

## VALENCE BOND METHODS

### Theory and applications

Valence bond theory is one of two commonly used methods in molecular quantum mechanics, the other is molecular orbital theory. This book focuses on the first of these methods, *ab initio* valence bond theory.

The book is split into two parts. Part I gives simple examples of two-electron calculations and the necessary theory to extend these to larger systems. Part II gives a series of case studies of related molecule sets designed to show the nature of the valence bond description of molecular structure. It also highlights the stability of this description to varying basis sets. There are references to the CRUNCH computer program for molecular structure calculations, which is currently available in the public domain. Throughout the book there are suggestions for further study using CRUNCH to supplement discussions and questions raised in the text.

The book will be of primary interest to researchers and students working on molecular electronic theory and computation in chemistry and chemical physics.

GORDON A. GALLUP was born (9 March 1927) and raised in St Louis, Missouri and attended the public schools there. After High School and a short stint in the US Navy, he attended Washington University (St Louis) and graduated with an AB in 1950. He received the PhD degree from the University of Kansas in 1953 and spent two years at Purdue University carrying out post-doctoral research. In 1955 he was appointed to the faculty of chemistry at the University of Nebraska and rose through the ranks, becoming full professor in 1964. He spent a year at the Quantum Theory Project at the University of Florida, and a year in England at the University of Bristol on an SERC fellowship. In 1993 he retired from teaching and since then has spent time as a research professor with the Department of Physics and Astronomy at the University of Nebraska. His research interests over the years include infrared spectroscopy and molecule vibrations, theory of molecular electronic structure, valence bond theory, electron scattering from atoms and molecules, and dissociative electron attachment. During his career he has held grants from the National Science Foundation, the Department of Energy, and others. He has had over 100 articles published in 10–15 different chemistry and physics journals, as well as articles in edited compendia and review books.

Cambridge University Press  
0521803926 - Valence Bond Methods: Theory and Applications  
Gordon A. Gallup  
Frontmatter  
[More information](#)

---

# VALENCE BOND METHODS

Theory and applications

GORDON A. GALLUP

*University of Nebraska*



Cambridge University Press  
0521803926 - Valence Bond Methods: Theory and Applications  
Gordon A. Gallup  
Frontmatter  
[More information](#)

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE  
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS  
The Edinburgh Building, Cambridge CB2 2RU, UK  
40 West 20th Street, New York, NY 10011-4211, USA  
477 Williamstown Road, Port Melbourne, VIC 3207, Australia  
Ruiz de Alarcón 13, 28014 Madrid, Spain  
Dock House, The Waterfront, Cape Town 8001, South Africa  
<http://www.cambridge.org>

© Gordon A. Gallup 2002

This book is in copyright. Subject to statutory exception  
and to the provisions of relevant collective licensing agreements,  
no reproduction of any part may take place without  
the written permission of Cambridge University Press.

First published 2002

Printed in the United Kingdom at the University Press, Cambridge

*Typeface* Times 11/14 pt    *System* L<sup>A</sup>T<sub>E</sub>X 2<sub>ε</sub> [TB]

*A catalogue record for this book is available from the British Library*

*Library of Congress Cataloguing in Publication data*

Gallup, G. A. (Gordon Alban), 1927–  
The valence bond method : theory and practice / G. A. Gallup.  
p. cm.

Includes bibliographical references and index.

ISBN 0 521 80392 6

1. Valence (Theoretical chemistry) I. Title.

QD469 .G35 2002

541.2'24–dc21

2002023398

ISBN 0 521 80392 6 hardback

Cambridge University Press  
0521803926 - Valence Bond Methods: Theory and Applications  
Gordon A. Gallup  
Frontmatter  
[More information](#)

---

To my wife Grace, for all her encouragement, and to the memory of our  
son, Michael, 1956–1995.

## Contents

<i>Preface</i>	page xiii
<i>List of abbreviations</i>	xv
<b>I Theory and two-electron systems</b>	
1 Introduction	3
1.1 History	3
1.2 Mathematical background	4
1.2.1 Schrödinger's equation	5
1.3 The variation theorem	9
1.3.1 General variation functions	9
1.3.2 Linear variation functions	9
1.3.3 A $2 \times 2$ generalized eigenvalue problem	14
1.4 Weights of nonorthogonal functions	16
1.4.1 Weights without orthogonalization	18
1.4.2 Weights requiring orthogonalization	19
2 H <sub>2</sub> and localized orbitals	23
2.1 The separation of spin and space variables	23
2.1.1 The spin functions	23
2.1.2 The spatial functions	24
2.2 The AO approximation	24
2.3 Accuracy of the Heitler–London function	27
2.4 Extensions to the simple Heitler–London treatment	27
2.5 Why is the H <sub>2</sub> molecule stable?	31
2.5.1 Electrostatic interactions	32
2.5.2 Kinetic energy effects	36
2.6 Electron correlation	38
2.7 Gaussian AO bases	38
2.8 A full MCVB calculation	38

viii	<i>Contents</i>	
	2.8.1 Two different AO bases	40
	2.8.2 Effect of eliminating various structures	42
	2.8.3 Accuracy of full MCVB calculation with 10 AOs	44
	2.8.4 Accuracy of full MCVB calculation with 28 AOs	44
	2.8.5 EGSO weights for 10 and 28 AO orthogonalized bases	45
3	H <sub>2</sub> and delocalized orbitals	47
	3.1 Orthogonalized AOs	47
	3.2 Optimal delocalized orbitals	49
	3.2.1 The method of Coulson and Fisher[15]	49
	3.2.2 Complementary orbitals	49
	3.2.3 Unsymmetric orbitals	51
4	Three electrons in doublet states	53
	4.1 Spin eigenfunctions	53
	4.2 Requirements of spatial functions	55
	4.3 Orbital approximation	58
5	Advanced methods for larger molecules	63
	5.1 Permutations	64
	5.2 Group algebras	66
	5.3 Some general results for finite groups	68
	5.3.1 Irreducible matrix representations	68
	5.3.2 Bases for group algebras	69
	5.4 Algebras of symmetric groups	70
	5.4.1 The unitarity of permutations	70
	5.4.2 Partitions	70
	5.4.3 Young tableaux and $\mathcal{N}$ and $\mathcal{P}$ operators	71
	5.4.4 Standard tableaux	72
	5.4.5 The linear independence of $\mathcal{N}_i\mathcal{P}_i$ and $\mathcal{P}_i\mathcal{N}_i$	75
	5.4.6 Von Neumann's theorem	76
	5.4.7 Two Hermitian idempotents of the group algebra	76
	5.4.8 A matrix basis for group algebras of symmetric groups	77
	5.4.9 Sandwich representations	79
	5.4.10 Group algebraic representation of the antisymmetrizer	80
	5.5 Antisymmetric eigenfunctions of the spin	81
	5.5.1 Two simple eigenfunctions of the spin	81
	5.5.2 The $\Xi$ function	84
	5.5.3 The independent functions from an orbital product	85
	5.5.4 Two simple sorts of VB functions	87
	5.5.5 Transformations between standard tableaux and HLSP functions	88
	5.5.6 Representing $\theta \mathcal{N}\mathcal{P}\mathcal{N}\Xi$ as a functional determinant	91

*Contents*

ix

6	Spatial symmetry	97
6.1	The AO basis	98
6.2	Bases for spatial group algebras	98
6.3	Constellations and configurations	99
6.3.1	Example 1. H <sub>2</sub> O	100
6.3.2	Example 2. NH <sub>3</sub>	102
6.3.3	Example 3. The $\pi$ system of benzene	105
7	Varieties of VB treatments	107
7.1	Local orbitals	107
7.2	Nonlocal orbitals	108
8	The physics of ionic structures	111
8.1	A silly two-electron example	111
8.2	Ionic structures and the electric moment of LiH	113
8.3	Covalent and ionic curve crossings in LiF	115
<b>II Examples and interpretations</b>		
9	Selection of structures and arrangement of bases	121
9.1	The AO bases	121
9.2	Structure selection	123
9.2.1	N <sub>2</sub> and an STO3G basis	123
9.2.2	N <sub>2</sub> and a 6-31G basis	123
9.2.3	N <sub>2</sub> and a 6-31G* basis	124
9.3	Planar aromatic and $\pi$ systems	124
10	Four simple three-electron systems	125
10.1	The allyl radical	125
10.1.1	MCVB treatment	126
10.1.2	Example of transformation to HLSP functions	129
10.1.3	SCVB treatment with corresponding orbitals	132
10.2	The He <sub>2</sub> <sup>+</sup> ion	134
10.2.1	MCVB calculation	134
10.2.2	SCVB with corresponding orbitals	135
10.3	The valence orbitals of the BeH molecule	136
10.3.1	Full MCVB treatment	137
10.3.2	An SCVB treatment	139
10.4	The Li atom	141
10.4.1	SCVB treatment	142
10.4.2	MCVB treatment	144
11	Second row homonuclear diatomics	145
11.1	Atomic properties	145
11.2	Arrangement of bases and quantitative results	146

x	<i>Contents</i>	
11.3	Qualitative discussion	148
11.3.1	B <sub>2</sub>	149
11.3.2	C <sub>2</sub>	152
11.3.3	N <sub>2</sub>	154
11.3.4	O <sub>2</sub>	157
11.3.5	F <sub>2</sub>	160
11.4	General conclusions	161
12	Second row heteronuclear diatomics	162
12.1	An STO3G AO basis	162
12.1.1	N <sub>2</sub>	164
12.1.2	CO	166
12.1.3	BF	168
12.1.4	BeNe	171
12.2	Quantitative results from a 6-31G* basis	173
12.3	Dipole moments of CO, BF, and BeNe	174
12.3.1	Results for 6-31G* basis	174
12.3.2	Difficulties with the STO3G basis	175
13	Methane, ethane and hybridization	177
13.1	CH, CH <sub>2</sub> , CH <sub>3</sub> , and CH <sub>4</sub>	177
13.1.1	STO3G basis	177
13.1.2	6-31G* basis	186
13.2	Ethane	187
13.3	Conclusions	189
14	Rings of hydrogen atoms	191
14.1	Basis set	192
14.2	Energy surfaces	192
15	Aromatic compounds	197
15.1	STO3G calculation	198
15.1.1	SCVB treatment of $\pi$ system	200
15.1.2	Comparison with linear 1,3,5-hexatriene	203
15.2	The 6-31G* basis	205
15.2.1	Comparison with cyclobutadiene	208
15.3	The resonance energy of benzene	208
15.4	Naphthalene with an STO3G basis	211
15.4.1	MCVB treatment	211
15.4.2	The MOCI treatment	212
15.4.3	Conclusions	213
16	Interaction of molecular fragments	214
16.1	Methylene, ethylene, and cyclopropane	214
16.1.1	The methylene biradical	215



	<i>Contents</i>	xi
16.1.2	Ethylene	215
16.1.3	Cyclopropane with a 6-31G* basis	218
16.1.4	Cyclopropane with an STO-3G basis	224
16.2	Formaldehyde, H <sub>2</sub> CO	225
16.2.1	The least motion path	226
16.2.2	The true saddle point	227
16.2.3	Wave functions during separation	228
	<i>References</i>	231
	<i>Index</i>	235

## Preface

One senses that it is out of style these days to write a book in the sciences all on one's own. Most works coming out today are edited compilations of others' articles collected into chapter-like organization. Perhaps one reason for this is the sheer size of the scientific literature, and the resulting feelings of incompetence engendered, although less honorable reasons are conceivable. Nevertheless, I have attempted this task and submit this book on various aspects of what is called *ab initio* valence bond theory. In it I hope to have made a presentation that is useful for bringing the beginner along as well as presenting material of interest to one who is already a specialist. I have taught quantum mechanics to many students in my career and have come to the conclusion that the beginner frequently confuses the intricacies of mathematical arguments with subtlety. In this book I have not attempted to shy away from intricate presentations, but have worked at removing, insofar as possible, the more subtle ones. One of the ways of doing this is to give good descriptions of simple problems that can show the motivations we have for proceeding as we do with more demanding problems.

This is a book on one sort of model or trial wave function that can be used for molecular calculations of chemical or physical interest. It is in no way a book on the foundations of quantum mechanics – there are many that can be recommended. For the beginner one can still do little better than the books by Pauling and Wilson[1] and Eyring, Walter, and Kimbal[2]. A more recent work is by Levine[3], and for a more “physicsish” presentation the book by Messiah[4] is recommended. These are a little weak on the practice of group theory for which Cotton[5] may serve. A more fundamental work on group theory is by Hammermesh[6]. Some further group theory developments, not to my knowledge in any other book, are in Chapter 5. Some of what we do with the theory of symmetric groups is based fairly heavily on a little book by Rutherford[7].

This is a book on *ab initio* valence bond (VB) theory. There is a vast literature on “valence bond theory” – much of it devoted to semiempirical and qualitative

discussions of structure and reactivity of many chemical substances. It is not my purpose to touch upon any of this except occasionally. Rather, I will restrict myself principally to the results and interpretation of the *ab initio* version of the theory. It must be admitted that *ab initio* VB applications are limited to smaller systems, but we shall stick to this more limited goal. Within what practitioners call *ab initio* VB theory there are, in broad terms, two different approaches.

- Calculations in which the orbitals used are restricted to being centered on only one atom of the molecule. They are legitimately called “atomic orbitals”. Treatments of this sort may have many configurations involving different orbitals. This approach may be considered a direct descendent of the original Heitler–London work, which is discussed in Chapter 2.
- Calculations in which the orbitals range over two or more atomic centers in the molecule. Although the resulting orbitals are not usually called “molecular orbitals” in this context, there might be some justification in doing so. Within this group of methods there are subcategories that will be addressed in the book. Treatments of this sort usually have relatively few configurations and may be considered descendents of the work of Coulson and Fisher, which is discussed in Chapter 3.

Each of these two approaches has its enthusiasts and its critics. I have attempted an even-handed description of them.

At various places in the text there are suggestions for further study to supplement a discussion or to address a question without a currently known answer. The CRUNCH program package developed by the author and his students is available on the Web for carrying out these studies.<sup>1</sup> This program package was used for all of the examples in the book with the exception of those in Sections 2.2–2.6.

I wish to thank Jeffrey Mills who read large parts of the manuscript and made many useful comments with regard to both style and clarity of presentation. Lastly, I wish to thank all of the students I have had. They did much to contribute to this subject. As time passes, there is nothing like a group of interested students to keep one on one’s toes.

Lincoln, Nebraska  
November 2001

Gordon A. Gallup

<sup>1</sup> See <http://phy-ggallup.unl.edu/crunch>

## List of abbreviations

AO	atomic orbital
CI	configuration interaction
CRUNCH	computational resource for understanding chemistry
DZP	double-zeta plus polarization
EGSO	eigenvector guided sequential orthogonalization
ESE	electronic Schrödinger equation
GAMESS	general atomic and molecular electronic structure system
GGVB	Goddard's generalized valence bond
GUGA	graphical unitary group approach
HLSP	Heitler–London–Slater–Pauling
LCAO	linear combination of atomic orbitals
LMP	least motion path
MCVB	multiconfiguration valence bond
MO	molecular orbital
MOCI	molecular orbital configuration interaction
RHF	spin-restricted Hartree–Fock
ROHF	spin-restricted open-shell Hartree–Fock
SEP	static-exchange potential
SCF	self-consistent-field
SCVB	spin coupled valence bond
UHF	unrestricted Hartree–Fock
VB	valence bond