SYMMETRY-ADAPTED BASIS SETS

Automatic Generation for Problems in Chemistry and Physics

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SYMMETRY-ADAPTED BASIS SETS

Automatic Generation for Problems in Chemistry and Physics

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Contents

<i>Preface</i>	ix
1. GENERAL CONSIDERATIONS	1
1.1 The need for symmetry-adapted basis functions	1
1.2 Fundamental concepts	2
1.3 Definition of invariant blocks	3
1.4 Diagonalization of the invariant blocks	5
1.5 Transformation of the large matrix to block-diagonal form	6
1.6 Summary of the method	7
2. EXAMPLES FROM ATOMIC PHYSICS	9
2.1 The Hartree-Fock-Roothaan method for calculating atomic orbitals	9
2.2 Automatic generation of symmetry-adapted configurations .	12
2.3 Russell-Saunders states	14
2.4 Some illustrative examples	15
2.5 The Slater-Condon rules	18
2.6 Diagonalization of invariant blocks using the Slater-Condon rules	20
3. EXAMPLES FROM QUANTUM CHEMISTRY	27
3.1 The Hartree-Fock-Roothaan method applied to molecules	27
3.2 Construction of invariant subsets	28
3.3 The trigonal group C_{3v} ; the NH_3 molecule	30

4. GENERALIZED STURMIANS APPLIED TO ATOMS	33
4.1 Goscinskian configurations	33
4.2 Relativistic corrections	38
4.3 The large- Z approximation: Restriction of the basis set to an $\mathcal{R}$ -block	42
4.4 Electronic potential at the nucleus in the large- Z approximation	43
4.5 Core ionization energies	46
4.6 Advantages and disadvantages of Goscinskian configurations	49
4.7 $\mathcal{R}$ -blocks, invariant subsets and invariant blocks	50
4.8 Invariant subsets based on subshells; Classification according to M_L and M_s	56
4.9 An atom surrounded by point charges	62
5. MOLECULAR ORBITALS BASED ON STURMIANS	71
5.1 The one-electron secular equation	71
5.2 Shibuya-Wulfman integrals and Sturmian overlap integrals evaluated in terms of hyperpherical harmonics	78
5.3 Molecular calculations using the isoenergetic configurations	85
5.4 Building $T_{\nu'\nu}^{(N)}$ and $\mathfrak{S}_{\nu'\nu}^{(N)}$ from 1-electron components	87
5.5 Interelectron repulsion integrals for molecular Sturmi- ans from hyperspherical harmonics	88
5.6 Many-center integrals treated by Gaussian expansions (Appendix E)	93
5.7 A pilot calculation	97
5.8 Automatic generation of symmetry-adapted basis functions	98
6. AN EXAMPLE FROM ACOUSTICS	101
6.1 The Helmholtz equation for a non-uniform medium	101
6.2 Homogeneous boundary conditions at the surface of a cube	101
6.3 Spherical symmetry of $v(\mathbf{x})$; nonseparability of the Helmholtz equation	103
6.4 Diagonalization of invariant blocks	105
7. AN EXAMPLE FROM HEAT CONDUCTION	111
7.1 Inhomogeneous media	111
7.2 A 1-dimensional example	112
7.3 Heat conduction in a 3-dimensional inhomogeneous medium	114

8. SYMMETRY-ADAPTED SOLUTIONS BY ITERATION	121
8.1 Conservation of symmetry under Fourier transformation . .	121
8.2 The operator $-\Delta + p_\kappa^2$ and its Green's function	122
8.3 Conservation of symmetry under iteration of the Schrödinger equation	123
8.4 Evaluation of the integrals	125
8.5 Generation of symmetry-adapted basis functions by iteration	127
8.6 A simple example	128
8.7 An alternative expansion of the Green's function that applies to the Hamiltonian formulation of physics	129
Appendix A REPRESENTATION THEORY OF FINITE GROUPS	131
A.1 Basic definitions	131
A.2 Representations of geometrical symmetry groups	132
A.3 Similarity transformations	133
A.4 Characters and reducibility	134
A.5 The great orthogonality theorem	136
A.6 Classes	141
A.7 Projection operators	142
A.8 The regular representation	144
A.9 Classification of basis functions	146
Appendix B STURMIAN BASIS SETS	149
B.1 One-electron Coulomb Sturmians	149
B.2 Löwdin-orthogonalized Coulomb Sturmians	151
B.3 The Fock projection	153
B.4 Generalized Sturmians and many-particle problems	154
B.5 Use of generalized Sturmian basis sets to solve the many- particle Schrödinger equation	155
B.6 Momentum-space orthonormality relations for Sturmian basis sets	156
B.7 Sturmian expansions of d -dimensional plane waves	158
B.8 An alternative expansion of a d -dimensional plane wave . .	159
Appendix C ANGULAR AND HYPERANGULAR INTEGRATION	161
C.1 Monomials, homogeneous polynomials, and harmonic polynomials	161
C.2 The canonical decomposition of a homogeneous polynomial	162

C.3	Harmonic projection	163
C.4	Generalized angular momentum	164
C.5	Angular and hyperangular integration	165
C.6	An alternative method for angular and hyperangular integrations	168
C.7	Angular integrations by a vector-pairing method	170
Appendix D	INTERELECTRON REPULSION INTEGRALS	173
D.1	The generalized Slater-Condon rules	173
D.2	Separation of atomic integrals into radial and angular parts	174
D.3	Evaluation of the radial integrals in terms of hypergeometric functions	175
D.4	Evaluation of the angular integrals in terms of Condon- Shortley coefficients	177
Appendix E	GAUSSIAN EXPANSION OF MOLECULAR STURMIANS	179
E.1	Expansions of Coulomb Sturmian densities in terms of Gaussians	179
Appendix F	EXPANSION OF DISPLACED FUNCTIONS IN TERMS OF LEGENDRE POLYNOMIALS	185
F.1	Displaced spherically symmetric functions	185
F.2	An alternative method	186
F.3	A screened Coulomb potential	187
F.4	Expansion of a displaced Slater-type orbital	188
F.5	A Fourier transform solution	190
F.6	Displacement of functions that do not have spherical symmetry	193
Appendix G	MULTIPOLE EXPANSIONS	195
Appendix H	HARMONIC FUNCTIONS	199
H.1	Harmonic functions for $d = 3$	199
H.2	Spaces of higher dimension	200
	<i>Bibliography</i>	207
	<i>Index</i>	221

Preface

In a number of previous papers and a book [Avery and Avery, 2006], two of us introduced the Generalized Sturmian Method applied to atoms. One of the interesting features of this method is that it leads to a secular equation of the form

$$\sum_{\nu} [\delta_{\nu',\nu} Z \mathcal{R}_{\nu} + T'_{\nu',\nu} - p_{\kappa} \delta_{\nu',\nu}] C_{\nu,\kappa} = 0 \quad (0.1)$$

where Z is the nuclear charge and where p_{κ} is not the energy but is a scaling factor related to the energy of an atomic state by

$$E_{\kappa} = -\frac{p_{\kappa}^2}{2} \quad (0.2)$$

In equation (0.1),

$$\mathcal{R}_{\nu} \equiv \sqrt{\frac{1}{n^2} + \frac{1}{n'^2} + \frac{1}{n''^2} + \dots} \quad (0.3)$$

ν being a collection of indices that label a configuration (a Slater determinant) and $n, n', n'', \dots$ being the principal quantum numbers of the atomic spin-orbitals that appear in the configuration. The matrix $T'_{\nu',\nu}$ represents the effects of interelectron repulsion. If interelectron repulsion is entirely neglected, the energy reduces to

$$E_0 = -\frac{1}{2}(Z\mathcal{R}_{\nu})^2 = -\frac{1}{2}Z^2 \left(\frac{1}{n^2} + \frac{1}{n'^2} + \frac{1}{n''^2} + \dots \right) \quad (0.4)$$

that is to say, it reduces to the energy of a set of completely independent electrons moving in the attractive Coulomb potential of the nucleus. We introduced a large- Z approximation, in which the basis set is restricted to configurations all of which correspond to the same value of R_{ν} , and we found that in this approximation, the energy of an atomic state is given by

$$E_{\kappa} \approx -\frac{1}{2}(Z\mathcal{R}_{\nu} - |\lambda_{\kappa}|)^2 \quad (0.5)$$

where λ_κ is a root of the energy-independent interelectron repulsion matrix $T'_{\nu',\nu}$. We found that for an isoelectronic series corresponding to a fixed number of electrons N , the large- Z approximation approached the experimental data more and more closely with increasing Z , provided that a simple correction was made for relativistic effects. We also found that the eigenfunctions of the simplified secular equation

$$\sum_{\nu} [T'_{\nu',\nu} - \lambda_\kappa \delta_{\nu',\nu}] C_{\nu,\kappa} = 0 \quad (0.6)$$

were Russell-Saunders states, i.e. simultaneous eigenfunctions of the total angular momentum operator L^2 , its z -component L_z , the total spin operator S^2 , and its z -component S_z . These Russell-Saunders states could be used as symmetry-adapted basis functions for more refined calculations, where the large- Z approximation was abandoned. This automatic generation of symmetry-adapted basis functions proved to be a great convenience.

In the present book, we are joined by Lektor Sten Rettrup, who has taught Group Theory and Quantum Chemistry for many years at the University of Copenhagen. The book results from a wish to go more deeply into the mathematical reasons behind the automatic generation of symmetry-adapted basis sets, which we observed when applying the Generalized Sturmian Method to atoms in the large- Z approximation. We believe that the same principles can be used in many problems encountered in physics and chemistry, where the size of the basis sets required for accurate solutions makes it desirable to use symmetry-adapted basis functions.

The first chapter discusses the general mathematical principles that underlie the automatic generation of symmetry-adapted basis functions, and subsequent chapters aim at developing and illustrating these basis principles. In Chapter 2, the principles are applied to atomic Hartree-Fock calculations followed by Configuration Interaction computations, while in Chapter 3, this is extended to molecules. As is well known, the number of configurations needed for accurate results in CI calculations is often extremely large - often in the millions. Therefore reducing this number by means of symmetry-adapted basis functions is highly desirable. We hope that Chapters 2 and 3 indicate paths one might follow to do this.

Chapter 4 reviews and extends our studies of the Generalized Sturmian method applied to atoms. Among the new topics not discussed previously, is the calculation of the effect on atoms when they are surrounded by symmetrical arrays of point charges. This effect is calculated using the Generalized Sturmian Method.

Chapter 5 sketches the extension of the Generalized Sturmian Method to molecules. Coulomb Sturmians have long been used as basis functions for solution for a single electron moving in the attractive field of two or more nuclei. Among the important pioneers in this field are C.E. Wulfman, V. Aquilanti and T. Koga. In Chapter 5, we try to show how Sturmian basis functions can be used in N -electron molecules. To do this, we need to evaluate many-center interelectron repulsion integrals involving Coulomb Sturmians, which are exponential-type orbitals. We propose a new method for evaluating these integrals making use of the Fock projection, which maps Coulomb Sturmians onto sets of 4-dimensional hyperspherical harmonics. The properties of hyperspherical harmonics are then used to evaluate the needed integrals.

In Chapters 6 and 7, we attempt to show how the basic principles for automatic generation of symmetry-adapted basis functions may be applied to other areas of physics. We hope that readers will find ways of applying these general principles to their own special areas of research. Chapter 8 discusses how symmetry-adapted basis functions can be generated by iteration.

Atomic units are used throughout this book: All lengths are in Bohrs and all energies are in Hartrees.

Programs for carrying out calculations of the type discussed in this book can be found at our website [Avery and Avery, 2006a]

<http://sturmian.kvante.org/symmetry>

These programs may be freely downloaded and modified for general use.

John Scales Avery, Sten Rettrup and James Emil Avery
Copenhagen, 2011