

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Graph Theoretic and Electronic
Properties of Fullerenes
&
Biasing Molecular Modelling
Simulations with Experimental
Residual Dipolar Couplings

Lukas N Wirz

2015

A thesis presented in partial fulfilment of the
requirements for the degree of
Doctor of Philosophy
at
Massey University, Albany
New Zealand

Contents

I	Graph theoretical and electronic properties of fullerenes	1
1	Introduction	5
1.1	A Short Introduction to Graph Theory and Embeddings . . .	9
1.2	Drawing fullerene graphs: Methods for planar embedding . .	13
1.3	The large isomer space	15
1.4	Generation of fullerene graphs	16
1.5	Transformation of fullerene graphs	17
1.6	Geometry of Fullerenes	23
1.7	Generating accurate 3D geometries	26
1.8	Fullerene symmetry	28
1.9	Shapes: Volume and surface area, sphericity and convexity .	33
1.10	Topological and chemical indicators	37
1.11	Perfect matchings and their molecular application	46
1.12	Thermodynamic stability and the graphene limit	51
1.13	Electronic aspects to structure and stability	56
1.14	The gas phase formation of fullerenes	57
2	Program Fullerene: A Software Package for Constructing and Analyzing Structures of Regular Fullerenes	61
2.1	Introduction	61
2.2	General structure and history of the program <i>Fullerene</i>	64
2.3	3D structure generation	65
2.4	Goldberg-Coxeter transformation	68
2.5	Stone Wales transformation and vertex insertions	70
2.6	Force-field optimizations and vibrational frequencies	71

2.7	Hamiltonian cycles	74
2.8	Hückel analysis	75
2.9	Stability of fullerenes	76
2.10	Topological Indicators	77
2.11	Volume, Surface Area and Deviation from Spherical Symmetry	80
2.12	2D Graph representations and Schlegel projections	84
2.13	Databases	87
2.14	Structure of <i>Fullerene</i> and libgraph	88
3	Non-face spiral fullerenes and general face-spiral algorithms	93
3.1	Introduction	93
3.2	Methods	95
3.3	Results and Discussion	97
3.4	The Halma and Leapfrog Transforms of NS-Fullerenes	110
3.5	Conclusions	112
3.6	The generalised face-spiral algorithm	114
4	Force fields for fullerenes and related polyhedra	119
4.1	Introduction	119
4.2	Computational Methods	121
4.3	A General Harmonic Force Field for Fullerenes	123
4.4	Results and Discussion	126
4.5	Summary and Conclusions	132
4.6	A force field for general polyhedral graphs and triangulations of the sphere	133
5	Hamilton Cycles in Fullerene Graphs	137
5.1	Introduction	137
5.2	Method	139
5.3	Results and discussion	140
5.4	The number of Hamilton cycles in $C_{10+10k}-D_{5+}$ (5,0) fullerene nanotubes	156
5.5	The number of Hamilton cycles in $C_{12+12k}-D_{6+}$ (6,0) fullerene nanotubes	162
6	Gaudienes	167
6.1	Introduction	167

6.2	Graph theoretical considerations	169
6.3	Computational methods	172
6.4	Molecular structures	173
6.5	Discussion and Conclusions	179
 II Biasing molecular dynamics simulations with experi- mental residual dipolar couplings		183
7	Introduction	187
7.1	Molecular dynamics	187
7.2	Residual dipolar couplings	198
8	Fitting alignment tensor components to experimental RDCs, CSAs and RQCs	217
8.1	Theory	218
8.2	Results	222
8.3	Conclusions	225
9	Expression of molecular alignment by a weight function	227
9.1	Expansion in magnetic field vectors	227
9.2	Expansion in spherical harmonics	229
9.3	Restraining in terms of magnetic field vectors	232
9.4	Restraining in terms of spherical harmonics	235
9.5	Implementation	237
9.6	Equivalence of spherical harmonics and tensor representations	240
9.7	Conclusion	242
10	Alignment Blocks	245
10.1	Restraining using alignment blocks	246
10.2	Application to $^2\text{F}_1^3\text{F}_1$ from human fibronectin (2CKU)	247
10.3	Conclusions and outlook	253
 References		257
 Statements of Contribution to Doctoral Thesis Containing Publica- tions		299

Acknowledgements

There are several people I have to thank for making my last 3.5 years possible and enjoyable: Peter Schwerdtfeger, for giving me the opportunity to come to Massey University, and shielding all of us from the administrators. Thank you for support and a lot of freedom. · Jane Allison, for being extremely motivating, always taking time to answer and discuss my questions, and for the cake! · James Avery, for teaching me how to write less bad code, how to think and write as a mathematician (for chemists) and patience when either failed. Thank you for inviting me to stay in Copenhagen for two-and-a-half enjoyable and productive months. · Florian Senn and Lukáš Pašteka for useful discussions, advice, and encouragement when I was in need of it. · Andrew Punnett for taming the bits and electrons (as well as explaining how to) on smaller and larger computers, whenever and in whichever way they misbehaved. · Jayson Cosme, Lukáš Pašteka, and Lukas Trombach for the daily fix of ping pong (table tennis, to be accurate). · And everyone else in CTCP for the throughout friendly and encouraging atmosphere.

List of Publications

- [1] Schwerdtfeger P, Wirz L, Avery J. Program fullerene: A software package for constructing and analyzing structures of regular fullerenes. *J Comput Chem* 2013, 34:1508–1526. doi:10.1002/jcc.23278.
- [2] Wirz LN, Tonner R, Avery J, Schwerdtfeger P. Structure and properties of the nonface-spiral fullerenes T-C₃₈₀, D₃-C₃₈₄, D₃-C₄₄₀, and D₃-C₆₇₂ and their halma and leapfrog transforms. *J Chem Inf Model* 2014, 54:121–130. doi:10.1021/ci4005578.
- [3] Schwerdtfeger P, Wirz LN, Avery J. The topology of fullerenes. *WIREs Comp Mol Sci* 2015, 5:96–145. doi:10.1002/wcms.1207.
- [4] Wirz LN, Allison JR. Fitting alignment tensor components to experimental RDCs, CSAs and RQCs. *J Biomol NMR* 2015, 62:25–29. doi:10.1007/s10858-015-9907-x.
- [5] Wirz LN, Tonner R, Hermann A, Sure R, Schwerdtfeger P. From small fullerenes to the graphene limit: A harmonic force-field method for fullerenes and a comparison to density functional calculations for Goldberg–Coxeter fullerenes up to C₉₈₀. *J Comput Chem* 2016, 37:10–17. doi:10.1002/jcc.23894.
- [6] Wirz LN, Allison JR. Comment on “a tensor-free method for the structural and dynamic refinement of proteins using residual dipolar couplings”. *J Phys Chem B* 2015, 119:8223–8224. doi:10.1021/acs.jpcc.5b02801.
- [7] Wirz LN, Babić D, Avery J, Schwerdtfeger P. Toward tight upper and lower bounds for Hamilton cycles in fullerene graphs 2015.
- [8] Sundholm D, Wirz LN, Schwerdtfeger P. Novel hollow all-carbon structures. *Nanoscale* 2015, 38:15886–15894. doi:10.1039/C5NR04370K.

Abstract

In this thesis two different models, that is levels of abstraction, are used to explore specific classes of molecular structures and their properties.

In part I, fullerenes and other all-carbon cages are investigated using graphs as a representation of their molecular structure. By this means the large isomer space, simple molecular properties as well as pure graph theoretical aspects of the underlying graphs are explored. Although chemical graphs are used to represent other classes of molecules, cavernous carbon molecules are particularly well suited for this level of abstraction due to their large number of isomers with only one atom type and uniform hybridisation throughout the molecule.

In part II, a force field for molecular dynamics, that is the step wise propagation of a molecular structure in time using Newtonian mechanics, is complemented by an additional term that takes into account residual dipolar couplings that are experimentally measured in NMR experiments. Adding this force term leads to more accurate simulated dynamics which is especially important for proteins whose functionality in many cases crucially depends on their dynamics. Large biomolecules are an example of chemical systems that are too large for treatment with quantum chemical methods but at the same time have an electronic structure that is simple enough for accurate simulations with a forcefield.