Lecture Notes in Chemistry

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W. Duch

GRMS or Graphical Representation of Model Spaces

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ACKNOWLEDGEMENTS

Over the years I have been blessed with a friendship of and collaboration with Jacek Karwowski. Although our opinions on virtually every subject differ diametrically we understand each other very well. Parts of the material on matrix element calculation and applications to the configuration interaction method presented in this book are related to the work we have done together when I was his graduate student. However, Jacek has declined the responsibility of being the co–author of these notes, despite the suggestion of a referee. The discussions with him were certainly of invaluable help.

Many people have influenced me through their books – I feel compelled here to name just a few titles but, being unable to do justice to all of them, I shall refrain from doing that. Many good books are quoted among the references.

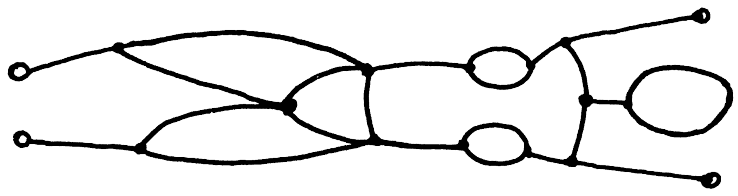
This work was started in Toruń, Poland, and finished far from home worries in Garching bei München. Hospitality of my host, Geerd H.F. Diercksen, who told me "have fun and get useful work done" (that suited very much to my taste), is gratefully acknowledged. My stay was financed by the Alexander von Humboldt Foundation that has been invaluable to so many foreign scientists working in Germany, providing us, i.e. the Humboldt fellows, not only with the money but also with advice and a cultural program. I would like to dedicate this volume to Dr. Heinrich Pfeiffer on the occasion of his 60th birthday and 30 years of work as Secretary General of the Alexander von Humboldt Foundation.

Excellent facilities of the Max–Planck Institutes in Garching have allowed me to acquire a new profession, namely that of a typesetter. It is much harder than I ever expected when I started this work. This manuscript was designed and prepared entirely by myself using a TEX system and a laser printer. Murphy's laws certainly apply to computerized typesetting: if you can loose a long text file you will and you will have to retype it. Ben Jeffreys is responsible for british spelling in some parts of this volume. In the rest errors abound.

1

Preface

The purpose of these notes is to give some simple tools and pictures to physicists and chemists working on the many–body problem. Abstract thinking and seeing have much in common – we say "I see" meaning "I understand", for example. Most of us prefer to have a picture of an abstract object. The remarkable popularity of the Feynman diagrams, and other diagrammatic approaches to many–body problem derived thereof, may be partially due to this preference. Yet, paradoxically, the concept of a linear space, as fundamental to quantum physics as it is, has never been cast in a graphical form. We know that



is a high–order contribution to a two–particle scattering process (this one invented by Cvitanović(1984)) corresponding to a complicated matrix element. The lines in such diagrams are labeled by indices of single–particle states. When things get complicated at this level it should be good to take a global view from the perspective of the whole many–particle space. But how to visualize the space of all many–particle states ? Methods of such visualization or graphical representation of the spaces of interest to physicists and chemists are the main topic of this work.

Notes on this subject have now been piling up on my desk for a couple of years and, although I have already managed to publish a few things about graphical representations, I have gradually realized that the scope of such a work is much broader

than my humble abilities allow. I received a formal training in physics and made my PhD in quantum chemistry. Working on applications of the symmetric group theory to the configuration interaction method I stumbled, motivated by Shavitt's work (1977), upon a graphical description of the configuration space. The physical meaning of Shavitt's graph was at that time unclear to most of the scientists who used it, the reason being a detoured way of approaching the problem via the unitary group theory. Years later I began to understand how useful the concept of a graphical representation of a space really is and how rich are its connections with the well–established branches of mathematics, like group theory, the theory of partitions, graph theory, integer programming, operations research or the theory of natural numbers. Thus, leaving the safe waters of my own speciality I have ventured into the unknown oceans of knowledge, discovering a number of fascinating books besides quite a few journals the existence of which I had never suspected. I have looked through shelves of books on mathematical subjects related to quantum mechanics, but even those books that refer directly to the bases of Hilbert or Banach tensor spaces (cf Singer 1970) fail to provide any geometrical pictures or to make connections with the graph theory or the group theory, while the number theory fits there as well as a third leg to trousers. Yet many examples may be found where Diophantine problems and graphical methods are related in a natural way, as with Dynkin diagrams in group–theoretical methods applied to unified models (cf Gilmore 1974; Slansky 1981). As Primas (1981) writes: *"The most important task of contemporary theoretical chemistry is to stimulate the mutual understanding of the various branches of chemistry and its neighboring sciences."*

On a piece of paper glued to the wall of an office in the Max–Planck–Institute for Astrophysics in Garching b. München I have found this quotation from T.S. Eliot's poem "The Rock"

All man are ready to invest their money
But most expect dividends
I say to you: Make perfect your will
I say: take no thought of the harvest,
But only of proper sowing.

Being a physicist of a saturation time (read: having no one to work for me) I have thus decided to limit the scope of the present work and leave some things for others, more mathematically gifted than myself, if they would find the subject interesting. In these notes I present simple tools, giving both the language and the methods of calculation, i.e. graphical representation of certain model spaces useful in many–body problem, plus the methods of matrix element calculation. This in itself took about 200 pages, so I decided to publish it separately as the first volume, leaving the mathematically more complicated Part **III**, as well as Part **IV** dealing with applications, for the second volume. My intention was to keep the whole work self–contained, in the sense that only a basic knowledge of mathematics is assumed and, although the list of references

is rather long, the reader should still be able to understand the text without digging through this literature.

Finally, if the reader, used to the impersonal style of most scientific papers, finds the personal tone of these notes rather distasteful, I should say that I have looked into my family tree searching in vain for any Polish king that would justify the use of a plural form "we".

2

Introduction

In which I am trying to explain why have I done it, what have I done, and what it is for.

Many–body experts like to start from the one–particle approximation. Even when geminals or group functions are used they are ultimately expanded in the one–particle basis (Wilson 1984). Computational difficulties with the explicitly correlated wavefunctions prevented the use of these methods for all but a few–electron systems (Handy 1978), although there are still some, who have not buried all their hopes, and whose results are promising (cf Jankowski and Malinowski 1980; Jeziorski *et al* 1984). Notwithstanding their hopes the majority votes for one–particle approximation, because it is fundamental to our intuitions and capable of high accuracy (cf Handy 1978).

Many–body equations, whatever is our choice, take place in the many–particle Hilbert space $\mathcal{H}$. The experts are usually so eager to solve their equations that they tend to forget that. This space is created from n–dimensional one–particle space $\mathcal{V}_n = \{|\phi_i\rangle\}_{i=1}^n$ called the orbital space and two–dimensional one–particle spin space $\mathcal{V}_2 = \{|\alpha\rangle, |\beta\rangle\}$. To be a little more general let's assume that we have a set of primitive objects (like orbital or geminal states) that are used in construction of many–particle states. It is convenient to formulate equations in a formalism that does not depend on the number of particles in the system nor on the size of the orbital space, i.e. to work in the Fock space (Kutzelnigg 1984). Finally however both the number of particles N and the number of orbitals n have to be specified, no matter what method we use. The full Hilbert space $\mathcal{H}_n^N$ has a very large dimension $\dim \mathcal{H}_n^N = \binom{2n}{N}$. In practice we are forced to truncate this space severely; managable dimensions for the present–day computers are of the order of 10^6 basis states. This truncated space $\tilde{\mathcal{H}}_n^N \subseteq \mathcal{H}_n^N$ is a part of the

physical model of our system, therefore it is called a model space.* The model space, as any other mathematical structure build from simpler objects, has a particular architecture. Primitive objects like orbital and spin states correspond here to building blocks or bricks that come only in a few sizes, while the space itself corresponds to a building. The architecture of a model Hilbert space may be visualized using simple graphs. We certainly do not want to inspect individual basis states if there are thousands of them, but we would like to see the relations between these states, recognize certain useful classes of states and develop some intuitions to tell the solid constructions (spaces giving good approximations) from the rickety ones (spaces giving poor approximations). The concept of a space structure is here implicit and I will use the word 'structure' in the same sense as it is used in any architectural context. In case of architectural objects we can also talk about shape. The concept of shape may not be precisely defined for a space, because there usually exist many different graphical representations that are topologically equivalent and thus preserve the structure of the space. However, if we fix the rules of a graphical representation and decide how to picture the primitive states we may talk about different shapes of spaces, and the shape will obviously depend on what kind of model spaces we are using and what kind of symmetries the basis states posses.

It is undoubtedly nice to see the structure of a space, but is it useful ? Summarizing the prospects of molecular quantum mechanics McWeeny and Pickup (1980) write: *"ab initio molecular calculations of 'chemical' accuracy, are going to be dominated more and more by the development of computers and highly efficient algorithms"*. The same is true in other branches of many–body theory (cf Wilson 1982), therefore computational aspects should not be ignored. Graphical representation should allow us to see the structure of a space and to teach the computer how to make use of this structure. Moreover the graphs should be constructed in such a way that would allow all required matrix elements to be obtained directly from the graphs, without recourse to the algebraic manipulations with the many–particle functions. Thus we come to the next concept – of a proper label for a state. Designation like $|^2P, M_S = \frac{1}{2}, M_L = 1\rangle$ is not a proper label because it doesn't say anything about the construction of this state from primitives or one–particle states. Weyl tableaux or Gelfand patterns may serve as an example of the proper labels. A properly constructed graph $\mathcal{G}$ should contain enough information about the basis states of many–particle space to facilitate the mapping:

$$\mathcal{G} : \hat{A}(\mathcal{H}) \rightarrow \mathbf{A}(\tilde{\mathcal{H}}_n^N)$$

of a differential or integral operator $\hat{A}$ acting in the infinite–dimensional space $\mathcal{H}$ to its matrix representative $\mathbf{A}$ in the model space $\tilde{\mathcal{H}}_n^N$. Biedenharn and Van Dam (1965) write " *One of the basic problems, if not the basic problem in spectroscopy, both atomic*

*In many–body perturbation theory the space of zeroth–order functions is sometimes called the model space; this is obviously not what is meant here.

and nuclear, is the construction of antisymmetric N–particle wave functions from the (degenerate) states of a given energy shell." The construction of such a wave functions is precisely what I hope to avoid, replacing it by graphical labels and graphical rules of matrix element evaluation. The theory should be simple, basically no more than an exercise in labeling of the many–particle states by a graphical means.

What kind of spaces can one visualize graphically ? Any kind of tensor spaces, i.e. all those with the bases being combinations of products of primitive states. Such states are well represented by Young tableaux or Gelfand patterns (cf Barut and Rączka 1980; Hammermesh 1962). One could say that any carrier space of $GL(n)$ can be represented in such way, but throughout this work I will try to avoid explicit use of a complicated mathematics, in particular the use of symmetric or unitary group theory. In those passages, where group–theoretical explanations are so natural that other seem clumsy, I have placed a warning sign **GT** to let the uninitiated skip them – material included there is by no means necessary to understand the rest of the text. I am very well aware that one can almost always dress the methodological developments in a now distinguished language of group theory. Condon and Shortley (1935) relate the following story:

> *When Dirac visited Princeton in 1928 he gave a seminar report on his paper showing the connection of the exchange energy with the spin variables of the electrons. In discussion following the report, Weyl protested that Dirac has said that he would derive the results without the use of group theory but, as Weyl said, all of Dirac's arguments were really applications of group theory. Dirac replied, "I said I would obtain the results without any previous knowledge of group theory".*

This anecdote* ilustrates very well the sense in which group theory is not used here. Personally I like group theory, especially when it is presented in the not–so–formal way (cf Lipkin 1965; Cvitanović 1984), and I do not manage to get along completely without it. But, as Condon and Shortley (1935) write in their book: *"Hence, if we can minimize the amount of new mathemathics he (i.e. the physicist) must learn in order to penetrate a new field we do him a real service"*. I am in favour of new mathematics; Wormer (1975) has rightly pointed that there always was a resistance to accept new mathematical ideas, even such 'obvious' (for us now) concepts like negative numbers or the use of letters in equations. There are cases where we certainly need powerful mathematical techniques (cf Primas 1980). Condon himself turned to group theory in his last book (Condon and Odabaşi 1980). But, to quote from his first book again " *the new developments bring with them so many new things to be learned that it seems inadvisable to add this additional burden to the load*". In some respects, because of this additional burden, we seem to fall back in our understanding of fundamental concepts,

*I am indebt to Prof. R. McWeeny for telling me this anecdote.

as a quick comparison between say Condon and Shortley's book and some of the latest quantum chemistry textbooks, will immediately show.

Symmetries, existing in the physical system we want to describe, are usually reflected in the construction and properties of the states of this system. Eigenstates of an operator $\hat{O}$ are called $\hat{O}$–adapted states and the space of these states $\hat{O}$–adapted space. Frequently construction of such states is too complicated to be worth the trouble; simpler basis sets are used instead and the space enlarged to ensure that the subspace of desired symmetry is included in it. For example, we may easily construct $\hat{\mathbf{L}}_z$–adapted states but the construction of $\hat{\mathbf{L}}^2$– adapted states is much more complicated. The states included in model space $\tilde{\mathcal{H}}_n^N$ are thus selected first on the basis of their symmetry. Furtner selection of basis states is based on their importance, frequently estimated by the perturbation theory; contrary to the selection by symmetry this does not complicate the construction of many–particle states. Estimates of importance are either used globally (this is sometimes called preselection, cf Shavitt 1977) or locally. Taking all two–particle, two–hole states relative to some Fermi vacuum is a global selection. Local selections demand checking individual states and admitting to $\tilde{\mathcal{H}}_n^N$ only those that give a contribution larger than certain threshold. Global selection leads to spaces with certain regular structure while local selection in general destroys it. As I will show in Part **IV** of this work the structure of a model space $\tilde{\mathcal{H}}_n^N$ is reflected in the structure of the matrices corresponding to the operators acting in this space. Although graphical representation is very useful for calculation of matrix elements no matter how the selection is done it is with the global selection and the regular structure of the corresponding matrices where the biggest gains should be expected.

Techniques of a graphical representation of many–particle basis states adapted to different symmetry operators should be helpful in case of a complicated fermion and boson systems, although here such ambitious applications are not presented. The formulas of many–body perturbation theory are very compact when many–particle states are used, and get very complicated when spin–adapted formalism is coupled with diagramatic reduction to one–particle level (El Baz and Castel 1972). Why do I hope that graphical representation of model spaces (or GRMS for short) will be effective as a computational method ? GRMS may be used just for visualization, i.e. the classification and labeling of many–particle states used in traditional many–body methods, but such a representation fosters a new way of thinking about the organization of computations. To some degree this is already evident from the succes of the unitary group approach. In applied quantum mechanics the unitary group approach (UGA) to the many–electron correlation problem is certainly one of the more popular subjects of research in recent years (cf Paldus 1976; Harter and Patterson 1976; Drake and Schlesinger 1977; Downward and Robb 1977; Shavitt 1977-1983; Paldus and Boyle 1980; Hinze 1981; Kent *et al* 1981; Payne 1982; Robb and Niazi 1984; Paldus and Wormer 1986). There are good reasons for this: the programs, based on UGA ideas, proved to be much more effective than the conventional ones (Siegbahn 1979,1980; Brooks *et al* 1979,1980; Lischka *et al*

1981; Saunders and van Lenthe 1983). Configuration interaction (CI) calculations with over one million terms (Saxe *et al* 1982; Diamond *et al* 1984) or potential curves for molecules like Cr_2 in $^{11}\Sigma_g^+$ state (Roos *et al* 1982) calculated with 220000 functions are without doubt remarkable achievements, but the applications did not stopped with CI. The unitary group approach was succesfully applied to the MCSCF method (Brooks *et al* 1980b; Shephard *et al* 1980,1982) complete active space SCF (Roos 1980; Roos *et al* 1980; Siegbahn *et al* 1980,1981), coupled electron pair approximation (CEPA) (Lischka 1982), open–shell electron propagator method (Born and Shavitt 1982), energy gradient calculations (Brooks *et al* 1980c) and crystal field theory (Zhenyi 1983). There are hopes for many other applications as well (Shavitt 1983b).

The theory that lies behind all these applications does not look simple to a profane eye. Pages and pages of coefficients and complicated diagrams are reported in all papers containing derivations of UGA based formulas (cf Payne 1982 or Robb and Niazi 1984). One has to admire the amount of work that Paldus had to perform writing his monumental paper (Paldus 1976) that has turned the attention of many scientists to the unitary group theory. However, despite the beauty of its mathematics one is tempted to ask – is it possible to find some shortcuts that lead to the same results in a more direct and simple way ?

I would like to argue here that the real power of this new computational methods lies not so much in the efficiency of matrix element calculations, as claimed by Paldus (1981), but rather in the new organisation of computations, fostered by the graphical representation of the $\hat{S}^2$–adapted basis, due to Shavitt (1977). The pre–graphical applications of UGA were not succesful (Robb and Hegarty 1978); however, once the insight from the graphical representation was gained it was possible to avoid the explicit use of graphs in some cases (Saunders and van Lenthe 1983). Thus in the graphical unitary group approach (GUGA) the emphasis should be placed rather on 'G' for 'graphical' than 'U' for 'unitary'. UGA results concerning matrix elements are easily obtained by simpler and at the same time more general means. Group theory need not to be mentioned in the derivation, except for comparison with the previous approaches. Shavitt's graph, introduced at first as a representation of a table of distinct rows in Paldus tableaux (Shavitt 1977) is now being slowly recognized as a representation of a many–electron model space (Shavitt 1983a), although the Gelfand basis (Gelfand and Tsetlin 1950; Barut and Rączka 1980) and A,B,C tableaux (Paldus 1976) are still presented as a prerequisite for understanding of the graph (cf Esser 1984).

Shavitt's graph has inspired us to develop the symmetric group graphical approach (SGGA) (Duch and Karwowski 1981–1985). Both GUGA and SGGA may be treated as a special cases of the graphical representation of model spaces. It should be emphasized that the graphs used in these approaches are rather different from other types of graphs used in physics. They do not represent chemical structures, interactions or formulae, but give a global description of many–particle model spaces. They are successors of the branching diagram (van Vleck 1932) describing the structure of a spin

space in a similar way as the SGA graph describes the structure of the space of orbital configurations. The graphs used in UGA and SGA are in fact different projections of the same three–dimensional graph describing $\hat{\mathbf{S}}^2$–adapted states. I shall explore other graphical representations of these states as well as states adapted to $\hat{\mathbf{S}}_z$, $\hat{\mathbf{L}}_z$, $\hat{\mathbf{L}}^2$, $\hat{\mathbf{J}}^2$ and spatial symmetry point group operators, and point out some connections of this theory to well–established branches of mathematics.

First part of this book deals with the architecture of many–particle model spaces, i.e. with the labeling and classification of their basis states. In the second part operators acting in the model space are introduced and techniques of deriving matrix elements straight from the graph are elaborated. In the finite–dimensional spaces of states built from primitive objects every operator is equivalent to a polynomial in the shift operators, i.e. operators that replace one primitive object by another. An elegant theory of matrix element calculations that fits very well to a graphical representation of model spaces is based on the use of these operators, called in the context of UGA 'generators of the unitary group'. The celebrated result of UGA (Paldus 1981) – segmentation of the two–generator product matrix elements – is obtained as an example of this approach. In the second volume matrix elements between states belonging to the degenerate representations of the point groups and matrix elements between $(\hat{\mathbf{L}}^2,\hat{\mathbf{S}}^2)$ eigenstates are considered. The structure of matrices representing operators acting in model spaces is elucidated in the last part. The insight, gained from understanding of this structure, is applied to various methods of solution of the Schrödinger equation. Experience gathered with computer programs dealing with graphs is also presented in the second volume. So far applications of group–theoretical approaches have influenced the techniques of computations rather than bringing with them new developments in the methods. It is my hope that investigation of the structure of matrix representations of operators may lead not only to computational efficiency but also to new methods. The effect of an extension of orbital basis, for some operators and some types of graphs, should have a predictable influence on the eigenvalues of matrices corresponding to these operators. Is it possible to obtain the eigenvalues in an infinite orbital basis set in this way, i.e. to solve the problem exactly ? Or to formulate the perturbation theory to account for an extension of the orbital basis ? These are new types of questions that can be stated in the context of GRMS and that conclude this work.

PART I

ARCHITECTURE OF MODEL SPACES