Dynamical Shift and Broadening of Core Excitons in Semiconductors

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(Received 8 July 1982)

A non-Hermitian eigenvalue equation is proposed to determine binding energies and widths of core excitons in semiconductors, taking into account the time dependence of screening effects through the dielectric matrix $\epsilon^{-1}(\vec{r}, \vec{r}'; \omega)$. Deviations from static screening contribute both an increase of the binding energy and a narrowing of the Auger width. Numerical estimates of both effects for the Si $2p$ transition give qualitative agreement with experimental data when the exciton size is reduced by band-structure effects.

PACS numbers: 71.35.+z, 71.45.-d

This Letter investigates theoretically the role of *incomplete electronic relaxation* on the position *and* the shape of inner-shell excitonic resonances in semiconductors. Specifically, it is suggested that analysis of these resonances may reveal the dynamical nature of the polarization of the medium that screens the electron-hole interaction. In fact, deviations from static screening, in addition to contributing an *increase* of the core-exciton binding energy, are shown to lead to a *decrease* of its spectral width relative to the spectral width of the core hole by itself (measured, e.g., by photoemission experiments).

The interpretation of the strong enhancement of the binding energy of core excitons in semiconductors (typically a few tenths of an electronvolt) as compared with the corresponding binding energy of valence (shallow) excitons (a few millielectronvolts) has been the subject of controversy.[1-5] The size of this effect has required treatments which go beyond traditional effective-mass theory.[6] Two possibilities have been proposed: (i) The mixing of Bloch functions about equivalent conduction minima (as in Si and Ge) is allowed for core excitons while it is forbidden for valence (indirect) excitons. Inclusion of this effect yields an increase of the binding energy and a decrease of the exciton radius.[1,2] (ii) Attractive central-cell corrections are stronger for core than for valence excitons because the hole wave function is more localized.[3]

The above effects are also present in the case of isocoric impurities with which the core-exciton problem has been traditionally associated.[7] However, this is correct insofar as one neglects dynamical effects and lattice relaxation which are of a different nature in the two cases.[8,9]

Both approaches (i) and (ii) aim mainly to improve the solution of the ordinary integral equation for excitons[6] and rest on the use of a statically screened electron-hole interaction. This can only be justified when the exciton binding energy is small in comparison to the characteristic energies entering the dielectric function, namely the valence energy gap.[9] When this condition is not met, dynamical corrections to the effective electron-hole interaction have to be considered. Attempts to include dynamical screening effects have already been made, either through the many-body formalism[4] or through a variational approach to the electronic polaron problem.[5] These dynamical effects, which may be envisaged as an incomplete electronic relaxation about the excited electron and the hole left behind, become progressively more important as the average distance between the electron and the hole is decreased, or, equivalently, as their binding energy is increased. As a consequence, the dynamical corrections and the (static) band-structure effects (i) and (ii) will tend to reinforce each other.

The occurrence of dynamical screening effects in the core-exciton problem can be most clearly revealed from a study of the relevant spectral widths. Specifically, we shall examine how the decay of the core hole influences the effective electron-hole interactions and how, in turn, the lifetime of the exciton is influenced by the incomplete relaxation of the surrounding medium.

The most general procedure for the study of excitons including all types of correlation effects is to consider the Bethe-Salpeter equation for the two-particle Green's function and to find its poles by a suitable reduction to an eigenvalue problem. This approach has so far been used for core excitons with the restriction to the series of ladder diagrams and with the neglect of Auger broadening.[4] Inclusion of this broadening requires a search for poles in the complex energy plane with a finite imaginary part Γ. With the restriction to the series of ladder diagrams of a dynamically screened electron-hole interaction and the inclu-

sion of Auger broadening, one is led to the following non-Hermitian eigenvalue problem[10]:

$$[E_c - (E_d + i\gamma)]A_{cd}(\Omega,\Gamma) + \sum_{c'd'} \langle c,d|H_{\rm eff}(\Omega,\Gamma)|c',d'\rangle A_{c'd'}(\Omega,\Gamma) = (\Omega - i\Gamma)A_{cd}(\Omega,\Gamma), \tag{1a}$$

where the electron-hole effective interaction Hamiltonian is given by[11]

$$\begin{aligned}\langle c,d|H_{\rm eff}(\Omega,\Gamma)|c',d'\rangle = &\int d^3x_1 d^3x_2 u_c^*(\vec{x}_1)u_d(\vec{x}_1)\frac{2}{|\vec{r}_1-\vec{r}_2|}u_{c'}(\vec{x}_2)u_{d'}^*(\vec{x}_2)\\ &- i\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega\delta}\int d^3x_1 d^3x_2 u_c^*(\vec{x}_1)u_{c'}(\vec{x}_1)\\ &\times\int d^3r_3\,\epsilon_T^{-1}(\vec{r}_1,\vec{r}_3;\omega)\frac{2}{|\vec{r}_3-\vec{r}_2|}u_d(\vec{x}_2)u_{d'}^*(\vec{x}_2)\\ &\times\left\{\frac{1}{\Omega+i\Gamma-(E_{c'}-E_d-i\gamma)-\omega}+\frac{1}{\Omega+i\Gamma-(E_c-E_{d'}-i\gamma)+\omega}\right.\\ &\left.+\frac{i\Gamma}{[\Omega+i\Gamma-(E_{c'}-E_d-i\gamma)-\omega]^2}+\frac{i\Gamma}{[\Omega+i\Gamma-(E_c-E_{d'}-i\gamma)+\omega]^2}\right\}.\end{aligned} \tag{1b}$$

In Eq. (1) the labels c and d stand for conduction and deep (core) band quantum numbers, respectively, E and $u(\vec{x})$ are single-particle energies and wave functions (including spin variables), γ is the core-hole spectral width, Ω is the excitation energy of the exciton, A are electron-hole amplitudes, ϵ_T^{-1} is the (time-ordered) dielectric matrix,[12] and δ is a positive infinitesimal. Notice that Eq. (1) is a self-consistent eigenvalue problem where both the Hamiltonian matrix and its eigenvectors A depend on the eigenvalues $\Omega - i\Gamma$. Equation (1) generalizes the equation considered in Ref. 4, which can be recovered in the limit $\gamma = \Gamma = 0$. Furthermore, in the static limit for the screening the ω integration can be performed analytically and Eq. (1) reduces to the ordinary integral equation for excitons.[6]

Core excitons in semiconductors are generally expected to extend over a few cells about the localized hole, and thus to experience both the central-cell part of the potential and its (dynamically) screened Coulomb tail. A proper way to attack the solution of Eq. (1) would then be to convert it into a local-orbital basis along the lines of previous work on optical properties,[13] quasiparticle states,[14] and screening of static impurities.[15] This procedure could, in fact, enable one to include accurately dynamical effects on top of band-structure effects, but it requires large-scale numerical computations.

However, qualitative trends as well as estimates of the size of dynamical effects can be obtained with limited effort as follows. Within the effective-mass limit of Eq. (1), the excitonic binding energy E_B can be determined by solving a Schrödinger-like equation with a dynamically screened electron-hole Coulomb interaction. The appropriate effective inverse dielectric constant that screens this Coulomb interaction is the real part of the expression

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

where $-\,{\rm Im}\{\epsilon^{-1}(\vec{q}=0;\omega)\}$ is the loss function. Consider, in particular, the Si $2p$ transition which has received much experimental[16,17] and theoretical[1-5] attention. If one takes the experimental value (0.2 eV[17]) for the broadening γ of the Si $2p$ hole in Eq. (2), E_B is increased by a mere 2 meV over the static effective-mass value (26.7 meV).[18] The amount of incomplete screening caused by the finite value of γ is thus not sufficient to account for the large experimental value (0.3 eV[16]) of the Si $2p$ core-exciton binding energy. Intervalley mixing and central-cell corrections are, however, completely neglected whenever the screened Coulomb potential is assumed to extend to vanishing electron-hole separation. To account for these effects, and yet keeping a simple numerical scheme, the short-range portion of the screened Coulomb potential can be replaced, e.g., by a spherical square well of fixed radius a about equal to the screening radius of Si[19] ($a = 4$ a.u.) and of variable depth V_0; for r larger than a the screened Coulomb potential is retained. The size of V_0 is estimated following the suggestion[3] that for the Si $2p$ hole the central-cell part of the potential alone has the critical value to produce a bound state. For the chosen a this critical value of V_0 is 7.9 eV.

In Table I the results of the self-consistent cal-

TABLE I. $E_B{}^D$, $E_B{}^S$: binding energy in the field of a square well of depth V_0 plus a dynamically or statically screened Coulomb tail, respectively (Ref. 18). $\gamma - \Gamma$: corresponding difference of spectral widths. All values are in electronvolts.

V_0	$E_B{}^D$	$E_B{}^S$	$\gamma - \Gamma$
7.0	0.093	0.078	0.039
8.0	0.186	0.150	0.058
9.0	0.370	0.291	0.073
10.0	0.649	0.512	0.081

culation where the Coulomb tail has been dynamically screened (column 2) are compared with the results of the corresponding calculation where the Coulomb tail has been statically screened (column 3) for various values of V_0. Deviations of the dynamical from the static calculation get larger as V_0, or equivalently E_B, increases, thereby showing the enhancement of the dynamical effects caused by the static central-cell corrections.

Direct comparison of these results with the experimental binding energy is, however, not meaningful on its own because the values of E_B in Table I depend rather steeply on V_0 while no specific criterion can be supplied to select a proper value of V_0. Nevertheless, the results of this calculation can be further utilized to estimate the size of a related physical quantity such as the difference between the broadening γ of the core hole and the broadening Γ of the core exciton according to the expression

$$\gamma - \Gamma = -\mathrm{Im}\{\tilde{\epsilon}_0^{-1}(E_B,\gamma)\}\,\frac{\langle F(\vec{r})|r^{-2}|F(\vec{r})\rangle}{\langle F(\vec{r})|F(\vec{r})\rangle}\,, \qquad (3)$$

which is also derived from the effective-mass limit of Eq. (1). The values of $\gamma - \Gamma$, calculated from Eq. (3) with E_B and the envelope function $F(\vec{r})$ taken from the previous dynamical calculation, are listed in column 4 of Table I. Notice that these values are *positive* and not negligible; in particular, the value of $\gamma - \Gamma$ corresponding to the experimental $E_B = 0.3$ eV is about 70 meV.

These results show that dynamical screening effects occurring within the core exciton may produce an appreciable narrowing of its spectral width. 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 electrons. The occurrence of this effect is then a fingerprint of dynamical screening since it cannot be obtained within the framework of a static theory.

It should be remarked at this point that Eq. (3) neglects the contribution of the additional decay channels where the bound electron itself participates in the hole-filling transitions and, at the same time, the hole is transferred from the core to a higher (valence) band (direct recombination[20]). Since the presence of these channels would tend to decrease the difference $\gamma - \Gamma$, a net narrowing of the spectral width can *only* result whenever dynamical screening effects are sufficiently large to compensate for the presence of the direct recombination channels. The net narrowing is indeed what has been experimentally observed in several cases[21,22] although some uncertainties might exist in the data. These uncertainties stem both from the poor identification in the absorption spectra of separate resonances within the excitonic series and from difficulties in isolating the sole contribution of the core hole to the spectral density in photoemission experiments. A critical revision of the experimental situation is then in order to set more accurate lower and upper limits on γ and Γ, respectively.

In conclusion, it has been shown that the occurrence of an observable narrowing of the core-excitation spectral width can be ascribed to dynamical screening effects. Whenever this occurs, dynamical effects are also expected to contribute significantly to the core-excitation binding energies.

The author is indebted to F. Bassani for his interest in this problem. Helpful discussions with M. Altarelli, M. Cini, R. Del Sole, L. Peliti, and E. Tosatti are gratefully acknowledged.

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Critical Quantum Fluctuations and Localization of the Small Polaron

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(Received 6 August 1982)

The first quantitative evidence of critical quantum fluctuations and superlocalization of the small polaron model in one, two, and three dimensions is presented. Starting from a discrete version of the Feynman path-integral representation of the partition function, the boson field is eliminated analytically and the polaron contribution is calculated by means of the standard Monte Carlo Method.

PACS numbers: 71.38.+i, 05.30.-d, 05.70.Jk

Phase transitions and phase diagrams of the ground state of quantum systems are essential for the characterization of the general behavior of these models. A special class of interesting problems is the coupled fermion-boson system. In this paper we want to discuss a lattice model in which one fermion is coupled to a boson field, a polaron. Here we report the results of an extensive Monte Carlo study of the thermodynamics of a small-polaron model.[1-4] There have been speculations about a possible phase transition connected with localization of the electron as a function of the electron-phonon coupling constant in continuum polaron models.[5] However, for the most interesting continuum model, the Fröhlich polaron, Feynman, using his path-integral formalism, has given a superior solution for the ground-state energy which does not exhibit any discontinuities.[6,7] Localization is also possible for the small polaron. For all lattice dimensionalities our results point to substantially enhanced, possibily critical, fluctuations for a critical value of the coupling constant.

For simplicity of notation we will now formulate the theory in one space dimension. The Holstein Hamiltonain reads

$$H = H_0 + H_1 + H_2, \tag{1a}$$

$$H_0 = \frac{1}{2M}\sum_{i=1}^{N} p_i^2, \tag{1b}$$

$$H_1 = \frac{M\Omega^2}{2}\sum_{i=1}^{N} x_i^2 + \lambda\sum_{i=1}^{N} x_i c_i^{\dagger} c_i, \tag{1c}$$

$$H_2 = -t\sum_{i=1}^{N} c_i^{\dagger} c_{i+1} + c_{i+1}^{\dagger} c_i. \tag{1d}$$