

even if this condition is not fulfilled, the level assignment can be made provided that the opposite relationship: $T_{1A}, T_{1B} \ll T_{1R}$ does *not* hold. The reason for this is, that as the population changes are dissipated into the spin system, they become more and more exhausted; the largest changes remain at the source, i.e., at the irradiated levels.

The TSI method—when it can be used—does not depend on the relative magnitudes of the relaxation times for an unambiguous result, and the intensity changes obtained are generally larger. The method requires a line-by-line search, but this feature is not really detrimental, since in most applications few lines need to be investigated.^{1a}

Experiments on the nuclear Overhauser effect require equipment for field-frequency stabilization² in order to maintain the irradiation field centered on a spectral line.

TSI experiments are readily performed with conventional field-sweep spectrometers. The frequency difference between the weak observation field and the strong irradiation field is offset so as to produce the TSI a short time (a small fraction of T_1) before the observation of the intensity change, and the amplitude of the irradiation field may be kept low while sweeping over the spectrum until the field reaches the vicinity of the line to be irradiated. When applied in this way, the irradiation will usually produce a population inversion by adiabatic fast passage³ rather than a population equalization by transitory saturation, and the intensity changes will be twice as large as those attainable by selective saturation.

Transitory selective *saturation* may be accomplished with frequency-sweep spectrometers by centering the irradiation rf field continuously on the line to be saturated, but at low amplitude except for a time T_2^* before recording the intensity change.

With frequency-sweep spectrometers, population inversion by adiabatic fast passage may be obtained e.g., by use of the so-called INDOR method,^{1c,4} provided that the time taken to sweep over the irradiated line is indeed short compared to the thermal relaxation times. If on the other hand the duration of the passage is long compared to the relaxation times, Overhauser-type rather than TSI-type population changes will occur.

¹ (a) K. Kuhlmann and J. D. Baldeschwieler, *J. Am. Chem. Soc.* **85**, 1010 (1963). (b) R. A. Hoffman, B. Gestblom, and S. Forsén, *J. Chem. Phys.* **39**, 486 (1963). (c) R. Kaiser, *ibid.*, p. 2435. (d) S. Forsén and R. A. Hoffman, *Acta Chem. Scand.* (to be published). (e) R. A. Hoffman, B. Gestblom, and S. Forsén, *J. Mol. Spectry.* (to be published). (f) S. Forsén, B. Gestblom, S. Gronowitz, and R. A. Hoffman, *Acta Chem. Scand.* (to be published).

² W. A. Anderson and R. Freeman, *J. Chem. Phys.* **37**, 85 (1962).

³ See, for example: (a) A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, England, 1961), pp. 34–36 and 65–68. (b) C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), pp. 18–23. (c) G. E. Pake, *Paramagnetic Resonance* (W. A. Benjamin Inc., New York, 1962), pp. 23–27.

⁴ E. B. Baker, *J. Chem. Phys.* **37**, 911 (1962).

Distribution of Space Charge in Homogeneous Metal Oxide Films and Semiconductors

J. ROSS MACDONALD

Texas Instruments Incorporated, P. O. Box 5474, Dallas, Texas

(Received 6 January 1964)

THE recent letter by Jepson¹ with most of the above title illustrates the lack of communication which develops between even slightly different fields containing common mathematical (or even physical) problems disguised by differences in nomenclature, notation, and applications. Jepson's analysis, like that of Butler's² on which it is based, is not properly tied in with previously published space-charge work^{3–15} (see Table I for a nonexhaustive listing); this has led to some unnecessary duplication of prior work, to inadequate problem definition, and to a concomitant lack of applicability conditions.

The treatments of Table I all assume that only one set of positive and negative charges is present and that charges of at least one sign are mobile. Thus, the results will apply to dielectrics and, somewhat less generally, to semiconductors. Valences of positive and negative charges are shown as positive numbers without distinguishing between the 1, 1 and n, n cases. Solutions given only in terms of quadratures are not defined as of closed form, but specific calculated potential-distance curves have usually been presented in these cases. Finally, items marked "D" are discussed below but hot carrier effects,¹⁶ spherical symmetry,¹⁷ and growing films¹⁸ are not.

We consider charges mobile which reach essentially their equilibrium positions during charging at the temperature of final space-charge measurement. On this basis, donors, acceptors, and vacancies will frequently be immobile in space-charge experiments. Although Jepson's and Butler's equations are appropriate only when charges of both sign are effectively mobile, mobility is not discussed. Recombination can give immobile charged centers an effective mobility,¹¹ but Jepson assumes full dissociation (zero recombination). His elliptic integral solution does, in fact, apply exactly in the case of fully dissociated charges of both sign mobile but has been suggested previously¹² and is equivalent to Jaffé's^{10,11} much earlier elliptic function solution. Although arbitrary charge valences are formally considered by Butler, discussion and potential-distance curves are restricted to the 1, 1 valence case, more fully treated in Refs. 10–12. The table shows that Grahame¹⁴ has found closed solutions in other valence cases for the single-blocking-electrode situation (where 1, 2 and 2, 1 are nonequivalent).

All treatments in Table I apply only in the absence of mobile charge-carrier degeneracy, particularly important for electrons or holes. Consider, e.g., an electron-donor situation where n , N_D , and N_C are the

TABLE I. Comparison of some static, one-dimensional space-charge analyses involving plane parallel electrodes.

Ref. No.	Positive charge valence, negative charge valence: z_p, z_n	Closed form for exact potential-distance relation	Static current	Charges of both signs mobile	Dissociation	Number of identical blocking plane electrodes
3-7	Equal	Yes	0	Yes	Full	1
8	Equal	Yes; showed two forms equivalent	0	Yes	Full	1
9	Equal	No	0	No	Arbitrary	1
10, 11	Equal	Yes	0	Yes	Full	2
12	Equal	No	0	No	Arbitrary	2
13	Equal	No	Arbitrary	No	Full	1, 2 (partly or completely blocking)
14	1, 2; 2, 1	Yes	0	Yes	Full	1
2	α, β	No	0	Probably; not discussed	Probably full; not discussed	2
1	Equal	Yes	0	D	Full	2
15	Equal	Yes No	0 Arbitrary	No	D ; small	2, partly blocking

concentrations of conduction-band electrons, immobile donors in the absence of space charge, and conduction band levels, and E_C , E_D , and E_F are conduction band, donor, and Fermi energy levels, respectively. Absence of degeneracy anywhere requires $n_{\max} \ll N_C$ or¹³ $\exp[(E_C - E_F)_{\min}/kT] \gg 1$. In the zero-current, arbitrary dissociation case, it follows from earlier work^{9,12,13} that this condition may be written

$$\exp(e\psi_1/kT) \ll (N_C/2N_D) [1 + (1+4R)^{1/2}] \\ \doteq (2N_C/N_D)^{1/2} \exp[(E_C - E_D)/2kT],$$

where the last part holds only for $R \gg \frac{1}{4}$; $R \equiv (2N_D/N_C) \exp[(E_C - E_D)/kT]$ is a recombination coefficient^{9,13} which is zero in the limit of full dissociation⁹; and ψ_1 is the potential (referenced to zero potential at a neutral point) at the position of maximum n . Thus, $\psi_1 = \psi_0 (\geq 0)$, the total p.d., in a one-blocking-electrode⁹ accumulation case, $\psi_1 = 0$ for the exhaustion case, and¹² $0 < \psi_1 < \psi_0/2$ in the usual two-blocking-electrodes case.

In the slightly dissociated ($R \gg 1$) situation with charges of a single sign mobile, the equations may be reduced to those of Jaffé^{10,11} for charges of both signs mobile under some conditions.^{9,11,12} Such reduction, recently carried out by Roberts and Tredgold¹⁵ for an electron-donor situation, led to a zero-current elliptic function solution differing from those of Jaffé and Jepson because of the different boundary conditions used. The conditions given for the validity of the reduction were incomplete, however, being obtained only for the neutral region and not guaranteeing non degeneracy. The accurate condition is^{9,12} $Rn_{\min}/N_D \gg 1$ or¹³ $\exp[(E_F - E_D)_{\min}/kT] \gg \frac{1}{2}$, depending on temperature and applied potential. This condition and that for non-

degeneracy lead to $\exp[(E_C - E_D)/kT] \gg \frac{1}{2}$, necessary but not sufficient for validity of the reduction. These conditions are necessary for the applicability of Jepson's and Butler's equations if charges of one sign are immobile and $R > 0$ (as it always is). For the usual blocking electrodes situation, n_{\min} occurs at the negative electrode, where $\psi = -\psi_a \equiv \psi_1 - \psi_0 < 0$, and it follows from earlier work^{9,12,13} that the reduction condition becomes

$$\exp(e\psi_a/kT) \ll [-\frac{1}{2} + (\frac{1}{4} + R)^{1/2}] \\ \doteq (2N_D/N_C)^{1/2} \exp[(E_C - E_D)/2kT],$$

where the last part, which should be compared to the corresponding nondegeneracy condition, holds only for $R \gg \frac{1}{4}$. Since $\psi_0 > \psi_a > \psi_0/2$ and usually $N_C \gg N_D$, the present condition is somewhat more restrictive.

¹ W. B. Jepson, J. Chem. Phys. **39**, 2377 (1963).

² J. N. Butler, J. Chem. Phys. **35**, 636 (1961).

³ G. Gouy, J. Phys. Radium **9**, 457 (1910).

⁴ D. L. Chapman, Phil. Mag. **25**, 475 (1913).

⁵ R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1929), 1st ed., pp. 282-283.

⁶ H. Müller, Cold Spr. Harb. Symp. Quant. Biol. **1**, 1 (1933).

⁷ G. Busch, Helv. Phys. Acta **29**, 197 (1956); L. Gold, J. Electron. Control **5**, 427 (1958); R. B. McQuistan, J. Appl. Phys. **34**, 3626 (1963).

⁸ J. R. Macdonald and M. K. Brachman, J. Chem. Phys. **22**, 1314 (1954).

⁹ J. R. Macdonald, J. Chem. Phys. **29**, 1346 (1958). See also H. Y. Fan, Phys. Rev. **62**, 388 (1942).

¹⁰ G. Jaffé, Ann. Physik **16**, 217 (1933). See also G. M. Anderson, J. Chem. Phys. **40**, 628 (1964).

¹¹ J. R. Macdonald, J. Chem. Phys. **22**, 1317 (1954). Some numerical calculations pertaining to the non-zero-current case have recently been published by J. Lindmayer and A. Slobodskoy, Solid-State Electronics **6**, 495 (1963).

¹² J. R. Macdonald, J. Chem. Phys. **30**, 806 (1959).

¹³ J. R. Macdonald, Solid State Electron. **5**, 11 (1962). References to much other space-charge work are given in this paper. See Appendix I for some nonzero recombination relations.

- ¹⁴ D. C. Grahame, *J. Chem. Phys.* **21**, 1054 (1953).
¹⁵ G. G. Roberts and R. H. Tredgold, *Phys. Letters* **2**, 6 (1962);
J. Phys. Chem. Solids **24**, 1263 (1963).
¹⁶ R. Stratton, *Phys. Rev.* **126**, 2002 (1962).
¹⁷ E. A. Guggenheim, *Trans. Faraday Soc.* **55**, 1714 (1959); **56**,
 1152 (1960); **58**, 86 (1962).
¹⁸ A. T. Fromhold, *J. Chem. Phys.* **38**, 282, 2041 (1963); *J.*
Phys. Chem. Solids **24**, 1081 (1963).

Symmetry Properties of Double-Resonance Spectra. II. Additional Comments and Errata

RICHARD ERNST

*Analytical Instrument Division, Varian Associates
 Palo Alto, California*

AND

JAY MARTIN ANDERSON

*Department of Chemistry, Bryn Mawr College
 Bryn Mawr, Pennsylvania*

(Received 9 January 1964)

IN two recent papers,^{1,2} Anderson and Baldeschwieler used certain antiunitary operators to demonstrate symmetry properties of frequency-sweep and field-sweep nuclear magnetic double-resonance spectra. In this letter, the properties of these operators are developed in further detail, and some errors in the previous papers^{1,2} are corrected. In addition, a simpler and more general proof of the symmetry theorem given in Ref. 1 is offered.

The properties of antiunitary operators are now discussed. The operator $\tilde{\lambda}_n$, defined both by Fulton and Baldeschwieler³ and also in Ref. 1, is antiunitary [consult Ref. 1 for definitions and notation, especially Eq. (14) of Ref. 1]. Because of the antiunitary property, the product operator $\tilde{\Lambda}$ cannot be defined^{1,3} simply by $\tilde{\Lambda} = \prod_i \tilde{\lambda}_i$, but must be defined by three equations similar to Eq. (14) of Ref. 1:

$$\begin{aligned} \tilde{\Lambda} | I(1), I(2), \dots, m(1), m(2), \dots \rangle &= \exp[i\pi \sum_i m_i] \\ &\times | I(1), I(2), \dots, -m(1), -m(2), \dots \rangle, \quad (1) \\ \tilde{\Lambda} i &= -i \tilde{\Lambda}, \quad (2) \end{aligned}$$

and

$$[\tilde{\Lambda}, \sum_i I_x(i)]_+ = [\tilde{\Lambda}, \sum_i I_y(i)]_+ = [\tilde{\Lambda}, \sum_i I_z(i)]_+ = 0. \quad (3)$$

The definition of the operator $\tilde{\Lambda}$ as a product of (for example, an even number) of $\tilde{\lambda}_i$'s would destroy the antiunitary nature of $\tilde{\Lambda}$ which is necessary in the theorems of Ref. 1. For, suppose $\tilde{\Lambda} = \tilde{\lambda}_1 \tilde{\lambda}_2$: then the result of operating $\tilde{\Lambda}$ on the function $| m_1, m_2 \rangle$ is

$$\begin{aligned} \tilde{\Lambda} | m_1, m_2 \rangle &= \tilde{\lambda}_1 \tilde{\lambda}_2 | m_1, m_2 \rangle = \tilde{\lambda}_1 | m_1, -m_2 \rangle e^{i\pi m_2} \\ &= | -m_1, -m_2 \rangle e^{i\pi(m_1 - m_2)}. \end{aligned}$$

This is not the result which the previous authors^{1,3}

require, namely, $\tilde{\Lambda} | m_1, m_2 \rangle = e^{i\pi(m_1 + m_2)} | -m_1, -m_2 \rangle$. This result is clearly seen if the effect of operating $\tilde{\lambda}_1 \tilde{\lambda}_2$ on a complex number is compared with operating $\tilde{\Lambda}$ on a complex number: $\tilde{\lambda}_1 \tilde{\lambda}_2 (a + bi) = a + bi \neq \tilde{\Lambda} (a + bi)$. For the same reason, the operator Q cannot be defined as in Ref. 1, but must be defined by equations parallel to Eqs. (26)–(28) of Ref. 1 and Eqs. (1)–(3) above.

Now the generalized proof of symmetry properties of double-resonance spectra is discussed. The symmetry theorem of Refs. 1 and 2 states that the frequency-sweep double-resonance spectrum of the A nuclei of a weakly coupled system consists of symmetrical groupings. The number of such symmetrical groupings is $r = (2nI_M + 1)(2n'I_{M'} + 1) \dots$, where there are n nuclei of type M , n' of type M' , and the A spectrum is observed while the X nucleus is strongly irradiated. The proof of this theorem has been given in Ref. 1, but that proof required an arduous examination of the Hamiltonian (consult the appendices to Ref. 1), whereas the present proof is based entirely on commutation properties and is more general. A preliminary theorem is given first.

Theorem 1. If a Hermitian operator A anticommutes with an arbitrary nonsingular linear or antilinear operator P ,⁴ then the eigenvalues of A are symmetrically placed about zero. For, let A have a set of eigenfunctions $\{\psi_i\}$, with eigenvalues $\{E_i\}$. Then $A\psi_i = E_i\psi_i$, and since A anticommutes with P , $AP\psi_i = -PA\psi_i = -PE_i\psi_i$. Since E_i is real, $A(P\psi_i) = -E_i(P\psi_i)$. For every eigenfunction ψ_i with eigenvalue E_i , there is an eigenfunction $P\psi_i$ with eigenvalue $-E_i$, and the eigenvalue spectrum is symmetric.

This theorem may be generalized to include normal operators A , but then the eigenvalues E_i may be complex, and P must be linear. A second theorem yields the symmetry rule.

Theorem 2. The spectrum of transition frequencies of a Hermitian operator $\mathcal{H} = A + B$ consists of r symmetrical groupings about the r transition frequencies of the operator B , if A commutes with B and anticommutes with an arbitrary nonsingular linear or antilinear operator P which commutes with B . Let $\{\psi_i\}$ be the simultaneous eigenfunctions of A and B with eigenvalues $\{E_i^A\}$ and $\{E_i^B\}$, respectively. Then, $(B + A)\psi_i = (E_i^A + E_i^B)\psi_i$. But $P(B + A)\psi_i = (B - A)P\psi_i = (E_i^B - E_i^A)P\psi_i$. For every eigenfunction ψ_i of \mathcal{H} with eigenvalue $E_i^B + E_i^A$, there exists an eigenfunction $P\psi_i$ with eigenvalue $E_i^B - E_i^A$. Therewith the transition frequencies are given by $\hbar\omega = E_i^B - E_j^B + (E_i^A - E_j^A)$ for the transition $\psi_j \rightarrow \psi_i$, and by $\hbar\omega = E_i^B - E_j^B - (E_i^A - E_j^A)$ for the transition $P\psi_j \rightarrow P\psi_i$. The symmetrical groupings consist of more than two lines if the differences $E_i^B - E_j^B$ are degenerate. This theorem may also be generalized to include normal operators A and B if P is restricted to being linear.

The hypotheses of the symmetry theorem of Ref. 1 are therefore fulfilled if only a suitable operator P can be found. The operator A is identified with \mathcal{H}_x [Eq.