Self-consistent calculations for shallow defects in semiconductors: I

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Abstract. Shallow defects in semiconductors are of major importance, both scientifically and technologically. These include donors, acceptors, isoelectronic impurities and various clusters, and may involve trapped carriers or bound excitons. Hopfield provided the key to understanding the more complicated defects by stressing their relation to atomic and molecular systems. We have developed a general computer program, SEMELE, to exploit this relation further. SEMELE provides a systematic and straightforward way of performing self-consistent calculations on shallow defects and is particularly suited to donor–acceptor pair and related systems.

In the present paper we discuss the main assumptions, together with the various ways of treating central-cell corrections. Results are given for excitons bound to neutral donors in GaP. A subsequent paper treats donor–acceptor pairs.

1. Introduction

The analogies between shallow defects in semiconductors and atomic or molecular systems have been known for many years. The simple donor strongly resembles a hydrogen atom, for example. More complicated systems like donor–acceptor pairs must be related to molecules instead. The key to understanding the various complex defects (bound excitons and groups of donors, acceptors or isoelectronic defects) has been Hopfield's (1964) classic paper[†] on 'quantum chemistry'. Hopfield observed that transition energies for many of these complicated defects could be obtained by scaling known atomic and molecular energies. In practice, the scaling only proves possible in certain limiting cases such as special values of the ratio of electron and hole masses or large defect separations. Simple interpolation can be difficult (especially when there are central-cell corrections) and it is usually much less accurate than the experimental data deserve. In the present paper we discuss a general program SEMELE (*Semi-conductor defect elec*tronic structure) which follows the philosophy proposed by Hopfield, albeit with some generalizations, but which is not restricted to special geometries or mass ratios and which can be applied even when there is no obvious molecular analogue.

The basic assumptions of Hopfield's approach are these. First, one concentrates on

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† Strictly, there was earlier work, notably by Lampert (1958) and in Kohn's footnote to the paper by Haynes (1960). But Hopfield's paper gave the first systematic treatment.

the envelope functions describing the conduction electrons and holes. If the full wave-functions have the form

$$\psi(r) = \phi(r)u_n(k_0, r) \tag{1.1}$$

where ϕ is the envelope function and $u_n(k_0, r)$ a band function for an extremum at k_0 of band n, then the band function can be ignored for very shallow defects. (There are two exceptions to this rule: one must remember the degeneracy of the valence band when applying the Pauli principle and also recognize the orthogonality properties of band functions associated with different bands.) Secondly, one may assume that the bands are isotropic and parabolic. The argument here is that, if suitable empirical band parameters are taken, the variation of energies with geometry (for example) is not sensitive to the simplifications of the band structure. The third assumption is that the central-cell correction can be represented in some simple way. We discuss various possibilities in §2. Hopfield proceeded to relate defect and molecular energies by scaling terms by carrier masses, charges and dielectric constants.

This approach has been very fruitful, giving insight as well as quantitative guidance. The present work goes beyond Hopfield's in a number of ways. There are no restrictions on effective masses or on defect geometries, so calculations are possible for defects as varied as very close donor–acceptor pairs and groups of up to 50 point defects with arbitrary geometry. Further, central-cell corrections can be included in a variety of ways, so that one can investigate their effects on different terms. Later in this paper we discuss central-cell effects on donor ionization energies and exciton binding energies.

2. The SEMELE program

The program SEMELE is based on the molecular Hartree–Fock program, ATMOL, of Dr V Saunders. This program (ATMOL) has been used widely for molecular calculations and for a number of solid-state applications. It is a flexible and robust program.

As we shall describe it, SEMELE performs self-consistent Hartree–Fock calculations on defects in semiconductors. There are two classes of restriction—program and model. Those imposed by the program limit the number of basis functions to 68 and the number of sites on which there are charges or basis functions to 50. Neither limit causes problems in practice. The other restrictions are those of the model, the most serious of which arise from the neglect of correlation (which can be estimated in certain cases) and the approximations concerning the isotropy of the band structure.

2.1. Scalings introduced by SEMELE

SEMELE differs from ATMOL by having additional computer code to make some of the modifications described in §1. Full details are given in a user's guide (Harker and Stoneham 1975). For present purposes it suffices to know that the changes have the following effects:

(i) Certain overlap integrals are set to zero because of the assumed orthogonality of the band functions $u_n(k_0, r)$.

(ii) Kinetic energy integrals are multiplied by the appropriate factor (m_0/m^*) to allow for the modified effective masses.

(iii) The Coulomb interactions involving holes are altered in sign as necessary because holes and electrons carry charges opposite in sign.

(iv) Where appropriate, interactions between the various nuclear and carrier charges are screened by multiplication by $1/\epsilon$, where ϵ is a dielectric constant.

It proves convenient to divide the electrons and holes into four groups: conduction electrons, core electrons, holes, and split-off holes. This division is partly to allow one to make the various changes systematically and partly to give extra flexibility. This flexibility takes the form of using different effective masses and screening constants for the core electrons and split-off holes, and of the option of splitting the valence band by shifting the split-off hole band. The core electrons are used only in the central-cell corrections, which we now discuss.

2.2. Central-cell corrections

The transition energies of donors and acceptors differ from those expected for a carrier trapped in a purely Coulombic potential. Whilst the reasons are varied in detail, the dominant effects can be attributed to the altered electronic structure at the defect site: the wavefunctions and charge density of the core electrons of the defect differ from those of the host atom replaced. The central-cell correction must be treated in some way if we hope to predict transition energies of shallow defects. Three options are available in SEMELE. For clarity, we describe them for donors:

(i) The effective mass of the donor electron can be adjusted to give the correct binding energy. If the donor ionization energy is E_D (in Rydbergs), then

$$m_e^* = E_D \epsilon^2 \tag{2.1}$$

where ϵ is the dielectric constant. This method, used by Hopfield, works quite well. The species dependence of m_e^* is a nuisance and has undesirable indirect effects on the extent of the wavefunction. But the prescription is satisfactory if the value of E_D is close to the effective-mass value.

(ii) An extra attractive potential can be added at each impurity site. Tradition usually favours a square-well potential, although this is inconvenient when several defects are involved and two-centre integrals occur. The most sensible choice for SEMELE proves to be a Gaussian potential of the form

$$V_i = A_i \exp(-|r - r_i|^2/\rho_i^2) \tag{2.2}$$

added to the Coulomb potential. The maximum depth, A_i, and range, ρ_i, are species-dependent. This option is not used in the present work.

(iii) The third option, and the one we prefer, recognises that the altered charge density of the defect core is a source of the central-cell corrections. Instead of treating each donor as a point charge $|e|$, one treats the donor as a point charge $Z|e|$ screened by $(Z - 1)$ core electrons. In most cases $Z = 5$ is convenient. Choices of core parameters are discussed in §3. The main point of this option is that the true defect core is mimicked by the model core chosen, and its properties are chosen phenomenologically.

3. Donors in GaP

Later we shall discuss the binding of excitons to neutral donors in GaP and the spectroscopy of donor–acceptor pairs, also in GaP. In both cases we need suitable wavefunctions for the isolated donor in a form which allows for central-cell corrections and yet is reasonably realistic and easy to use. GaP is an important material technologically and an enormous amount of accurate data is available. But GaP is also complicated. The conduction band has three minima at the zone edge, for example, which means the band structure is very far from the isotropic model we assume. For this reason, a successful

choice of parameters can be regarded as verification of the assumptions of Hopfield's approach.

We adopt the approach described in §2, namely, we represent a donor by a conduction electron of mass m_e^* moving outside a core consisting of a charge $5|e|$ and four core electrons. The core electrons have mass m_0 and their interactions with each other and with the point charge are unscreened. The interaction of the donor electron with the core is screened by a dielectric constant ϵ. We shall take $\epsilon = 11.02$, following recent re-evaluations (Vink *et al* 1973), although our earliest work used the previously-accepted value 10.75. Our choice of $m_e^* = 0.33\, m_0$ is close to the values assumed by Faulkner (1968) in his work on isoelectronic defects, and has the advantage of giving an effective Rydberg $m^* e^4/2\epsilon^2\hbar^2$ of 37 meV, close to estimates of the donor binding energy in the absence of central-cell corrections.

The choice of trial wavefunctions for both core and donor electrons must be made. For the four core electrons, it is convenient to have just a single parameter to vary. The spatial wavefunctions were taken to be linear combinations of two basis functions, namely

$$
\left.
\begin{aligned}
\psi_{1s}^c &\sim \exp\left(-\alpha r\right) \\
\psi_{2s}^c &\sim r \exp\left(-\tfrac{1}{2}\alpha r\right)
\end{aligned}
\right\}
\tag{3.1}
$$

which were orthogonalized automatically by the program. When α is infinite, there is no central-cell correction; as α falls, the core spreads out and the binding of the donor electron increases. Values of α as a function of E_D, the donor ionization energy, are given in the following paper. For present purposes it suffices to know that varying α changes the central-cell correction.

A more flexible choice is made for the donor-electron wavefunction, the basis functions being chosen as follows. First we note that, for a potential varying asymptotically as r^{-1}, the wavefunction at large distances varies as (some polynomial in r) $\times$ $\exp\left(-\beta r\right)$ (Newton 1966) in which

$$
\beta = \frac{m^*}{m_0} E_D
\tag{3.2}
$$

when β is in atomic units and E_D is in Rydbergs. The 'quantum defect' method exploits this asymptotic behaviour, using functions like $r^{\nu-1}\exp\left(-\beta r\right)$. Two of the four functions included in our basis for isolated donors are of this type:

$$
\left.
\begin{aligned}
\psi_1 &\sim \exp\left(-\beta r\right) \\
\psi_2 &\sim r \exp\left(-\beta r\right).
\end{aligned}
\right\}
\tag{3.3}
$$

In addition we include two functions following Hopfield's suggestion. If the effective mass were adjusted to give E_D correctly, then the exponent which corresponds would be γ, where

$$
\gamma = \epsilon E_D
\tag{3.4}
$$

with E_D in Rydbergs and γ in atomic units. The other two functions included for isolated donors (where only s functions are needed) are:

$$
\left.
\begin{aligned}
\psi_3 &\sim \exp\left(-\gamma r\right) \\
\psi_4 &\sim r \exp\left(-\tfrac{1}{2}\gamma r\right).
\end{aligned}
\right\}
\tag{3.5}
$$

We note that it is essential to avoid exponents smaller than β, since these would give incorrect asymptotic behaviour. Also, clearly, it is important that the core electron functions be more compact than the donor electron functions, so that $\alpha \gg \beta, \gamma$. These conditions are obeyed in all the cases treated. This is the reason we took $Z = 5$ with four core electrons; the values of α needed for $Z = 3$ and two electrons proved too small.

4. Exciton bound to a neutral donor in GaP

The earliest work on bound excitons (Haynes 1960) suggested that an exciton could be bound to a neutral donor by an energy E_{BX}, defined in terms of the reaction:

$$[\oplus e\ eh] + E_{BX} \rightarrow [\oplus e] + [eh] \tag{4.1}$$

where the square brackets indicate bound systems and $\oplus$ represents the ionized donor. Results for various donors in silicon suggested that E_{BX} and E_D were proportional (Haynes rule), although more recent experimental work (eg Dean *et al* 1970) has shown that for GaP

$$E_{BX} = AE_D + B \tag{4.2}$$

is appropriate, and that for InP (White *et al* 1972) the relation is still more complex. Clearly it would be valuable to establish the way in which central-cell corrections affect E_{BX} and E_D, since these corrections underly equations like (4.2). In this section we give the first quantitative treatment of the relation between E_{BX} and E_D.

4.1. The free exciton

The free exciton is a system for which the assumptions of §2 are particularly bad. The main point is that the electron–hole correlation is responsible for much of the exciton binding energy E_X, and this correlation is not treated well by Hartree–Fock methods. When the electron and hole masses are very different, the problem is not important. When the two masses are very similar however, as in GaP (where there is the added complication of the conduction band structure), the problem could be severe. Fortunately, most of the difficulties resolve themselves, partly because of the precise values of the crystal parameters but mainly for reasons of principle. One point is that we shall be seeking an energy difference between free and bound excitons, and the correlation terms cancel to a large extent. A second point is that the 'quantum chemistry' approach is partly empirical, since some experimental data are used in choosing parameters. Thus the method is able to interpolate successfully even in cases where the assumptions do not hold strictly.

We have used a hole mass m_h^* of $0.38\ m_0$, since this gives the correct effective-mass acceptor energy in the simplest theory and also a good exciton energy. It is a plausible average of the light- and heavy-hole masses of $0.17\ m_0$ and $0.67\ m_0$. In the simplest hydrogenic model of the exciton, E_X is (m_x/ϵ^2) Rydbergs, where m_x is the reduced mass of the electron and hole. The result, about 19.8 meV, is far too large, for experiment gives about 10 meV. However, SEMELE gives rather more than 40% of the hydrogenic result, mainly because electron–hole correlation is treated badly. The SEMELE result, about 8.6 meV, is fortuitously close to experiment, so that the same choice of m_h^* gives good acceptor and exciton energies using SEMELE. One can interpret this quantitative

agreement by saying that there is a large cancellation of both the errors from neglect of correlation and those from neglect of the complexities of the band structure. The exciton energy is relatively insensitive to the basis used, so we have made the following choice. For the hole wavefunction, we include terms based on both the quantum defect and Hopfield approaches, together with some extra terms to give more flexibility. Four 1s functions are included (exponents 0·0162, 0·114, 0·080 and 0·040 au) and two 2s functions (exponents 0·081 and 0·040 au). The same basis was used for the electron as for the donor. Thus, for each donor, three calculations were done: isolated donor, isolated exciton, and exciton bound to neutral donor.

4.2. The bound exciton

We have calculated the exciton binding energy for a range of central-cell corrections typical of donors in GaP. The results are summarized in figure 1, where they are compared with experiment.
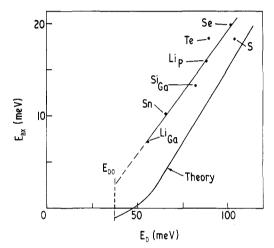

Figure 1. The binding of excitons to neutral donors in GaP as a function of donor binding energy. The experimental data are from Dean (1972) and the theory is that of the present paper. The two curves are $E_{BX} = 0.268E_X - 7.51$ meV for the experimental results and $E_{BX} = 0.324 E_X - 17.04$ meV for the theory. E_{DO} is the donor energy in the absence of a central-cell correction.

The first point to emerge is that the qualitative agreement with experiment is good. At all except the smallest central-cell corrections, both theory and experiment agree that a generalized Haynes rule, as in (4.2), holds. Further, for very low central-cell corrections, one would expect the curve to flatten off as it is plausible that correlation terms will keep E_{BX}, the exciton binding, positive in all cases. The curvature is shown by the calculations, although the E_{BX} does become negative because of the inadequate treatment of correlation. The curvature only begins to manifest itself for donors with smaller central-cell corrections than are met in practice.

The second point of importance is that the quantitative agreement with experiment is satisfactory. The bound exciton is one of the most searching tests of SEMELE, both

of the simplifications of the band structure and of the correlation. Three conclusions can be drawn. Firstly, the quantum chemistry method can give quite accurate quantitative predictions, even when the band structure is relatively unfavourable. The value of the slope is especially good. Secondly, it seems that the neglected correlation terms cancel to a large extent between the free and bound exciton cases. The residual correlation terms are probably the main reason for the discrepancies, which should be compared with the 11·2 meV difference between the free exciton energy predicted by SEMELE and the hydrogenic value m_x/ϵ^2 using the same parameters. As one would expect, the differences between theory and experiment are less for the deeper donors, where the central-cell terms become more important than correlation. Other possible reasons for the discrepancies include the simplification of the band structure and our neglect of any distinction between the roles of electronic and ionic screening. We have checked that the choice of basis is not important by doing calculations with a much more extended basis for the case of no central-cell correlation. Thirdly, we have verified the conjecture often made qualitatively that, for donors with central-cell corrections, a generalized Haynes rule like (4.2) is expected. It remains to be seen whether the different forms of (4.2) for different systems are correctly predicted.

5. Summary

We have developed a general computer program, SEMELE, for the treatment of complex shallow defects in semiconductors. The program uses a generalization of Hopfield's 'quantum chemistry' approach and has been applied successfully to bound exciton systems; in the following paper, application to donor–acceptor pairs is discussed. The method is readily extended to defects of much greater complexity, and its importance lies in its flexibility and convenience of application to a wide range of shallow defects.

Acknowledgments

References

Dean P J 1972 *Luminescence of Crystals, Molecules and Solutions* ed F Williams (New York: Plenum Press) pp 538–52
Dean P J, Faulkner R A and Kimura S 1970 *Phys. Rev.* B2 4062–76
Faulkner R A 1968 *Phys. Rev.* 175 991–1010
Harker A H and Stoneham A M 1975 *AERE Report R-7773*
Haynes J R 1960 *Phys. Rev. Lett.* 4 361–5
Hopfield J J 1964 *Proc. Int. Conf. on Physics of Semiconductors, Paris* pp 725–35
Lampert M 1958 *Phys. Rev. Lett.* 1 450–4
Newton R G 1966 *Quantum Theory of Scattering* (New York: McGraw-Hill)
Vink A T, van der Heyden R L A and van der Does de Bye J A W 1973 *J. Luminesc.* 8 105–25
White A M, Dean P J, Taylor L L and Clarke R C 1972 *J. Phys. C: Solid St. Phys.* 5 L110-3