$

whereby an external (test) charge probes the density response of the system in the ground state. The effective and the ordinary inverse dielectric matrices coincide, however, in the *static limit* when γ vanishes and the differences $\omega-(\epsilon_{c'}-\epsilon_d)$ and $\omega-(\epsilon_c-\epsilon_d)$ can be neglected in comparison to the characteristic energies in the loss matrix $-\mathrm{Im}[\epsilon_R^{-1}(\vec{r}_1,\vec{r}_3;\omega')]$, which are at least of the order of the valence energy gap. When these conditions are met, as in the case of valence (shallow) excitons, Eq. (2.18) reduces to the ordinary integral equations for excitons with static screening.[23] For core excitons, however, deviations from static screening (the so-called *dynamical corrections*) need to be considered.

D. Effective eigenvalue equation

Equation (2.18) is not yet, in general, an eigenvalue equation, since it depends parametrically on the frequency ω, although this frequency has been assumed to be close to the position Ω of the core-exciton resonance. To determine the proper value of ω consistently with the assumptions of Sec. II B, we *average* Eq. (2.18) over ω with the weighting function $D(\omega)$ of the form (2.15) which represents the probability for the exciton to be formed by radiation at frequency ω. This averaging procedure thus bears some resemblance to the experimental situation where the absorption spectrum is weighted by the monochromator spectral function. One is then led to the following non-Hermitian eigenvalue problem:

$$[\epsilon_c-\epsilon_d-i\gamma-(\Omega-i\Gamma)]\bar{A}(d,c)-\sum_{d'c'}\bar{A}(d',c')\int d\vec{x}_1 d\vec{x}_2 u_c^*(\vec{x}_1)u_{c'}(\vec{x}_1)$$

$$\times\int d\vec{r}_3 \epsilon^{-1}_{dc,dc'}(\vec{r}_1,\vec{r}_3;\Omega+i\Gamma)\frac{2}{|\vec{r}_3-\vec{r}_2|}u_d(\vec{x}_2)u_{d'}^*(\vec{x}_2)=0 , \quad (2.21)$$

where the suffix r labeling degenerate eigenvectors has been dropped.[25] We note the following features.

(i) The eigenvalue $\Omega-i\Gamma$ of Eq. (2.21) needs to be consistent with the energy dependence of the Hamiltonian matrix. Moreover, the Hamiltonian matrix is *non-Hermitian,* its skew Hermitian part arising from the finite values of γ and Γ. Both facts are familiar for the quasiparticle equation which is derived from Dyson's equation.[21]

(ii) Equation (2.21) generalizes the equation reported in Ref. 2 which can be recovered in the limit of stable excitons when $\gamma=\Gamma=0$. In this case, the reduction of the Bethe-Salpeter equation to an eigenvalue problem is achieved by performing a complex integration along an infinitesimal contour enclosing the pole of the function (2.8) located along the *real* energy axis at E_S-E_0.[11,13]

III. PHYSICAL INTERPRETATION

This section is devoted to gaining physical insight into the main analytical result of this paper, Eq. (2.21), and to discussing the observable consequences of dynamical screening predicted from that equation.

A. Exponential decay of the core hole

The Eq. (2.21) derived in Sec. II reduces, in the limit $\gamma=\Gamma=0$, to the equation for true bound states which follows from the Bethe-Salpeter equation by established procedures. We shall now explore this connection by arguing that Eq. (2.21) with γ and Γ finite could have been guessed directly from the corresponding true bound-state equation with $\gamma=\Gamma=0$ on physical grounds. In fact, the effective electron-hole potential in Eq. (2.21) can be recast

in the following form that shows the time-dependence of the interaction by Fourier-transforming the frequency integration in Eq. (2.19) into a time integration:

$$\int d\vec{r}_3 \epsilon^{-1}_{dc,dc'}(\vec{r}_1,\vec{r}_3;\Omega+i\Gamma)\frac{2}{|\vec{r}_3-\vec{r}_2|} = \int_0^\infty dt\, e^{-2\gamma t} W(\vec{r}_1,\vec{r}_2;t) \times (e^{i(\Omega-\epsilon_c'+\epsilon_d)t}+e^{i(\Omega-\epsilon_c+\epsilon_d)t}), \quad (3.1)$$

where we have set $\gamma \simeq \Gamma$ as a first approximation. Here the core-hole decay factor $\exp(-2\gamma t)$ combines with the time-dependent screened potential $W(\vec{r}_1,\vec{r}_2;t)$ defined by Eq. (2.10) to yield the effective potential

$$W_{\text{eff}}(\vec{r}_1,\vec{r}_2;t)=e^{-2\gamma t}W(\vec{r}_1,\vec{r}_2;t)\ . \quad (3.2)$$

The Auger decay of the core hole thus reduces its response to the excited electron by allowing only an *incomplete relaxation,* and might thereby influence the exciton's binding energy and lifetime.[26]

One may wonder at this point how the exponential factor in Eq. (3.2) represents the lifetime effects related to the Auger decay of the core hole. One knows, in fact, that[27] deviations from the exponential decay occur both for short times [i.e., for $(E_R-E_{th})t \lesssim 1$, where E_R is the resonance energy and E_{th} is the onset of the continuum] and for large times (i.e., for $\Gamma t \gtrsim 1$). In particular, the decay law starts as a quadratic function of time and ends as an inverse power law, thereby being larger in both cases than the exponential approximation. However, for typical semiconductors one expects the exponential approximation to hold since the characteristic *screening time* (i.e., the reciprocal of the characteristic energies entering the loss function) lies well within its limits of validity.

B. Direct recombination channels

The structure of the eigenvalue equation (2.21) is of the type obtained by an effective Hamiltonian method,[10] whereby the Schrödinger equation is reduced into the subspace of a set of approximate bound states by suitably eliminating the continuum channels through projection-operator techniques. The effective Hamiltonian which results is, in general, non-Hermitian and energy dependent.

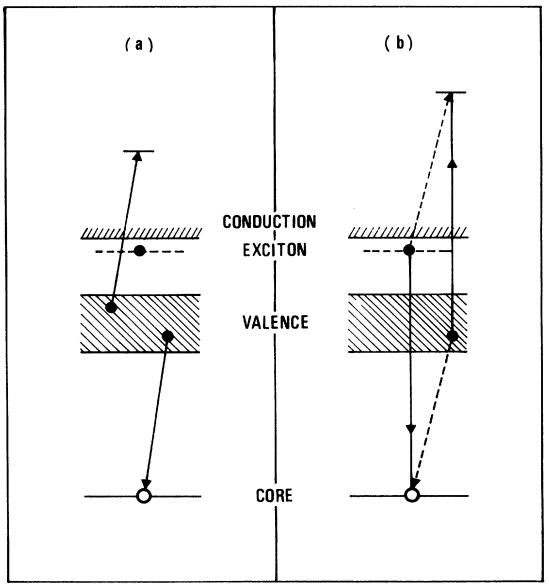

FIG. 1. (a) Auger process; (b) direct recombination.

On the other hand, the approach to the core-exciton eigenvalue problem through Green's functions that we have used has enabled us to separate from the outset two-particle from single-particle effects, and to treat both the Auger decay of the core hole and the dynamical screening effects in the electron-hole interaction in an essentially phenomenological way through the width γ and the loss matrix $-\text{Im}[\epsilon_R^{-1}(\vec{r}_1,\vec{r}_2;\omega)]$, respectively.

This approach, however, has left out the so-called direct recombination channels[28] where the bound electron itself fills the hole and, at the same time, a new hole is produced in a higher (valence) band (Fig. 1). Note that the Auger channels contain at least two holes, whereas the direct recombination channels contain a single hole in the valence band. This feature can be important for the experimental detection of the core exciton.[29]

The contribution of the direct recombination channels to the core-exciton eigenvalue equation (2.21) can be represented by adding the following term to the interaction Hamiltonian:

$$\langle c,d\,|\,H_{DR}\,|\,c',d'\rangle=\sum_{v'',c''}\frac{\langle c,v''\,|\,v(1-P)\,|\,d,c''\rangle\langle c'',d'\,|\,v(1-P)\,|\,v'',c'\rangle}{\Omega-(\epsilon_{c''}-\epsilon_{v''})+i\delta}\ . \quad (3.3)$$

Here the labels v'' and c'' refer to a valence band and to a highly excited conduction state, respectively, the Kapur-Peierls[10] boundary conditions are appropriate to a decaying state, and the matrix elements read, in the usual notation,

$$\langle c,v''\,|\,v(1-P)\,|\,d,c''\rangle=\int d\vec{x}_1 d\vec{x}_2 u_c^*(\vec{x}_1)u_{v''}^*(\vec{x}_2)\frac{2}{|\vec{r}_1-\vec{r}_2|}[u_d(\vec{x}_1)u_{c''}(\vec{x}_2)-u_{c''}(\vec{x}_1)u_d(\vec{x}_2)]\ . \quad (3.4)$$

It can be inferred from Eq. (3.3) that the sole contribution of the direct recombination channels would yield a value Γ of the core-exciton width larger than the corresponding value γ of the core-hole width. This is to be expected, because the direct recombination channels are suppressed in the $(N-1)$-particle problem for the core hole. However, values of Γ *smaller* than γ have been reported experimentally.[8,9] This net narrowing of the spectral width in passing from the core hole to the core exciton can thus *only* result whenever dynamical screening ef-

fects in the Auger channels are sufficiently large to compensate for the presence of the direct recombination channels, as discussed below.

C. Effective-mass limit and the narrowing effect

The net narrowing of the spectral width discussed above can be predicted *analytically* from the effective-mass limit of Eq. (2.21). To this end, one has to follow the steps leading the usual effective-mass equation for excitons,[23] retaining the full effective inverse dielectric function and not just its static limit. The results are as follows.

(i) The excitonic binding energy E_B $(=\epsilon_c^{\text{bottom}}-\epsilon_d-\Omega)$ can be determined by solving a Schrödinger-like equation with an attractive electron-hole Coulomb interaction screened by the real part of the effective inverse dielectric function

$$\tilde{\epsilon}_0^{-1}(E_B,\Gamma+\gamma)=1-\frac{2}{\pi}\int_0^\infty d\omega\frac{-\mathrm{Im}[\epsilon^{-1}(\vec{q}=0;\omega)]}{\omega+E_B-i(\Gamma+\gamma)}\ , \tag{3.5}$$

where $-\mathrm{Im}[\epsilon^{-1}(\vec{q}=0;\omega)]$ is the loss function.

(ii) The difference $\gamma-\Gamma$ can then be calculated from the expression

$$\gamma-\Gamma=-\mathrm{Im}[\tilde{\epsilon}_0^{-1}(E_B,\Gamma+\gamma)]\int d\vec{r}\,F^*(\vec{r})\frac{2}{r}F(\vec{r})\ , \tag{3.6}$$

where $F(\vec{r})$ is the (normalized) envelope function solution of the effective-mass equation with eigenvalue $-E_B$.

Assume now that this simplified version of the core-exciton eigenvalue problem has been solved to self-consistency. From Eq. (3.5) one then verifies that the imaginary part of the effective inverse dielectric function is negative for any value of its arguments, thereby yielding positive values for the difference $\gamma-\Gamma$ in Eq. (3.6). Deviations from static screening can thus indeed lead to *a narrowing of the Auger width* in passing from the core hole to the core exciton. Pictorially, this effect can be described by saying that the presence of the electron orbiting about the hole hinders the Auger filling of the hole by the remaining (valence) electrons.[30] This intuitive physical representation of the narrowing effect and its experimental observation give confidence that the core-exciton eigenvalue equation (2.21) could be extrapolated in practice beyond the limits within which it was derived.

In addition to the narrowing effect, dynamical screening also leads to an increase of the binding energy over its static value obtained by setting $E_B=\Gamma+\gamma=0$ in Eq. (3.5). In fact, for finite values of E_B and $\Gamma+\gamma$ the effective dielectric constant $\tilde{\epsilon}_0(E_B,\Gamma+\gamma)$ [defined as the reciprocal of the real part of Eq. (3.5)] is smaller than its static value, i.e., the macroscopic dielectric constant ϵ_0. A plot of $\tilde{\epsilon}_0(E_B,\Gamma+\gamma)$ as a function of E_B for various values of $\Gamma+\gamma$ is shown in Fig. 2 for the case of silicon.[31] Physically, these curves represent two distinct effects, namely (i) the curve with $\Gamma+\gamma=0$ shows that electronic relaxation is reduced when the electron orbits at shorter range about the core hole or, equivalently, when the excitonic binding energy E_B is increased, and (ii) the curves with $\Gamma+\gamma\neq 0$ show that, in addition, the decay of the core hole induces an incomplete electronic relaxation. The increase of the excitonic binding energy over its static screening value will result mostly from dynamical effects of the type of (i).

Numerical estimates of these dynamical effects have been reported in Ref. 1 for the case of the Si $2p$ transition. They were based on a suitable modification of the effective-mass limit discussed above to include band-structure effects, such as intervalley mixing and central-cell corrections, in an effective manner. Typically, dynamical screening effects may yield a 20—30 % increase of the binding energy over its static value and a comparable percentage decrease of the spectral width.

D. Normalization condition

The normalization condition (2.17) with $r=s$ merits some comments. This condition is altogether trivial in the lowest approximation when the exciton is built up as a linear superposition of single electron-hole—pair excitations from the Hartree-Fock ground state and screening effects due to multiple electron-hole pairs are neglected. When screening effects are introduced, however, Eq. (2.17) becomes nontrivial since the coefficients $\bar{A}$ refer only to a subset of the states needed to describe the exciton. In this case, Eq. (2.17) can be supported by the theory of Refs. 14 and 15, whereby the coefficients of multiple electron-hole pairs are expressed in terms of those for single pairs.

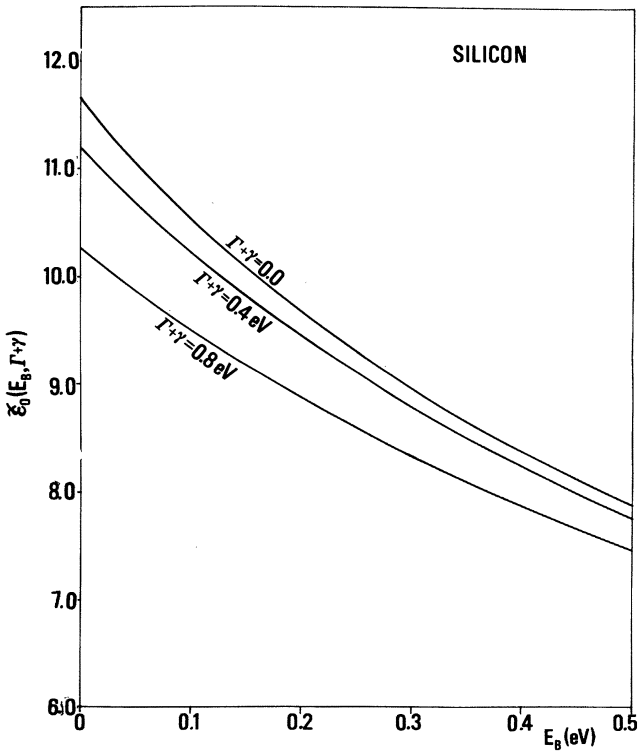

FIG. 2. Effective dielectric constant (silicon) versus the excitonic binding energy E_B for various values of the sum $\Gamma+\gamma$ of the core-exciton and core-hole widths.

IV. CONCLUDING REMARKS

An eigenvalue equation to determine binding energies and spectral widths of core excitons in semiconductors has been derived, taking into account the time dependence of screening effects through the dielectric matrix $\epsilon^{-1}(\vec{r},\vec{r}';\omega)$. Dynamical screening effects have been shown to lead to an observable narrowing of the core-exciton width, accompanied by an increase of the core-exciton binding energy over its value for static screening.

These dynamical effects are missing in the isochoric impurity problem[32] to which the core-exciton problem has been traditionally associated.[33] This association has rested on the intuitive replacement of the massive core hole by a static charge which is localized at a lattice site and acts as an external potential on the excited electron and on the polarizable medium. This picture, however, disregards the quantum nature of the core hole which manifests itself in the scattering with the excited electron regardless of the large value of its effective mass. In our approach this leads to a modification of the polarization of the medium where the core hole and the excited electron are embedded.

The eigenvalue equation (2.21) might be solved numerically in a local-orbital basis (cf. the Appendix) which is appropriate when the excitonic size deviates appreciably from its effective-mass value. This method could be applied particularly to the study of surface core excitons[9,34] where dynamical effects are expected to be enhanced by the localization of the surface states.

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APPENDIX

In this Appendix the core-exciton eigenvalue equation (2.21) is converted into a local-orbital representation along the approach introduced by Altarelli and Bassani for intermediate binding.[35]

The conversion is achieved by expanding the single-particle conduction Bloch functions $\psi_{n\vec{k}}(\vec{r})$ in the matrix elements of (2.21) into orbitals $\varphi_\mu(\vec{r}-\vec{l})$ localized about the lattice sites $\vec{l}$:[36]

$$\psi_{n\vec{k}}(\vec{r})=\sum_{\{\mu\}}\left[N^{-1/2}\sum_{\vec{l}}e^{i\vec{k}\cdot\vec{l}}\varphi_\mu(\vec{r}-\vec{l})\right]c_{\mu n}(\vec{k})\ . \tag{A1}$$

Here N is the number of lattice sites, $\vec{k}$ is the Bloch wave vector, n is a band index, and the c's are expansion coefficients to be determined from the band structure. The number of indices $\{\mu\}$ depends on the portion of conduction bands one is willing to include. For the core bands, on the other hand, the φ are atomic orbitals and c reduces to $\delta_{\mu d}$.

Manipulations lead to the eigenvalue equation for singlet excitons with Bloch vector $\vec{Q}=0$:

$$\sum_{\mu',d',\vec{l}\,'}[\delta_{\mu\mu'}\delta_{dd'}\delta_{\vec{l}\,\vec{l}\,'}+\langle\mu d\,\vec{l}\,|H_{\rm eff}(\Omega,\Gamma)|\,\mu' d'\,\vec{l}\,'\rangle]\times\bar{A}(\mu',d',\vec{l}\,')=0\ . \tag{A2}$$

Here $\bar{A}(\mu,d,\vec{l})$ is the lattice Fourier transform of the expansion coefficients $\bar{A}(\mu,d,\vec{k})$ in the basis of the Bloch sums within large parentheses in Eq. (A1), and the electron-hole effective interaction Hamiltonian in local-orbital representation reads

$$\begin{aligned}\langle\mu d\,\vec{l}\,|H_{\rm eff}(\Omega,\Gamma)|\,\mu' d'\,\vec{l}\,'\rangle=&N^{-1}\sum_{n,\vec{k}}e^{i\vec{k}\cdot\vec{l}}N^{-1}\sum_{n',\vec{k}\,'}e^{-i\vec{k}\,'\cdot\vec{l}\,'}\sum_{\nu,\nu'}\frac{c^*_{\nu n}(\vec{k})c_{\mu n}(\vec{k})c^*_{\mu' n'}(\vec{k}\,')c_{\nu' n'}(\vec{k}\,')}{\Omega+\epsilon_d-\epsilon_n(\vec{k})+i(\gamma-\Gamma)}\\&\times\sum_{\vec{m},\vec{m}\,'}e^{i\vec{k}\,'\cdot\vec{m}\,'}e^{i(\vec{k}\,'-\vec{k})\cdot\vec{m}}\,i\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega\delta}W_{\nu\nu'\vec{m},dd'\vec{0}}(\vec{m}\,';\omega)\\&\times\left[\frac{1}{\Omega+i\Gamma-[\epsilon_{n'}(\vec{k}\,')-\epsilon_d-i\gamma]-\omega}+\frac{1}{\Omega+i\Gamma-[\epsilon_n(\vec{k})-\epsilon_d-i\gamma]+\omega}\right],\end{aligned} \tag{A3}$$

with the notation

$$W_{\nu\nu'\vec{m},dd'\vec{0}}(\vec{m}\,';\omega)=\int d\vec{r}\,d\vec{r}\,'\varphi^*_\nu(\vec{r}-\vec{m})\varphi_{\nu'}(\vec{r}-\vec{m}-\vec{m}\,')W(\vec{r},\vec{r}\,';\omega)\varphi^*_{d'}(\vec{r}\,')\varphi_d(\vec{r}\,')\ . \tag{A4}$$

Equations (A3) and (A4) omit the negligible overlap between core (atomic) orbitals centered at different lattice sites; the direct RPA term, whose expression[35] is not affected by screening, has also been omitted.

The matrix elements (A4) can be evaluated by utilizing the Hanke and Sham formalism within the so-called time-dependent screened Hartree-Fock approximation.[37,38] The desired values of Ω and Γ then result from the vanishing of the determinant of the matrix within square brackets in Eq. (A2).

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