

Self-consistent calculations for shallow defects in semiconductors: II. Donor–acceptor pairs

A M Stoneham and A H Harker

Theoretical Physics Division, Atomic Energy Research Establishment, Harwell, Oxfordshire, OX11 0RA.

Received 11 November 1974

Abstract. A general method has been developed for performing self-consistent calculations for shallow defects or defect complexes in semiconductors. Results are given here for donor–acceptor pairs in GaP and a comparison is made of the various treatments of central-cell corrections and the effects arising from the overlap of the donor and acceptor wavefunctions.

Whilst no detailed refitting of host parameters is attempted, it seems likely that the current estimate of the bandgap (2.339 eV) is too large, and the latest estimates of the dielectric constant may also be inaccurate.

1. Introduction

One of the classes of defect central to the development of commercial electro-optic devices consists of donor–acceptor pair systems (eg Dean 1973). In these systems, an electron trapped at a donor may recombine with a hole trapped at an acceptor, giving luminescence with an energy E_{LUM} approaching that of the bandgap, E_{GAP} .

The donor–acceptor pairs are of great scientific interest, in addition to their technological virtues. Extremely accurate spectroscopy is possible, giving recombination energies and other details of the transitions as a function of the donor–acceptor separation. The theory of the trends with separation of the transition energy, E_{LUM} , is the subject of the present paper. We shall demonstrate the use of the general computer program SEMELE (Stoneham and Harker 1975, to be referred to as I), comparing earlier treatments of the theory with a more accurate approach and commenting on the implications for the parameters of the host lattice.

2. General

In this section we outline previous work on donor–acceptor systems, the choice of suitable systems to test different aspects of the theory and the values of parameters for the various systems studied.

2.1. Earlier theories

The results which have been the mainstay of the interpretation of donor–acceptor recombination data are given by Hopfield (1964), whose ‘quantum chemistry’ approach to shallow defects is followed in the present paper. The essence of his conclusions is that

at large separations R , where the donor and acceptor wavefunctions do not overlap

$$\Delta E \equiv E_{\text{GAP}} - E_{\text{LUM}} \simeq E_{\text{A}} + E_{\text{D}} - e^2/\epsilon R \quad (2.1)$$

where E_{D} is the donor ionization energy, E_{A} the acceptor ionization energy and ϵ the dielectric constant (usually taken as the static constant). At very small separations, where the Coulomb fields of the ionized donor and acceptor would cancel to a great extent, Hopfield argues:

$$\Delta E \simeq E_{\text{EXC}} \quad (2.2)$$

where E_{EXC} is the exciton binding energy.

We shall be concerned primarily with $\Delta E(R)$, together with the effects of central-cell corrections on the various energies. We shall not be discussing the many small corrections to (2.1) proposed by other workers. These include multipole corrections, elastic interactions, polaron effects, van der Waals terms and corrections from the wavevector dependence of the dielectric constant. However, it is worth stressing that the van der Waals terms are not important. The original discussion of this contribution (Trumbore and Thomas 1965) was based on empirical arguments. Revised estimates of the dielectric constant reduced the need for these terms. Further, quantitative estimates are possible (Stoneham 1975) based on the observed polarizabilities of donors and acceptors (Dean and Patrick 1970), which show that the van der Waals terms must be only a few per cent of the original estimates. The problem has been complicated by the incorrect screening used by many workers (including some otherwise-scrupulous analyses, for example, Vink *et al* 1973): the van der Waals term should contain an ϵ^{-2} factor, not the ϵ^{-1} commonly found (McLachlan 1965, Israelachvili 1972). In essence, the instantaneous dipole on one centre induces a dipole proportional to ϵ^{-1} on the other and the interaction of these two dipoles is screened by a further ϵ^{-1} factor.

There have been four earlier calculations of the separation dependence of ΔE which go beyond (2.1). The earliest, due to Williams (1960) took into account the overlap of the donor and acceptor wavefunctions. This work was extended later by Mehrkam and Williams (1972), whose work we discuss in more detail in §3. Hopfield (1964) quotes otherwise-unpublished calculations in his review. His work appears to cover many of the aspects treated later by Mehrkam and Williams and his results have the added virtue of going over to (2.2) at small spacings. Bindemann and Unger (1973) adopted a strategy different in detail, using 'floating' wavefunctions centred on sites other than the donor and acceptor. Their method also behaves reasonably at short distances. Calculations for molecular H_2 (Hurley 1954, Rosen 1931) suggest the Bindemann–Unger treatment should give rather better energies than the Mehrkam–Williams method.

2.2. Choice of system

There are several sets of accurate data for donor–acceptor pair recombination. We shall discuss two systems in GaP: the sulphur–carbon pairs and, to a lesser extent, the sulphur–zinc pairs. The host crystal, GaP, is convenient because of the accurate experimental data and because it has a rather low degree of ionicity, so that polaron effects are unlikely to be important. The GaP: (Zn, S) system has been discussed by Mehrkam and Williams and it is for this reason we describe briefly some calculations in §4. But the major part of the work (§3) is on GaP: (S, C). The advantages of this system are that the most detailed experimental information is available (Dean 1973, Vink *et al* 1973) and that the carbon is a very shallow acceptor for which an unsophisticated treatment of central-cell correc-

tions suffices. The sulphur donor is fairly deep and is suitable for comparing the merits of different treatments of the central-cell terms.

2.3. Choice of parameters

We shall need to choose values of the dielectric constant ϵ , the effective masses m_e^* and m_h^* , and the band gap E_{GAP} . In addition to these host lattice properties, the effective radii for the core electrons must be established for a description of the central-cell corrections (cf § 3 of the preceding paper).

We shall normally use the following parameters for GaP:

$$\left. \begin{aligned} \epsilon &= 11.02 && \text{(Vink } et \text{ al 1973),} \\ m_e^* &= 0.33 m_0 && \text{(I, to fit effective-mass donor energy),} \\ m_h^* &= 0.38 m_0 && \text{(I, to fit effective-mass acceptor energy),} \\ E_{\text{GAP}} &= 2.339 \text{ eV} && \text{(Dean 1973).} \end{aligned} \right\} \quad (2.3)$$

Different parameters are used occasionally. In special cases, notably GaP: (Zn, S), we compare results with earlier work using $\epsilon = 10.75$, and so we alter the dielectric constant. In other cases, central-cell corrections are included by modifying m_e^* . We shall also see that our calculations cast doubt on the assumed values of ϵ and E_{GAP} .

As described in I, the donor core can be represented by a nuclear charge $Z = 5$ and four electrons in orbitals with wavefunctions proportional to $\exp(-\alpha r)$ and $r \exp(-\frac{1}{2}\alpha r)$. The parameters α can be varied to give the correct central-cell correction. In I we needed to know only that the α controlled the central-cell correction. Here we need to know the precise relation between α and the donor binding. The results of such calculations are given in figure 1. All choices of basis function and all scalings are as described in I. However, there is one slight difference. For systems with more than one centre, as for a donor-acceptor pair, there are advantages in using a Gaussian basis in calculating the molecular integrals. These advantages are very considerable when more than two centres are involved. The program used has an option for expanding the Slater orbitals chosen as a sum of Gaussians. The approximations introduced are slight if enough Gaussians (typically 3 or 4) are used and arise mainly from the poor description of the cusp in the 1s core functions. The results in figure 1 have used an expansion in terms of three Gaussians. The same expansion was used in all subsequent calculations.

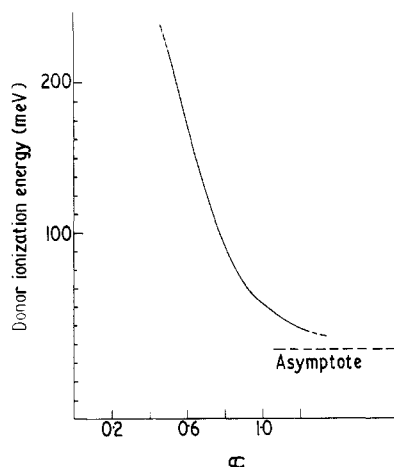


Figure 1. Donor ionization energies in GaP for various choices of core wavefunctions. These results use $Z = 5$, and 1s and 2s functions $\exp(-\alpha r)$ and $r \exp(-\frac{1}{2}\alpha r)$ for the four core electrons. This parameterization is appropriate when each Slater function is fitted by three Gaussian functions. The asymptote is for $\alpha \rightarrow \infty$.

2.4. Different levels of calculation

We have calculated the variation of the donor-acceptor pair energy with separation using five different levels of approximation, which we now summarize in 2.4.1-2.4.5. The wavefunction parameters used are listed in table 1.

Table 1. Parameters used in various calculations for GaP: (S, C)

Method	ϵ	m_e^*/m_0	m_h^*/m_0	Functions	Exponents (au)
Mehrkam-Williams	11.02	0.672	0.672	1s (D, A)	0.0609
				2p (D, A)	0.0609
Asymmetric	11.02	0.930	0.414	1s (D)	0.0844
				1s (A)	0.0376
				2p (D)	0.0844
				2p (A)	0.0276
Extended asymmetric	11.02	0.930	0.414	1s, 2p (D)	0.0844
				2s, 2p (D)	0.0422
				1s, 2p (A)	0.0376
				2s, 2p (A)	0.0188
Full SEMELE	11.02	0.33	0.414	1s (D)	0.0842
				1s, 2s, 2p (D)	0.0502
				2s, 2p (D)	0.0421
				1s, 2p (A)	0.0376
				2s, 2p (A)	0.0188
		1.0 (core electrons)		1s (donor core)	0.75
				2s (donor core)	0.375
<u>Parameters used for GaP (Zn, S)</u>					
Mehrkam-Williams	10.75	0.705	0.705	1s, 2p (D, A)	0.0581
Extended asymmetric	10.75	0.705	0.705	1s, 2p (D, A)	0.029

2.4.1. *Coulombic form (case I)*. This form uses equation (2.1) and is asymptotically correct at large distances. But, since donor-acceptor spectra are often used to determine the dielectric constant ϵ , the results may show unduly good agreement with experiment. In particular, one should note that the largest separations for which there are accurate data are only two or three times the effective Bohr radii: the true asymptotic régime and the range of spacings seen in practice do not overlap.

2.4.2. *Mehrkam-Williams form (case II)*. In its most basic version, Mehrkam and Williams (1972) assume a total wavefunction of the form $\psi_e(r_e - R_D) \psi_h(r_h - R_A)$, where R_D and R_A give the donor and acceptor positions. The one-particle functions ψ have the form:

$$\psi(r) = N(1 + \sigma\beta Z) \exp(-\beta r) \quad (2.4)$$

where $N(\sigma, \beta)$ is a normalization and the Z axis is the axis of the defect. This form of ψ is the simplest which shows most features of interest and it makes several major approximations. First, all asymmetry of donor and acceptor is ignored, even if E_D and E_A differ. The parameters σ and β are the same for both the electron and hole. Secondly, the central-cell corrections are incorporated by altering the effective masses. Both electron and hole are assumed to have a mass m^* given by

$$\frac{m^*}{m_0} = \frac{1}{2}\epsilon^2(E_A + E_D) \quad (2.5)$$

where E_A and E_D are measured in Rydbergs. This scheme was used in Hopfield's earlier calculations. Thirdly, the exponent β was not treated as a full variation parameter. It was fixed by the relation:

$$\beta = \frac{m_0}{m^*} \epsilon a_0 \frac{2a_0}{E_A + E_D} \quad (2.6)$$

where a_0 is the Bohr radius. This value of β was held constant for a range of spacings. Note too that the β parameter for the 2p component of ψ is the same as for the 1s component; for the hydrogen atom, β_{2p} is half β_{1s} . The parameter σ is varied freely, altering the weights of 1s and 2p in the one-electron functions to minimize energy. Mehrkam and Williams call this process 'configuration admixture', a misleading phrase, totally different in meaning to the standard useage of molecular physics (eg Condon and Shortley 1935, Slater 1963, Coulson 1963, McWeeney and Sutcliffe 1969).

2.4.3. *Simple asymmetric form (case III)*. This corresponds to the Mehrkam-Williams model in all respects but one: the asymmetry of donor and acceptor is included. Instead of (2.5), the electron and hole masses are defined by:

$$\frac{m^*}{m_0} = \epsilon^2 E_D \quad (2.7)$$

and

$$\frac{m_h^*}{m_0} = \epsilon^2 E_A \quad (2.8)$$

where again E_A and E_D are measured in Rydbergs. The orbital exponents for electron and hole are then fixed by the relations:

$$\beta_e = \frac{m_0 \epsilon}{m_e^*} a_0 = a_0 / \epsilon E_D \quad (2.9)$$

and

$$\beta_h = \frac{m_0 \epsilon}{m_h^*} a_0 = a_0 / \epsilon E_A. \quad (2.10)$$

The asymmetry may be quite considerable. For the GaP: (S, C) system, for example, β_e is only 45% of β_h .

2.4.4. *Extended basis form (case IV)*. This is a generalization of case III, but with a more general form of the one-particle functions ψ . Instead of only 1s and 2p functions, with exponents β defined by (2.9) or (2.10), the following set of functions is used:

Exponent β : 1s and 2p functions

Exponent $\beta/2$: 2s and 2p functions;

that is, four basis functions for the donor and four different ones for the acceptor.

2.4.5. *Full central-cell approach (case V)*. In this form, the central-cell corrections for the donor are included by using a realistic core, as described in § 2.3 of this paper and § 3 of the preceding paper. Additional 2p basis functions are included, with exponents as for the 2s functions. In the cases we shall be treating, the *acceptor* is treated as in case IV, namely by a specially-chosen effective mass. This approximation should be reasonable for the shallow carbon acceptor, which we discuss primarily, where the ionization energy is only 46.4 meV.

Table 2. Predictions of various models for ΔE , the difference between the bandgap and the donor-acceptor recombination energy. The difference is in meV and is positive when the energy of luminescence predicted is less E_{GAP} . Spacings are in atomic units. The singlet-triplet splitting uses the full SEMELE method.

Spacing (au)	Coulombic	Mehrkam-Williams	Asymmetric	Extended asymmetric	Full SEMELE	Singlet-triplet splitting
10	-96.26	-13.95	-11.47	17.23	12.92	9.22
20	27.17	34.80	37.05	40.41	36.79	9.30
30	68.31	65.99	67.38	67.82	65.73	9.03
40	88.88	85.93	86.45	86.53	85.71	6.95
60	109.46	107.48	107.45	107.46	107.96	3.30

3. Results for GaP: (S, C)

The ionization energies for the two component defects are 104.2 meV (S) and 46.4 meV (C). Results for all five methods and spacings $R = 10, 20, 30, 40$ and 60 au are given in table 2 and shown in figure 2. With the parameters adopted, the exciton energy is 8.6 meV (preceding paper) in the open-shell Hartree-Fock procedure used here. This is compatible with the observed values (albeit fortuitously so) and we shall use this value to obtain results for zero spacing. We shall compare the various methods in § 5.

3.1. Coulomb form

As mentioned, this is asymptotically exact at large R . However, it gives a divergence at small R . In the present case (2.1) predicts a transition energy higher than that for the free exciton when $R < R_0 \sim 9.2 \text{ \AA}$, and results for smaller spacings will surely be unreliable.

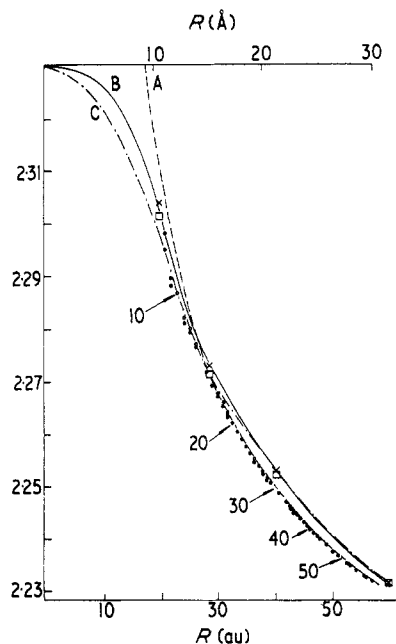


Figure 2. Recombination energies for the GaP: (S, C) donor-acceptor pair in various approximations: Curve A, Coulombic method; curve B, full SEMELE; curve C, extended asymmetric; the points \square , asymmetric; and \times , Mehrkam-Williams. The experimental data \circ are taken from Deans (1973).

3.2. Mehrkam-Williams form

This method also becomes unreliable at small R , overestimating the transition energy considerably when $R \lesssim R_0$. The reason for the overestimate is the relative inflexibility of the choice of basis. Like all the methods described, this method should converge satisfactorily on the asymptote (2.1) at large spacings. But one important point emerges, relevant for all the methods II-V. The effective Bohr radius is of the order of 8.7 Å and the largest spacings studied are rather less than 30 Å. The overlaps are still significant at these distances and it is not trivial to deduce values parameters like ϵ from the experimental data.

The p-like admixture decreases at large separations and is listed in table 3.

Table 3. s-p admixture on the donor in the Mehrkam-Williams and the Asymmetric cases for GaP: (S, C). The values quoted are the weights of the normalized s and p functions. The charge density between the donor and acceptor is *reduced* by the admixture. Results for other methods show similar trends, but are more complicated because of the more extended basis used.

Method	Separation (au)				
	10	20	30	40	60
Mehrkam-Williams	0.232	0.189	0.120	0.067	0.0155
Asymmetric	0.421	0.246	0.140	0.076	0.019

3.3. Simple asymmetry

As with cases I and II, problems occur for small separations. The general features of II and III agree qualitatively, both as regards energies (table 2) and admixtures of p-like terms (table 3). The admixtures reduce the charge densities in the overlap region. Quantitatively, asymmetry makes a difference of more than 1 meV out to distances of order 20 Å and differences in the donor p-admixture of more than 1% to similar distances.

3.4. Extended basis

This is the simplest method which avoids problems at small spacings. The electron-hole recombination energy appears to converge properly onto the exciton energy at small R and to the asymptote at large R .

3.5. Full central-cell approach

Like the extended basis method, this form gives the correct asymptotic behaviour at both large and small R . However, there is quite a large difference in the values of the transition energy given by this method and the extended basis method at 10 au and 20 au separations. Available experimental data are compatible with both; it is not easy to decide which is the most successful, partly because other complications (eg multipole corrections) are significant.

Our calculations have also been repeated for the spin triplet system, although this has not been observed. The singlet-triplet splittings are listed in table 2.

4. Results for GaP: (Zn, S)

We have treated this system in much less detail and quote results here primarily to verify the Mehrkam–Williams results and to see the effects of extending the basis used without other sophistications. Consequently, we have used different crystal parameters, namely:

$$\epsilon = 10.75 \quad m_c^* = m_h^* = 0.705. \quad (4.1)$$

The effective masses and exponents $\beta \equiv 0.0581$ au have been chosen using (2.5), (2.6) and the ionization energies of 104.2 meV (S) and 64 meV (Zn).

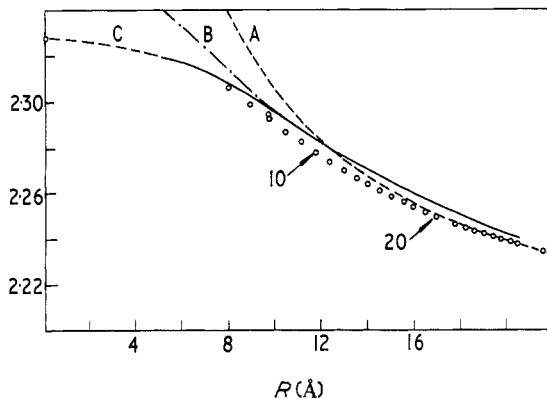


Figure 3. Recombination energies for the GaP: (Zn, S) donor–acceptor pair in various approximations: Curve A, Coulombic; curve B, Mehrkam–Williams; and curve C, extended asymmetric. The experimental data (○) are taken from Dean (1973).

The results given in table 4 were obtained with the present program. Mehrkam and Williams give their results in diagrammatic form only; suffice it to say that our data and theirs appear to agree provided one includes a constant shift of their results of the sort described in their paper.

The main difference between the calculations of the Mehrkam–Williams form (case II) and those with a more extended basis (as for case II, but with additional 2s and 2p functions with exponents $\beta/2$) is at small separations. The more extended basis avoids the divergence mentioned in §3.

5. Discussion

We now compare various aspects of the different approximations, with the aim of deciding which approaches can be used reliably and conveniently in calculations of

Table 4. Predictions of ΔE in meV for GaP: (S, Zn)

Method	Separation (au)				
	10	20	24	30	40
Coulombic	-84.8	41.7	62.8	83.8	104.9
Mehrkam–Williams	0.2	46.9	60.7	77.5	97.5
Extended basis	20.1	47.9	61.1	77.7	97.8

donor-acceptor pair spectra. Convenience is important, whilst not an overriding factor. Suffice it to say that we believe the SEMELE program to be particularly straightforward to use; the calculations have been automated, and the program combines simplicity of use with great flexibility.

The first point to discuss is the choice of basis functions. Can one successfully use just a single s and a single p function on each site? The answer seems to be no. Both the Mehrkam-Williams and asymmetric approaches behave very badly at small spacings R . Indeed, both predict the wrong sign for ΔE at small R . But the other approaches (including that of Bindemann and Unger 1973, whose floating functions are equivalent to an expansion in many spherical harmonics with related radial factors) behave properly at small spacings. These successful approaches include the extended basis and full SEMELE methods. We shall return to the results at large spacings later.

The second point concerns the way in which the central-cell corrections are included. Again, the small-separation cases are the strongest tests. There are effects at large spacings but these are masked by the purely Coulombic part of ΔE . Deviations from (2.1) should show a strong model-dependence because of the different asymptotic wavefunctions, but their value is a small fraction of ΔE at most. The results of table 2 or figure 2 show large differences between the two methods whose behaviour is satisfactory; that is, between the extended basis form and the full SEMELE form. We have not been able to use experiment to decide between these two, partly because the experimental data in the critical 10–20 au range are very incomplete. The problem is complicated further by the need for extra theoretical corrections at small R , like multipole corrections. But the full SEMELE form makes more realistic assumptions about the form of the central-cell corrections, so one would expect its predictions to be the most reliable.

The third point concerns the intermediate and larger spacings. At the largest spacings, the Coulombic part of ΔE (see (2.1)) dominates, and all theories do reasonably well. Indeed, at these spacings it is the parameterizations of the host dielectric constant and bandgap which are the most important factors. The present calculations suggests that the standard parameters adopted ($E_{\text{GAP}} = 2.339$ eV and $\epsilon = 11.02$) may be in error. The important point is that the estimates of these parameters are based on the Coulombic form (2.1) at the larger spacings. But the 'large' spacings usually used (to 70 Å for GaP: (O, C) by Vink *et al.*, but more commonly only 20–30 Å) are only a few times larger than the effective Bohr radii and overlap terms are still significant. Thus the usual parameters E_{GAP} and ϵ are empirical parameters, useful only for interpolation and limited extrapolation, and not correct crystal parameters. It would be a major undertaking to reparameterize the spectra and we have not done this. But the results do suggest that the band gap is 2 to 3 meV smaller than assumed (giving 2.336 to 2.337 eV). This new value is consistent with all the data with which we are familiar. It also implies a slightly lower exciton binding than usual, about 8 meV instead of 10 meV. This too is consistent with other data (see eg Czaja 1971).

Thus, at large spacings, all the approaches work satisfactorily with a proper choice of parameters. The parameters differ significantly between the best fit of the Coulombic form (2.1) and a fit of the methods with overlap corrections. This difference in choice of parameters is also conspicuous at intermediate spacings, where the predictions of ΔE for all the models with overlap cross the curve for (2.1) at a spacing of two or three effective Bohr radii. Since the crossover appears for all models, it is unlikely to be an artefact and, indeed, one can make plausible arguments for the small- and large- R behaviour which imply a crossover. However, the crossover could be eliminated for practical purposes if the empirical host parameters were used for the Coulombic form (2.1) and correct host

parameters for the other methods. Further, if the band gap is reduced to 2.337 eV, only the full SEMELE approach is satisfactory at smaller R .

Differences between the models become apparent at intermediate spacings, where all show trends of the right qualitative form. But, whilst the more advanced methods (extended basis and full SEMELE) give results which lead naturally to the correct small- R behaviour, the two other methods (Mehrkam-Williams and asymmetric) give satisfactory corrections over such a small range of spacings that there is rather little advantage in using them.

Acknowledgments

We are indebted to Dr V Saunders (Atlas Laboratory) for the copy of ATMOL on which SEMELE is based, and to Drs P J Dean, D C Herbert and A M White (RRE Malvern) for stimulating discussions.

References

- Bindemann R and Unger K 1973 *Phys. Stat. Solidi* **56(b)** 563-71
Condon E U and Shortley G H 1935 *Theory of Atomic Spectra* (London: Cambridge UP) ch 15
Coulson C A 1961 *Valence* (London: Oxford UP)
Czaja W 1971 *Phys. Kondens. Mater.* **12** 226-36
Dean P J 1973 *Prog. Solid St. Chem.* **8** 1-126
Dean P J and Patrick L 1970 *Phys. Rev.* **B2** 1888-99
Hopfield J J 1964 *Proc. Int. Conf. on Semiconductors, Paris* pp 725-35
Hurley A C 1954 *Proc. R. Soc.* **226** 179-90
Israelachvili J N 1972 *Proc. R. Soc.* **A331** 39-51
McLachlan A D 1965 *Discuss. Faraday Soc.* **40** 238-46
McWeeny R M and Sutcliffe B T 1969 *Methods of Molecular Quantum Mechanics* (New York: Academic Press)
Mehrkam L and Williams F E 1972 *Phys. Rev.* **B6** 3753-6
Rosen N 1931 *Phys. Rev.* **38** 2099-104
Slater J C 1963 *Quantum Theory of Molecules and Solids: I* (New York: McGraw-Hill) p 45
Stoneham A M 1975 *Theory of Defects in Solids* (London: Oxford UP)
Stoneham A M and Harker A H 1975 *J. Phys. C: Solid St. Phys.* **8** 1102-8
Trumbore F A and Thomas D G 1965 *Phys. Rev.* **137** A1030-7
Vink A T, van der Heyden R L A and van der Does de Bye J A W 1973 *J. Luminescence* **8** 105-25
Williams F E 1960 *J. Phys. Chem. Solids* **12** 265-73