

## Spatially extended quasiparticles in disordered alloys

Abdoul Aziz Mbaye, Frédéric Raymond, and Christian Vèrié

*Laboratoire Physique du Solide et Energie Solaire, Centre National de la Recherche Scientifique,  
Parc de Sophia Antipolis, rue Bernard Grégory, F-06560 Valbonne, France*

(Received 15 March 1983; revised manuscript received 29 December 1983)

Recent experiments in the spectroscopy of free or impurity-bound electrons and excitons in semiconductor alloys show that these quasiparticles are differently affected by the same disorder state. In this paper, we present a formal theory to account for disorder effects on the properties of quasiparticles. To this end, a new alloy model is described. Based on a representation of the composition fluctuations within the quasiparticle extent, this theory treats the effective alloy medium "felt" by the quasiparticle of a given spatial extent. Its relations with the single-site and virtual-crystal approximation are obtained in the two limiting cases (site-localized limit and highly extended quasiparticle cases). Trends in disorder effects on quasiparticles as functions of their extent are briefly discussed from a simple model of propagating quasiparticles.

### I. INTRODUCTION

Spatially extended quasiparticles have elicited wide spread interest in semiconductor physics. However, despite the considerable literature on their properties in pure crystals, they have seldom been studied in disordered alloys.<sup>1-4</sup> Recent experiments on the spectroscopy of such quasiparticles in semiconductors (e.g., excitons)<sup>1,2</sup> show that they are affected differently by the statistical disorder state. It also appears from these studies<sup>1,2</sup> that their characteristic spatial extent (e.g., Bohr radius for free excitons) is an important parameter for the determination of the disorder effects on their properties. Some semiempirical schemes have been derived to account for such effects in some particular cases, e.g., free excitons in CdS<sub>1-x</sub>Se<sub>x</sub>.<sup>1</sup> This paper is a contribution to a formal theory which accounts for such effects through the definition of the effective alloy medium "felt" by quasiparticles.

The concept of quasiparticles has been introduced to account for a specific interaction of an excited electron with other particles or elementary excitations in solids. This interaction extends over a finite region in the solid. This region will be referred to as the quasiparticle extent (for free excitons, this region is limited to the relative motion of the electron-hole pair). In this work, its size is taken as a parameter characteristic of the considered interaction. Typical examples are Frenkel and Wannier excitons. In the first example, the excited electron interacts strongly with the valence states of its origin atom. This interaction is, therefore, localized within an atomic cell volume supporting the original Frenkel-exciton model as an excited state of an atom (site-localized quasiparticle). On the other hand, a Wannier exciton has a Bohr radius extended over many interatomic distances.<sup>5</sup> These two kinds of quasiparticles will be affected differently by the alloy disorder state.

In this paper we will assume that *the disorder state in the alloy does not directly affect the specific interaction of the excited electron with elementary excitations and other particles*. The disorder effect on the quasiparticle properties is assumed to arise from the fluctuations of the alloy

potential *within the range of its specific interaction*. This has been postulated by Goede *et al.*<sup>1</sup> to account for experimental observations of excitons in CdS- and CdSe-based alloys. These authors considered a virtual-crystal alloy effective medium and additional disorder effects (spectral line broadening) as a result of the above-mentioned fluctuations.

The problem of disorder effects on quasiparticles, therefore, reduces to the choice of an appropriate effective alloy medium, capable of properly describing the disorder effects arising from only the fluctuations of the local medium within the quasiparticle extent. Note that neither the single-site<sup>6-12</sup> nor the virtual-crystal<sup>13</sup> (VCA) alloy models would be suitable for this purpose since these models are appropriate, respectively, for the site-localized limit and for the description of infinitely extended quasiparticles. The clustering of similar atoms which are responsible for structures with spikes in alloy density of states are not considered in this work. After the construction of a new alloy representation in Sec. II, our formal theoretical approach is given in Sec. III. We derive its limit for site-localized quasiparticles in Sec. IV. From a simple quasiparticle model, we discuss in Sec. V the general trends in the disorder effects on quasiparticles as functions of their spatial extent.

### II. ALLOY REPRESENTATION

As previously stated we assume that quasiparticles in alloys ( $A_x B_{1-x}$ ) are affected by the only fluctuations of the alloy potential in the local medium within their extent. We now *assume* that the effect of the local medium on the quasiparticle is only determined by the amount  $c \neq x$  of  $A$ -type atoms it contains, but not on the particular way the  $cN_0$   $A$ -type atoms are distributed upon the  $N_0$  sites in the medium. Considering these assumptions, the actual potential in this local medium may be replaced by the linear average

$$V(\vec{r}) = \sum_{[l]} c V_A(\vec{r} - \vec{l}) + (1-c) V_B(\vec{r} - \vec{l}). \quad (2.1)$$

$[I]$  denotes the indices of the  $N_0$  sites within the local cell. This potential locally equals the one that the quasiparticle would experience from a *macroscopic* crystal of composition  $c$ , i.e.,  $A_c B_{1-c}$ , treated in the VCA. Hence this virtual crystal is defined by its only composition  $c$  and will be referred to as *subcrystal*  $c$ . Therefore the subcrystal  $c$  represents any local medium embodied in the quasiparticle extent and which contains  $cN_0$  atoms of type  $A$ .

The local medium in the quasiparticle extent must contain  $0, 1, 2, \dots$  or  $N_0$   $A$ -type atoms and may be represented respectively by a subcrystal  $c = 0, 1/N_0, \dots, N_0/N_0 (=1)$ . For a given quasiparticle extent ( $N_0$ ) the ensemble of subcrystals denoted by  $[c]$  is therefore taken as the representation of the disorder state in the alloy. Each subcrystal is associated with the probability  $P(c)$  that the local medium contains  $cN_0$   $A$ -type atoms. This probability distribution is closely related to the type of solid solution  $A_x B_{1-x}$ .

From a mathematical viewpoint, the pair  $[c, P(c)]$  will be the statistical ensemble over which an average of subcrystal (disorder) related quantities will be performed.<sup>14</sup> Two remarks must be made before closing this section: First, the subcrystal potential is given by

$$V_c(\vec{r}) = \sum_{\vec{I}} cV_A(\vec{r} - \vec{I}) + (1-c)V_B(\vec{r} - \vec{I}), \quad (2.2)$$

where  $\vec{I}$  runs over all sites of the lattice underlying the actual alloy. Second, for a given quasiparticle extent ( $N_0$ ), the ensemble average of any subcrystal-dependent quantity  $Z(c)$  is given by

$$Z = \sum_{[c]} Z(c)P(c) \quad (2.3a)$$

with

$$\sum_{[c]} P(c) = 1. \quad (2.3b)$$

From the conservation of total number of  $A$ - and  $B$ -type atoms in  $A_x B_{1-x}$  we also have

$$\sum_{[c]} cP(c) = x. \quad (2.3c)$$

Provided with this new alloy representation, we turn to the derivation of the formal theory of disorder effects on quasiparticles in alloys.

### III. FORMAL THEORY

We study the ensemble-averaged disorder effects on quasiparticles in alloys. Such effects appear through the spectroscopy of quasiparticles as spectral line shift and broadening,<sup>1,2</sup> which are related to the so-called self-energy or coherent potential describing the effective medium.

This effective medium is chosen such that the ensemble average of the additional disorder scattering suffered by the quasiparticle from the fluctuating local medium embodied in its extent vanishes identically. This defines a leveled-out effective medium for this quasiparticle. Argyres<sup>15</sup> has developed a general self-energy expansion

technique that is valid for any *a priori* statistical ensemble representing the disorder state in alloys. He expressed the self-energy in terms of the fluctuating part of the Hamiltonian via the introduction of projection operators. These operators affect the ensemble average over the *chosen* statistical ensemble.

In the subcrystal  $c$  the Hamiltonian is given by

$$H_c = -\frac{\hbar^2}{2m}\Delta + V_c. \quad (3.1)$$

It can be rewritten as

$$H_c = H_0 + V, \quad (3.2a)$$

where

$$H_0 = -\frac{\hbar^2}{2m}\Delta + \sum_{\vec{I}} [xV_A(\vec{r} - \vec{I}) + (1-x)V_B(\vec{r} - \vec{I})] \quad (3.2b)$$

and

$$V = (c-x) \sum_{\vec{I}} [V_A(\vec{r} - \vec{I}) - V_B(\vec{r} - \vec{I})] = \alpha\Delta_{AB}(r), \quad (3.2c)$$

where  $\alpha = c - x$  stands for the deviation of the subcrystal composition  $c$  from the macroscopically observed composition  $x$ , and

$$\Delta_{AB}(\vec{r}) = \sum_{\vec{I}} [V_A(\vec{r} - \vec{I}) - V_B(\vec{r} - \vec{I})]. \quad (3.2d)$$

$H_0$  is the virtual-crystal Hamiltonian, while  $V$  describes the disorder- (subcrystal) dependent part of the Hamiltonian.  $V$  fluctuates through the subcrystal ensemble due to its dependence on  $c$  (or  $\alpha$ ). The periodic nature of  $\Delta_{AB}(r)$  is merely a consequence of the fact we have constructed the subcrystals such that they possess the translational periodicity required for the ensemble-averaged observables of the alloy.

By using Eq. (3.2a), the self-energy  $\Sigma^0(E)$  associated with the alloy effective medium can be computed from the technique developed by Argyres.<sup>15</sup> (See Appendix A.) We obtain (with  $Q$  and  $Q'$  operating on everything to their right)

$$\Sigma^0(E) = \sum_{m=1}^{\infty} QV(Q'G^0V^m)^{-1}. \quad (3.3a)$$

The superscript in  $\Sigma^0$  refers to the use of the VCA Green function  $G^0$ . The ensemble-averaged Green function  $G(E)$  is given by

$$G(E) = [E - H_0 - \Sigma^0(E)]^{-1}. \quad (3.3b)$$

$Q$  is the projection operator to effect the average over the subcrystal ensemble, and  $Q' = 1 - Q$ . Hence, for any subcrystal-dependent quantity  $Z(c)$ ,

$$Q(Z) = \sum_{[c]} Z(c)P(c) \quad (3.4a)$$

gives the ensemble average of  $Z$  while

$$Q'(Z) = Z(c) - Q(Z) \quad (3.4b)$$

gives it subcrystal-dependent (or fluctuating) part of  $Z$ . Both operators act only on the quantity on their right, and commute with disorder- (subcrystal) independent operators such as  $\Delta_{AB}$  or  $G^0$ . Therefore, Eq. (3.2c) becomes

$$\Sigma^0(E) = \sum_{m=1}^{\infty} K_m(N_0; P) \Delta_{AB} (G^0 \Delta_{AB})^{m-1} \quad (3.5a)$$

with

$$K_m(N_0; P) = Q \alpha (Q' \alpha)^{m-1},$$

which, for  $m \geq 2$ , reads as (see Appendix B)

$$K_m(N_0; P) = Q(\alpha^m) - \sum_{l=2}^{m-2} K_l(N_0; P) Q(\alpha^{m-l}). \quad (3.5b)$$

The  $K_m(N_0; P)$ 's depend on the statistical nature of the disorder state ( $P$ ) and on the quasiparticle spatial extent ( $N_0$ ), while  $\Delta_{AB}(r)$  describes the chemical difference between the substituted atomic species.

The implicit dependence of  $K_m$  on the quasiparticle extent ( $N_0$ ) may be easily illustrated by the following: When the quasiparticle extends to the *whole alloy*, i.e.,  $N_0 = N$ ,  $N$  being the total (infinite) lattice-site number, the only possible value of  $c$  is  $c = x$ . The subcrystal ensemble then reduces to one subcrystal of composition  $x$ , i.e.,  $P(c \neq x) = 0$  and  $P(c = x) = 1$ .<sup>16</sup> This case corresponds to the VCA.  $\alpha$  thus vanishes identically and so do all the  $K_m$ 's and hence  $\Sigma^0(E)$ . This agrees with the intuitive argument that infinitely extended quasiparticles are not affected by the alloy disorder state and are well described by the VCA.

The present formal theory takes into account the disorder-state characteristics through the probability distribution  $P(c)$  of local compositions  $c$  and the disorder-strength operator  $\Delta_{AB}$  together with the spatial extent of the considered quasiparticle ( $N_0$ ). The way disorder affects extended quasiparticles will be studied later. Now we study our non-self-consistent formal theory at the limit of site-localized quasiparticles.

#### IV. SITE-LOCALIZED QUASIPARTICLES IN RANDOMLY-DISORDERED ALLOYS

In this section we study the particular case of *site-localized* quasiparticles in an *ideal solid solution*  $A_x B_{1-x}$  (random disorder). By site-localized quasiparticles, we mean that the interacting particles involved in the quasiparticle formation are located within the same atomic unit volume (e.g., Frenkel exciton). The quasiparticle may, hence, be thought of as an excited state of the atom. In this case the number of sites  $N_0$  is unity ( $N_0 = 1$ ). The only possible values of the composition  $c$  (concentration of  $A$ ) in the local medium within this site-localized quasiparticle extent are  $c = 0$  ( $\alpha = 0 - x$ ) and  $c = 1$  ( $\alpha = 1 - x$ ); these values correspond to the cases when the site is occupied by a  $B$ - or  $A$ -type atom, respectively. From the randomness ( $P_0$ ) of the disorder state, the respective probabilities of such events are

$$\begin{aligned} P_0(A) &= x, \\ P_0(B) &= 1 - x. \end{aligned} \quad (4.1)$$

That is,

$$P_0(c=0) = P_0(B) = P_0(\alpha = -x) = 1 - x, \quad (4.2)$$

$$P_0(c=1) = P_0(A) = P_0(\alpha = 1 - x) = x.$$

This completely determines the probability distribution law ( $P_0$ ) of the fluctuating composition  $c$  upon the subcrystal ensemble. The statistical factors  $K_m(N_0; P_0)$  are, hence, explicitly known and given by (see Appendix C)

$$K_1(N_0; P_0) = 0, \quad (4.3)$$

$$K_m(N_0; P_0) = x(1-x)(1-2x)^{m-2}, \quad m \geq 2.$$

Hereafter, we shall use a quasiparticle one-band tight-binding model. This greatly simplifies the notation. It is also particularly suitable for site-localized quasiparticles and yields a good understanding of the approximations used here. In this case, the previously defined operators must be rewritten in terms of site-localized quantities.

We have

$$H_0 = \sum_i \bar{\epsilon} |i\rangle \langle i| + \sum_{\substack{i \neq j \\ i,j}} t_{ij} |i\rangle \langle j| \quad (4.4)$$

and

$$\Delta_{AB} = -U \sum_i |i\rangle \langle i| = -U \quad (4.5)$$

with

$$\bar{\epsilon} = x\epsilon_A + (1-x)\epsilon_B,$$

$$U = \epsilon_B - \epsilon_A.$$

Here  $|i\rangle$  denotes the site-localized Wannier function at the  $i$ th site of the lattice. The site-excitation energy in the actual alloy is either  $\epsilon_A$  or  $\epsilon_B$ , depending on whether the site is occupied by an  $A$ - or  $B$ -type atom. This site-diagonal VCA Green function matrix element is

$$G_{00}^0(z) = \langle i | G^0(z) | i \rangle = \int \frac{\rho^0(E')}{z - \bar{\epsilon} - E'} dE', \quad (4.6)$$

where  $\rho^0(E)$  is the quasiparticle density of states per site associated with the VCA Hamiltonian  $H_0$ . From Eqs. (3.5a) and (4.3), the self-energy expression becomes

$$\Sigma^0(E) = \sum_{m=2}^{\infty} x(1-x)(1-2x)^{m-2} (-1)^m U^m V_{m-1}(G^0), \quad (4.7)$$

where

$$V_m(G^0) = \sum_{l_1, l_2, \dots, l_{m-1}} G_{0l_1}^0 G_{l_1 l_2}^0 \cdots G_{l_{m-1} 0}^0 \quad (4.8a)$$

with

$$G_{l_1 l_2}^0 = \langle l_1 | G^0 | l_2 \rangle. \quad (4.8b)$$

The  $V_m(G)$ 's are, from usual scattering theory, the amplitude of probability for a site-localized quasiparticle described by the propagator  $G^0$  to be scattered from the origin site and to come back on to this site after  $m$  other independent scattering events. Some approximations

must be made to derive close form for the self-energy. To this end, we rewrite Eq. (4.8a) as

$$V_m(G^0) = (G_{00}^0)^m + \sum_{l_1, \dots, l_{m-1}} G_{0l_1}^0 G_{l_1 l_2}^0 \times \dots \times G_{l_{m-1} 0}^0, \quad (4.8c)$$

where the prime means that at least one of the  $l_i$  is different from 0. The first term in (4.8c) corresponds to the multiple scattering of the quasiparticle by the same scatterer at a given site (*single site*), while the second term gives the *multisite* scattering contribution since it involves at least two sites.

For the non-self-consistent expansion [Eq. (4.7)], we consider the only single-site scattering. Equation (4.7) then becomes

$$\Sigma^0(E) = \sum_{m=2}^{\infty} x(1-x)(1-2x)^{m-2} \times (-1)^m U^m (G_{00}^0)^{m-1} \quad (4.9a)$$

$$= \frac{x(1-x)U^2 G_{00}^0(E)}{1 + (1-2x)UG_{00}^0(E)}. \quad (4.9b)$$

Equation (4.9b) can be easily proved to be the average- $t$ -matrix approximation (ATA) self-energy expression. In fact, the usual ATA reads as<sup>17</sup>

$$\langle t \rangle = \frac{x(\epsilon_A - \bar{\epsilon})}{1 - (\epsilon_A - \bar{\epsilon})G_{00}^0} + \frac{(1-x)(\epsilon_B - \bar{\epsilon})}{1 - (\epsilon_B - \bar{\epsilon})G_{00}^0} \quad (4.10a)$$

and

$$\sigma(E) = \frac{\langle t \rangle}{1 + \langle t \rangle G_{00}^0(E)}. \quad (4.10b)$$

$\sigma(E)$  in Eq. (4.10b) is the total ATA site-excitation energy and appears as  $\sigma(E) = \bar{\epsilon} + \Sigma^0(E)$ . Replacing (4.10a) in (4.10b) we obtain Eq. (4.9b). Note that  $U = \epsilon_B - \epsilon_A$ .

Thus our non-self-consistent self-energy expansion [Eq. (4.7)] is proved. This arises from the fact that the VCA has been taken to describe the reference medium in the self-energy calculation.<sup>15</sup>

## V. EXTENDED QUASIPARTICLES IN RANDOMLY DISORDERED ALLOYS

Disorder effects on the properties of spatially extended quasiparticles have been experimentally proved to decrease as their spatial extent increases.<sup>1,2</sup> However, although this experimental observation is well understood on purely intuitive grounds, there exists no theoretical approach which gives a clear description of such effects. Such a theory must be able to describe properly the effective alloy medium "felt" by spatially extended quasiparticles such as free or bound excitons in semiconductor alloys.

In this section, it is our purpose to derive from the formal theory reported in Sec. III a closed form for the non-self-consistent self-energy  $\Sigma^0(E)$  which (i) is able to describe disorder effects on extended quasiparticles as function of their spatial extent and which (ii) arises from

the same set of approximations as the ATA (Sec. IV). Here, we are only concerned with propagating (free) quasiparticles. The cases of spatially extended quasiparticles trapped by the potential fluctuations or by impurities in alloys will be studied elsewhere.

In addition to the assumptions stated in Sec. I, we assume the motion of the quasiparticle is identified with the site-to-site motion of its core.<sup>18</sup> Off-diagonal disorder is neglected.

From the random-disorder approximation, the probability distribution  $P$  of this fluctuating composition is given by

$$P(c) = P(\alpha = c - x) = \binom{N_0}{n} x^n (1-x)^{N_0-n}, \quad (5.1)$$

where  $n = cN_0$ . The self-energy is

$$\Sigma^0(E) = \sum_{m=2}^{\infty} K_m(N_0; P) (-1)^m U^m V_{m-1}(G^0). \quad (5.2)$$

An approximate expression for the  $K_m(N_0; P)$ , which together with our hypothesis on the  $V_m(G^0)$  form a self-contained set of approximations, is derived in Appendix D and is given by

$$K_m(N_0; P) = \frac{1}{N_0^{m-1}} x(1-x)(1-2x)^{m-2}, \quad m \geq 2. \quad (5.3)$$

Therefore, using  $V_m(G^0) = (G_{00}^0)^m$ , we obtain the disorder-induced modification of the quasiparticle energy  $\Sigma^0(E)$ , which reads as

$$\Sigma^0(E) = \frac{(U^2/N_0)x(1-x)G_{00}^0(E)}{1 + (1-2x)(U/N_0)G_{00}^0(E)}. \quad (5.4)$$

Equation (5.4) expresses the alloy effective medium "felt" by the quasiparticle with a given spatial extent ( $N_0$ ). It is consistent with both the ATA for  $N_0 = 1$  and with VCA for  $N_0 = \infty$ . In the latter case, it physically expresses the statistical strong law of large numbers.<sup>16</sup> To our knowledge, it is the first theoretical attempt to describe the effective alloy medium "felt" by spatially extended quasiparticles as functions of their extent. This problem must not be confused with the widely studied clustering effects in alloys. Applications of the present theory to free excitons in semiconductor alloys are under active consideration. Before closing this section, however, some salient results embodied in Eq. (5.4) must be noted.

$N_0$  can also be rewritten as the ratio of the volume within the local medium and the atomic unit volume defined, respectively, by their equivalent spherical radii  $R$  and  $R_0$ ; we have  $N_0 = (R/R_0)^3$ . In most alloy theories<sup>6-10</sup>  $U = \epsilon_B - \epsilon_A$  is the disorder scattering strength. Therefore, from Eq. (5.4), it appears the disorder scattering strength felt by the extended quasiparticle in the effective medium is shielded. It decreases monotonically from its single-site ( $N_0 = 1$ ) value  $U$  to 0 asymptotically for infinitely extended quasiparticles ( $N_0 = \infty$ ) which thus experience no disorder effects. Therefore, the most extended quasiparticles are the least affected by the statistical disorder state. As a consequence the VCA gives a good approximation for the effective medium "felt" by very extended quasiparticles, even if the intrinsic disorder

scattering strength  $U$  is not small compared to their bandwidth. For sufficiently extended quasiparticles, i.e.,  $(1-2x)(U/N_0)^*G_{00}^0 \ll 1$ , the self-energy reads as

$$\Sigma^0(E) = x(1-x)(R/R_0)^3 U^2 G_{00}^0(E). \quad (5.5)$$

This equation (5.5) may be used to interpolate Wannier exciton energy in semiconductor alloys. It is also analogous to the equation obtained by Goede *et al.*<sup>1</sup> and others.<sup>19</sup> Note that these authors assumed a direct proportionality of disorder-induced line broadening of excitons in  $\text{CdS}_{1-x}\text{Se}_x$  with the random mean square of the fluctuating exciton energy in the local medium (i.e.,  $(R/R_0)^{3/2}[x(1-x)]^{1/2}$ ). In this case  $U = \epsilon_B - \epsilon_A$  appears as the first-order derivative of exciton energy with regard to composition, and  $R$  is about twice the Bohr radius.<sup>1</sup> Detailed studies of these excitons from the present theoretical approach are planned to be published elsewhere. An important feature of disorder effects in the weak scattering limit needs to be emphasized. In this limit the usual single-site approximations [ATA and coherent-potential approximation (CPA)] agree to  $O(U^2)$ .<sup>20</sup> Both predict a symmetric behavior of disorder effects as a function of composition about  $x=0.5$ . This is known as Nordheim's rule. For extended quasiparticles, this rule may be expected to break down since, even at this limit, an asymmetric variation is introduced by the composition dependence of the quasiparticle extent  $R$  interpolated between its values in the extreme pure constituents. This behavior has been experimentally observed by Goede *et al.* in the variation of free-exciton spectral line broadening as a function of composition in  $\text{CdS}_{1-x}\text{Se}_x$  alloys.<sup>1</sup>

## VI. CONCLUDING REMARKS

In this paper we have reported a new formal theoretical approach for the disorder effects on spatially extended quasiparticles such as free excitons in alloys. The present theory, however, is non-self-consistent, due to the choice of the virtual-crystal alloy as the reference medium to derive the self-energy expression. Yet the asymptotic  $R^{-3/2}$  variation law of the effective disorder scattering strength felt by extended quasiparticles suggests that non-self-consistency (CPA-like) is needed for the description of the effective alloy medium felt by *very* extended quasiparticles such as Wannier excitons in semiconductors (weak scattering limit).

However, such a self-consistent description would be necessary to study the persistence and amalgamation of the properties of spatially extended quasiparticles in alloys as functions of  $x$ ,  $U$ , and  $R$  (or  $N_0$ ). Such a study has only been done for  $N_0=1$ .<sup>21</sup> Another quantitative result of this work is that, as expected, disorder effects on extended quasiparticles (spectral line broadening and shift) decrease as their spatial extent (typically one Bohr radius for free excitons) increases. These vanish for *infinitely* extended quasiparticles, in agreement with the statistical strong law of large numbers.<sup>16</sup> Such trends have been briefly discussed from a simple quasiparticle model.<sup>17</sup> The present formalism is being applied to free excitons in semiconductor alloys. From the close relation of such quasiparticles (used experimentally as disorder probe<sup>1,2,22</sup>)

with the Bloch states in the upper valence and lower conduction bands, the present approach would allow the prediction of the relevance of disorder effects on semiconductor alloy band edges, i.e., on the optical band gap (extrinsic bowing effects). Detailed results are planned to be published elsewhere.

## ACKNOWLEDGMENTS

Part of this work was supported by a grant from the Centre National de la Recherche Scientifique. One of the authors (A.A.M.) would like to thank Dr. F. Ducastelle for stimulating discussions at the beginning of this work.

## APPENDIX A

The Hamiltonian describing the quasiparticle in a given subcrystal reads as

$$H = H_0 + V. \quad (A1)$$

$H_0$  and  $V$  are defined in Sec. III. From Eqs. (2.3c) and (3.2c), the ensemble average of  $V$  is identically 0. The macroscopic properties of the system are obtained from averages over all possible subcrystals weighted by their respective probabilities. The operator  $Q$  defined in Eq. (3.4) is a projector:  $Q^2=Q$ . The related operator  $Q'=1-Q$ , which gives the subcrystal-dependent part of any quantity  $Z$ , is such that  $QQ'=Q'Q=0$  and  $(Q')^2=Q'$ . Now let the VCA, subcrystal-dependent, and ensemble-average Green functions be, respectively,

$$G^0(E) = (E - H_0)^{-1}, \quad (A2a)$$

$$G_c(E) = (E - H_0 - V)^{-1}, \quad (A2b)$$

$$G(E) = QG_c(E) = [E - H_0 - \Sigma^0(E)]^{-1}, \quad (A2c)$$

where  $\Sigma^0(E)$  is the so-called self-energy operator.

From the definition of  $G_c(E)$ , we have

$$(E - H_0 - V)G_c(E) = 1, \quad (A3)$$

$$G_c = QG_c + Q'G_c = G + Q'G_c. \quad (A4)$$

Operating on it with  $Q$  and  $Q'$  separately, we obtain (with  $Q$  and  $Q'$  operating on everything to their right)

$$(E - H_0 - QV)G - QVQ'G_c = 1, \quad (A5a)$$

$$(E - H_0 - Q'V)Q'G_c - Q'VG = 0, \quad (A5b)$$

since  $[H_0, Q] = QQ' = 0$ . From (A5b) we obtain  $Q'G_c$  in terms of  $G$ . We substitute it into (A5a) to find the following exact equation for  $G$ :

$$[E - H_0 - QV - QV(E - H_0 - Q'V)^{-1}Q'V]G = 1. \quad (A6)$$

Hence, from (A2c) and (A6) we obtain

$$\Sigma^0(E) = Q[V + V(E - H_0 - Q'V)^{-1}Q'V]. \quad (A7a)$$

Note again that  $Q$  and  $Q'$  operate on everything to their right. From the expansion

$$(E - H_0 - Q'V)^{-1} = G^0 + G^0Q'VG^0 + G^0Q'VG^0Q'VG^0 + \dots, \quad (A7b)$$

$\Sigma^0(E)$  becomes

$$\Sigma^0(E) = Q(V + VG^0Q'V + VG^0Q'VG^0Q'V + \dots) \quad (\text{A8a})$$

$$= \sum_{m=1}^{\infty} QV(G^0Q'V)^{m-1}. \quad (\text{A8b})$$

This established Eq. (3.3a).

### APPENDIX B

Equations (3.3a) can be rewritten in the following form:

$$\Sigma^0(E) = \sum_{m=2}^{\infty} Q\alpha(Q'\alpha)^{m-1}\Delta_{AB}(G^0\Delta_{AB})^{m-1}. \quad (\text{B1})$$

This arises from the fact that

$$[Q, G^0] = [Q', G^0] = 0.$$

$Q$  and  $Q'$  commute with any subcrystal-independent operator. From (B1),  $K_m(N_0; P)$  appears as

$$K_m(N_0; P) = Q\alpha(Q'\alpha)^{m-1}. \quad (\text{B2})$$

Some properties of the operators  $Q$  and  $Q'$  are quoted in Sec. II. We also have

$$K_M(N_0; P) = Q\alpha(Q'\alpha)^{M-2}Q'\alpha. \quad (\text{B3})$$

Equation (2.3c) also reads as  $Q'\alpha = \alpha$ . Hence,

$$K_m(N_0; P) = Q\alpha(Q'\alpha)^{m-3}Q'(\alpha^2). \quad (\text{B4})$$

That is,

$$K_m(N_0; P) = Q\alpha(Q'\alpha)^{m-3}\alpha^2 - Q(\alpha^2)Q\alpha(Q'\alpha)^{m-3}. \quad (\text{B5})$$

The second term on the right-hand side of Eq. (B5) may be rewritten using (B2). Equation (B5) becomes

$$K_m(N_0; P) = Q\alpha(Q'\alpha)^{m-3}\alpha^2 - Q(\alpha^2)K_{m-2}(N; P) \quad (\text{B6})$$

This procedure (B3)–(B6) may be repeated starting from the first term on the right-hand side of (B6). It is an easy task to set it to be recurrent for  $1 < k < m - 1$ . Note that  $K_1(N_0; P) = Q(\alpha) = 0$  from Eq. (2.3c):

$$K_m(N_0; P) = Q\alpha(Q'\alpha)^{m-k-1}\alpha^k - \sum_{l=2}^k K_{m-l}(N_0; P)Q(\alpha^l). \quad (\text{B7})$$

Indeed, assuming (B7) is true for a given  $k$  and applying the procedure (B3)–(B6) to the first term in (B7), we have

$$Q\alpha(Q'\alpha)^{m-k} = Q\alpha(Q'\alpha)^{m-k-2}Q'(\alpha^{k+1}) \\ = Q\alpha(Q'\alpha)^{m-k-2}\alpha^{k+1} - Q(\alpha^{k+1}) \quad (\text{B8})$$

$$- K_{m-k-1}(N_0; P). \quad (\text{B9})$$

From (B9) and (B7), we obtain

$$K_m(N_0; P) = Q\alpha(Q\alpha)^{m-(k+2)}\alpha^{k+1} \\ - \sum_{l=2}^{k+1} K_{m-l}(N_0; P)Q(\alpha^l). \quad (\text{B10})$$

Once this is demonstrated, we apply (B7) to the case  $k = m - 1$ . We thus obtain

$$K_m(N_0; P) = Q(\alpha^m) - \sum_{l=2}^{m-2} K_{m-l}(N_0; P)Q(\alpha^l). \quad (\text{B11})$$

$K_m(N_0; P)$  appears as a combination of products of the moments  $Q(\alpha^l)$  of  $\alpha$  in the probability distribution  $P$ . Therefore they may be calculated, once the quasiparticle extent ( $N_0$ ), which gives the possible values of  $c$  (hence, values of  $\alpha$ ), and the solid-solution type, which determines the respective probabilities  $P(c)$  of the local compositions  $c$  (or  $\alpha$ ), are given.

Before concluding this appendix we give the  $K_m$ 's for  $m = 1-4$ :

$$K_1(N_0; P) = Q(\alpha) = 0,$$

$$K_2(N_0; P) = Q(\alpha^2),$$

$$K_3(N_0; P) = Q(\alpha^3),$$

$$K_4(N_0; P) = Q(\alpha^4) - [Q(\alpha^2)]^2.$$

### APPENDIX C

For *site-localized* quasiparticles in ideal solid solutions (*random disorder*), the number of  $N_0$  sites within the quasiparticle extent (1 atomic volume) is given by  $N_0 = 1$ . There are only two possible values for the composition  $c$  (concentration of  $A$  atoms in the local medium),  $c = 0$  and 1. These two values correspond, respectively, to the cases where the considered site is occupied by a  $B$ - or  $A$ -type atom. They also correspond to  $\alpha = 0 - x$  and  $1 - x$ , respectively. Under the random-disorder approximation, the respective probabilities of such events are given by

$$P(c = 0) = P(\alpha = 0 - x) = P(B) = 1 - x, \quad (\text{C1})$$

$$P(c = 1) = P(\alpha = 1 - x) = P(A) = x.$$

Equation (C1) completely determines the probability distribution law  $P$  of subcrystals in the statistical ensemble (see Sec. II). In such a case, the moments of  $\alpha$  involved in the  $K_m(1; P)$ 's are given by

$$Q(\alpha^m) = (1-x)(-x)^m + x(1-x)^m \quad (\text{C2})$$

From this, we obtain

$$K_1(1; P) = 0,$$

$$K_2(1; P) = Q(\alpha^2) = x(1-x), \quad (\text{C3})$$

$$K_3(1; P) = Q(\alpha^3) = x(1-x)(1-2x),$$

$$K_4(1; P) = Q(\alpha^4) - [Q(\alpha^2)]^2 = x(1-x)(1-2x)^2.$$

Equation (C3) suggests that

$$K_m(1; P) = x(1-x)(1-2x)^{m-2}, \quad m \geq 2. \quad (\text{C4})$$

This relation is true for  $2 \leq m \leq 4$ . Its validity can be established by recurrence. From Eqs. (C2), (C4), and (B11) we have

$$K_m(1;P) = x(1-x) \left[ (1-x)^{m-1} - (-x)^{m-1} - \sum_{l=2}^{m-2} (1-2x)^{l-2} [(1-x)^{m-1}x + (1-x)(-x)^{m-1}] \right] \\ = x(1-x)(I_0 - I_1 - I_2), \quad (C5)$$

where

$$I_0 = (1-x)^{m-1} - (-x)^{m-1}, \quad (C6a)$$

$$I_1 = \sum_{l=2}^{m-2} (1-2x)^{l-2} (1-x)^{m-l} x, \quad (C6b)$$

$$I_2 = \sum_{l=2}^{m-2} (1-2x)^{l-2} (-x)^{m-l} (1-x). \quad (C6c)$$

Expanding  $I_1$  we obtain

$$I_1 = - \sum_{l=2}^{m-2} \sum_{k=0}^{l-2} \binom{l-2}{k} (1-x)^{m-k-2} (-x)^{k+1}, \quad (C7)$$

where  $\binom{l}{k}$  has its usual significance in combinatorial analysis. The double sum in Eq. (C7) is then rewritten in order to group the terms with the same power of  $(-x)$ ;  $I_1$  becomes

$$I_1 = - \sum_{j=0}^{m'-2} \left[ \sum_{k=j}^{m'-2} \binom{k}{j} \right] (1-x)^{m'-j} (-x)^{j+1} \quad (C8)$$

with

$$m' = m - 2.$$

For  $n > j$  it can be shown that

$$N(n, j) = \sum_{k=j}^n \binom{k}{j} = \binom{n+1}{j+1}. \quad (C9a)$$

$N(n, j)$  reads as

$$N(n, j) = \sum_{l=0}^{n-j} \binom{n-l}{j} \quad (C9b)$$

$$= \sum_{l=0}^{n-j} \binom{n-l}{n-j-l}. \quad (C9c)$$

Using the general combinatorial relation

$$\binom{n+1}{k} = \binom{n}{k} + \binom{n}{k-1}, \quad (C9d)$$

together with (C9c), we have

$$N(l, j) = \binom{n+1}{n-j} = \binom{n+1}{j+1}. \quad (C9e)$$

We obtain from Eqs. (C9e) and (C8)

$$I_1 = - \sum_{j=0}^{m'} \binom{m'-1}{j+1} (1-x)^{m'-j} (-x)^{j+1} \quad (C10a)$$

$$= - [(1-2x)^{m'-1} - (1-x)^{m'-1}] (1-x)^2. \quad (C10b)$$

A similar result may be obtained for  $I_2$ :

$$I_2 = [(1-2x)^{m'-1} - (-x)^{m'-1}] x^2.$$

Therefore, replacing  $I_0, I_1, I_2$  in (C5), we finally obtain  $K_m$  in the form given in Eq. (C4)

#### APPENDIX D

To derive a closed expression for the self-energy for spatially extended quasiparticles (effective medium) which satisfies the two requirements (i) and (ii) in Sec. V, we must use the same assumptions for  $V_m(G^0)$  as in the ATA. That is, in Eq. (4.8c) we consider the only single-site contributions to the scattering processes for each site within the quasiparticle spatial extent (local medium). These contributions are thus *additive*. Since all sites are identical, the single-site contribution from the local medium is proportional to the number of sites therein, i.e., to  $N_0$ . Now, we define a more appropriate notation where the site number is used rather than the concentration: from the  $Q(\alpha^m)$ 's involved in the  $K_m$ 's we first obtain the  $Q(\eta^m)$ 's, where  $\eta = N_0 \alpha = N_0(c-x)$ .  $\eta$  is the fluctuation of the number of sites occupied by  $A$ -type atom, in the local cell. We have, from general properties of moments,

$$Q(\eta^m) = N_0^m Q(\alpha^m). \quad (D1)$$

From Eq. (3.5b) one can easily show

$$K_m^{(\eta)}(N_0; P) = N_0^m K(N_0; P), \quad (D2)$$

$K_m^{(\eta)}(N_0; P)$  being the statistical factor calculated from the random variable  $\eta$  instead of  $\alpha$ . The approximation stated above is more easily expressed by using the  $K_m^{(\eta)}$ 's. We have

$$K_m^{(\eta)}(N_0; P) = \sum_{n=0}^{N_0} P(n) (n - \bar{n})^m, \quad (D3)$$

where  $n = cN_0$ , and  $\bar{n} = xN_0$ .  $P(n)$  is given by Eq. (5.1). Expanding (D3) we obtain

$$Q(\eta^m) = \sum_{l=0}^m \binom{m}{l} (-1)^{m-l} (\bar{n})^{m-l} Q(n^l) \quad (D4)$$

with

$$Q(n^l) = \sum_{n=0}^{N_0} P(n) n^l. \quad (D5)$$

Equation (D5) is then calculated using the general properties of the discrete binomial distribution law.<sup>23</sup>

$$Q(\eta^l) = \left[ x \frac{\partial}{\partial x} \right]^l (x+y)^{N_0}, \quad \text{for } x+y=1 \quad (D6a)$$

$$= \sum_{k=1}^l \frac{N_0!}{(N_0-k)!} S_l^{(k)} x^k, \quad (D6b)$$

where  $S_l^{(k)}$  are the Stirling numbers of the second kind.<sup>24</sup> From (D4) and (D6),

$$Q(\eta^m) = \sum_{l=0}^m \binom{m}{l} (-1)^{m-l} N_0^{m-l} \times \sum_{k=1}^l \frac{N_0!}{(N_0-k)!} S_l^{(k)} x^{m-l-k}. \quad (\text{D7})$$

There  $Q(\eta^m)$  is a polynomial of order  $m$  in  $N_0$  and where the lowest-order power of  $N_0$  is 1. For self-containedness with respect to the assumption about  $V_m(G^0)$ , the only term in the  $K_m^{(\eta)}(N_0;P)$  proportional to  $N_0$  must be taken into account. This term is easily obtained from (D7) by setting  $l=m$ . It is given by

$$K_m^{(\eta)}(N_0;P) = Q(\eta^m) = N_0 \sum_{k=1}^m (-1)^{k-1} (k-1)! S_m^{(k)} x^k, \quad (\text{D8})$$

since the contribution from the sum in Eq. (3.5b) is at least of order  $N_0^2$ . Equation (D8) can be rewritten as<sup>25</sup>

$$K_m^{(\eta)}(N_0;P) = N_0 C^{(m)}(x), \quad (\text{D9})$$

where the  $C^{(m)}(x)$  are the so-called Kubo's cumulants of the random variable  $\eta$  (or  $\alpha$ ). Here, we use an approxi-

mate closed form for the  $C^{(m)}$ 's which has been previously reported by Ehrenreich and Schwartz.<sup>26</sup> It reads as

$$C^{(m)}(x) = x(1-x)(1-2x)^{m-2}, \quad m \geq 2. \quad (\text{D10})$$

As mentioned in Refs. 17 and 26, this approximation is exact for  $m < 3$  and gives correctly the leading terms in  $x$  and  $1-x$  for  $m > 3$ . Therefore, the self-energy expression we derive from Eq. (D10) will be exact through  $O(U^3)$ , the same as that for the ATA obtained in Refs. 17 and 26. From (D2), (D9), and (D10) we finally obtain

$$K_m^{(\eta)}(N_0;P) = \frac{1}{N_0^m} K_m^{(\eta)}(N_0;P) = \frac{1}{N_0^{m-1}} x(1-x)(1-2x)^{m-2}, \quad m \geq 2. \quad (\text{D11})$$

It must be emphasized that (D11) is a single-site approximation for  $K_m(N_0;P)$ . It does not account for the pairing or higher-order clustering terms which have been neglected. These latter terms are at least of order  $N_0^2$ . Therefore our theory still gives the *leveled-out* effective medium "felt" by extended quasiparticles in alloys, in a perfect analogy to the ATA for site-localized quasiparticles ( $N_0=1$ ).

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