MONASH University

# Thesis Title

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# Copyright notice

# Abstract

The abstract should outline the main approach and findings of the thesis and must not be more than 500 words.

# Declaration

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes (insert number) original papers published in peer reviewed journals and (insert number) submitted publications. The core theme of the thesis is (insert theme). The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the (insert name of academic unit) under the supervision of (insert name of supervisor).

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of (insert chapter numbers) my contribution to the work involved the following:

I have / have not renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

**Student name:** John J. Johnson

| **Thesis chapter** | **Publication title** | **Status (published, in press, accepted or returned for revision)** | **Nature and % of student contribution** | **Co-author name(s), nature and % of co-author's contribution** | **Co-author(s), Monash student Y/N** |
|---|---|---|---|---|---|
| 2 | xx | xx | xx | xx | N |
| 3 | xx | xx | xx | xx | N |
| 4 | xx | xx | xx | xx | N |
| 5 | xx | xx | xx | xx | N |

**Student signature:**

**Date:**

# Acknowledgements

Generally anyone that helped you in your research journey should be acknowledged here.

Large credit of this thesis template goes to Rob J Hyndman. His original template can be found at his github repositary.

# Abbreviations

| | |
|---|---|
| $BF_4^-$ | tetrafluoroborate |
| $C_1mim^+$ | 1,3-dimethylimidazolium |
| $C_1mpyr^+$ | N,N-dimethylpyrrolidinium |
| $NTf_2^-$ | *bis*(trifluoromethylsulfonyl)amide |
| $N(CN)_2^-$ | dicyanamide |
| mes | mesylate |
| tos | tosylate |
| $PF_6^-$ | hexafluorophosphate |

# Chapter 1

# Introduction

This chapter contains a summary of the context in which your research is set.

Imagine you are writing for your fellow PhD students. Topics that are well-known to them do not have to be included here. But things that they may not know about should be included.

Resist the temptation to discuss everything you've read in the last few years. And you are not writing a textbook either. This chapter is meant to provide the background necessary to understand the material in subsequent chapters. Stick to that.

You will need to organize the literature review around themes, and within each theme provide a story explaining the development of ideas to date. In each theme, you should get to the point where your ideas will fit in. But leave your ideas to later chapters. This way it is clear what has been done beforehand, and what new contributions you are making to the research field.

## 1.1 Rmarkdown

The big advantage of using Rmarkdown is that it allows you to include your R code directly into your thesis, to ensure there are no errors in copying and pasting, and that everything is reproducible. It also helps you stay better organized.

For details on using *R Markdown* see http://rmarkdown.rstudio.com.

### 1.1.1 Syntax

Superscript: +/- 2 kJ $mol^{-1}$

Subscript $C_3$mim

Lists:

I. Make sure you have two spaces after I.
II. Point 2

1) List
2) Point 2

a. Point 1
b. Point 2

- unordered list
  - sub-item 1
  - sub-item 2

Bold: **Bolded** or **Bolded**

Italics: *Italicised* or *Italicised*

## 1.2 Citing references

This is an example of citing is the style of RMarkdown with reference to authors Makridakis and Hibon [1] and Makridakis et al. [2] and Chatfield et al. [see 3] also Ord, Koehler, and Snyder [4].[5–8]

This template also works with `autocite` (latex notation) which will raise the citations to superscript.[4]

## 1.3 Including Figures From File

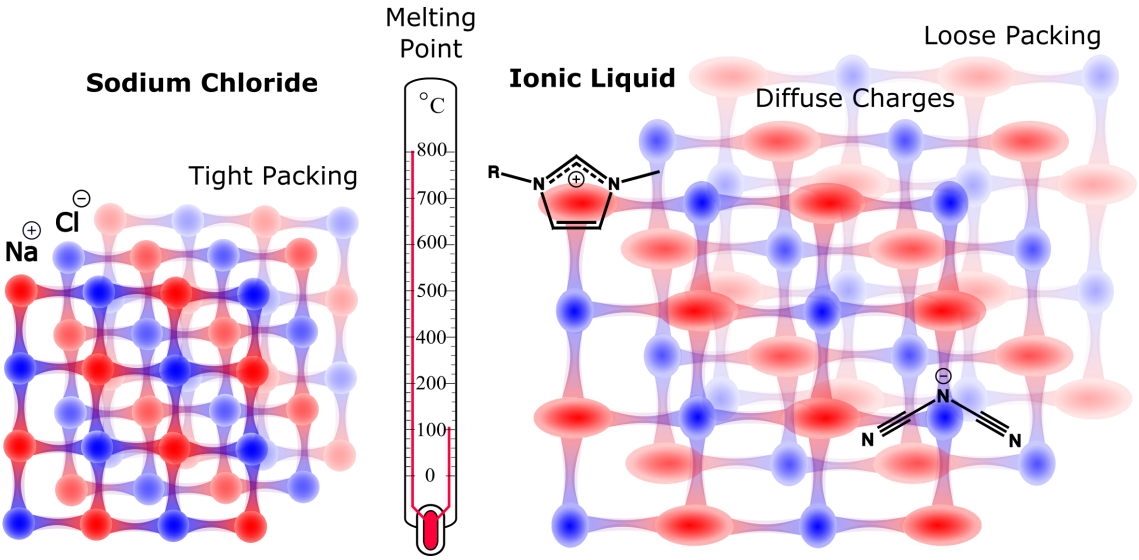


**Figure 1.1:** *The caption for my figure :).*

## 1.4 Equations

Inline equations are surrounded by \$ ($y_t$) and displayed equations look like:

$$y_t - y_{t-4} = \beta(x_t - x_{t-4}) + \gamma(z_t - z_{t-4}) + \theta_1\varepsilon_{t-1} + \Theta_1\varepsilon_{t-4} + \varepsilon_t \tag{1.1}$$

and generate equation numbers.

Inline r commands can be called and even used to process data on the spot. In the following equation 2+3 is evaluated during rendering to produce $\Theta_1 = 5$. In RStudio `addins` function `Input LaTex Math` simplifies the syntax of inserting equations.

Dalton Transactions

PAPER

View Article Online
View Journal | View Issue



Cite this: *Dalton Trans.*, 2014, **43**, 11145

# The use of localised orbitals for the bonding and mechanistic analysis of organometallic compounds†

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www.rsc.org/dalton

Through a series of examples we show how, upon orbital localisation, the outcome of an electronic structure calculation reveals features, such as bonding and oxidation states, which are controversial to grasp by alternative methods. The approach can also be applied to the analysis of reaction mechanisms. Because of the insight it provides in a limited execution time, we believe that this approach, known since the early developments of computational quantum chemistry, could find wider applications in the organometallic community than it actually has and facilitate communication between computational and experimental chemists.

## Introduction

*Is there a bond between atoms X and Y? What is the oxidation state of atom X?* Both are central questions in chemistry, to which we can often answer on the basis of the knowledge we built on related systems. However, as chemical research pushes its limits towards the synthesis of compounds with novel properties, new situations arise for which it is difficult to make an assignment. When this occurs, computational quantum chemistry is asked to resolve the issue. Indeed, computational quantum chemistry is capable, within its own limitations, of providing a picture of the system of interest at a resolution which is in general not accessible by experimental means. However, the solution of the quantum chemical problem comes in a form (a set of nuclear coordinates and electronic orbitals) which has to be reconciled with accepted chemical concepts. Concepts such as bonding and oxidation states are deep-rooted in the chemist's way of thinking and are so useful to guide the design of new compounds that we do not want to abandon them. And the problem lies there: *how do we reduce the N-body solution to a set of estimates of chemical concepts*. Many methods have been devised for this purpose. Among these, we recall population analysis (Mulliken[1] and variants[2,3]), the theory of atoms in molecules,[4] and molecular orbital analysis (including the natural bonding orbitals[5]). All these methods are widely used in the theoretical community, each with its own advantages and limitations, such that some researchers may prefer one over the other. In this communication we want to call attention to the use of localised molecular orbitals to perform the analysis. The approach dates back to the work of Boys in the sixties,[6,7] but is not much used by the organometallic community. In contrast, it is much more employed (in the form of maximally localised Wannier functions[8,9]) in condensed matter research where it has important applications.[10] Through a few examples drawn from our current research and cases discussed in the literature, we will show how localised molecular orbitals may be conveniently used to answer the opening questions. It is not our intention to criticize previous work, nor to propose that the use of this procedure should substitute other analysis techniques. We just want to share with the reader the clear cut picture of the electronic structure which arises from the application of the localisation procedure.

## Methods

Orbital localisation consists of finding the unitary transformation $U$ acting on the Kohn–Sham orbitals $\varphi_i^{KS}$,

$$\varphi_n^{loc} = \sum_i U_{in} \varphi_i^{KS}$$

which minimizes the spread functional $\Omega$

$$\Omega = \sum_n \left[ \langle \varphi_n^{loc} | r^2 | \varphi_n^{loc} \rangle - \langle \varphi_n^{loc} | r | \varphi_n^{loc} \rangle^2 \right]$$

The procedure consists of first performing a standard density functional theory (DFT) calculation within the Kohn–

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†Electronic supplementary information (ESI) available: Supporting Fig. S1–5. Details of the calculation of localised orbitals and orbital centroids in Gaussian09. Cartesian coordinates of atoms and orbital centroids in the complexes analyzed. See DOI: 10.1039/c4dt00251b

## 1.6 References

[1] S. Makridakis and M. Hibon. Accuracy of forecasting: an empirical investigation (with discussion). *Journal of Royal Statistical Society (A)* **142** (1979), 97–145.

[2] S. Makridakis, A. Anderson, R. Carbone, R. Fildes, M. Hibon, R. Lewandowskiand J. Newton, E. Parzen, and R. Winkler. The accuracy of extrapolation (time series) methods: results of a forecasting competition. *Journal of Forecasting* **1** (1982), 111–153.

[3] C. Chatfield, A. B. Koehler, J. K. Ord, and R. D. Snyder. A new look at models for exponential smoothing. *The Statistician* **50** (2001), 147–159.

[4] J. K. Ord, A. B. Koehler, and R. D. Snyder. Estimation and prediction for a class of dynamic nonlinear statistical models. *Journal of American Statistical Association* **92** (1997), 1621–1629.

[5] R. G. Brown. *Statistical forecasting for inventory control.* 1959.

[6] R. G. Brown. *Smoothing, forecasting and prediction of discrete time series.* 1963.

[7] C. E. Holt. *Forecasting trends and seasonals by exponentially weighted averages.* O.N.R. Memorandum 52/1957. Carnegie Institute of Technology, 1957.

[8] P. R. Winters. Forecasting sales by exponentially weighted moving averages. *Management Science* **6** (1960), 324–342.

# Chapter 2

# Results and Analysis

## 2.1 Data

Included in this template is a file called `sales.csv`. We can load in this data set using the command in the following `R` chunk:

```
# Loading the data
sales <- read.csv("data/sales.csv")
```

Notice only `R` syntax is contained in the chunk and even the comments are different. Any data you use in your thesis can go into the data directory. It is recommended that munging is scripted in R and form part of your thesis files (possibly hidden in the output) to ensure reproducibility.

## 2.2 Creating Figures and Self Referencing

Figure 2.1 shows time plots of the data we loaded in the last chunk. Notice how figure captions and references work. Chunk names can be used as figure labels with `fig:` prefixed. Never manually type figure numbers, as they can change when you add or delete figures. This way, the figure numbering is always correct.

This is a reference to the next chapter, chapter 2, and this is a reference to the next section (2.3).

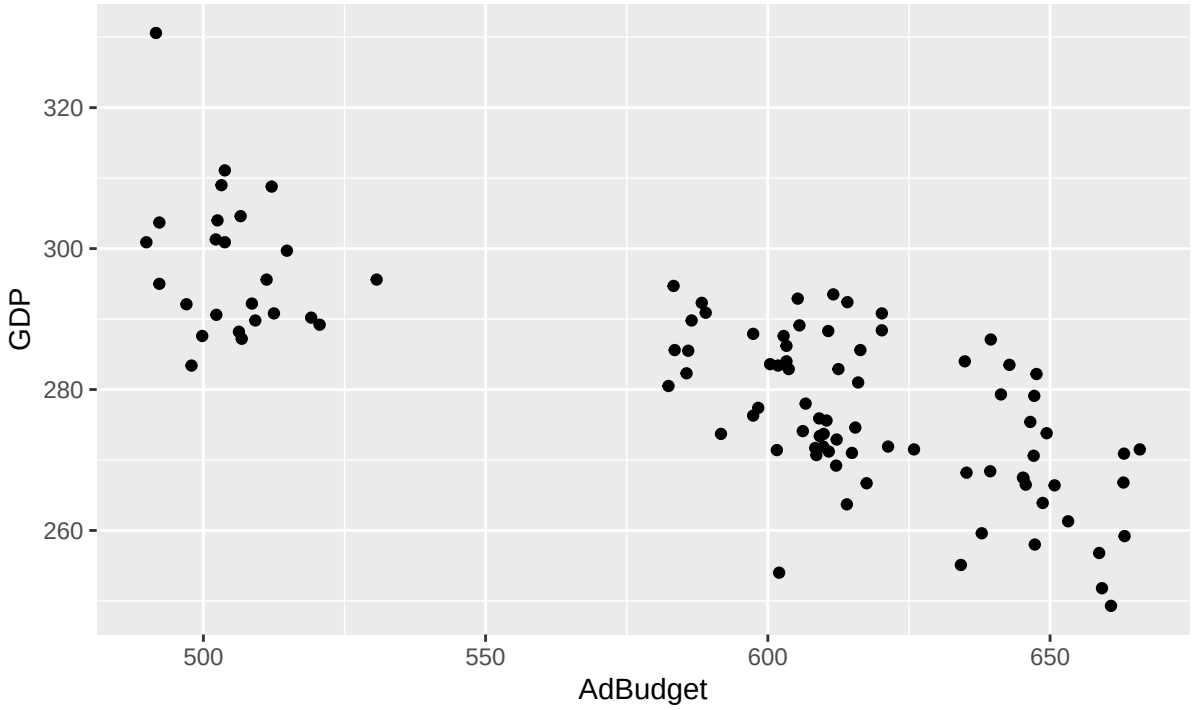


**Figure 2.1:** *This is a figure caption!*

## 2.3 Tables

### 2.3.1 knitLatex xTab Table

| X | Sales | AdBudget | GDP |
|---|---|---|---|
| Mar-81 | 1020.2 | 659.2 | 251.8 |
| Jun-81 | 889.2 | 589.0 | 290.9 |
| Sep-81 | 795.0 | 512.5 | 290.8 |
| Dec-81 | 1003.9 | 614.1 | 292.4 |
| Mar-82 | 1057.7 | 647.2 | 279.1 |

**Table 2.1:** *Table with 'knitLatex'*

Again, notice the automatically generated table numbers. In this case, we need to generate the label ourselves.

The `knitLatex` package is useful for generating tables from R output. Other packages can do similar things including the `kable` function in `knitr` which is somewhat simpler but you have less control over the result. If you use `knitLatex` to generate tables, don't forget to

include `results="asis"` in the chunk settings. The options of xTab can be found here: https://cran.r-project.org/web/packages/knitLatex/knitLatex.pdf.

### 2.3.2 Knitr Kable Table

| X | Sales | AdBudget | GDP |
|---|---|---|---|
| Mar-81 | 1020.2 | 659.2 | 251.8 |
| Jun-81 | 889.2 | 589.0 | 290.9 |
| Sep-81 | 795.0 | 512.5 | 290.8 |
| Dec-81 | 1003.9 | 614.1 | 292.4 |
| Mar-82 | 1057.7 | 647.2 | 279.1 |

For more options from `kable_styling` see https://cran.r-project.org/web/packages/kableExtra/kableExtra.pdf.

### 2.3.3 Markdown Table

For simple tables Markdown syntax is extremely easy. Additionally you can use an online Table generator (https://www.tablesgenerator.com/markdown_tables). In the example below colons on the left left-align the columns.

| My | Header |
|---|---|
| This | is |
| a | Markdown |
| Table | Easy! |

### 2.3.4 Manual Table

Kable typically take in data.frames which can be made before creating the table.

| Text1 | Text2 | Text3 |
|---|---|---|
| Yes | 1 | 20.0 |
| No | 2 | 40.5 |

**Have fun!**

# Appendices

# Appendix A

# Additional stuff

You might put some computer output here, or maybe additional tables.

Note that `\appendix` must appear before your first appendix although this is not required for other appendices.