

## BRIEF TECHNICAL NOTES

HINNE HETTEMA

Department of Chemistry, University of Auckland, Private Bag 92109  
Auckland, New Zealand

I wish to be brief on most of the technical points raised by the present collection of papers. The results of most of these have been excellently summarised in later, commonly available work which is relatively well known. In this technical introduction, I provide an overview of the book and some additional brief comments on individual papers.

In editing a book such as this, one is faced with an obvious dilemma. On the one hand it is possible to significantly edit the papers, provide a host of comments, and perhaps even alter portions of the material to fit a modern day description. Such an approach would have made the current project both infeasible and also, to a large extent, uninteresting. Most of the material presented here has been excellently recaptured in later, commonly known works, and modern formulations of the theory are readily available. So I have chosen the other option: I have striven to provide very faithful translations and exact copies of the formulae as they appear in the original material, and have refrained from heavy editing. This section, however, points out some of the more obvious typographical mistakes in the original formulae.

A brief remark about the selection: I have chosen to collect theoretical papers that are, it is hoped, of interest to both the theorist and the experimentalist in physical chemistry. Since the advent of theoretical science in the United States, the two have been intimately connected, so there is not much of a gap to bridge here.

### 1. An overview of the book

The book is divided into six different parts. The first part consists of papers that deal almost exclusively with the interaction between nuclear and electronic motion in molecules. It contains a translation of the original paper of Born and Oppenheimer on what is now commonly called the Born–Oppenheimer approximation. This very complicated paper, in which the rotational energy of a molecule is derived as a fourth order perturbation in the nuclear motion parameter, is still the basis of most quantum chemistry today.

The second part deals with the theory of atoms, and the choice here has been to highlight the use of explicitly correlated functions in the theory of atoms with

more than one electron and the  $1/Z$  expansion of the electronic energy. We have thus left out all theoretical work on one-electron atoms, on which much of the theory of more-electron atoms is based. This choice is justified by the observation that papers dealing with the one-electron atoms are in a sense more “basic” papers in the development of quantum theory, and it was not our aim to provide another introduction to or a set of translations of this interesting and widely studied subject. Here we have collected some of the papers of Hylleraas, who performed some of the first “exact” calculations on two-electron atoms, partly motivated by the question whether quantum mechanics was leading to numerically correct answers for these complicated systems. He found that the answers obtained were correct.

The third part deals with the theory of the chemical bond. It contains (of course) the seminal paper by Heitler and London, as well as a more general paper by London on the chemical bond and the quantum theory of homopolar valence numbers. The Heitler–London theory gave rise to the valence bond (VB) approach in quantum chemistry. There is also a paper with some “exact” calculations on  $H_2$  by Hylleraas, which present a computationally accurate view of the hydrogen bond.

The fourth part deals with spectroscopy. Since this part also contains some of the papers of Hund which are relevant to the theory of the chemical bond, there is an overlap with the third part here. I have chosen to place Hund’s work in the spectroscopy section, mainly because spectroscopy is what Hund set out to do. The Hund–Mulliken or molecular orbital (MO) approach to the chemical bond, some of which is piloted here, became prominent after the emergence of quantum chemistry in the United States, mainly through the series of papers by Pauling. Much of the material discussed in this section can also be found in the books by Herzberg (Herzberg 1950; Herzberg 1966).

The fifth part discusses the theory of intermolecular interactions. Again, London is an influential figure here. In fact, his first paper with Heitler on the theory of the hydrogen bond was a spinoff of an earlier attempt to solve the problem of van der Waals interactions.

The sixth and last part of this collection consists of Hückel’s theory of the double bond.

## **2. A few remarks on the papers**

We will now give some details on the parts and the individual papers, where necessary. Our aim is not to point out all the specialties of the derivations; indeed, part of the aim of the present book is to make these available to the modern reader.

The formulae and tables from the original papers are copied as they appear in the originals, including some errors. Below, we include a few remarks on the individual papers (where necessary) and point out some of the obvious typographical errors which appear in the originals.

2.1. Chapter 1. *M. Born and J.R. Oppenheimer, Ann. d. Physik Lpz.*

**84**, 457 (1927)

This complicated paper describes the separation of electronic and nuclear coordinates in a molecular quantum-mechanical problem. The internal coordinates of the molecule are indicated by  $\xi$ , the translation and rotation coordinates by  $\zeta$ . The equation for the minimum of the electronic energy is derived [Eq. (40)], and the problem of molecular vibration [Eq. (46)] as well as molecular rotation [Eq. (69)] is discussed.

Special remarks:

1. In formula (7), the “ $K$ ” on the operator of the kinetic energy should be subscripted.

The theoretical derivation of this paper is also presented, in a somewhat more accessible form, in the book by Born and Huang (Born and Huang 1950).

2.2. Chapter 2. *J. von Neumann and E. Wigner, Physik. Z.* **30**, 467 (1929)

There is a superfluous right bracket in the lower line equation of Eq. (4).

2.3. Chapter 5. *E.A. Hylleraas, Z. Physik* **48**, 469 (1929)

The numerical computations in this paper are very complicated. A few remarks on problems with the formulae

1. In Eq. (14a) the  $\psi$  is missing after the expression for the potential energy.
2. In Eq. (26d) the  $Y$  is missing after  $l(l+1)$ .
3. In the “Note added in proof” the summation over  $k$  starts at 1.

2.4. Chapter 6. *E.A. Hylleraas, Z. Physik* **54**, 347 (1929)

After Eq. (8) and before Eq. (8a) the boundary condition is stated to be  $\beta = 0$ . This should be  $t = 0$ , since there is no  $\beta$  appearing elsewhere in the paper.

2.5. Chapter 8. *E.A. Hylleraas, Z. Physik* **65**, 209 (1930)

In Eq. (8a) in one of the integrals the  $d\tau$  is missing. In Table 7 the theoretical value for  $\text{Li}^+$  should be 75.272; cf. the table in Chapter 7.

2.6. Chapter 11. *E.A. Hylleraas, Z. Physik* **71**, 739 (1931)

Because of the complicated formulae in this paper, there are a few typographical mistakes in the original. We have located the following:

1. In formula (9c) there is a  $c$  missing in the last term.
2. The first term of formula (14a) should read  $xy''$ .
3. Formula (16a) should be headed by  $m = 1$ , reading from the text above.

4. In formula (18) the “2” second derivative is missing.
5. In formula (23) in the fourth line there should be a + sign between the second and third terms in the square brackets.
6. In formula (25a) in the second line there should be  $\tau + \frac{1}{2}$ .

2.7. Chapter 18. E. Wigner and E.E. Wittmer, *Z. Physik* **51**, 859 (1928)

1. Below Eq. (14a) one of the nuclear coordinates should be  $Z'$ .

2.8. Chapter 20. H.A. Kramers, *Z. Physik* **53**, 429 (1929)

This paper uses the word *Grade*, which strictly means degree, for the number of elements of a group. I have therefore chosen to translate it into “order”, giving the word “Grade” in square brackets immediately behind it.

2.9. Chapter 22. R. Eisenschitz and F. London, *Z. Physik* **60**, 491 (1930)

In footnote 12 as well as in Section I.2 the operators are called “Einzeloperatoren” and the matrix  $\mathbb{T}$  is called an “Einzelmatrix”. I have translated these into “projection operators” and “projection matrix”, although the literal translation is “single” operator and “single” matrix. To my current knowledge, the word “Einzeloperator” or “Einzelmatrix” is no longer used in German.

2.10. Chapter 25. H. Eyring and M. Polanyi, *Z. Phys. Chemie B* **12**, 279 (1931)

In Eq. (9) there should be an “=” sign instead of a “-” sign in the equation for  $\eta_2$ . In Eq. (11) there should be  $f(b)$  in the fifth term instead of  $fb$ .

### 3. A note on styles and peculiarities of translation

It is neither an exaggeration nor an unfair criticism to state that all the papers as published in the present volume would face severe difficulties in getting published “as is” in the present-day scientific literature. The style of publishing a paper has simply changed too much over time.

A major difference between the papers collected in the present volume and today’s scientific publications is the speed with which they were reviewed, typeset and printed. For instance: Hylleraas’ paper on the ground state of the helium atom, while a substantial contribution both in size and content, was received by the *Z. Phys.* on 16 March 1928, has a “note added in proof” dated April 1928, and it was printed in the May issue of the *Zeitschrift*. This is a speed which nowadays is rarely met in scientific publication, notwithstanding the increased efficiency with which present-day publishers can handle the publication process.

Consequently, many of the papers are stylistically very close to a true scientific communication. They contain, to a much larger extent than many of today’s

papers, hints, surmises, suggestions for further research and personal opinions of their authors. I have thought it best to retain these elements of (personal) style and not revert too much to the more impersonal mode of conversation which dominates today's scientific publishing. Any initial uneasiness of a late twentieth century reader should soon pass. The personal styles are exactly what makes these papers interesting and exciting reading today: they show to a large extent the process of science in the making, particularly if the science that is in the making is a major portion of the core of today's physical and theoretical chemistry. And we find that the construction, after the birth of the "new" quantum mechanics as embodied in the Schrödinger equation and Heisenberg's matrix mechanics, was taking place at breakneck speed.

It is therefore not really a surprise that perhaps the best single-word description of the stylistic difference is that most of the scientific papers collected in this volume seem to be "unfinished". There are, however, considerable differences in style between all the authors and I have done my best to retain these differences as far as possible.

A few general remarks on peculiarities associated with translation. In German texts, the word *Bild* is often used to denote a conceptualisation of the physical situation. I have translated it into the word "picture", or "model", though these have a somewhat different semantic field.

Another similar problem with the translation is the word *Kräftespiel*, which, translated literally, means a "game of forces". Meant is the complex dynamic equilibrium between forces that lead to homopolar, or covalent, chemical bonds between equal atoms. The word "game" can be used quite well in this sense in German or Dutch, but seems silly in English. Hence my translation into "equilibrium of forces" or something very similar, depending on the context.

#### 4. Bibliography

- Born and Huang (1950), *The Dynamical Theory of Crystal Lattices*, Oxford.
- Herzberg, G. (1950). *Spectra of Diatomic Molecules*, Volume I of *Molecular Spectra and Molecular Structure*. New York: Van Nostrand Reinhold.
- Herzberg, G. (1966). *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Volume III of *Molecular Spectra and Molecular Structure*, New York: Van Nostrand Reinhold.