Atomistic Models

Concepts in Computational Chemistry

Per-Olof Åstrand

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CONCEPTS IN COMPUTATIONAL CHEMISTRY

CONTENTS

PREFACE

This text is to a large extent a result of teaching two courses in molecular modeling and computational chemistry at the Norwegian University of Science and Technology (NTNU) in Trondheim. An introductory course in *Molecular Modeling* has been given annually since 2002 on the M.Sc. level based on the book by Leach (Leach 2001). This course gives an introduction to and an overview of the topic, including the basic elements in computational quantum chemistry, force fields and molecular simulations, as well as some more specialized topics as free-energy calculations and solvation models. A biannual course on the Ph.D. level, *Advanced Molecular Modeling*, has been given since 2004 based on own lecture notes and review papers. These notes have previously been used in a course organized by Prof. Kurt V. Mikkelsen at Aarhus University (1995) and annually at the University of Copenhagen (1997-2002). For this course, two sets of lecture notes, *Intermolecular Interactions* and *Simulations of Liquids*, were developed, where the notes on *Intermolecular Interactions* are based on an introductory chapter in my Ph.D. thesis (Åstrand 1994). The notes have also been used in a course on *Intermolecular Interactions* at the University of Tromsø in 2002, and at a summer school in *Molecular Dynamics and Chemical Kinetics: Exploitation of Solar Energy* at the University of Copenhagen annually since 2013. This text is therefore the result of lecture notes gathered and updated continuously over the years.

There are many excellent books in the field of computational and theoretical chemistry, but

they are often specialized in one or a few of the topics important for a general course in molecular modeling. So it is rather the lack of a book with the, according to me, desired composition (table of contents) for a general text on molecular modeling than the lack of good texts on each of the topics that lead to that eventually this project was initiated.

The clear separation between content and style in LaTeX (Lamport 1994) makes it pivotal in organizing and developing a complex document. In addition, the PGF and TikZ graphics systems for TeX have been used extensively to construct the graphics leading to that all figures in the document are included as in-line LaTeX code. Consequently, the graphics appear in a consistent way and can be easily updated as the document is developed. All references with a doi are clickable in the reference lists as a result of using BibTex together with the doi package. Also text marked with brown (with one exception) are clickable with a link to an external web-page. Developing a complex LaTeX document has many similarities to software development. Since the repository only consists of text files (including the figures when PGF/TikZ is used), it is therefore natural to use a version control system and for this project *git* (Chacon and Straub 2014) is used.

There is a multitude of software available to do the actual calculations using the methods discussed in this text. If possible, I have so far chosen to use software that is generally available in the Ubuntu Linux-based system. Avogadro is used as a molecule editor (Hanwell et al. 2012) to generate input files for the quantum chemical calculations, and for the quantum chemical calculations NWChem (Valiev et al. 2010) has been used.

There are of course many persons that have contributed indirectly to this text. I am in particular grateful to my Ph.D. thesis adviser Prof. Gunnar Karlström (Lund University) and to my postdoc adviser Prof. Kurt V. Mikkelsen (University of Copenhagen). Since the notes have been used extensively in courses over the years, I am also grateful to all the students that have commented on different parts of the original notes or in other ways given feedback.

I also would like to thank Bookboon for publishing this text, and in particular I would like to thank Karin Hamilton Jakobsen at Bookboon for the encouragement to actually convert a set of separate notes into one coherent document. I support the idea of Bookboon to distribute free ebooks for students.

First edition

The 1st edition is by no means a complete book on molecular modeling, it is rather a compendium containing some of the chapters relevant for a general course in molecular modeling and computational chemistry. Apart from a brief introduction, this edition consists of two chapters on computational quantum chemistry and force fields, respectively. Since this text is published as an e-book only, it is, as for a software, possible to publish corrections and additions frequently. The goal is to publish a new edition annually as long as I use the text myself in teaching, so comments on the content are most welcome.

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ABOUT THE AUTHOR

Per-Olof Åstrand was born in Sätila in western Sweden in 1965 and grew up in Tygelsjö just south of Malmö in the very southern part of Sweden. After a compulsory military service, he moved to Lund in 1985 to study at Lund University for a degree in chemical engineering which was completed in 1990. He then started on a Ph.D. degree in theoretical chemistry with Gunnar Karlström as thesis supervisor and Anders Wallqvist as cosupervisor. His thesis work was on the development of the polarizable force field named NEMO (Wallqvist and Karlström 1989), and the Ph.D. thesis (Åstrand 1994) included also theoretical work on far infrared spectroscopy in collaboration with Anders Engdahl and Bengt Nelander as well as molecular dynamics simulations with Per Linse and Kurt V. Mikkelsen using the NEMO force field.

He moved to Denmark in 1995 for a postdoc with Kurt V. Mikkelsen, first one year at Aarhus University and then at the University of Copenhagen in 1996-97. In 1998, he moved to Risø National Laboratory just north of Roskilde outside Copenhagen, and in 2001-02 he was part time at the University of Copenhagen and at Risø. In this period he was also a part of a collaboration with Kenneth Ruud and Trygve Helgaker at the University of Oslo. At the end of the period, he also received a grant from NorFA to spend two months with Kenneth Ruud at the University of Tromsø in the most northern part of Norway.

In 2002, he was appointed as full professor in computational chemistry at the Norwegian University of Science and Technology (NTNU) in Trondheim, Norway and he thereby moved to his third Scandinavian country. He has been teaching molecular modeling and computational chemistry based on the book by Leach (Leach 2001) since 2002 (since 2013 the course is shared with Titus S. van Erp). He has also been teaching basic physical chemistry (2002-2005) and an interdisciplanary course (2006-2008). In 2008, he established a new chemistry-oriented course for the new nanotechnology engineering program in statistical thermodynamics based on the book by Dill and Bromberg (Dill and Bromberg 2003; 2011), which he has been teaching since then. He is also giving a biannual Ph.D. course in advanced molecular modeling since 2004 with a focus on the theory of intermolecular forces, the connection between force fields and quantum mechanics as well as the connection between microscopic and macroscopic polarization.

Since his Ph.D. work, his research has covered a broad range of theoretical chemistry including applied quantum chemistry, vibrational motion, force-field development and molecular dynamics simulations. Many of the projects have been carried out in close collaboration with experimental groups, most noteably work on far infrared spectroscopy on bimolecular complexes (Anders Engdahl and Bengt Nelander, Lund), THz spectroscopy on liquid water (Cecilie Rønne and Søren R. Keiding, Aarhus), azobenzenes in optical storage materials (P. S. Ramanujam and Søren Hvilsted, Risø), and more recently work on heterogenous catalysis (Magnus Rønning and De Chen, NTNU) and electrically insulating properties of dielectric liquids (Lars Lundgaard, SINTEF Energy, and Mikael Unge, ABB Corporate Research). In the academic year 2009/10, he spent a sabbatical at Northwestern University with George C. Schatz and Mark A. Ratner. Since 2011, he is the leader (elected) of the Computational Chemistry section of the Norwegian Chemical Society.

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INTRODUCTION

1.1   What is molecular modeling?

With molecular models we mean models where a molecule is constituted by atoms connected by chemical (covalent) bonds (see figure 1.1 for two examples). Molecular models are normally based on a mechanistic model for describing the structure of molecules and other molecular properties as well as the interactions between molecules. Using the here quite ill-defined term *atom* rather than nucleus for the constituents of a molecule indicates that the constituent of interest consists of both a nucleus and core electrons (whereas the valence electrons mainly form the covalent bonds between the atoms), and we also therefore refer to the models discussed in this text as *atomistic models*. The letters in the figure denote the position of the atoms: H for hydrogen, C for carbon, N for nitrogen, O for oxygen, etc., and the solid lines denote covalent bonds, i.e. electron pairs shared by the two connected atoms. Another common way to depict the structure of molecules is with ball-and-stick models, where two molecules are shown in figure 1.2. Here a colour code is used for each element: black for C, red for O, blue for N, white for H, etc.

The terms *molecular modeling, computational chemistry* and *theoretical chemistry* are often used interchangeably and the distinctions, if ever been meaningful, have more or less lost their meaning. A text on computational chemistry should in my opinion include the aspects of how to solve the problem on a modern computer system including the choice of algorithms, parallelization on large-scale clusters and optimization on gpu-accelerators. The subtitle of this text *Concepts in Computational Chemistry* indicates that we rather focus on what is needed from a user perspective to understand the methods in computational chemistry rather than the implementation of the methods. The so far never-ending rapid development of computer technology has evidently lead to a revolution in chemistry, and computational chemistry has become an accompanying analysis technique in line with many common experimental characterization techniques. So the role of high-performance computers is indisputable, but in this text we assume that we have the required computer
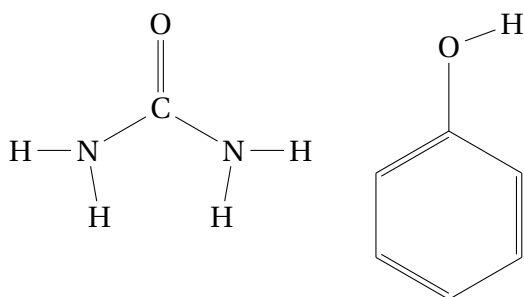

Figure 1.1: Chemical structure for urea (left) and phenol (right). In phenol, the hydrogens on the phenyl ring are suppressed.
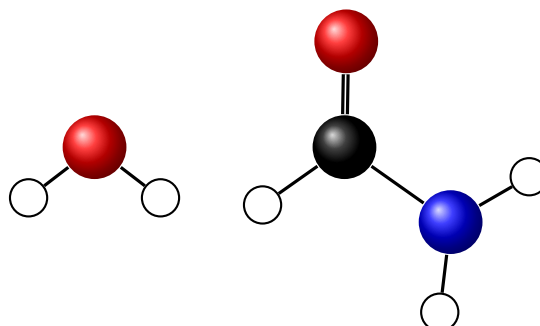
Figure 1.2: Ball-and-stick representation of water (left) and formamide (right).

resources in terms of both hardware and software at hand. Theoretical chemistry, although by many often used as a synonym for quantum chemistry, is the widest term including theoretical development (i.e. new equations), computational chemistry (i.e. how to solve the equations on a computer), and how to apply the methods in different applications which requires a detailed knowledge of each particular application area. Theoretical chemistry is also a wider concept than molecular modeling and includes also thermodynamics, chemical kinetics and molecular informatics.

Computer modeling is in many cases an attractive alternative to experiments with the requirement that the accuracy of the modeled property rivals that of the experiment. Computer-based simulations are in most cases less expensive and less time-consuming than to carry out the corresponding experiments, and in addition simulations can more easily be performed at extreme conditions, e.g. at very high pressures or temperatures, or with hazardous components, e.g. with explosives or poisonous molecules, than experiments. In simulations, it is also easier to investigate different contributions, e.g. from a non-zero temperature or from a solvent, to a property since in calculations we often add up various contributions which thus can be analyzed individually whereas we in an experiment often only get a single number as the result. Similarly, it is often possible to partition the computed property into various terms or in other ways to analyze the computed result in terms of properties that cannot be measured experimentally. As an example, the electrostatics of a molecule is commonly analyzed in terms of partial atomic charges, a property that cannot be measured experimentally.

When presenting a method in computational chemistry, we are thus interested in three different things: the theory behind the method describing which properties that can be computed (at least in principle), the accuracy of the method, and finally, how the results can be analyzed to provide further insights about the studied system. To stop after the second step is a pity, then an accurate calculations is not more valuable than an accurate experiment since it only provides "a single number".

1.2   Brief summary

The most fundamental way to describe a molecular system theoretically is with quantum mechanics. In molecular quantum mechanics (quantum chemistry), we normally approximate both nuclei and electrons as point particles, i.e. each particle has a mass, an electric charge and possibly also a spin. Nevertheless, the molecular problem in quantum mechanics is complicated and only the hydrogen atom (one nucleus and one electron) in a clamped-nucleus approach (the nucleus is kept in a fixed position in space and has no kinetic energy) has been solved analytically. The goal is to solve the Schrödinger equation for molecular systems, but for many-electron atoms and all molecules this can only be achieved by approximate models solved numerically. A major part of computational chemistry is therefore devoted to approximate methods for calculating molecular energies and properties including very accurate molecular-orbital methods to include electron correlation, methods based on density-functional theory, and phenomenologically based force-field methods. If the wavefunction of a molecule is known, however, all information about the molecule can be extracted from its wavefunction. An introduction to computational methods in quantum

chemistry is given in chapter 2.

Although we briefly introduce classical electrostatics in chapter 2, we are often interested in the interaction between a molecular system and an electromagnetic field. The obvious example is spectroscopy where the molecular system is perturbed by an applied electromagnetic field and the response is measured. Another example is organic solar cells (e.g. Grätzel cellswhere the light of the sun is absorbed by a photosensitizer and the excited electron is separated from the hole leading to an electrical current. Also long-range intermolecular interactions can be described in terms of electrostatics using the same basic concepts, i.e. a molecule is interacting with the electrostatic potential, electric field, etc. arising from the charge distribution of the surrounding molecules. The proper starting point of this branch of molecular modeling are Maxwell's equations.

At least historically, quantum chemical calculations are computationally too expensive to be used for very large systems (thousands of atoms) or in molecular dynamics simulations where the interatomic forces have to be computed repeatedly (perhaps millions of times). This gap is filled by force fields, i.e. simple and approximate models for the molecular energy as well as intermolecular interactions that is feasible for large-scale molecular dynamics simulations. Force fields are here first introduced phenomenologically and subsequently in a more systematic way by deriving each term in a force field from quantum chemistry. An introduction to force fields is given in chapter 3.

A quantum chemical calculation gives in principle information about the properties of a
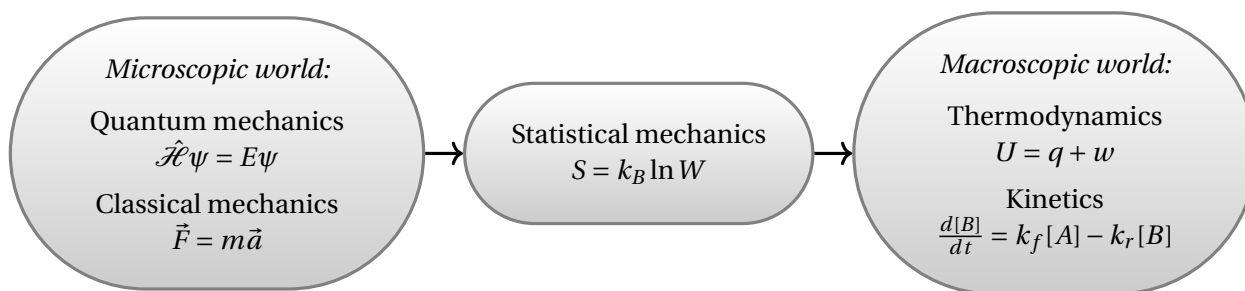
Figure 1.3: Statistical thermodynamics provides the connection between the microscopic and the macroscopic world.

molecular system at the temperature 0 K. To obtain properties for a liquid or solution for example at room temperature and ambient pressure, we need to employ statistical thermodynamics. Statistical thermodynamics (statistical mechanics is used as an equivalent term in this text) is the theory that provides the link between the microscopic world described by quantum mechanics (and sometimes classical mechanics) and the macroscopic world described by thermodynamics and chemical kinetics (see figure 1.3). A key component of statistical thermodynamics is the partition function and all thermodynamics properties of a system can be provided from the partition function provided that it is known. This is not the case for a realistic system as a molecular liquid, so the problem of calculating the properties of a liquid is instead turned into a sampling scheme where liquid configurations are sampled from the correct distribution (e.g. at a given temperature, pressure and density) using molecular dynamics or Monte Carlo simulations. Another major part of computational chemistry is therefore devoted to simulations of molecular liquids.

A chemical event, e.g. a chemical reaction or the absorption of a photon, is in most cases local in space where the actual event involves perhaps 5-10 atoms whereas the total system may consist of thousands of atoms as well as fast in time, often on the femtosecond scale. Consequently, multiscale and multiphysics methods in theoretical chemistry have been developed over the years.

In molecular informatics, which may be subdivided into chemoinformatics and bioinformatics, molecular properties are related to how the system functions (photovoltaic cell, electrochemical battery, drug, etc.) by statistics without an underlying mechanistic model and is therefore a separate branch of theoretical and computational chemistry.

Many of the grand challenges in chemistry today are strongly connected to severe problems for our society, as for example a sustainable production of energy and electricity, clean water and food production, the environment, and nano-scale devices for the next generation of information technology. In all these cases, modeling on the atomistic scale have already provided or can give substantial contributions.

MOLECULAR QUANTUM MECHANICS

Quantum mechanics, together with statistical mechanics, is the foundation of theoretical chemistry and molecular modeling. Quantum mechanics applied on molecular systems, quantum chemistry, provides the chemical model for describing chemical bonds and reactions, intermolecular interactions and molecular properties. Quantum chemistry also provides the foundation for many less sophisticated (coarse-grained) models for describing molecules such as force fields.

Previous knowledge in quantum mechanics is expected in line with an undergraduate course in physical chemistry (see "Recommended Literature" at the end of the chapter), and many of the sections in this chapter are regarded as repetition which is also reflected in the form of the presentation. The goal of the first sections are to provide the fundamentals of quantum mechanics and quantum chemistry needed in the forthcoming sections and chapters. For a more complete presentation of quantum chemistry, specialized texts on the subject are recommended at the end of the chapter.

2.1   The Schrödinger equation

The Schrödinger equation (Schrödinger 1926) is here presented as a hypothesis that has proven to be incredibly useful, and we do not aim at giving a motivation for its existence or the way it looks like. Knowing the solution to the Schrödinger equation provides all the necessary information of a microscopic system at the temperature 0 K. The time-dependent Schrödinger equation is given as

$$\hat{\mathscr{H}}\Psi(\vec{r}_{1\ldots N}, t) = i\hbar \frac{\partial \Psi(\vec{r}_{1\ldots N}, t)}{\partial t} \ , \tag{2.1.1}$$

where $\hbar = h/2\pi$ and h is Planck's constant, t is the time, Ψ is the wavefunction where $\vec{r}_{1\ldots N}$ is a short-hand notation for the position vectors of N particles, $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N$. The Hamiltonian, $\hat{\mathscr{H}}$, is the energy operator and is divided into a kinetic energy operator, $\hat{\mathscr{T}}$, and a potential energy operator, $\hat{V}$, as

$$\hat{\mathscr{H}} = \hat{\mathscr{T}} + \hat{V} \ . \tag{2.1.2}$$

The kinetic energy operator, $\hat{\mathscr{T}}$, is the sum of the kinetic energy operator of all particles in the system,

$$\hat{\mathscr{T}} = \sum_{i=1}^{N} \frac{-\hbar^2}{2m_i} \nabla_i^2 \ , \tag{2.1.3}$$

where m_i is the particle mass of particle i, N is the number of particles, and ∇_i^2 is the Laplacian of particle i given in Cartesian coordinates as

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \ , \tag{2.1.4}$$

where $\vec{r}_i = (x_i, y_i, z_i)$ is the position vector in Cartesian coordinates. The potential energy operator, $\hat{V}(\vec{r}_{1...N})$, is unique for each type of system, and in chemistry we are mainly interested in the Hamiltonian for molecular systems which is discussed in section 2.2.

If the Hamiltonian is a function of only the spatial variables, $\vec{r}_{1...N}$, and not of the time, separation of variables is used to simplify the Schrödinger equation. The wavefunction is thus written as the product of a spatial wavefunction, $\psi(\vec{r}_{1...N})$ and a time-dependent function, $\theta(t)$,

$$\Psi(\vec{r}_{1...N}, t) = \psi(\vec{r}_{1...N})\theta(t) \, , \tag{2.1.5}$$

which is plugged into the Schrödinger equation in eq. (2.1.1) leading to

$$\frac{1}{\psi}\hat{\mathcal{H}}\psi = \mathrm{i}\hbar\frac{1}{\theta}\frac{\partial\theta}{\partial t} \, . \tag{2.1.6}$$

Since the left-hand side is a function of only $\vec{r}_{1...N}$ and the right-hand side is a function of only t, both sides have to be equal to a constant, identified as the energy E. This leads to the time-independent Schrödinger equation for the spatial part,

$$\hat{\mathcal{H}}\psi = E\psi \, , \tag{2.1.7}$$

and to a trivial solution for the time-dependent part,

$$\theta(t) = C\,\mathrm{e}^{\frac{-\mathrm{i}Et}{\hbar}} \, , \tag{2.1.8}$$

where C is a constant. For most Hamiltonians (but not all), the solution to the time-independent Schrödinger equation in eq. (2.1.7) is *quantized*,

$$\hat{\mathcal{H}}\psi_n = E_n\psi_n \, , \tag{2.1.9}$$

which is interpreted as that a quantum particle is in a state n with discrete energy levels at E_n. Eq. (2.1.9) is an eigenvalue problem, where E_n are the eigenvalues and ψ_n are the eigenfunctions of the operator $\hat{\mathcal{H}}$. The time-independent Schrödinger equation[1] is solvable analytically only for a few model systems, where some of them are discussed in appendix 2.A.

2.2 The molecular Hamiltonian

In quantum chemistry, a molecule is represented by n electrons and N nuclei, where an electron has a charge $-e$ and a mass m_e, and a nucleus I has a charge $Z_I e$ and a mass m_I. Both the nuclei and the electrons are regarded as point charges, i.e. they have no extension in space. The kinetic energy operator, $\hat{\mathcal{T}}$, for a molecule is given by a trivial extension of eq. (2.1.3) as a sum of the kinetic energy for all nuclei and electrons,

$$\hat{\mathcal{T}} = \underbrace{\sum_{I=1}^{N}\frac{-\hbar^2}{2m_I}\nabla_I^2}_{\text{nuclei}} + \underbrace{\sum_{i=1}^{n}\frac{-\hbar^2}{2m_e}\nabla_i^2}_{\text{electrons}} \, . \tag{2.2.1}$$

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[1]In the remaining part of the text, the time-independent Schrödinger equation in eq. (2.1.9) is referred to as the Schrödinger equation. Also, the eigenfunctions in eq. (2.1.9), ψ_n, are referred to as the wavefunction. If the time dependence is included, we will explicitly refer to the time-dependent Schrödinger equation and the time-dependent wavefunction, respectively.

The potential energy operator, $\hat{V}$, for a molecule is given by the Coulomb interaction between point charges for all the nuclei and electrons,

$$\hat{V} = \underbrace{\sum_{\substack{I=1,\\J=I+1}}^{N} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0 R_{IJ}}}_{\text{nucleus-nucleus}} + \underbrace{\sum_{i=1}^{n}\sum_{I=1}^{N} \frac{-Z_I e^2}{4\pi\varepsilon_0 r_{iI}}}_{\text{electron-nucleus}} + \underbrace{\sum_{\substack{i=1,\\j=i+1}}^{n} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{\text{electron-electron}} , \tag{2.2.2}$$

which is thus divided into nucleus-nucleus, electron-nucleus and electron-electron interactions. Here $Z_I e$ is the charge of nucleus I so that Z_I is the atomic number of the nucleus, e.g. $Z_I = 1$ for hydrogen and $Z_I = 6$ for carbon, and e is the elementary charge so that the charge of the electron is $-e$. We normally use capital letter subscripts, $I, J, K, \ldots$, to denote nuclei and small letter subscripts, $i, j, k, \ldots$, to denote electrons. If the distance involves only nuclei, it is denoted by R, whereas r is used if the distance involves at least one electron. In quantum chemistry, it is common to use atomic units (instead of SI units), where some constants are set equal to ± 1, see table 2.1. In atomic units, the molecular Hamiltonian for the kinetic energy operator becomes

$$\hat{\mathcal{T}} = \underbrace{-\frac{1}{2}\sum_{I=1}^{N} \frac{1}{m_I}\nabla_I^2}_{\text{nuclei}} - \underbrace{\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2}_{\text{electrons}} , \tag{2.2.3}$$

charge of electron: $e = -1$	length:	1 bohr = 0.529177 Å
mass of electron: $m_e = 1$	energy:	1 hartree = 2625.4996 kJ/mol
$\hbar = h/2\pi = 1$		1 hartree = 27.2113845 eV
$4\pi\varepsilon_0 = 1$		

Table 2.1: Atomic units. Constants set to ±1 (to the left) and some common unit conversions (to the right).

and for the potential energy operator we get

$$\hat{V} = \underbrace{\sum_{\substack{I=1, \\ J=I+1}}^{N} \frac{Z_I Z_J}{R_{IJ}}}_{\text{nucleus-nucleus}} + \underbrace{\sum_{i=1}^{n} \sum_{I=1}^{N} \frac{-Z_I}{r_{iI}}}_{\text{electron-nucleus}} + \underbrace{\sum_{\substack{i=1, \\ j=i+1}}^{n} \frac{1}{r_{ij}}}_{\text{electron-electron}} \quad . \tag{2.2.4}$$

We can thus write the molecular Hamiltonian $\hat{\mathcal{H}}^{\text{mol}}$ as

$$\hat{\mathcal{H}}^{\text{mol}} = \hat{\mathcal{T}}_n + \hat{\mathcal{T}}_e + \hat{V}_{nn} + \hat{V}_{en} + \hat{V}_{ee} , \tag{2.2.5}$$

i.e. the kinetic energy operators of the nuclei and electrons, respectively, as well as the nucleus-nucleus, nucleus-electron and electron-electron Coulomb interaction operators.

2.3 Some basic properties of the wavefunction

We will essentially only list some of the basic properties of the wavefunction needed in the forthcoming sections. For a more systematic introduction to basic molecular quantum mechanics, see e.g. (Atkins and Friedman 2010).

According to Born's interpretation of the wavefunction (Born 1926), $\psi_i^* \psi_i \, d\tau$ is interpreted as the probability for a particle in state i to be in a volume element $d\tau$. Here, ψ_i^* denotes the complex conjugate of ψ_i, i.e. the wavefunction may be complex including both a real and an imaginary part, however the probability $\psi_i^* \psi_i \, d\tau$ has by construction only a real part which is a requirement for an observable. Assuming that a probability for state i, $\rho_i(\vec{r})$, is *normalized*, i.e. the probability to find a particle anywhere in space is 1, we have

$$\int_{\text{all space}} \rho_i \, d\tau = \int_{\text{all space}} \psi_i^* \psi_i \, d\tau = 1 , \tag{2.3.1}$$

and we refer to this condition as if the wavefunction is normalized. Here $d\tau$ is the volume element, which in Cartesian coordinates for a single particle is $d\tau = dx \, dy \, dz$ and in spherical polar coordinates it is $d\tau = r^2 \sin(\theta) \, dr \, d\theta \, d\varphi$, respectively. In this text, the integration limits are dropped if we integrate over all space so that

$$\int_{\text{all space}} \ldots d\tau \equiv \int \ldots d\tau . \tag{2.3.2}$$

If we return to the time-dependent wavefunction in eqs. (2.1.5) and (2.1.8) putting C to 1 in eq. (2.1.8),

$$\Psi(t) = \psi \, e^{\frac{-iEt}{\hbar}} , \tag{2.3.3}$$

we see that if ψ is normalized, also $\Psi(t)$ is normalized. If we in general have

$$\Psi^*(t)\Psi(t) = \psi^*\psi , \tag{2.3.4}$$

we refer to the state as being *stationary*. For an operator $\hat{\Omega}$, the *expectation value*, $\langle\Omega\rangle_i$, is defined as

$$\langle\Omega\rangle_i \equiv \frac{\int \psi_i^* \hat{\Omega} \psi_i \, \mathrm{d}\tau}{\int \psi_i^* \psi_i \, \mathrm{d}\tau} , \tag{2.3.5}$$

for a system in state i. For a normalized wavefunction, it becomes

$$\langle\Omega\rangle_i = \int \psi_i^* \hat{\Omega} \psi_i \, \mathrm{d}\tau . \tag{2.3.6}$$

If ψ_i is an eigenfunction of $\hat{\Omega}$,

$$\langle\Omega\rangle_i = \frac{\int \psi_i^* \hat{\Omega} \psi_i \, \mathrm{d}\tau}{\int \psi_i^* \psi_i \, \mathrm{d}\tau} = \frac{\Omega_i \int \psi_i^* \psi_i \, \mathrm{d}\tau}{\int \psi_i^* \psi_i \, \mathrm{d}\tau} = \Omega_i , \tag{2.3.7}$$

i.e. the expectation value is equal to the eigenvalue, Ω_i. Thus we can write the energy, E_i, as an expectation value of the Hamiltonian as

$$E_i = \int \psi_i^* \hat{\mathscr{H}} \psi_i \, \mathrm{d}\tau , \tag{2.3.8}$$

for a normalized wavefunction. To simplify the notation, the *Dirac bra-c-ket* notation is introduced,

$$\langle\psi_i|\hat{\Omega}|\psi_j\rangle \equiv \langle i|\hat{\Omega}|j\rangle \equiv \int \psi_i^* \hat{\Omega} \psi_j \, \mathrm{d}\tau , \tag{2.3.9}$$

where $\langle\psi_i|$ or $\langle i|$ is the *bra* of state i and $|\psi_j\rangle$ or $|j\rangle$ is the *ket* of state j. The molecular Hamiltonian is *hermitian*, i.e. it fulfils

$$\int \psi_i^* \hat{\Omega} \psi_j \, \mathrm{d}\tau = \int \left(\hat{\Omega}\psi_i\right)^* \psi_j \, \mathrm{d}\tau , \tag{2.3.10}$$

which leads to that its eigenvalues are real and that the eigenfunctions are orthogonal (see exercise 2.1 to show this). Since energies, or to be more precise energy differences, are measurable quantities and therefore the energies have to be real, it is a requirement that the molecular Hamiltonian is hermitian. For *orthonormal* states (i.e. orthogonal and normalized),

$$\int \psi_i^* \psi_j \, \mathrm{d}\tau \equiv \langle\psi_i|\psi_j\rangle \equiv \langle i|j\rangle = \delta_{ij} \tag{2.3.11}$$

where δ_{ij} is the Kroenecker delta function (1 if $i = j$; 0 if $i \neq j$).

2.4 The Born-Oppenheimer approximation

In the Born-Oppenheimer approximation, the molecular wavefunction, $\psi(\vec{R}_{1...N}, \vec{r}_{1...n})$, is approximated as the product of an electronic, ψ^{el}, and a nuclear, ψ^{nuc}, wavefunction,

$$\psi(\vec{R}_{1...N}, \vec{r}_{1...n}) \approx \psi^{\mathrm{el}}(\vec{r}_{1...n}; \vec{R}_{1...N}) \, \psi^{\mathrm{nuc}}(\vec{R}_{1...N}) , \tag{2.4.1}$$
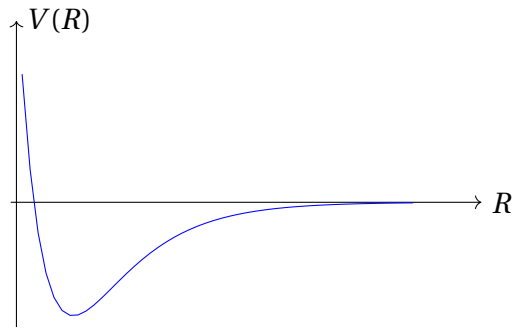
Figure 2.1: Sketch of a potential energy surface, $V(R)$, for a regular diatomic molecule. The minimum of $V(R)$ corresponds to the equilibrium bond length of the molecule.

where ψ^{el} is a function of the electronic coordinates, $\vec{r}_{1\ldots n}$, and depends *parametrically* on the nuclear coordinates, $\vec{R}_{1\ldots N}$.[2] It means that we solve the Schrödinger equation for ψ^{el} for a given molecular geometry, the *clamped-nucleus approach*. The corresponding Hamiltonian, $\hat{\mathscr{H}}^{\text{el}}$, is given as

$$
\begin{aligned}
\hat{\mathscr{H}}^{\text{el}} &= -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\sum_{I=1}^{N}\frac{Z_I}{r_{iI}} + \sum_{\substack{i=1\\j=i+1}}^{n}\frac{1}{r_{ij}} + \sum_{\substack{I=1\\J=I+1}}^{N}\frac{Z_I Z_J}{R_{IJ}}\\
&= \hat{\mathscr{T}}_e + \hat{\mathscr{V}}_{en} + \hat{\mathscr{V}}_{ee} + \hat{\mathscr{V}}_{nn}\,,
\end{aligned}
\tag{2.4.2}
$$

i.e. the kinetic term for the nuclei is ignored in the clamped-nucleus approach as compared to the molecular Hamiltonian in eq. (2.2.5). The last term on the right-hand side in eq. (2.4.2), the nucleus-nucleus potential energy, becomes a "constant" contribution to the molecular energy since the nuclear positions are regarded as parameters and not as variables in the electronic wavefunction ψ^{el}. The Schrödinger equation for the electronic state i becomes

$$
\hat{\mathscr{H}}^{\text{el}}\psi_i^{\text{el}} = \varepsilon_i^{\text{el}}\psi_i^{\text{el}}\,.
\tag{2.4.3}
$$

If eq. (2.4.3) is solved repeatedly for different molecular geometries, $\vec{R}_{1\ldots N}$, a *potential energy surface* is obtained for each state i, $\varepsilon_i^{\text{el}}(\vec{R}_{1\ldots N})$. Normally, we refer to the ground state energy surface, $\varepsilon_0^{\text{el}}(\vec{R}_{1\ldots N})$, as the potential energy surface, $V(\vec{R}_{1\ldots N})$,

$$
V(\vec{R}_{1\ldots N}) \equiv \varepsilon_0^{\text{el}}(\vec{R}_{1\ldots N})\,,
\tag{2.4.4}
$$

where a typical potential energy surface for a diatomic molecule is depicted in figure 2.1. The zero-level of the energy scale is normally shifted for $V(\vec{R}_{1\ldots N})$ as compared to $\varepsilon_0^{\text{el}}(\vec{R}_{1\ldots N})$ so that $V(\vec{R}_{1\ldots N})$ approaches zero for an infinite separation of two fragments, whereas $\varepsilon_0^{\text{el}}(\vec{R}_{1\ldots N})$ approaches zero for an infinite separation of all nuclei and electrons. We define the Hamiltonian for the nuclei as

$$
\hat{\mathscr{H}}^{\text{nuc}} = -\sum_{I=1}^{N}\frac{1}{2m_I}\nabla_I^2 + V(\vec{R}_{1\ldots N})\,,
\tag{2.4.5}
$$

---

[2]Note the distinction between $f(x,y)$ and $f(x;y)$. In the first case, x and y are both variables, but in the second case, y is a parameter, i.e. it has a single, constant value.

and the corresponding Schrödinger equation becomes

$$\hat{\mathcal{H}}^{\mathrm{nuc}} \psi_k^{\mathrm{nuc}} = \varepsilon_k^{\mathrm{nuc}} \psi_k^{\mathrm{nuc}} \,. \tag{2.4.6}$$

By applying the Born-Oppenheimer approximation, we have thus separated quantum chemistry into two problems: the electronic problem in eq. (2.4.3) solved for a given molecular geometry, and a nuclear problem in eq. (2.4.6) where the potential energy surface is obtained by solving the electronic Schrödinger equation for a set of molecular geometries. In this chapter, we focus entirely on the electronic structure of molecules by discussing methods for solving eq. (2.4.3). In a forthcoming chapter on molecular structure and vibrational motion, we will discuss how to solve eq. (2.4.6).

2.5 Atomic orbitals

2.5.1 One-electron atom

The starting point for solving the electronic Schrödinger equation is the *one-electron atom*. The position of the nucleus is regarded as fixed by adopting the Born-Oppenheimer approximation in section 2.4. The Hamiltonian, $\hat{\mathcal{H}}^{\mathrm{el}}$, for an electron interacting with a

l	0	1	2	3	4	5
name	s	p	d	f	g	h

(a) Symbols used for the quantum number l

n	l	m_l	name
1	0	0	$1s$
2	0	0	$2s$
2	1	$0, \pm 1$	$2p$

(b) Solutions allowed for $n = 1, 2$

Table 2.2: Notation for atomic orbitals

nucleus becomes in atomic units,

$$\hat{\mathcal{H}}^{\text{el}} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \, , \tag{2.5.1}$$

where Z is the charge of the nucleus and r is the distance between the electron and the nucleus. The Hamiltonian thus consists of a kinetic energy operator for the electron and the Coulomb interaction between the electron and the nucleus. The solutions to the Schrödinger equation is in spherical polar coordinates given as (see appendix 2.A.5)

$$\psi_{nlm_l}(r, \theta, \varphi) = R_{nl}(r) Y_{lm_l}(\theta, \varphi) \, , \tag{2.5.2}$$

where $R_{nl}(r)$ is a radial function and $Y_{lm_l}(\theta, \varphi)$ is a spherical harmonics. The solution depends on three quantum numbers, the principal quantum number n and two angular quantum numbers l and m_l, which are restricted to the following integer values:

$n = 1, 2, 3, \ldots$

$l = 0, 1, 2, \ldots, n - 1$

$m_l = 0, \pm 1, \pm 2, \ldots, \pm l$

The naming convention for atomic orbitals is given in table 2.2, giving the notation of $1s$, $2s$, $2p$, etc. orbitals. We thus have three $2p$-functions, normally denoted $2p_x$, $2p_y$ and $2p_z$. For $n = 3$, we get $3s$, $3p$ (with the components $3p_x$, $3p_y$ and $3p_z$), and $3d$ functions. The d-functions have five components, normally labeled d_{xy}, d_{xz}, d_{yz}, d_{z^2}, and $d_{x^2 - y^2}$. It is also noted that the atomic orbitals form an orthonormal set of functions,

$$\int \psi_{nlm_l}^*(r, \theta, \varphi) \, \psi_{n'l'm_l'}(r, \theta, \varphi) \, d\tau = \delta_{nn'} \delta_{ll'} \delta_{m_l m_l'} \, . \tag{2.5.3}$$

Each electron has a spin, with a spin quantum number, m_s,

$$m_s = \pm \frac{1}{2} \, . \tag{2.5.4}$$

Each *spatial* atomic orbital in eq. (2.5.2), may thus accomodate two electrons without violating the Pauli principle for fermions (each electron has a unique set of n, l, m_l, and m_s). The electron configuration for an atom is given according to the Aufbau principle as for example

He $1s^2$

Ne $1s^2 2s^2 2p^6$

Cl $1s^2 2s^2 2p^6 3s^2 2p^5$ or Ne $3s^2 2p^5$
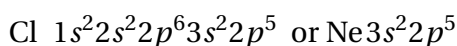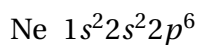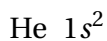
2.5.2 Two-electron atom

If we next regard the Hamiltonian of the two-electron atom, still within the clamped-nucleues approach,

$$\hat{\mathcal{H}}^{\text{el}} = \underbrace{-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}}_{\hat{\mathcal{H}}_i} \underbrace{-\frac{1}{2}\nabla_j^2 - \frac{Z}{r_j}}_{\hat{\mathcal{H}}_j} + \frac{1}{r_{ij}} \,, \tag{2.5.5}$$

where we have two electrons i and j interacting with a single nucleus. The Hamiltonian consists of five terms: a kinetic energy for each electron, the Coulomb interaction between each electron and the nucleus, and the repulsive Coulomb interaction between the two electrons. If we as a first approximation ignore the electron repulsion, the Hamiltonian becomes

$$\hat{\mathcal{H}}^{\text{el}} = \hat{\mathcal{H}}_i + \hat{\mathcal{H}}_j \,, \tag{2.5.6}$$

i.e. two one-electron Hamiltonians of the type in eq. (2.5.1) each with a solution given by eq. (2.5.2). Denoting a one-electron wavefunction, an atomic orbital, with $\phi_i(\vec{r}_i)$, we may anticipate that the Schrödinger equation becomes using variable separation

$$\left(\hat{\mathcal{H}}_i + \hat{\mathcal{H}}_j\right)\phi_i(\vec{r}_i)\phi_j(\vec{r}_j) = \left(\varepsilon_i + \varepsilon_j\right)\phi_i(\vec{r}_i)\phi_j(\vec{r}_j) \,, \tag{2.5.7}$$

where ε_i is an orbital energy. Since electrons are fermions, they are, however, indistinguishable and the wavefunction has to be anti-symmetric with respect to the exchange of

two electrons. If both electrons are put into the $1s$ orbital, an occupation denoted $1s^2$, the wavefunction may as a first attempt be written as

$$\psi(i, j) = 1s(i)\, 1s(j) \,, \tag{2.5.8}$$

where the notation $\vec{r}_i \equiv i$ and $\vec{r}_j \equiv j$ is adopted. In eq. (2.5.8), the electrons are indistinguishable but the wavefunction is not anti-symmetric. It is the total wavefunction, however, including also the spin in addition to the spatial coordinates, that has to be anti-symmetric. Denoting a spin-orbital, $\chi_i(\vec{r}_i, s_i)$,

$$\chi_i(\vec{r}_i, s_i) \equiv \phi_i(\vec{r}_i)\, \sigma_i(s_i) \,, \tag{2.5.9}$$

where σ_i can be either α for $m_s = \frac{1}{2}$ or β for $m_s = -\frac{1}{2}$. However, the wavefunction,

$$\psi(i, j) = 1s(i)\,\alpha(i) \times 1s(j)\,\beta(j) \,, \tag{2.5.10}$$

is not anti-symmetric (nor are the electrons indistinguishable). Constructing the following linear combinations of the spin-functions,

$$\frac{1}{\sqrt{2}}\left(\alpha(i)\beta(j) + \alpha(j)\beta(i)\right) \qquad \text{symmetric} \,,$$
$$\frac{1}{\sqrt{2}}\left(\alpha(i)\beta(j) - \alpha(j)\beta(i)\right) \qquad \text{anti-symmetric} \,,$$

gives a symmetric and an anti-symmetric spin-function. Here it is assumed that the spin-functions are orthonormal, i.e.

$$\langle \alpha(i) | \beta(j) \rangle = \delta_{\alpha\beta}\delta_{ij} \,, \tag{2.5.11}$$

giving the normalization factor, $1/\sqrt{2}$, above. The wavefunction,

$$\psi(i, j) = 1s(i)1s(j) \times \frac{1}{\sqrt{2}}\left(\alpha(i)\beta(j) - \alpha(j)\beta(i)\right) \,, \tag{2.5.12}$$

is thus acceptable since the wavefunction is anti-symmetric and the electrons are indistinguishable and in line with our chemical picture that the helium atom has a $1s^2$ configuration with a spin-up and and a spin-down electron given schematically in figure 2.2a with two electrons in the orbital with the lowest energy. For an excited state of He, e.g. $1s(1)\,2s(2)$, see figures 2.2b and (c), the spatial part of the wavefunction becomes

$$\frac{1}{\sqrt{2}}\left(1s(i)2s(j) \pm 1s(j)2s(i)\right) \,, \tag{2.5.13}$$

where the plus sign gives a symmetric function and the minus sign gives an anti-symmetric function. If they are then combined with appropriate spin functions, anti-symmetric wavefunctions can be constructed for both the singlet state and the triplet state.

(a) Ground state **(b)** Singlet excited state **(c)** Triplet excited state
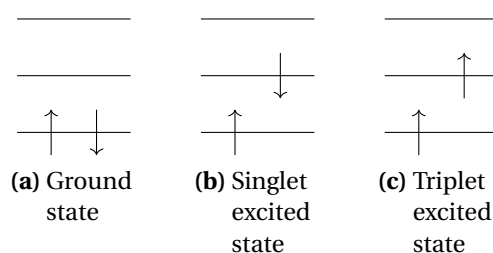
Figure 2.2: Some electronic states for the He atom

2.5.3 n-electron atom

Generalizing to an n-electron atom, a Slater determinant (Heisenberg 1926, Dirac 1926, Slater 1929),

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(n) & \chi_2(n) & \cdots & \chi_n(n) \end{vmatrix}, \tag{2.5.14}$$

gives the correct symmetry of the wavefunction as expressed by spin-orbitals.

2.6 Molecular orbitals

A fundamental approximation in molecular orbital theory is to construct molecular orbitals, φ_i, as a linear combination of m atomic orbitals, ϕ_j, the LCAO approximation,

$$\varphi_i = \sum_{j=1}^{m} c_{ij} \phi_j, \tag{2.6.1}$$

where c_{ij} is an orbital coefficient. For the hydrogen molecule, H_2, a molecular orbital, σ_i (where σ indicates that it is a σ-bond), may be written as a linear combination of two atomic orbitals, a $1s$ orbital for the first hydrogen atom, $1s_A$, and a $1s$ orbital for the second hydrogen atom, $1s_B$,

$$\sigma_i = c_{iA} 1s_A + c_{iB} 1s_B. \tag{2.6.2}$$

Using only two atomic orbitals for the hydrogen molecule, the solutions may be found trivially by regarding the symmetry of the molecule. If the two nuclei are placed at $(x_e, 0, 0)$ and $(-x_e, 0, 0)$, respectively, the probability to find an electron in x and $-x$ will be equal because of symmetry reasons. Assuming real wavefunctions,

$$\psi^2(x) = \psi^2(-x), \tag{2.6.3}$$

which has two solutions, a *symmetric* and an *anti-symmetric* solution,

$$\psi(x) = \psi(-x) \quad \text{and} \quad \psi(x) = -\psi(-x). \tag{2.6.4}$$

(a) Ground state   **(b)** Triplet excited state

Figure 2.3: Molecular orbital diagrams of the hydrogen molecule

Thus, $1s_A$ and $1s_B$ are two identical functions (atomic orbitals), centered around x_e and $-x_e$, respectively. Furthermore, $c_{Ai} = c_{Bi}$ or $c_{Ai} = -c_{Bi}$. If the atomic orbitals are orthonormal, see eq. (2.5.3), orthonormal molecular orbitals are given by
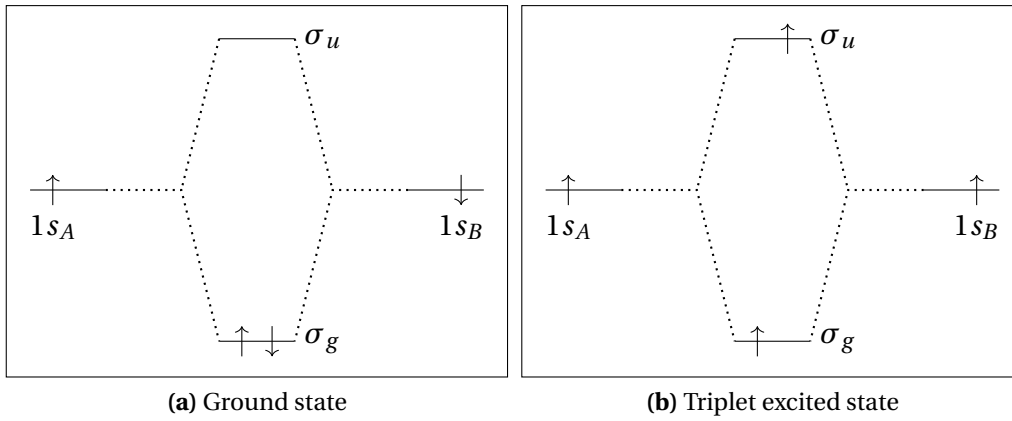
$$\sigma_g = \frac{1}{\sqrt{2}}\left(1s_A + 1s_B\right) \quad \text{and} \quad \sigma_u = \frac{1}{\sqrt{2}}\left(1s_A - 1s_B\right), \tag{2.6.5}$$

where σ_g (the subscript g denotes *gerade*, German for *even*) is a bonding σ-orbital and σ_u (the subscript u denotes *ungerade*, German for *odd*) is an antibonding σ-orbital. Following the Aufbau principle, the orbital with the lower energy σ_g will be doubly occupied (two electrons with opposite spin), whereas σ_u is unoccupied.

In general, the molecular wavefunction may be written as a Slater determinant of molecular orbitals. For a molecule with n electrons, $\frac{n}{2}$ molecular orbitals are occupied (two electrons with opposite spin in each molecular orbital), whereas the remaining molecular orbitals are unoccupied. As an example, the ground state of the hydrogen molecule, ψ_0, may thus be written as a Slater determinant of the occupied spin-orbitals,

$$\psi_0 = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left(\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)\right), \tag{2.6.6}$$

where $\chi_1(j) = \sigma_g(j)\alpha(j)$ and $\chi_2(j) = \sigma_g(j)\beta(j)$ and the wavefunction is normalized. Molecular orbitals may be depicted in molecular orbital (MO) diagrams, given for the hydrogen molecule in its ground state in figure 2.3a. If we regard the triplet state of the hydrogen molecule, the MO diagram is given in figure 2.3b, the wavefunction, ψ_1, becomes

$$\psi_1 = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_1(1) & \chi_3(1) \\ \chi_1(2) & \chi_3(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_u(1)\alpha(1) \\ \sigma_g(2)\alpha(2) & \sigma_u(2)\alpha(2) \end{vmatrix}, \tag{2.6.7}$$

where we have used the notation $\chi_3(j) = \sigma_u(j)\alpha(j)$.

2.6.1   Energy of the hydrogen molecule

The electronic Hamiltonian for the hydrogen molecule is

$$\hat{\mathscr{H}}^{\text{el}} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z_A}{r_{1A}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{1B}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R_{AB}} \ , \tag{2.6.8}$$

which we rewrite as

$$\hat{\mathscr{H}}^{\text{el}} = \hat{\mathscr{H}}_1 + \hat{\mathscr{H}}_2 + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R_{AB}} \ , \tag{2.6.9}$$

where the one-electron term, $\hat{\mathscr{H}}_i$, for electron i is given as

$$\hat{\mathscr{H}}_i = -\frac{1}{2}\nabla_i^2 - \frac{Z_A}{r_{iA}} - \frac{Z_B}{r_{iB}} \ . \tag{2.6.10}$$

We introduce

$$E_0 = E_0(1) + E_0(2) + E_0(1,2) + \frac{Z_A Z_B}{R_{AB}} \ , \tag{2.6.11}$$

where the last term on the right-hand side is a classical Coulomb energy between the two nuclear charges. For the one-electron contribution to electron 1, we get for the ground state of the hydrogen molecule in eq. (2.6.6), using the expectation value for the energy in

eq. (2.3.8) (see exercise 2.3),

$$
\begin{aligned}
E_0(1) &= \langle \psi_0 | \hat{\mathcal{H}}_1 | \psi_0 \rangle \\
&= \frac{1}{2} \left(\langle \chi_1(1) | \hat{\mathcal{H}}_1 | \chi_1(1) \rangle + \langle \chi_2(1) | \hat{\mathcal{H}}_1 | \chi_2(1) \rangle \right) \\
&= \langle \sigma_g(1) | \hat{\mathcal{H}}_1 | \sigma_g(1) \rangle \, .
\end{aligned}
\tag{2.6.12}
$$

Analogously,

$$
E_0(2) = \langle \sigma_g(2) | \hat{\mathcal{H}}_2 | \sigma_g(2) \rangle \, .
\tag{2.6.13}
$$

The two-electron term, $E_0(1,2)$, becomes (again see exercise 2.3)

$$
E_0(1,2) = \langle \sigma_g(1) \sigma_g(2) | \frac{1}{r_{12}} | \sigma_g(1) \sigma_g(2) \rangle \, ,
\tag{2.6.14}
$$

which may be rephrased as

$$
E_0(1,2) = \int \sigma_g^*(1) \sigma_g^*(2) \frac{1}{r_{12}} \sigma_g(1) \sigma_g(2) \, \mathrm{d}\tau = \int \rho(1) \frac{1}{r_{12}} \rho(2) \, \mathrm{d}\tau \, ,
\tag{2.6.15}
$$

where we in line with Born's interpretation in eq. (2.3.1) relate the electron density for a molecular orbital as $\rho(j) = \sigma^*(j)\sigma(j)$. Thus, $E(1,2)$ is interpreted as a Coulomb interaction between two charge distributions and these Coulomb terms are normally denoted as J_{ij}. We therefore rewrite eq. (2.6.11) as

$$
E_0 = H_1 + H_2 + J_{12} + \frac{Z_A Z_B}{R_{AB}} \, ,
\tag{2.6.16}
$$

where we also have adopted the notation $H_j \equiv E_0(j)$ for the one-electron terms.

In addition, the energy of the triplet state of the hydrogen molecule, see eq. (2.6.7) for its wavefunction, is obtained (see exercise 2.3). The one-electron terms become analogous to the ground state,

$$
E_1(j) = \frac{1}{2} \left(\langle \sigma_g(j) | \hat{\mathcal{H}}_j | \sigma_g(j) \rangle + \langle \sigma_u(j) | \hat{\mathcal{H}}_j | \sigma_u(j) \rangle \right) ,
\tag{2.6.17}
$$

but the two-electron term, $E_1(1,2)$, becomes

$$
\begin{aligned}
E_1(1,2) &= \underbrace{\frac{1}{2} \left(\langle \sigma_g(1) \sigma_u(2) | \frac{1}{r_{12}} | \sigma_g(1) \sigma_u(2) \rangle + \langle \sigma_u(1) \sigma_g(2) | \frac{1}{r_{12}} | \sigma_u(1) \sigma_g(2) \rangle \right)}_{J_{12}} \\
&\quad - \underbrace{\langle \sigma_g(1) \sigma_u(2) | \frac{1}{r_{12}} | \sigma_g(2) \sigma_u(1) \rangle}_{K_{12}} \, .
\end{aligned}
\tag{2.6.18}
$$

Again, the first term on the right-hand side is interpreted as a Coulomb interaction, J_{ij}, whereas the second term is referred to as an *exchange* integral and is denoted as K_{ij}. The energy for the triplet state of the hydrogen molecule thus becomes

$$
E_1 = H_1 + H_2 + J_{12} - K_{12} + \frac{Z_A Z_B}{R_{AB}} \, .
\tag{2.6.19}
$$

Since an exchange integral, K_{ij}, has a positive sign, it means that the triplet state in eq. (2.6.7) has a lower energy than the corresponding excited singlet state,

$$\psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_u(1)\beta(1) \\ \sigma_g(2)\alpha(2) & \sigma_u(2)\beta(2) \end{vmatrix}, \tag{2.6.20}$$

and the interpretation is that the electrons are more delocalized when the system is in the triplet state.

2.6.2 Energy of a Slater determinant

The Slater determinant in eq. (2.5.14) is rewritten as

$$|\psi\rangle = \hat{\mathscr{A}} |\chi_1(1)\chi_2(2)\ldots\chi_n(n)\rangle, \tag{2.6.21}$$

where $\hat{\mathscr{A}}$ is the antisymmetrizing operator generating the correct Slater determinant by operating on the direct product of spin-orbitals. $\hat{\mathscr{A}}$ is given as

$$\hat{\mathscr{A}} = \frac{1}{\sqrt{n!}} \sum_{p=0}^{n-1} (-1)^p \hat{\mathscr{P}}^{(p)} = \frac{1}{\sqrt{n!}} \left(\hat{1} - \sum_{i=1}^{n}\sum_{j=i+1}^{n} \hat{\mathscr{P}}_{ij}^{(1)} + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\sum_{k=j+1}^{n} \hat{\mathscr{P}}_{ijk}^{(2)} - \ldots \right), \tag{2.6.22}$$

where $\hat{1}$ is the identity operator, $\hat{\mathscr{P}}_{ij}^{(1)}$ is a permutation operator permuting the coordinates of two electrons i and j,

$$\hat{\mathscr{P}}_{ij}^{(1)}|\chi_i(i)\chi_j(j)\rangle = |\chi_j(i)\chi_i(j)\rangle \,. \tag{2.6.23}$$

Analogously, $\hat{\mathscr{P}}_{ijk}^{(2)}$ gives all possible permutations of the coordinates of three electrons,

$$\hat{\mathscr{P}}_{ijk}^{(2)}|\chi_i(i)\chi_j(j)\chi_k(k)\rangle = |\chi_k(i)\chi_i(j)\chi_j(k)\rangle + |\chi_j(i)\chi_k(j)\chi_i(k)\rangle \,, \tag{2.6.24}$$

etc. By convention, we order the orbitals in the direct products in eqs. (2.6.23) and (2.6.24) by the label of the electronic coordinates. It can be shown that $\hat{\mathscr{A}}$ commutes with $\hat{\mathscr{H}}$,

$$\left[\hat{\mathscr{A}}, \hat{\mathscr{H}}\right] = \hat{\mathscr{A}}\hat{\mathscr{H}} - \hat{\mathscr{H}}\hat{\mathscr{A}} = 0 \,, \tag{2.6.25}$$

and that

$$\hat{\mathscr{A}}\hat{\mathscr{A}} = \sqrt{n!}\hat{\mathscr{A}} \,. \tag{2.6.26}$$

Eqs. 2.6.25 and (2.6.26) are derived in exercise (2.4). We rewrite the electronic Hamiltonian in eq. (2.4.2) in line with eq. (2.6.9) as

$$\hat{\mathscr{H}}^{\text{el}} = \hat{\mathscr{T}}_e + \hat{\mathscr{V}}_{en} + \hat{\mathscr{V}}_{ee} + \hat{\mathscr{V}}_{nn} = \sum_{i=1}^{n} \hat{h}(i) + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \hat{g}(i,j) + \hat{\mathscr{V}}_{nn} \,, \tag{2.6.27}$$

i.e. the one-electron term $\hat{h}(i)$ is the motion of electron i in the potential of all the nuclei and includes thus the $\hat{\mathscr{T}}_e$ and $\hat{\mathscr{V}}_{ne}$ terms and $\hat{g}(i,j)$ is the two-electron term including the electron-electron Coulomb repulsion term $\hat{\mathscr{V}}_{ee}$. The energy of the Slater determinant in eq. (2.6.21) is given as

$$\begin{aligned}
E_0 &= \langle\psi|\hat{\mathscr{H}}^{\text{el}}|\psi\rangle \\
&= \langle\hat{\mathscr{A}}\chi_1(1)\chi_2(2)\ldots\chi_n(n)|\hat{\mathscr{H}}^{\text{el}}|\hat{\mathscr{A}}\chi_1(1)\chi_2(2)\ldots\chi_n(n)\rangle \\
&= \sqrt{n!}\langle\chi_1(1)\chi_2(2)\ldots\chi_n(n)|\hat{\mathscr{H}}^{\text{el}}|\hat{\mathscr{A}}\chi_1(1)\chi_2(2)\ldots\chi_n(n)\rangle \\
&= \sum_{p=0}^{n-1}(-1)^p \langle\chi_1(1)\chi_2(2)\ldots\chi_n(n)|\hat{\mathscr{H}}^{\text{el}}|\hat{\mathscr{P}}^{(p)}\chi_1(1)\chi_2(2)\ldots\chi_n(n)\rangle \,. \tag{2.6.28}
\end{aligned}$$

The nucleus-nucleus Coulomb operator, $\hat{\mathscr{V}}_{nn}$, only depends on the nuclear coordinates,

$$\langle\psi|\hat{\mathscr{V}}_{nn}|\psi\rangle = V_{nn}\langle\psi|\psi\rangle = V_{nn} \,, \tag{2.6.29}$$

where we have used that ψ is normalized. V_{nn} is thus reduced to a classical Coulomb interaction energy as in eq. (2.6.11) for the hydrogen molecule. Using that the spin-orbitals form an orthonormal set, only the identity operator $\hat{1}$ in the expansion of $\hat{\mathscr{A}}$ in eq. (2.6.22) gives a contribution to the energy of the one-electron operator $\hat{h}(i)$, e.g.

$$\begin{aligned}
&\langle\chi_1(1)\chi_2(2)\ldots\chi_n(n)|\hat{h}(1)|\chi_1(1)\chi_2(2)\ldots\chi_n(n)\rangle \\
&= \langle\chi_1(1)|\hat{h}(1)|\chi_1(1)\rangle\langle\chi_2(2)|\chi_2(2)\rangle\ldots\langle\chi_n(n)|\chi_n(n)\rangle \\
&= \langle\chi_1(1)|\hat{h}(1)|\chi_1(1)\rangle = h_1 \,. \tag{2.6.30}
\end{aligned}$$

For the one-electron operator, all energy terms including a permutation gives zero, e.g.

$$\langle \chi_1(1)\chi_2(2)\ldots\chi_n(n)|\hat{h}(1)|\hat{\mathscr{P}}_{12}^{(1)}\chi_1(1)\chi_2(2)\ldots\chi_n(n)\rangle$$
$$= \langle \chi_1(1)|\hat{h}(1)|\chi_2(1)\rangle\langle\chi_2(2)|\chi_1(2)\rangle\ldots\langle\chi_n(n)|\chi_n(n)\rangle = 0\,, \tag{2.6.31}$$

where the second term on the right-hand side with the integration over the coordinates of electron 2 is zero because of the orthogonality of the spin-orbitals 1 and 2. For the same reason, only the identity operator $\hat{1}$ and the two-electron permutation operator $\hat{\mathscr{P}}_{ij}^{(1)}$ in eq. (2.6.22) give contributions for the two-electron operator $g(i,j)$. The term for the identity operator for electrons 1 and 2 becomes

$$\langle \chi_1(1)\chi_2(2)\chi_3(3)\ldots\chi_n(n)|\hat{g}(1,2)|\chi_1(1)\chi_2(2)\chi_3(3)\ldots\chi_n(n)\rangle$$
$$= \langle \chi_1(1)\chi_2(2)|\hat{g}(1,2)|\chi_1(1)\chi_2(2)\rangle\langle\chi_3(3)|\chi_3(3)\rangle\ldots\langle\chi_n(n)|\chi_n(n)\rangle$$
$$= \langle \chi_1(1)\chi_2(2)|\hat{g}(1,2)|\chi_1(1)\chi_2(2)\rangle = J_{12}\,, \tag{2.6.32}$$

and is referred to as a Coulomb integral in line with eq. (2.6.15) for the hydrogen molecule. The second term for $\hat{\mathscr{P}}_{12}^{(1)}$ becomes

$$\langle \chi_1(1)\chi_2(2)\chi_3(3)\ldots\chi_n(n)|\hat{g}(1,2)|\hat{\mathscr{P}}_{12}^{(1)}\chi_1(1)\chi_2(2)\chi_3(3)\ldots\chi_n(n)\rangle$$
$$= \langle \chi_1(1)\chi_2(2)|\hat{g}(1,2)|\chi_2(1)\chi_1(2)\rangle\langle\chi_3(3)|\chi_3(3)\rangle\ldots\langle\chi_n(n)|\chi_n(n)\rangle$$
$$= \langle \chi_1(1)\chi_2(2)|\hat{g}(1,2)|\chi_2(1)\chi_1(2)\rangle = K_{12}\,, \tag{2.6.33}$$

where K_{12} is denoted an exchange integral in line with eq. (2.6.18). The combination of Slater determinants and orthonormal orbitals to reduce the molecular energy into a sum of one- and two-electron integrals is referred to as the Slater-Condon rules (Slater 1929, Condon 1930). In eqs. (2.6.32) and (2.6.33), we put electrons 1 and 2 in orbitals 1 and 2, however we integrate over the electronic coordinates so the electrons could have had any labels. We can therefore drop the electron labels and write the Coulomb and exchange integrals as

$$J_{12} = \langle \chi_1\chi_2|\hat{g}|\chi_1\chi_2\rangle \qquad \text{and} \qquad K_{12} = \langle \chi_1\chi_2|\hat{g}|\chi_2\chi_1\rangle\,, \tag{2.6.34}$$

respectively, but where we now have to be observant on the order of the orbitals in the integrals. The energy in eq. (2.6.28) may thus be written as

$$E_0 = \sum_{i=1}^{n} h_i + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\left(J_{ij} - K_{ij}\right) + V_{nn}\,, \tag{2.6.35}$$

where the minus sign for the exchange integrals arises from the $(-1)^p$ factor in eq. (2.6.28). Utilizing that the self-interaction J_{ii} is exactly cancelled by K_{ii}, see eqs. (2.6.32) and (2.6.33), eq. (2.6.35) is rewritten as

$$E_0 = \sum_{i=1}^{n} h_i + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij} - K_{ij}\right) + V_{nn}\,. \tag{2.6.36}$$

For a closed-shell system, we put two electrons in each spatial orbital but with opposite spin. As an example, we take

$$\chi_1(1) = \varphi_1(1)\alpha(1) \quad \text{and} \quad \chi_2(2) = \varphi_1(2)\beta(2) \tag{2.6.37}$$

Let us compute the exchange integral in eq. (2.6.33) for this pair of orbitals,

$$
\begin{aligned}
K_{12} &= \langle \chi_1(1)\chi_2(2)|\hat{g}(1,2)|\chi_1(2)\chi_2(1)\rangle \\
&= \langle \varphi_1(1)\varphi_2(2)|\hat{g}(1,2)|\varphi_1(2)\varphi_2(1)\rangle\langle \alpha(1)|\beta(1)\rangle\langle \alpha(2)|\beta(2)\rangle = 0 \qquad (2.6.38)
\end{aligned}
$$

which becomes zero because of the orthogonality of the spin functions, see eq. (2.5.11). Therefore half of the exchange integrals in eq. (2.6.36) vanish so that

$$
E_0 = 2\sum_{i=1}^{n/2} h_i + \sum_{i=1}^{n/2}\sum_{j=1}^{n/2}\left(2J_{ij} - K_{ij}\right) , \qquad (2.6.39)
$$

where the sums now run over the number of doubly occupied orbitals.

2.7   The variational principle

Variation theory is a method to obtain approximate solutions to the Schrödinger equation. We denote the exact wavefunction with ψ_i and an approximate trial function by $\tilde{\psi}_i$. The exact eigenenergies are denoted E_i. The energy of the trial function, $\tilde{E}_i$, is written as an expectation value,

$$
\tilde{E}_i = \frac{\langle \tilde{\psi}_i|\hat{\mathcal{H}}|\tilde{\psi}_i\rangle}{\langle \tilde{\psi}_i|\tilde{\psi}_i\rangle} , \qquad (2.7.1)
$$

which is termed the Rayleigh ratio. The *variation theorem* states (shown in exercise 2.5)

$$
\tilde{E}_0 \geq E_0 \quad \text{for any choice of } \tilde{\psi}_i , \qquad (2.7.2)
$$

where the equal sign holds only if the trial function is equal to the exact wavefunction. Consequently, the energy serves as a measure of how good the trial wavefunction is, and we search for a trial function with the lowest possible energy. An important use case of the variational principle is when the trial function is expanded in a set of m functions, ϕ_p,

$$
\tilde{\psi}_0 = \sum_{p=1}^{m} c_p \phi_p , \qquad (2.7.3)
$$

where c_p is a coefficient to be determined. The Rayleigh ratio in eq. (2.7.1) becomes

$$
\tilde{E}_0 = \frac{\displaystyle\sum_{p,q=1}^{m} c_p c_q H_{pq}}{\displaystyle\sum_{p,q=1}^{m} c_p c_q S_{pq}} , \qquad (2.7.4)
$$

where we have used the notation $H_{pq} = \langle \phi_p|\hat{\mathcal{H}}|\phi_q\rangle$ and $S_{pq} = \langle \phi_p|\phi_q\rangle$, respectively. Applying the variation theorem in eq. (2.7.2) to this trial function leads to the following conditions

$$
\frac{\partial \tilde{E}_0}{\partial c_r} = 0 \quad \forall r . \qquad (2.7.5)
$$

The result is obtained as a *secular equation* (see exercise 2.6)

$$\sum_{p=1}^{m} c_p \left(H_{pr} - \tilde{E}_0 S_{pr} \right) = 0 \quad \forall r \,, \tag{2.7.6}$$

which is fulfilled if its *secular determinant* is zero (also see exercise 2.6),

$$|\mathbf{H} - \tilde{E}_0 \mathbf{S}| = 0 \,, \tag{2.7.7}$$

where H_{pr} is a matrix element of **H** and S_{pr} is a matrix element of **S**. This method is termed the Rayleigh-Ritz method.

2.8 Perturbation theory

2.8.1 Time-independent perturbation theory

Rayleigh-Schrödinger perturbation theory (RSPT) is introduced (see e.g. (Hirschfelder et al. 1964)). The purpose is to solve the eigenvalue problem for the Hamiltonian, $\hat{\mathcal{H}}$,

$$\hat{\mathcal{H}} |\psi_k\rangle = \left(\hat{\mathcal{H}}_0 + \lambda \hat{\mathcal{H}}_1 \right) |\psi_k\rangle = \varepsilon_k |\psi_k\rangle \,, \tag{2.8.1}$$

where the Hamiltonian is divided into two parts, $\hat{\mathscr{H}}_0$ and $\hat{\mathscr{H}}_1$. It is assumed that the solutions are known for the unperturbed Hamiltonian $\hat{\mathscr{H}}_0$,

$$\hat{\mathscr{H}}_0|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}|\psi_i^{(0)}\rangle \,, \tag{2.8.2}$$

whereas $\hat{\mathscr{H}}_1$ is regarded as a perturbation and λ is an order parameter. It is thus implied that $\hat{\mathscr{H}}_1$ in some sense is small compared to $\hat{\mathscr{H}}_0$ and thus that the zeroth-order wavefunction, $\psi_k^{(0)}$, is also relatively close to the exact wavefunction, ψ_k. Both the wavefunction, ψ_k, and the energies, ε_k, are expanded in λ as

$$\varepsilon_k = \varepsilon_k^{(0)} + \lambda\varepsilon_k^{(1)} + \lambda^2\varepsilon_k^{(2)} + \ldots \qquad \text{and} \qquad |\psi_k\rangle = |\psi_k^{(0)}\rangle + \lambda|\psi_k^{(1)}\rangle + \lambda^2|\psi_k^{(2)}\rangle + \ldots \,, \tag{2.8.3}$$

where $|\psi_k^{(n)}\rangle$ and $\varepsilon_k^{(n)}$ are the nth order corrections to the wavefunction and the energy, respectively. We proceed by putting eq. (2.8.3) into the Schrödinger equation in eq. (2.8.1),

$$\left(\hat{\mathscr{H}}_0 + \lambda\hat{\mathscr{H}}_1\right)\left(|\psi_k^{(0)}\rangle + \lambda|\psi_k^{(1)}\rangle + \lambda^2|\psi_k^{(2)}\rangle + \ldots\right) =$$
$$= \left(\varepsilon_k^{(0)} + \lambda\varepsilon_k^{(1)} + \lambda^2\varepsilon_k^{(2)} + \ldots\right)\left(|\psi_k^{(0)}\rangle + \lambda|\psi_k^{(1)}\rangle + \lambda^2|\psi_k^{(2)}\rangle + \ldots\right) \,. \tag{2.8.4}$$

This equation must hold for each order n in λ^n leading to for the lowest orders:

$$n = 0 \qquad\qquad \hat{\mathscr{H}}_0|\psi_k^{(0)}\rangle \qquad\quad = \varepsilon_k^{(0)}|\psi_k^{(0)}\rangle \tag{2.8.5}$$

$$n = 1 \qquad \hat{\mathscr{H}}_0|\psi_k^{(1)}\rangle + \hat{\mathscr{H}}_1|\psi_k^{(0)}\rangle \quad = \varepsilon_k^{(0)}|\psi_k^{(1)}\rangle + \varepsilon_k^{(1)}|\psi_k^{(0)}\rangle \tag{2.8.6}$$

$$n = 2 \qquad \hat{\mathscr{H}}_0|\psi_k^{(2)}\rangle + \hat{\mathscr{H}}_1|\psi_k^{(1)}\rangle \quad = \varepsilon_k^{(0)}|\psi_k^{(2)}\rangle + \varepsilon_k^{(1)}|\psi_k^{(1)}\rangle + \varepsilon_k^{(2)}|\psi_k^{(0)}\rangle \,, \tag{2.8.7}$$

i.e. the leading term in the expansion is the zeroth-order solution in eq. (2.8.2). The normalization of $\psi_k^{(m)}$ is chosen according to *intermediate normalization* as

$$\langle\psi_k^{(m)}|\psi_k^{(n)}\rangle = \delta_{mn} \,. \tag{2.8.8}$$

The energy for each order n are obtained by projecting eqs. (2.8.5)–(2.8.7) by $\langle\psi_k^{(0)}|$, then using eq. (2.8.2) and applying the condition in eq. (2.8.8), which leads to

$$n = 1 \qquad\qquad \varepsilon_k^{(1)} = \langle\psi_k^{(0)}|\hat{\mathscr{H}}_1|\psi_k^{(0)}\rangle \tag{2.8.9}$$

$$n = 2 \qquad\qquad \varepsilon_k^{(2)} = \langle\psi_k^{(0)}|\hat{\mathscr{H}}_1|\psi_k^{(1)}\rangle \,. \tag{2.8.10}$$

The first-order correction to the energy, $\varepsilon_k^{(1)}$, is given as the expectation value of the perturbation operator, $\hat{\mathscr{H}}_1$. For obtaining a first-order correction to the wavefunction in Rayleigh-Schrödinger perturbation theory, it is expanded in the spectrum of the unperturbed wavefunction,

$$|\psi_k^{(1)}\rangle = \sum_{j=1}^{\infty} c_{kj}^{(1)}|\psi_j^{(0)}\rangle \,, \tag{2.8.11}$$

and by projecting with $\langle\psi_j^{(0)}|$, we obtain

$$\langle\psi_j^{(0)}|\psi_k^{(1)}\rangle = c_{kj}^{(1)} \,. \tag{2.8.12}$$

The intermediate normalization condition in eq. (2.8.8) gives that $c_{kk}^{(1)} = 0$, which leads to

$$|\psi_k^{(1)}\rangle = \sum_{j \neq k}^{\infty} |\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|\psi_k^{(1)}\rangle \ . \tag{2.8.13}$$

Furthermore, eq. (2.8.6) is rewritten as

$$\left(\varepsilon_k^{(0)} - \hat{\mathcal{H}}_0\right)|\psi_k^{(1)}\rangle = \left(\hat{\mathcal{H}}_1 - \varepsilon_k^{(1)}\right)|\psi_k^{(0)}\rangle \ , \tag{2.8.14}$$

which is projected by $\langle \psi_j^{(0)}|$ giving

$$\left(\varepsilon_k^{(0)} - \varepsilon_j^{(0)}\right)\langle \psi_j^{(0)}|\psi_k^{(1)}\rangle = \langle \psi_j^{(0)}|\hat{\mathcal{H}}_1|\psi_k^{(0)}\rangle \quad \text{for all } j \text{ apart from } j = k \ . \tag{2.8.15}$$

Thus $c_{kj}^{(1)}$ in eq. (2.8.12) becomes

$$c_{kj}^{(1)} = \frac{\langle \psi_j^{(0)}|\hat{\mathcal{H}}_1|\psi_k^{(0)}\rangle}{\varepsilon_k^{(0)} - \varepsilon_j^{(0)}} \quad \text{for } j \neq k \ . \tag{2.8.16}$$

The first-order correction to the wavefunction in eq. (2.8.13) may thus be written as

$$|\psi_k^{(1)}\rangle = \sum_{j \neq k}^{\infty} \frac{\langle \psi_j^{(0)}|\hat{\mathcal{H}}_1|\psi_k^{(0)}\rangle}{\varepsilon_k^{(0)} - \varepsilon_j^{(0)}}|\psi_j^{(0)}\rangle \ . \tag{2.8.17}$$

Eqs. (2.8.10) and (2.8.17) are combined to give the second-order contribution to the energy,

$$\varepsilon_k^{(2)} = \langle \psi_k^{(0)}|\hat{\mathcal{H}}_1|\psi_k^{(1)}\rangle = \sum_{j \neq k}^{\infty} \frac{\langle \psi_k^{(0)}|\hat{\mathcal{H}}_1|\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|\hat{\mathcal{H}}_1|\psi_k^{(0)}\rangle}{\varepsilon_k^{(0)} - \varepsilon_j^{(0)}} \ . \tag{2.8.18}$$

Also the second-order correction to the energy, $\varepsilon_k^{(2)}$, is thus given in terms of the solution to the zeroth-order problem in eq. (2.8.2). From eq. (2.8.18), it becomes, however, apparant where Rayleigh-Schrödinger perturbation theory fails. When $\varepsilon_k^{(0)} \approx \varepsilon_j^{(0)}$, eq. (2.8.18) diverges.

2.8.2   Time-dependent perturbation theory

We consider a time-dependent Hamiltonian, $\hat{\mathcal{H}}(t)$, partitioned as

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_0 + \lambda \hat{\mathcal{H}}_1(t) \tag{2.8.19}$$

where $\hat{\mathcal{H}}_1(t)$ is a time-dependent perturbation and λ is an order parameter as in eq. (2.8.1). $\hat{\mathcal{H}}_0$ is the time-independent Hamiltonian for the unperturbed system for which the wavefunction is stationary (see eq. (2.3.4)),

$$|\Psi_n^{(0)}(t)\rangle = e^{\frac{-i\varepsilon_n^{(0)}t}{\hbar}}|\psi_n^{(0)}\rangle = e^{-i\omega_n t}|\psi_n^{(0)}\rangle \tag{2.8.20}$$

where we introduced $\omega_n = \varepsilon_n^{(0)}/\hbar$ in the last step. The solution to the time-independent Schrödinger equation in eq. (2.1.9) is known for the Hamiltonian $\hat{\mathcal{H}}_0$,

$$\hat{\mathcal{H}}_0|\psi_n^{(0)}\rangle = \varepsilon_n^{(0)}|\psi_n^{(0)}\rangle \tag{2.8.21}$$

where $\psi_n^{(0)}$ forms an orthonormal set (see eq. (2.3.11)),

$$\langle \psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn} . \tag{2.8.22}$$

We also assume that before the perturbation is turned on (chosen as $t = 0$), we are in state p so that

$$|\Psi(0)\rangle = |\psi_p^{(0)}\rangle . \tag{2.8.23}$$

The evolution in time of the wavefunction $\Psi(t)$ is given by the time-dependent Schrödinger equation in eq. (2.1.1),

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{\mathcal{H}}(t)|\Psi(t)\rangle . \tag{2.8.24}$$

We proceed by expanding the wavefunction $\Psi(t)$ in the solutions of the unperturbed system,

$$|\Psi(t)\rangle = \sum_{n=0}^{\infty} a_n(t)|\Psi_n^{(0)}(t)\rangle = \sum_{n=0}^{\infty} a_n(t)\,e^{-i\omega_n t}|\psi_n^{(0)}\rangle , \tag{2.8.25}$$

where we used eq. (2.8.20) and $a_n(t)$ are time-dependent coefficients to be determined. We combine eqs. (2.8.25) and (2.8.24) leading to

$$\hat{\mathscr{H}}(t) \sum_{n=0}^{\infty} a_n(t) \, \mathrm{e}^{-\mathrm{i}\omega_n t} |\psi_n^{(0)}\rangle = \mathrm{i}\hbar \frac{\partial}{\partial t} \sum_{n=0}^{\infty} a_n(t) \, \mathrm{e}^{-\mathrm{i}\omega_n t} |\psi_n^{(0)}\rangle \qquad (2.8.26)$$

Using eq. (2.8.19) and the dot notation (Newton's notation) for time derivatives,

$$\dot{a}_n(t) \equiv \frac{\mathrm{d}a_n(t)}{\mathrm{d}t} \qquad (2.8.27)$$

we get

$$\sum_{n=0}^{\infty} \left(\varepsilon_n^{(0)} a_n(t) \, \mathrm{e}^{-\mathrm{i}\omega_n t} |\psi_n^{(0)}\rangle + a_n(t) \lambda \hat{\mathscr{H}}_1(t) \, \mathrm{e}^{-\mathrm{i}\omega_n t} |\psi_n^{(0)}\rangle \right) =$$

$$\sum_{n=0}^{\infty} \left(\mathrm{i}\hbar \dot{a}_n(t) \, \mathrm{e}^{-\mathrm{i}\omega_n t} |\psi_n^{(0)}\rangle + \varepsilon_n^{(0)} a_n(t) \, \mathrm{e}^{-\mathrm{i}\omega_n t} |\psi_n^{(0)}\rangle \right) \qquad (2.8.28)$$

where two of the terms cancel each other. Projecting by

$$\langle \Psi_m^{(0)}(t)| = \langle \psi_m^{(0)}| \, \mathrm{e}^{\mathrm{i}\omega_m t} \qquad (2.8.29)$$

gives

$$\sum_{n=0}^{\infty} a_n(t) \langle \psi_m^{(0)}| \lambda \hat{\mathscr{H}}_1(t) |\psi_n^{(0)}\rangle \, \mathrm{e}^{\mathrm{i}\omega_{mn} t} = \mathrm{i}\hbar \dot{a}_m(t) \, , \qquad (2.8.30)$$

where $\omega_{mn} = \omega_m - \omega_n$ and we have used the orthonormality condition in eq. (2.8.22). We expand the time-dependent coefficients $a_n(t)$ in the order parameter λ,

$$a_n(t) = \sum_{i=0}^{\infty} \lambda^i a_n^{(i)}(t) \, . \qquad (2.8.31)$$

After substituting eq. (2.8.31) into eq. (2.8.30), the resulting equation has to hold for each order of $\lambda^i, i = 0, 1, \ldots, \infty$. For $i = 0$, we get the unperturbed and time-independent wavefunction so $a_n^{(0)} = \delta_{pn}$ from eq. (2.8.23). For $i = 1$, we get

$$\mathrm{i}\hbar \dot{a}_m^{(1)}(t) = \sum_{n=0}^{\infty} a_n^{(0)} \langle \psi_m^{(0)}(t)| \hat{\mathscr{H}}_1(t) |\psi_n^{(0)}\rangle \, \mathrm{e}^{\mathrm{i}\omega_{mn} t} = \langle \psi_m^{(0)}| \hat{\mathscr{H}}_1(t) |\psi_p^{(0)}\rangle \, \mathrm{e}^{\mathrm{i}\omega_{mp} t} \, , \qquad (2.8.32)$$

where we in the last step have used that $a_n^{(0)} = \delta_{pn}$. We can integrate this equation, assuming that the perturbation is turned on at $t = 0$, as

$$a_m^{(1)}(t) - a_m^{(1)}(0) = \frac{-\mathrm{i}}{\hbar} \int_0^t \langle \psi_m^{(0)}| \hat{\mathscr{H}}_1(t') |\psi_p^{(0)}\rangle \, \mathrm{e}^{\mathrm{i}\omega_{mp} t'} \, \mathrm{d}t' \, , \qquad (2.8.33)$$

where $a_m^{(1)}(0) = 0$ is given by the initial condition at $t = 0$ in eq. (2.8.23) and $a_m^{(0)}(0) = \delta_{mp}$. If $\hat{\mathscr{H}}_1(t)$ is of the form $\hat{\mathscr{H}}_1(t) = \hat{V} f(t)$ where $\hat{V}$ is independent of time and $f(t)$ is a function of time only,

$$a_m^{(1)}(t) = \frac{-\mathrm{i}}{\hbar} \langle \psi_m^{(0)}| \hat{V} |\psi_p^{(0)}\rangle \int_0^t f(t') \, \mathrm{e}^{\mathrm{i}\omega_{mp} t'} \, \mathrm{d}t' \, . \qquad (2.8.34)$$
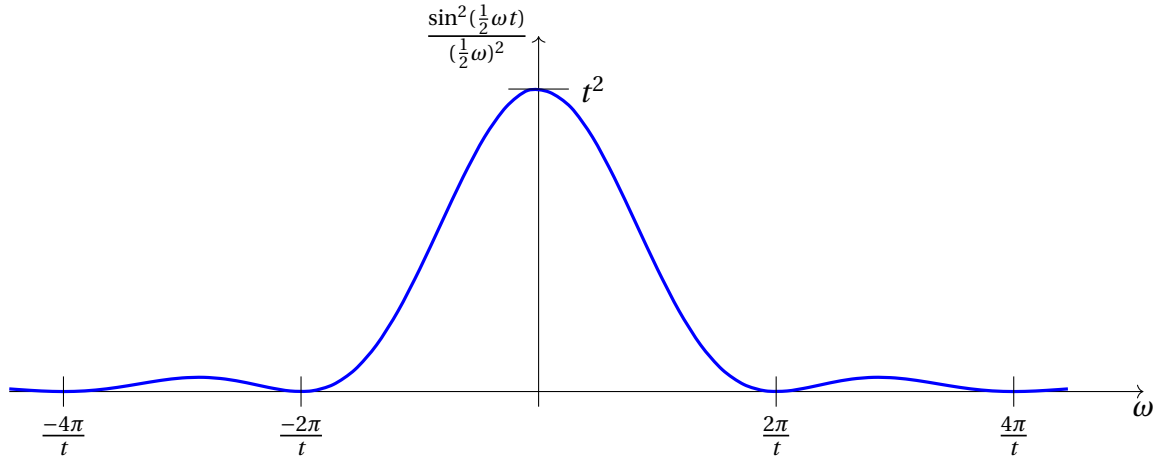
Figure 2.4: The probability $\frac{\sin^2(\frac{1}{2}\omega t)}{(\frac{1}{2}\omega)^2}$ versus ω. It is noted that the central peak grows as t^2 and narrows as $1/t$.

If the wavefunction in eq. (2.8.25) is normalized,

$$\int \Psi^*(t)\Psi(t)\,\mathrm{d}\tau = \sum_{m=0}^{\infty} |a_m(t)|^2 = 1 \,, \tag{2.8.35}$$

where $|a_m(t)|^2$ has the interpretation of being the probability, $P_{p\to m}(t)$, of the system being in state m at time t if it was in state p at $t = 0$,

$$P_{p\to m}(t) = |a_m(t)|^2 \,. \tag{2.8.36}$$

Further developments depend on the form of $f(t)$, where examples are Fermi's golden rule in section 2.8.2.1 and the frequency-dependent polarizability in section 2.9.4.

2.8.2.1 Fermi's golden rule

If it is assumed that the perturbation, $\hat{\mathscr{H}}_1(t)$, is independent of time apart from being turned on at $t = 0$, we have from eq. (2.8.34) that $f(t') = 1$ leading to (see exercise 2.13)

$$a_m^{(1)}(t) = -\frac{\langle \psi_m^{(0)} | \hat{V} | \psi_p^{(0)} \rangle}{\hbar} \frac{\mathrm{e}^{\mathrm{i}\omega_{mp}t} - 1}{\omega_{mp}} \,, \quad m \neq p \,. \tag{2.8.37}$$

Utilizing eq. (2.8.35) to first order in λ, we get (see exercise 2.14)

$$P_{p\to m}^{(1)}(t) = |a_m^{(1)}(t)|^2 = 4|\langle \psi_m^{(0)} | \hat{V} | \psi_p^{(0)} \rangle|^2 \frac{\sin^2(\frac{1}{2}\omega_{mp}t)}{\hbar^2 \omega_{mp}^2} \,, \quad m \neq p \,, \tag{2.8.38}$$

which is the first-order probability for the transition from state p to state m. This probability is shown as a function of ω_{mp} in Figure 2.4, where the most likely transitions are to states whose energies lie under the central peak. Since this peak is given by the first zeros of $\sin(x)$, the energies of the most probable states satisfy

$$\hbar\omega_{mp} = |E_p - E_m| < \frac{2\pi\hbar}{t} \,. \tag{2.8.39}$$

Furthermore, it is supposed that there is a continuum of states around state m, and that we would like to know the probability of the transition into this group of states rather than into a single state m. Let us assume that $|\langle\psi_m^{(0)}|\hat{V}|\psi_p^{(0)}\rangle|^2$ is a smooth and slowly varying function of m and let $\rho(E_m)$ be the density of states around E_m. The probability of a transition from state p to a state around m becomes

$$P_{p\to m}^{(1)}(t) = |\langle\psi_m^{(0)}|\hat{V}|\psi_p^{(0)}\rangle|^2 \int_* \rho(E_m) \frac{\sin^2\left(\frac{\omega_{mp}t}{2}\right)}{\left(\frac{\omega_{mp}}{2}\right)^2}\, \mathrm{d}E_m \qquad (2.8.40)$$

where $\mathrm{d}E_m = \hbar\,\mathrm{d}\omega_\mathrm{m}$ and the asterisk indicates that we integrate only over a small region around E_m. For large enough t, the central peak will include all the states around E_m. If we also assume that $\rho(E_m)$ is a slowly varying function of E_m, we get

$$P_{p\to m}^{(1)}(t) = |\langle\psi_m^{(0)}|\hat{V}|\psi_p^{(0)}\rangle|^2 \rho(E_m) \int_* \frac{\sin^2\left(\frac{\omega_{mp}t}{2}\right)}{\left(\frac{\omega_{mp}}{2}\right)^2}\, \mathrm{d}E_m \qquad (2.8.41)$$

For large t the area under the central peak is essentially all the area and we can extend the limits to $\pm\infty$ and use

$$\int_{-\infty}^{\infty} \frac{\sin^2(x)}{x^2}\, \mathrm{d}x = \pi \qquad (2.8.42)$$

The probability is written in terms of the transition rate Γ as

$$P_{p\to m}^{(1)}(t) = \Gamma t \qquad (2.8.43)$$

so that

$$\Gamma = \frac{2\pi}{\hbar} |\langle\psi_m^{(0)}|\hat{V}|\psi_p^{(0)}\rangle|^2 \rho(E_m)\,, \qquad \text{where } |E_p - E_m| < \frac{2\pi\hbar}{t}\,, \qquad (2.8.44)$$

which is known as *Fermi's golden rule*. A similar result may be obtained by noting that as t becomes large the probability in figure 2.4 becomes more and more peaked around $E_m = E_p$. Since it has the total area $2\pi t/\hbar$, it therefore approaches $\frac{2\pi t}{\hbar}\delta(E_p - E_m)$ apart from negligible oscillations in the wings. We thus have

$$\Gamma = \frac{2\pi}{\hbar} |\langle\psi_m^{(0)}|\hat{V}|\psi_p^{(0)}\rangle|^2 \delta(E_p - E_m) \qquad (2.8.45)$$

as an alternative form of Fermi's golden rule.

2.8.3 Use cases for perturbation theory

In this text, we will use perturbation theory in several different ways. In general we partition the Hamiltonian $\hat{\mathscr{H}}$ in eq. (2.8.1) into

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \lambda\hat{\mathscr{H}}_1\,, \qquad (2.8.46)$$

where we can solve the Schrödinger equation for $\hat{\mathscr{H}}_0$ and we regard $\hat{\mathscr{H}}_1$ as a perturbation. The first application area is presented in section 2.9 when $\hat{\mathscr{H}}_0$ is the molecular Hamiltonian

in eq. (2.4.2) and $\hat{\mathcal{H}}_1$ is the interaction with an electric field, i.e. the perturbation in eq. (2.8.46) is a physical perturbation of the system.

Secondly, if we are not able to solve the Schrödinger equation for the Hamiltonian $\hat{\mathcal{H}}$ but instead we have a solution for an approximate Hamiltonian $\hat{\mathcal{H}}_0$, we can regard the difference between the exact and the approximate Hamiltonian as a perturbation,

$$\hat{\mathcal{H}}_1 = \hat{\mathcal{H}} - \hat{\mathcal{H}}_0 \,, \tag{2.8.47}$$

and apply perturbation theory to include corrections to $\hat{\mathcal{H}}_0$. The typical example is that we cannot solve the Schrödinger equation for the molecular Hamiltonian in eq. (2.4.2). Rather we introduce the Hartree-Fock approximation as in section 2.10, and in section 2.12.2 we use perturbation theory to correct for the Hartree-Fock approximation in Møller-Plesset perturbation theory.

Finally in a very similar use case, we do a Taylor expansion of the Hamiltonian around $\hat{\mathcal{H}}_0$,

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \sum_{n=1}^{\infty} \frac{1}{n!} \lambda^n \hat{\mathcal{H}}_n \,, \tag{2.8.48}$$

where we again assume that we can solve the Schrödinger equation for $\hat{\mathcal{H}}_0$ and we include $\hat{\mathcal{H}}_n$ as perturbations order by order. Here the standard example is vibrational motion in molecules where we do a Taylor example of the potential energy surface, and $\hat{\mathcal{H}}_0$ is

the harmonic oscillator, given for a diatomic molecule in appendix 2.A.2, and the leading correction from perturbation theory arises from the anharmonicity of the potential energy surface.

2.9   First and second-order electric properties

2.9.1   Multipole expansion

The starting point is classical electrostatics where we regard a set of point charges interacting with a test charge. The interaction energy, V, between a charge distribution described by a set of N point charges, q_i, and a test charge, q_t is given by Coulomb's law as (using atomic units)

$$V = \sum_{i=1}^{N} \frac{q_i q_t}{R_{it}} \, , \tag{2.9.1}$$

where R_{it} is the distance between particles i and t. Note that the Coulomb interactions within the set of N point charges are not included in eq. (2.9.1). The electrostatic potential in a point t, φ_t, is *defined* from the interaction energy V obtained by placing a test charge q_t in point t,

$$V = q_t \varphi_t \, , \tag{2.9.2}$$

which leads to the following definition of the electrostatic potential in point t from the charge distribution,

$$\varphi_t = \sum_{i=1}^{N} \frac{q_i}{R_{it}} \tag{2.9.3}$$

Consequently, the electrostatic potential at point charge i, φ_i, arising from the test charge, t, is given as

$$\varphi_i = \frac{q_t}{R_{it}} \tag{2.9.4}$$

so that the potential energy can be written as

$$V = \sum_{i=1}^{N} \varphi_i q_i \, . \tag{2.9.5}$$

The next step is to carry out a *multipole expansion*, i.e. a Taylor expansion of the electrostatic potential at each point i around a common origin where it is assumed that $|\vec{R}_{Oi}| \ll |\vec{R}_{tO}|$ for the Taylor expansion to converge rapidly. For a Taylor expansion in Cartesian coordinates, the electrostatic potential at particle i, φ_i, becomes (see figure 2.5)

$$
\begin{aligned}
\varphi_i \;\; &= \;\; \frac{q_t}{|\vec{R}_{ti}|} = \frac{q_t}{|\vec{R}_{tO} + \vec{R}_{Oi}|} \\[2mm]
&= \;\; \varphi_O + R_{i,\alpha} \nabla_{i,\alpha} \varphi_O + \frac{1}{2} R_{i,\alpha} R_{i,\beta} \nabla_{i,\beta} \nabla_{i,\alpha} \varphi_O + \dots \\[2mm]
&= \;\; \varphi_O^{(0)} + R_{i,\alpha} \varphi_{O,\alpha}^{(1)} + \frac{1}{2} R_{i,\alpha} R_{i,\beta} \varphi_{O,\alpha\beta}^{(2)} + \dots \\[2mm]
&= \;\; \sum_{m=0}^{\infty} \frac{1}{m!} R_{i,\alpha_1} \dots R_{i,\alpha_m} \varphi_{O,\alpha_1 \dots \alpha_m}^{(m)} \, ,
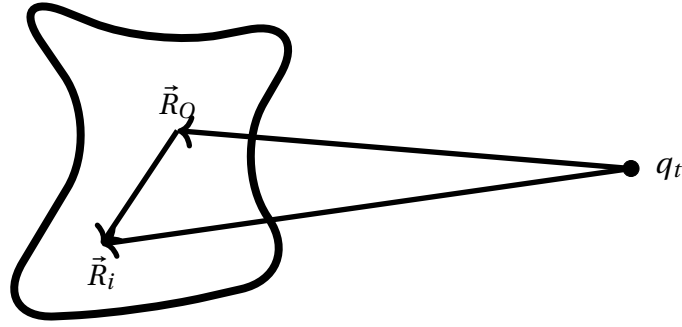\end{aligned}
\tag{2.9.6}
$$

Figure 2.5: Molecular multipole expansion. For each particle (electron or nucleus) i, a Taylor expansion of the electrostatic potential is carried out around a common origin $\vec{R}_O$. Note that $\vec{R}_i$ is used to denote a *point* so that the distance vector is given by $\left(\vec{R}_i - \vec{R}_O\right)$. In general, the explicit reference to the origin is however dropped and thus $\vec{R}_i$ may be interpreted both as the point and the distance vector. The explicit reference to the origin is only needed in a few cases, for example to investigate the origin dependence of molecular properties (see exercises 2.7 and 2.8).

where φ_O (also written as $\varphi_O^{(0)}$) is the electrostatic potential evaluated at the origin $\vec{R}_O$ given as $q_t/|\vec{R}_{tO}|$ and $\varphi_{O,\alpha_1...\alpha_m}^{(m)}$ is the mth derivative of the electrostatic potential with respect to a Cartesian coordinate x, y or z calculated at the origin O. The Einstein summation convention is used for the subscripts α and β denoting the Cartesian coordinates x, y and z. In the last line of eq. (2.9.6), a special notation is used for $m = 0$, where the whole term is reduced to $\varphi_O^{(0)}$. Using the Taylor expansion of the electrostatic potential in eq. (2.9.6), the interaction energy, V, in eq. (2.9.1) becomes

$$
\begin{aligned}
V &= \sum_{i=1}^{N} q_i \varphi_O + q_i R_{i,\alpha} \varphi_{O,\alpha}^{(1)} + \frac{1}{2} q_i R_{i,\alpha} R_{i,\beta} \varphi_{O,\alpha\beta}^{(2)} + \dots \\
&= \left(\sum_{i=1}^{N} q_i\right) \varphi_O + \left(\sum_{i=1}^{N} q_i R_{i,\alpha}\right) \varphi_{O,\alpha}^{(1)} + \frac{1}{2} \left(\sum_{i=1}^{N} q_i R_{i,\alpha} R_{i,\beta}\right) \varphi_{O,\alpha\beta}^{(2)} + \dots \\
&= q^{\text{mol}} \varphi_O + \mu_\alpha^{\text{mol}} \varphi_{O,\alpha}^{(1)} + \frac{1}{2} Q_{\alpha\beta}^{\text{mol}} \varphi_{O,\alpha\beta}^{(2)} + \dots \\
&= \sum_{m=0}^{\infty} \frac{1}{m!} M_{\alpha_1...\alpha_m}^{(m)} \varphi_{O,\alpha_1...\alpha_m}^{(m)} ,
\end{aligned}
\tag{2.9.7}
$$

where an electric moment of order m, $M_{\alpha_1...\alpha_m}^{(m)}$, is defined as

$$
M_{\alpha_1...\alpha_m}^{(m)} = \sum_{i=1}^{N} M_{i,\alpha_1...\alpha_m}^{(m)} = \sum_{i=1}^{N} q_i \prod_{p=1}^{m} R_{i,\alpha_p} .
\tag{2.9.8}
$$

In particular, the charge, q ($m = 0$), the dipole moment, μ_α ($m = 1$), and the second moment, $Q_{\alpha\beta}$ ($m = 2$), are defined as

$$
q = \sum_{i=1}^{N} q_i , \qquad \mu_\alpha = \sum_{i=1}^{N} q_i R_{i,\alpha} , \qquad Q_{\alpha\beta} = \sum_{i=1}^{N} q_i R_{i,\alpha} R_{i,\beta} .
\tag{2.9.9}
$$

The electric field, $E_{k,\alpha}$, in point k is defined as minus the gradient of the electrostatic potential in the same point k,

$$
E_{k,\alpha} = -\varphi_{k,\alpha}^{(1)} ,
\tag{2.9.10}
$$

which is consistent with the definition of the force as $F_\alpha = -\nabla_\alpha V$, so that the electric field is the force acting on a particle with unit charge. The electric field gradient, $E_{k,\alpha\beta}$, is trivially defined as

$$E_{k,\alpha\beta} = -\varphi_{k,\alpha\beta}^{(2)} , \qquad (2.9.11)$$

and in general the m-th derivative of the electric field, $E_{k,\alpha_1...\alpha_m}$, is defined as

$$E_{k,\alpha_1...\alpha_m} = -\varphi_{k,\alpha_1...\alpha_m}^{(m)} . \qquad (2.9.12)$$

The interaction energy in eq. (2.9.7) is written in terms of the electric field as

$$V = q\varphi_O - \sum_{m=1}^{\infty} \frac{1}{m!} M_{\alpha_1...\alpha_m}^{(m)} E_{O,\alpha_1...\alpha_m}^{(m)} . \qquad (2.9.13)$$

The electrostatic potential at the origin, φ_O, from a point charge, q_t, is given by using eq. (2.9.4) as

$$\varphi_O = \frac{q_t}{R_{Ot}} = q_t T^{(0)}(R_{Ot}) , \qquad (2.9.14)$$

where the T-tensor (or interaction tensor) of rank 0 is defined as

$$T^{(0)}(R_{ij}) = \frac{1}{R_{ij}} . \qquad (2.9.15)$$

We now introduce the more compact notation,

$$T^{(0)}(R_{ij}) \equiv T^{(0)}_{ij} \; . \tag{2.9.16}$$

The gradients of the potential as well as the electric field and its gradients are thus obtained from the gradients of the T-tensor. The T-tensor of rank 1 is defined as

$$T^{(1)}_{ij,\alpha} \equiv \nabla_{j,\alpha} T^{(0)}_{ij} = \nabla_{j,\alpha} \frac{1}{R_{ij}} = \frac{-R_{ij,\alpha}}{R^3_{ij}} \; , \tag{2.9.17}$$

where $R_{ij,\alpha}$ is a component of the vector connecting particles i and j, $R_{ij,\alpha} = R_{j,\alpha} - R_{i,\alpha}$.

Example 2.1: Force on a point charge

Since the potential energy V for a charge q_j in an electrostatic potential φ_j is given by eq. (2.9.5) as $V = q_j \varphi_j$, the force $F_{j,\alpha}$ is given as

$$F_{j,\alpha} = -\nabla_{j,\alpha} V = q_j E_{j,\alpha} \tag{2.9.18}$$

where we in the second step have used the definition of the electric field in eq. (2.9.10), the electric field is the force on a point charge with the value $+1$. If the electrostatic potential arises from a charge q_i

$$F_{j,\alpha} = -\nabla_{j,\alpha} q_i T^{(0)}_{ij} q_j = -q_i T^{(1)}_{ij,\alpha} q_j \tag{2.9.19}$$

so that

$$E_{j,\alpha} = -q_i T^{(1)}_{ij,\alpha} \tag{2.9.20}$$

Since $R_{ij,\alpha} = -R_{ji,\alpha}$, we have

$$T^{(1)}_{ji,\alpha} = -T^{(1)}_{ij,\alpha} \; . \tag{2.9.21}$$

The T-tensor of rank 2 is consequently given as

$$T^{(2)}_{ij,\alpha\beta} = \nabla_{j,\beta} T^{(1)}_{ij,\alpha} = \frac{3R_{ij,\alpha} R_{ij,\beta} - \delta_{\alpha\beta} R^2_{ij}}{R^5_{ij}} \; , \tag{2.9.22}$$

where $\delta_{\alpha\beta}$ is the Kroenecker delta function. The $T^{(2)}$-tensor is traceless,

$$T^{(2)}_{ij,\alpha\alpha} = T^{(2)}_{ij,xx} + T^{(2)}_{ij,yy} + T^{(2)}_{ij,zz} = 0 \; . \tag{2.9.23}$$

We also have

$$T^{(3)}_{ij,\alpha\beta\gamma} = -\frac{1}{R^7_{ij}} \left(15 R_{ij,\alpha} R_{ij,\beta} R_{ij,\gamma} - 3R^2_{ij} \left(R_{ij,\alpha} \delta_{\beta\gamma} + R_{ij,\beta} \delta_{\alpha\gamma} + R_{ij,\gamma} \delta_{\alpha\beta} \right) \right) , \tag{2.9.24}$$

and

$$
\begin{aligned}
T_{ij,\alpha\beta\gamma\delta}^{(4)} \;=\;\; & \frac{1}{R_{ij}^9} \Big(105 R_{ij,\alpha} R_{ij,\beta} R_{ij,\gamma} R_{ij,\delta} \\
- \;\; & 15 R_{ij}^2 \Big(R_{ij,\alpha} R_{ij,\beta}\delta_{\gamma\delta} + R_{ij,\alpha} R_{ij,\gamma}\delta_{\beta\delta} + R_{ij,\alpha} R_{ij,\delta}\delta_{\beta\gamma} \\
+ \;\; & R_{ij,\beta} R_{ij,\gamma}\delta_{\alpha\delta} + R_{ij,\beta} R_{ij,\delta}\delta_{\alpha\gamma} + R_{ij,\gamma} R_{ij,\delta}\delta_{\alpha\beta} \Big) \\
+ \;\; & 3 R_{ij}^4 \Big(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} \Big) \Big) \, .
\end{aligned}
\tag{2.9.25}
$$

In general, we have

$$
T_{ij,\alpha_1\ldots\alpha_n}^{(n)} = \nabla_{j,\alpha_n}\ldots\nabla_{j,\alpha_1}\left(\frac{1}{R_{ij}}\right) .
\tag{2.9.26}
$$

Eqs. (2.9.21) and eq. (2.9.23) are generalized to

$$
T_{ji,\alpha_1\ldots\alpha_n}^{(n)} = (-1)^n \, T_{ij,\alpha_1\ldots\alpha_n}^{(n)} \qquad \text{and} \qquad T_{ij,\alpha_1\ldots\alpha_m\alpha_m\ldots\alpha_n}^{(n)} = 0 \, .
\tag{2.9.27}
$$

Normally, the second moment in eq. (2.9.9) is instead given as its traceless counterpart, the quadrupole moment. As an illustration, the interaction energy, V, between a test charge, q_t, and the second moment of the charge distribution is regarded,

$$
V = \frac{1}{2} Q_{O,\alpha\beta} T_{Ot,\alpha\beta}^{(2)} q_t \, .
\tag{2.9.28}
$$

A constant contribution, Δ, is added to each of the diagonal terms of $Q_{O,\alpha\beta}$,

$$
\tilde{Q}_{O,\alpha\beta} = Q_{O,\alpha\beta} + \Delta\,\delta_{\alpha\beta} \, ,
\tag{2.9.29}
$$

The modified interaction energy, $\tilde{V}$, becomes

$$
\tilde{V} = V + \frac{1}{2}\Delta\,\delta_{\alpha\beta} T_{Ot,\alpha\beta}^{(2)} q_t = V + \frac{1}{2}\Delta\, T_{Ot,\alpha\alpha}^{(2} q_t = V \, ,
\tag{2.9.30}
$$

where we have used that the $T^{(2)}$-tensor is traceless (eq. (2.9.23)). It is thus noted that the trace of the second moment does not contribute to the interaction energy since Δ can be chosen as

$$
\Delta = -\frac{1}{3} Q_{\gamma\gamma} \, .
\tag{2.9.31}
$$

Therefore, the quadrupole moment is defined as (Buckingham 1967)

$$
\Theta_{\alpha\beta} = \frac{3}{2} Q_{\alpha\beta} - \frac{1}{2} Q_{\gamma\gamma}\delta_{\alpha\beta} \, ,
\tag{2.9.32}
$$

where a factor of $3/2$ is introduced to be consistent with the literature. Since the quadrupole moment is traceless, it only contains five independent components. This is equivalent to d-orbitals for describing atomic orbitals, where we have five orbitals in spherical polar coordinates as compared to six d-orbitals in Cartesian coordinates. Similarly, the quadrupole moment describes a second-order shape/anisotropy of the charge distribution, and the term $\left(x^2 + y^2 + z^2\right)$ is isotropic.

2.9.1.1 Units

Even if SI units are recommended, they are often not suitable in chemistry since they become inconviently large or small. A typical length of a covalent bond is in the order of 0.1 nm, which indeed would be a suitable unit, but historically we instead use ångström (1 Å = 0.1 nm) so a typical bond length is around 1-2 Å. In quantum chemistry, we also commonly use the atomic unit system, which was introduced in table 2.1, where for example the charge of an electron is -1.

For dipole moments, we normally use the unit debye, which is a CGS unit and also has its origin in the electrostatic unit (esu) system. 1 D is the dipole moment of two charges with different sign, but equal magnitude of 0.2081943 e, separated by 1 Å. The conversion factor from atomic units thus becomes 1 $e \cdot$ bohr = 2.541766 D. In SI units, we have 1 D = $3.33564 \cdot 10^{-30}$ C·m. A typical molecular dipole moment is of the magnitude $1 - 10$ D. Using the smallest available SI prefix yocto for $1 \cdot 10^{-24}$, would still mean that the magnitude of a typical molecular dipole moment would be around $1 \cdot 10^{-6}$ yC·m, illustrating what we above meant with "inconviently small".

For quadrupole moments, the buckingham unit is used, where 1 B = 1 DÅ, i.e. the quadrupole moment of two dipoles of the magnitude 1 D, but opposing directions, placed with a distance 1 Å from each other. The conversion factor from atomic units becomes 1 $e \cdot$ bohr^2 = 1.344911 B.
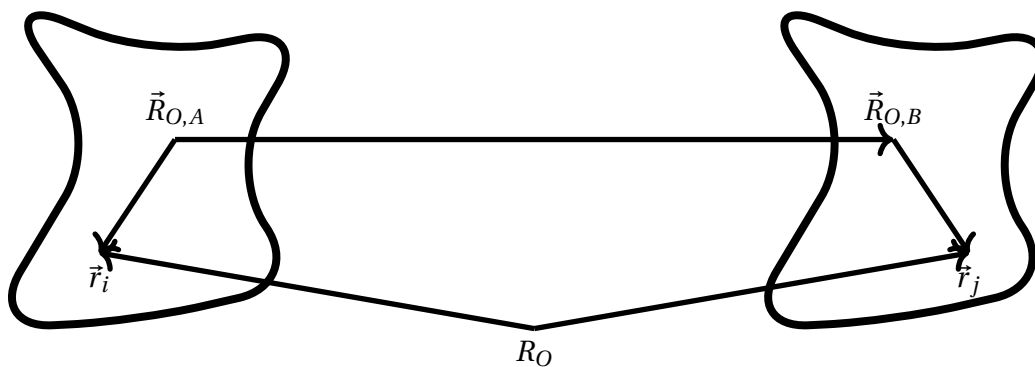
Figure 2.6: Molecular multipole expansions for intermolecular interactions. The distance vector $\vec{R}_{AB}$ is defined as $\vec{R}_{AB} = \vec{R}_{O,B} - \vec{R}_{O,A}$. Furthermore, $\vec{R}_j = \vec{r}_j - \vec{R}_O$ and $\vec{R}_i = \vec{r}_i - \vec{R}_O$.

2.9.1.2   Multipole expansion of two interacting molecules

Two charge distributions, *A* and *B*, are considered, where system *A* has N_A point charges and system *B* has N_B point charges. The Coulomb interaction energy *between* the two charge distributions is

$$V_{AB} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{|\vec{R}_j - \vec{R}_i|} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{|\vec{r}_j - \vec{r}_i + \vec{R}_{AB}|} \tag{2.9.33}$$

where the distance vectors are defined in figure 2.6. If $\vec{r}_i$ and $\vec{r}_j$ are small compared to $\vec{R}_{AB}$, a multipole expansion may be carried out around $\vec{r}_i = 0$ and $\vec{r}_j = 0$. The multipole expansion of two interacting charge distributions becomes

$$
\begin{aligned}
V_{AB} &= \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{|\vec{r}_j - \vec{r}_i + \vec{R}|} \\
&= \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \Bigg(q_i T_{AB}^{(0)} q_j + q_i T_{AB,\alpha}^{(1)} q_j r_{j,\alpha} + \frac{1}{2} q_i T_{AB,\alpha\beta}^{(2)} q_j r_{j,\alpha} r_{j,\beta} + \dots \\
&\quad - q_i r_{i,\alpha} T_{AB,\alpha}^{(1)} q_j - q_i r_{i,\alpha} T_{AB,\alpha\beta}^{(2)} q_j r_{j,\beta} - \frac{1}{2} q_i r_{i,\alpha} T_{AB,\alpha\beta\gamma}^{(3)} q_j r_{j,\beta} r_{j,\gamma} + \dots \\
&\quad + \frac{1}{2} q_i r_{i,\alpha} r_{i,\beta} T_{AB,\alpha\beta}^{(2)} q_j + \frac{1}{2} q_i r_{i,\alpha} r_{i,\beta} T_{AB,\alpha\beta\gamma}^{(3)} q_j r_{j,\gamma} \\
&\quad + \frac{1}{4} q_i r_{i,\alpha} r_{i,\beta} T_{AB,\alpha\beta\gamma\delta}^{(4)} q_j r_{j,\gamma} r_{j,\delta} + \dots \Bigg),
\end{aligned}
\tag{2.9.34}
$$

where the definition of the *T*-tensor in eq. (2.9.21) has been adopted. It is noted that minus sign appearing in the linear terms in $r_{i,\alpha}$ (and subsequently also for other odd order terms in $r_{i,\alpha}$) arises from the definition of $\vec{R}_{AB} = \vec{R}_{O,B} - \vec{R}_{O,A}$ as pointing from $\vec{R}_{O,A}$ to $\vec{R}_{O,B}$ (see figure 2.6). Defining an electric moment of order *m* as in eq. (2.9.8), eq. (2.9.34) can be rewritten as,

$$V_{AB} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{|\vec{r}_j - \vec{r}_i + \vec{R}|} = \sum_{m,n=0}^{\infty} \frac{(-1)^m}{m! n!} M_{i,\alpha_1\dots\alpha_m}^{(m)} T_{AB,\alpha_1\dots\alpha_{m+n}}^{(m+n)} M_{j,\alpha_{m+1}\dots\alpha_{m+n}}^{(n)}. \tag{2.9.35}$$

2.9.2   Polarizability in an external field

The dipole-dipole polarizability, $\alpha_{\alpha\beta}$, is defined as the linear response to an electric field, E_β, (Buckingham 1967)

$$\mu_\alpha^{\text{ind}} = \alpha_{\alpha\beta} E_\beta \,, \tag{2.9.36}$$

where μ_α^{ind} is the induced dipole moment. Frequently, we use a model of representing a molecular systems by a set of point particles, and we denote the polarizability for particle i as $\alpha_{i,\alpha\beta}$. Analogously to eq. (2.9.36), we define $\alpha_{i,\alpha\beta}$ by

$$\mu_{i,\alpha}^{\text{ind}} = \alpha_{i,\alpha\beta} E_{i,\beta} \,, \tag{2.9.37}$$

where $\mu_{i,\alpha}^{\text{ind}}$ is the induced dipole moment of particle i and $E_{i,\beta}$ is the local electric field at particle i. The electrostatic interaction energy, V_{ele}, between a dipole moment and an electric field is given in eq. (2.9.7) as

$$V_{\text{ele}} = -\mu_\beta^{\text{ind}} E_\beta \,. \tag{2.9.38}$$

In classical theory, there is, however, an additional energy term arising from the work required to create the induced dipole moment, the self-energy V_{self}. The polarizability describes the mobility of charges within a charge distribution. The work V_{self} required to move a charge, q, in an external force, F_β, is

$$V_{\text{self}} = \int_0^{\vec{R}} F_\beta \, \mathrm{d}R_\beta \,. \tag{2.9.39}$$

Using that the force is $F_\beta = qE_\beta$ and the induced dipole moments is $\mathrm{d}\mu_\beta^{\text{ind}} = q\,\mathrm{d}R_\beta$ gives

$$V_{\text{self}} = \int_0^{\vec{\mu}^{\text{ind}}} E_\beta \, \mathrm{d}\mu_\beta^{\text{ind}} \overset{(2.9.36)}{=} \int_0^{\vec{\mu}^{\text{ind}}} \left(\alpha_{\alpha\beta}\right)^{-1} \mu_\alpha^{\text{ind}} \, \mathrm{d}\mu_\beta^{\text{ind}} = \frac{1}{2}\left(\alpha_{\alpha\beta}\right)^{-1} \mu_\alpha^{\text{ind}} \mu_\beta^{\text{ind}} = \frac{1}{2}\mu_\beta^{\text{ind}} E_\beta \,, \tag{2.9.40}$$

where we have used partial integration in the second last step (see exercise 2.9). The total energy termed the induction energy, V_{ind}, is the sum of the electrostatic energy and the self-energy,

$$V_{\text{ind}} = -\mu_\beta^{\text{ind}} E_\beta + \frac{1}{2}\mu_\beta^{\text{ind}} E_\beta = -\frac{1}{2}\mu_\beta^{\text{ind}} E_\beta = -\frac{1}{2}\alpha_{\alpha\beta} E_\beta E_\alpha \,. \tag{2.9.41}$$

The self-energy thus cancels exactly half of the electrostatic energy. It is furthermore noted that the induction energy is quadratic in the electric field.

2.9.3   A molecule in an external potential

2.9.3.1   Dipole and quadrupole moment

To study a molecule in an external electrostatic potential, Rayleigh-Schrödinger perturbation theory (see section 2.8.1) is adopted. The Hamiltonian for a molecule in an external potential may be written as

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_{\text{mol}} + \lambda\hat{V} \,, \tag{2.9.42}$$

where $\hat{\mathscr{H}}_{\text{mol}}$ is the molecular Hamiltonian discussed in section 2.2, λ is an order parameter that determines the order in the perturbation expansion, and $\hat{V}$ is the interaction operator between a molecular charge distribution and an external electrostatic potential,

$$\hat{V} = \sum_{I=1}^{N} Z_I \varphi_I - \sum_{i=1}^{n} \varphi_i \, , \tag{2.9.43}$$

where the minus sign arises from the charge of the electron. As in section 2.2, we regard a molecule consisting of N nuclei and n electrons. Using the multipole expansion of the electrostatic potential in eq. (2.9.6), the interaction operator in eq. (2.9.43) becomes

$$\hat{V} = \sum_{m=0}^{\infty} \frac{1}{m!} \left(\sum_{I=1}^{N} Z_I R_{I,\alpha_1} \dots R_{I,\alpha_m} - \sum_{i=1}^{n} r_{i,\alpha_1} \dots r_{i,\alpha_m} \right) \varphi_{O,\alpha_1 \dots \alpha_m}^{(m)} \, . \tag{2.9.44}$$

The operator for a molecular electronic moment is identified as

$$\hat{\mathscr{M}}_{\alpha_1 \dots \alpha_m}^{(m)} = \sum_{I=1}^{N} Z_I \prod_{p=1}^{m} R_{I,\alpha_p} - \sum_{i=1}^{n} \prod_{p=1}^{m} r_{i,\alpha_p} \, . \tag{2.9.45}$$

Consequently, the first-order energy in eq. (2.8.9) using Rayleigh-Schrödinger perturbation theory becomes

$$\varepsilon_0^{(1)} = \langle \psi_0^{(0)} | \hat{V} | \psi_0^{(0)} \rangle = \sum_{m=0}^{\infty} \frac{1}{m!} \langle \psi_0^{(0)} | \hat{\mathscr{M}}_{\alpha_1 \dots \alpha_m}^{(m)} | \psi_0^{(0)} \rangle \varphi_{O,\alpha_1 \dots \alpha_m}^{(m)} \, . \tag{2.9.46}$$

By comparison to eq. (2.9.7), the molecular charge, q^{mol}, $(m = 0)$ is trivially given as

$$q^{\text{mol}} = \sum_{I=1}^{N} Z_I - n \, , \tag{2.9.47}$$

the molecular dipole moment, μ_α^{mol}, $(m = 1)$ is identified as

$$\mu_\alpha^{\text{mol}} = \sum_{I=1}^{N} Z_I R_{I,\alpha} + \langle \psi_0^{(0)} | - \sum_{i=1}^{n} r_{i,\alpha} | \psi_0^{(0)} \rangle \, , \tag{2.9.48}$$

and the molecular second moment, $Q_{\alpha\beta}^{\text{mol}}$, $(m = 2)$ is identified as

$$Q_{\alpha\beta}^{\text{mol}} = \sum_{I=1}^{N} Z_I R_{I,\alpha} R_{I,\beta} + \langle \psi_0^{(0)} | - \sum_{i=1}^{n} r_{i,\alpha} r_{i,\beta} | \psi_0^{(0)} \rangle \, , \tag{2.9.49}$$

The molecular moment of order m is given as

$$M_{\alpha_1 \dots \alpha_m}^{(m)} = \sum_{I=1}^{N} Z_I R_{I,\alpha_1} \dots R_{I,\alpha_m} + \langle \psi_0^{(0)} | - \sum_{i=1}^{n} r_{i,\alpha_1} \dots r_{\alpha_m} | \psi_0^{(0)} \rangle \, . \tag{2.9.50}$$

The first-order correction to the energy becomes

$$\begin{aligned} \varepsilon_0^{(1)} &= q^{\text{mol}} \varphi_O + \mu_\alpha^{\text{mol}} \varphi_{O,\alpha}^{(1)} + \frac{1}{2} Q_{\alpha\beta}^{\text{mol}} \varphi_{O,\alpha\beta}^{(2)} + \dots \\ &= q^{\text{mol}} \varphi_O - \mu_\alpha^{\text{mol}} E_{O,\alpha} - \frac{1}{2} Q_{\alpha\beta}^{\text{mol}} E_{O,\alpha\beta} + \dots \\ &= \sum_{m=0}^{\infty} \frac{1}{m!} M_{\alpha_1 \dots \alpha_m}^{(m)} \varphi_{O,\alpha_1 \dots \alpha_m}^{(m)} \, . \end{aligned} \tag{2.9.51}$$

It has thus been demonstrated by comparing to eq. (2.9.7) that the first-order energy corresponds to classical electrostatics.

2.9.3.2 Electrostatic potential

Rewriting eq. (2.9.43) as the electrostatic interaction between a molecule and a test charge q_t, we get

$$\hat{V} = \sum_{I=1}^{N} \frac{Z_I q_t}{R_{It}} - \sum_{i=1}^{n} \frac{q_t}{r_{it}} \; . \tag{2.9.52}$$

The electrostatic potential at the test charge, φ_t, is given by eq. (2.9.3) leading to

$$\hat{\varphi}_t = \sum_{I=1}^{N} \frac{Z_I}{R_{It}} - \sum_{i=1}^{n} \frac{1}{r_{it}} \; , \tag{2.9.53}$$

so that

$$\hat{V} = \hat{\varphi}_t q_t \; . \tag{2.9.54}$$

Again using the first-order correction to the energy from Rayleigh-Schrödinger perturbation theory in eq (2.8.9),

$$\varepsilon_0^{(1)} = \langle \psi_0^{(0)} | \hat{V} | \psi_0^{(0)} \rangle = \langle \psi_0^{(0)} | \hat{\varphi}_t | \psi_0^{(0)} \rangle q_t \; , \tag{2.9.55}$$

where thus the electrostatic potential in point t from a molecule becomes

$$\varphi_t = \langle \psi_0^{(0)} | \hat{\varphi}_t | \psi_0^{(0)} \rangle = \sum_{I=1}^{N} \frac{Z_I}{R_{It}} - \langle \psi_0^{(0)} | \sum_{i=1}^{n} \frac{1}{r_{it}} | \psi_0^{(0)} \rangle \; . \tag{2.9.56}$$

2.9.3.3 Polarizability

For the second-order contribution to the energy in eq. (2.8.18),

$$\varepsilon_0^{(2)} = \sum_{p=1}^{\infty} \frac{1}{\varepsilon_0^{(0)} - \varepsilon_p^{(0)}} \langle \psi_0^{(0)} | \hat{V} | \psi_p^{(0)} \rangle \langle \psi_p^{(0)} | \hat{V} | \psi_0^{(0)} \rangle \,, \tag{2.9.57}$$

it is noted that only the terms in $\hat{V}$ including explicit dependence on the electronic coordinates, $r_{i,\alpha}$, are non-zero since the electronic states are orthogonal, i.e. $\langle \psi_p^{(0)} | \psi_q^{(0)} \rangle = \delta_{pq}$. Thus the term for $m = 0$ in eq. (2.9.44) as well as all nuclear contributions to $\hat{\mathcal{M}}_{\alpha_1 \dots \alpha_m}^{(m)}$ in eq. (2.9.45) vanish. The second-order energy becomes

$$
\begin{aligned}
\varepsilon_0^{(2)} &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{m! n!} \left(\sum_{p=1}^{\infty} \frac{1}{\varepsilon_0^{(0)} - \varepsilon_p^{(0)}} \langle \psi_0^{(0)} | \hat{\mathcal{M}}_{\alpha_1 \dots \alpha_m}^{(m)} | \psi_p^{(0)} \rangle \langle \psi_p^{(0)} | \hat{\mathcal{M}}_{\beta_1 \dots \beta_m}^{(m)} | \psi_0^{(0)} \rangle \right) \\
&\times \quad \varphi_{O,\alpha_1 \dots \alpha_m}^{(m)} \varphi_{O,\beta_1 \dots \beta_n}^{(n)} \,.
\end{aligned}
\tag{2.9.58}
$$

Adopting the following notation for a polarizability, $P_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n}^{(m,n)}$,

$$P_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n}^{(m,n)} = \sum_{p=1}^{\infty} \frac{1}{\varepsilon_0^{(0)} - \varepsilon_p^{(0)}} \langle \psi_0^{(0)} | \hat{\mathcal{M}}_{\alpha_1 \dots \alpha_m}^{(m)} | \psi_p^{(0)} \rangle \langle \psi_p^{(0)} | \hat{\mathcal{M}}_{\beta_1 \dots \beta_n}^{(n)} | \psi_0^{(0)} \rangle \,, \tag{2.9.59}$$

eq. (2.9.58) is rewritten as

$$\varepsilon_0^{(2)} = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{m! n!} P_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n}^{(m,n)} \varphi_{O,\alpha_1 \dots \alpha_m}^{(m)} \varphi_{O,\beta_1 \dots \beta_n}^{(n)} \,. \tag{2.9.60}$$

The leading term ($m = 1, n = 1$) becomes

$$\varepsilon_0^{(2)} = \sum_{p=1}^{\infty} \left(\frac{1}{\varepsilon_0^{(0)} - \varepsilon_p^{(0)}} \langle \psi_0^{(0)} | - \sum_{i=1}^{n} r_{i,\alpha} | \psi_p^{(0)} \rangle \varphi_{O,\alpha}^{(1)} \langle \psi_p^{(0)} | - \sum_{i=1}^{n} r_{i,\beta} | \psi_0^{(0)} \rangle \varphi_{O,\beta}^{(1)} \right) \,. \tag{2.9.61}$$

Defining the molecular dipole-dipole polarizability ($m = 1$, $n = 1$), $\alpha_{\alpha\beta}^{\text{mol}}$, as

$$\alpha_{\alpha\beta}^{\text{mol}} = 2 \sum_{p=1}^{\infty} \frac{\langle \psi_0^{(0)} | - \sum\limits_{i=1}^{n} r_{i,\alpha} | \psi_p^{(0)} \rangle \langle \psi_p^{(0)} | - \sum\limits_{i=1}^{n} r_{i,\beta} | \psi_0^{(0)} \rangle}{\varepsilon_p^{(0)} - \varepsilon_0^{(0)}} \,, \tag{2.9.62}$$

where we note the factor of 2 and the reverse of sign in the denominator as compared to eq. (2.9.59). This leads to

$$
\begin{aligned}
\varepsilon_0^{(2)} &= -\frac{1}{2} \alpha_{\alpha\beta}^{\text{mol}} \varphi_{O,\beta}^{(1)} \varphi_{O,\alpha}^{(1)} + \dots \\
&= -\frac{1}{2} \alpha_{\alpha\beta}^{\text{mol}} E_{O,\beta} E_{O,\alpha} + \dots \,,
\end{aligned}
\tag{2.9.63}
$$

so that the expression for the induction energy in eq. (2.9.41) has been obtained. This second-order energy quadratic in the electric field is therefore termed the induction energy.

2.9.4 Frequency-dependent polarizabilities

We use the general result from time-dependent perturbation theory in eq. (2.8.34),

$$a_m^{(1)}(t) = \frac{-\mathrm{i}}{\hbar} \langle \psi_m^{(0)} | \hat{V} | \psi_p^{(0)} \rangle \int_0^t f(t') \, \mathrm{e}^{\mathrm{i}\omega_{mp} t'} \, \mathrm{d}t' , \qquad (2.9.64)$$

so that the first-order correction to the time-dependent wavefunction is

$$\Psi^{(1)}(t) = \sum_k a_k^{(1)}(t) \, \mathrm{e}^{-\mathrm{i}\omega_k t} | \psi_k^{(0)} \rangle . \qquad (2.9.65)$$

The Hamiltonian, $\hat{\mathscr{H}}(t)$, is as in eq. (2.8.19), divided into

$$\hat{\mathscr{H}}(t) = \hat{\mathscr{H}}_0 + \lambda \hat{\mathscr{H}}_1(t) , \qquad (2.9.66)$$

where $\hat{\mathscr{H}}_1(t) = \hat{V} f(t)$. Here we regard the response to an oscillating electric field,

$$\hat{\mathscr{H}}_1(t) = 2\hat{V} \, \mathrm{e}^{\varepsilon t} \cos(\omega t) = \hat{V} \left(\mathrm{e}^{(\varepsilon + \mathrm{i}\omega) t} + \mathrm{e}^{(\varepsilon - \mathrm{i}\omega) t} \right) , \qquad (2.9.67)$$

where the term $\mathrm{e}^{\varepsilon t}$ ensures that the field is turned on in a distant path. The parameter ε is supposed to be small and will be allowed to approach zero giving a steady-state response

when the field has been turned on a for a long time. Now we intgrate eq. (2.9.64),

$$
\begin{aligned}
a_k^{(1)}(t) &= \frac{-\mathrm{i}}{\hbar} \langle \psi_k^{(0)} | \hat{V} | \psi_p^{(0)} \rangle \int_{-\infty}^{t} \mathrm{e}^{(\varepsilon + \mathrm{i}\omega_{kp} + \mathrm{i}\omega)t'} + \mathrm{e}^{(\varepsilon + \mathrm{i}\omega_{kp} - \mathrm{i}\omega)t'} \, \mathrm{d}t' \\
&= \frac{-1}{\hbar} \langle \psi_k^{(0)} | \hat{V} | \psi_p^{(0)} \rangle \left(\frac{\mathrm{e}^{(\varepsilon + \mathrm{i}\omega_{kp} + \mathrm{i}\omega)t'}}{\omega_{kp} + \omega - \mathrm{i}\varepsilon} + \frac{\mathrm{e}^{(\varepsilon + \mathrm{i}\omega_{kp} - \mathrm{i}\omega)t'}}{\omega_{kp} - \omega - \mathrm{i}\varepsilon} \right)\Bigg|_{-\infty}^{t} \\
&= \frac{-1}{\hbar} \langle \psi_k^{(0)} | \hat{V} | \psi_p^{(0)} \rangle \left(\frac{\mathrm{e}^{(\varepsilon + \mathrm{i}\omega_{kp} + \mathrm{i}\omega)t}}{\omega_{kp} + \omega - \mathrm{i}\varepsilon} + \frac{\mathrm{e}^{(\varepsilon + \mathrm{i}\omega_{kp} - \mathrm{i}\omega)t}}{\omega_{kp} - \omega - \mathrm{i}\varepsilon} \right) \\
&\stackrel{\varepsilon \to 0}{=} \frac{-1}{\hbar} \langle \psi_k^{(0)} | \hat{V} | \psi_p^{(0)} \rangle \left(\frac{\mathrm{e}^{\mathrm{i}(\omega_{kp} + \omega)t}}{\omega_{kp} + \omega} + \frac{\mathrm{e}^{\mathrm{i}(\omega_{kp} - \omega)t}}{\omega_{kp} - \omega} \right).
\end{aligned}
\tag{2.9.68}
$$

We now regard time-dependent dipole moment of the ground state ($p = 0$),

$$
\mu_\alpha(t) = \langle \Psi(t) | \hat{\mu}_\alpha | \Psi(t) \rangle,
\tag{2.9.69}
$$

with

$$
\Psi(t) = \psi_0^{(0)} \, \mathrm{e}^{-\mathrm{i}\omega_0 t} + \sum_{k \neq 0}^{\infty} \lambda a_k^{(1)}(t) \psi_k^{(0)} \, \mathrm{e}^{-\mathrm{i}\omega_k t}
\tag{2.9.70}
$$

Considering each order i in λ^i, we get for $i = 0$,

$$
\mu_\alpha^{(0)} = \langle \psi_0^{(0)} | \hat{\mu}_\alpha | \psi_0^{(0)} \rangle
\tag{2.9.71}
$$

and for $i = 1$,

$$
\mu_\alpha^{(1)} = \sum_{k \neq 0}^{\infty} \langle \psi_0^{(0)} | \hat{\mu}_\alpha | \psi_k^{(0)} \rangle \, \mathrm{e}^{-\mathrm{i}\omega_{k0} t} \, a_k^{(1)}(t) + \langle \psi_k^{(0)} | \hat{\mu}_\alpha | \psi_0^{(0)} \rangle \, \mathrm{e}^{\mathrm{i}\omega_{k0} t} \left(a_k^{(1)}(t) \right)^*
\tag{2.9.72}
$$

Using eq. (2.9.68) with $\hat{V} = -\hat{\mu}_\beta E_\beta$ and $p = 0$,

$$
\begin{aligned}
\mu_\alpha^{(1)} &= \frac{E_\beta}{\hbar} \sum_{k \neq 0}^{\infty} \left(\langle \psi_0^{(0)} | \hat{\mu}_\alpha | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{\mu}_\beta | \psi_0^{(0)} \rangle \frac{\mathrm{e}^{\mathrm{i}\omega t}}{\omega_{k0} + \omega} + \frac{\mathrm{e}^{-\mathrm{i}\omega t}}{\omega_{k0} - \omega} \right. \\
&\quad + \left. \langle \psi_0^{(0)} | \hat{\mu}_\beta | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{\mu}_\alpha | \psi_0^{(0)} \rangle \frac{\mathrm{e}^{-\mathrm{i}\omega t}}{\omega_{k0} + \omega} + \frac{\mathrm{e}^{\mathrm{i}\omega t}}{\omega_{k0} - \omega} \right) \\
&= \frac{E_\beta}{\hbar} \left(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t} \right) \sum_{k \neq 0}^{\infty} \left(\frac{\langle \psi_0^{(0)} | \hat{\mu}_\alpha | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{\mu}_\beta | \psi_0^{(0)} \rangle}{\omega_{k0} - \omega} \right. \\
&\quad + \left. \frac{\langle \psi_0^{(0)} | \hat{\mu}_\alpha | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{\mu}_\beta | \psi_0^{(0)} \rangle}{\omega_{k0} + \omega} \right)
\end{aligned}
\tag{2.9.73}
$$

Using the definition of the polarizability in eq. (2.9.36) slightly extended to include frequency-dependence,

$$
\mu_\alpha^{(1)} = \alpha_{\alpha\beta}(\omega) E_\beta \left(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t} \right),
\tag{2.9.74}
$$

leads to the following result for the frequency-dependent polarizability,

$$
\alpha_{\alpha\beta}(\omega) = \frac{1}{\hbar} \sum_{k \neq 0}^{\infty} \left(\frac{\langle \psi_0^{(0)} | \hat{\mu}_\alpha | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{\mu}_\beta | \psi_0^{(0)} \rangle}{\omega_{k0} - \omega} + \frac{\langle \psi_0^{(0)} | \hat{\mu}_\alpha | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{\mu}_\beta | \psi_0^{(0)} \rangle}{\omega_{k0} + \omega} \right).
\tag{2.9.75}
$$

2.10   The Hartree-Fock approximation

The starting point for the Hartree-Fock approximation (Hartree 1928, Fock 1930, Roothan 1951) is the energy for the Slater determinant in eq. (2.6.36) using the more compact notation in eq. (2.6.34),

$$
\begin{aligned}
E_0 &= \sum_{i=1}^{n} h_i + \frac{1}{2} \sum_{i,j=1}^{n} \left(J_{ij} - K_{ij} \right) + V_{nn} \\
&= \sum_{i=1}^{n} \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{n} \left(\langle \chi_i \chi_j | \hat{g} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \hat{g} | \chi_j \chi_i \rangle \right) + V_{nn} \,.
\end{aligned}
\tag{2.10.1}
$$

The Slater determinant is an approximate wavefunction and we can thus minimize the energy in eq. (2.10.1) using the variational principle in section 2.7 by optimizing the orbitals. We would, however, like to retain that the orbitals form an orthonormal set, and this condition is imposed by a constrained minimization using the method of Lagrangian multipliers. The Lagrangian, $\tilde{E}_0$, becomes

$$
\tilde{E}_0 = E_0 - \sum_{i,j=1}^{n} \lambda_{ij} \left(\langle \chi_i | \chi_j \rangle - \delta_{ij} \right) = E_0 - \sum_{i,j=1}^{n} \lambda_{ij} \left(S_{ij} - \delta_{ij} \right) \,,
\tag{2.10.2}
$$

where we have one Lagrangian multiplier λ_{ij} for each pair of orbitals and δ_{ij} is the Kroenecker delta function indicating the required orthonormality of the orbitals. We define an element of the overlap matrix S_{ij} as

$$
S_{ij} = \langle \chi_i | \chi_j \rangle \,.
\tag{2.10.3}
$$

A small variation of the Lagrangian, $\delta \tilde{E}_0$ becomes

$$
\delta \tilde{E}_0 = \delta E_0 - \sum_{i,j=1}^{n} \lambda_{ij} \left(\langle \delta \chi_i | \chi_j \rangle + \langle \chi_i | \delta \chi_j \rangle \right) \,,
\tag{2.10.4}
$$

where a small variation of the energy E_0 in eq. (2.10.1) becomes

$$
\begin{aligned}
\delta E_0 &= \sum_{i=1}^{n} \langle \delta \chi_i | \hat{h} | \chi_i \rangle + \langle \chi_i | \hat{h} | \delta \chi_i \rangle \\
&+ \frac{1}{2} \sum_{i,j=1}^{n} \left(\langle \delta \chi_i \chi_j | \hat{g} | \chi_i \chi_j \rangle + \langle \chi_i \delta \chi_j | \hat{g} | \chi_i \chi_j \rangle + \langle \chi_i \chi_j | \hat{g} | \delta \chi_i \chi_j \rangle + \langle \chi_i \chi_j | \hat{g} | \chi_i \delta \chi_j \rangle \right) \\
&- \left(\langle \delta \chi_i \chi_j | \hat{g} | \chi_j \chi_i \rangle + \langle \chi_i \delta \chi_j | \hat{g} | \chi_j \chi_i \rangle + \langle \chi_i \chi_j | \hat{g} | \delta \chi_j \chi_i \rangle + \langle \chi_i \chi_j | \hat{g} | \chi_j \delta \chi_i \rangle \right) \\
&= \sum_{i=1}^{n} \langle \delta \chi_i | \hat{h} | \chi_i \rangle + \langle \chi_i | \hat{h} | \delta \chi_i \rangle \\
&+ \sum_{i,j=1}^{n} \langle \delta \chi_i \chi_j | \hat{g} | \chi_i \chi_j \rangle + \langle \chi_i \chi_j | \hat{g} | \delta \chi_i \chi_j \rangle - \langle \delta \chi_i \chi_j | \hat{g} | \chi_j \chi_i \rangle - \langle \chi_i \chi_j | \hat{g} | \delta \chi_j \chi_i \rangle
\end{aligned}
\tag{2.10.5}
$$

In the last step, we have used that i and j are just dummy indexes and can be interchanged. Introducing two operators, the Coulomb operator,

$$
\hat{\mathscr{J}}_j | \chi_i \rangle = \langle \chi_j | \hat{g} | \chi_j \rangle | \chi_i \rangle \,,
\tag{2.10.6}
$$

and the exchange operator,

$$\hat{\mathscr{K}}_j |\chi_i\rangle = \langle \chi_j |\hat{g}|\chi_i\rangle |\chi_j\rangle \,, \tag{2.10.7}$$

where the operator *exchanges* the orbital it operates on. We thus get

$$
\begin{aligned}
\delta E_0 &= \sum_{i=1}^{n} \langle \delta\chi_i |\hat{h}|\chi_i\rangle + \langle \chi_i |\hat{h}|\delta\chi_i\rangle \\
&+ \sum_{i,j=1}^{n} \langle \delta\chi_i |\hat{\mathscr{J}}_j - \hat{\mathscr{K}}_j |\chi_i\rangle + \langle \chi_i |\hat{\mathscr{J}}_j - \hat{\mathscr{K}}_j |\delta\chi_i\rangle \,.
\end{aligned}
\tag{2.10.8}
$$

Defining the Fock operator $\hat{f}$ as

$$\hat{f} = \hat{h} + \sum_{j=1}^{n} \left(\hat{\mathscr{J}}_j - \hat{\mathscr{K}}_j \right) \,, \tag{2.10.9}$$

so that the total Hartree-Fock Hamiltonian, $\hat{\mathscr{H}}_{\mathrm{HF}}$, becomes

$$\hat{\mathscr{H}}_{\mathrm{HF}} = \sum_{i=1}^{n} \hat{f}_i \,, \tag{2.10.10}$$

where the subscript i denotes that we have one Fock operator for each electron in the system. We get

$$\delta E_0 = \sum_{i=1}^{n} \langle \delta\chi_i |\hat{f}_i|\chi_i\rangle + \langle \chi_i |\hat{f}_i|\delta\chi_i\rangle \tag{2.10.11}$$

so that the total Lagrangian becomes

$$\delta \tilde{E}_0 = \sum_{i=1}^{n} \langle \delta\chi_i |\hat{f}_i|\chi_i\rangle + \langle \chi_i |\hat{f}_i|\delta\chi_i\rangle - \sum_{i,j=1}^{n} \lambda_{ij} \left(\langle \delta\chi_i |\chi_j\rangle + \langle \chi_i |\delta\chi_j\rangle \right) \,. \tag{2.10.12}$$

Assuming that *either* a small variation $\langle \delta\chi_i|$ or $|\delta\chi_i\rangle$ leads to that the variational principle is fulfilled, i.e. $\delta \tilde{E}_0 = 0$, gives two relations to be fulfilled simultaneously,

$$\sum_{i=1}^{n} \langle \delta\chi_i |\hat{f}_i|\chi_i\rangle - \sum_{i,j=1}^{n} \lambda_{ij} \langle \delta\chi_i |\chi_j\rangle = 0 \,, \tag{2.10.13}$$

and

$$\sum_{i=1}^{n} \langle \chi_i |\hat{f}_i|\delta\chi_i\rangle - \sum_{i,j=1}^{n} \lambda_{ij} \langle \chi_i |\delta\chi_j\rangle = 0 \,. \tag{2.10.14}$$

Using that

$$\langle \delta\chi_i |\hat{f}_i|\chi_i\rangle = \langle \chi_i |\hat{f}_i|\delta\chi_i\rangle^* \tag{2.10.15}$$

and subtracting eq. (2.10.13) from the complex conjugate of eq. (2.10.14) from each other, we get

$$\sum_{i,j=1}^{n} \left(\lambda_{ij} - \lambda_{ji}^* \right) \langle \delta\chi_i |\chi_j\rangle = 0 \,, \tag{2.10.16}$$

so that the condition is fulfilled if λ_{ij} is an element of a Hermitian matrix. In the next step, eq. (2.10.13) is rewritten as a set of eigenvalue problems rather than an expectation value,

$$\hat{f}_i|\chi_i\rangle = \sum_{j=1}^{n} \lambda_{ij}|\chi_j\rangle \quad \forall i \,. \tag{2.10.17}$$

We can now make a specific choice of the orbitals in eq. (2.10.17) by a unitary transformation so that λ_{ij} becomes a diagonal matrix. With the notation $\epsilon_i = \lambda_{ii}$,

$$\hat{f}_i|\chi_i\rangle = \epsilon_i|\chi_i\rangle \quad \forall i \,, \tag{2.10.18}$$

where this choice of orbitals is termed the *canonical* orbitals and ϵ_i is an orbital energy. Eq. (2.10.18) is referred to as the Hartree-Fock equations and is a set of coupled eigenvalue equations since the Fock operator in eq. (2.10.9) depends on all the orbitals through the Coulomb and exchange operators in eqs. (2.10.6) and (2.10.7), respectively. An iterative method, the self-consistent field (SCF) method is therefore commonly employed with a set of starting orbitals to get an initial guess of $\hat{f}_i$. Eq. (2.10.18) is then solved for this set of $\hat{f}_i$ providing an updated set of orbitals and thereby also an updated $\hat{f}_i$, and the procedure is repeated until convergence is reached.

Rewriting the quantum mechanical expression for the molecular electrostatic potential in eq. (2.9.56) in terms of a Slater determinant,

$$\varphi_t = \sum_{I=1}^{N} \frac{Z_I}{R_{It}} - \sum_{i=1}^{n} \langle \chi_i | \frac{1}{r_{it}} | \chi_i \rangle \,, \tag{2.10.19}$$

where the second term on the right-hand side is the integral that appears for the Coulomb operator in eq. (2.10.6). The averaging over one of the electronic coordinates in the definitions of the Coulomb and exchange operators in eqs. (2.10.6) and (2.10.7) thus leads to that the two-electron Coulomb term in eq. (2.10.5) has been replaced by the interaction between one electron and the average electrostatic potential in eq. (2.10.8). We refer to this kind of approximation as a mean-field approximation.

The orbital energy ϵ_i can be obtained as an expectation value,

$$\epsilon_i = \langle \chi_i | \hat{f}_i | \chi_i \rangle \approx h_i + \sum_{j=1}^{n} \left(J_{ij} - K_{ij} \right) , \tag{2.10.20}$$

where we instead of integrating over the Fock operator $\hat{f}_i$ return to the initial two-electron integrals. Consequently the energy for a Slater determinant in eq. (2.10.1) becomes within the Hartree-Fock approximation

$$E_0 = \sum_{i=1}^{n} \epsilon_i - \frac{1}{2} \sum_{i,j=1}^{n} \left(J_{ij} - K_{ij} \right) + V_{nn} , \tag{2.10.21}$$

and is thus not just the sum over the orbital energies. In eq. (2.10.21), we have also added the classical nucleus-nucleus interaction energy.

2.11   Basis set expansion

We have to represent the spin-orbitals mathematically in some way to be able to do actual calculations to solve the Hartree-Fock equations in eq. (2.10.18). The set of basis functions, in quantum chemistry termed the *basis set* can be chosen in different ways. We will return to different choices for the basis set, here we just assume that a spin-orbital, χ_i is expanded in m basis functions ϕ_p (Roothan 1951),

$$|\chi_i\rangle = \sum_{p=1}^{m} c_{ip} |\phi_p\rangle , \tag{2.11.1}$$

where c_{ip} is an orbital coefficient. The Hartree-Fock equations in eq. (2.10.18) become

$$\hat{f}_i \sum_{p=1}^{m} c_{ip} |\phi_p\rangle = \epsilon_i \sum_{j=1}^{m} c_{ip} |\phi_p\rangle \qquad \forall i . \tag{2.11.2}$$

We introduce the following matrix notation

$$\boldsymbol{\phi} = \left(\phi_1, \phi_2, \dots \phi_m \right) , \tag{2.11.3}$$

$$\mathbf{c}_i = \begin{pmatrix} c_{1i} \\ c_{2i} \\ \vdots \\ c_{mi} \end{pmatrix} \quad \text{and} \quad \mathbf{C} = \begin{pmatrix} c_{11} & c_{12} & \dots & c_{1n} \\ c_{21} & c_{22} & \dots & c_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ c_{m1} & c_{m2} & \dots & c_{mn} \end{pmatrix} \tag{2.11.4}$$

so that we can write

$$\chi_i = \boldsymbol{\phi} \cdot \mathbf{c}_i \qquad \text{and} \qquad \boldsymbol{\chi} = \boldsymbol{\phi} \cdot \mathbf{C} \,. \tag{2.11.5}$$

We also define the Fock matrix as

$$\mathbf{F} = \begin{pmatrix} \langle \phi_1 | \hat{f} | \phi_1 \rangle & \langle \phi_1 | \hat{f} | \phi_2 \rangle & \dots & \langle \phi_1 | \hat{f} | \phi_m \rangle \\ \langle \phi_2 | \hat{f} | \phi_1 \rangle & \langle \phi_2 | \hat{f} | \phi_2 \rangle & \dots & \langle \phi_2 | \hat{f} | \phi_m \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \phi_m | \hat{f} | \phi_1 \rangle & \langle \phi_m | \hat{f} | \phi_2 \rangle & \dots & \langle \phi_m | \hat{f} | \phi_m \rangle \end{pmatrix} \,. \tag{2.11.6}$$

In addition, the overlap matrix is defined as

$$\mathbf{S} = \begin{pmatrix} \langle \phi_1 | \phi_1 \rangle & \langle \phi_1 | \phi_2 \rangle & \dots & \langle \phi_1 | \phi_m \rangle \\ \langle \phi_2 | \phi_1 \rangle & \langle \phi_2 | \phi_2 \rangle & \dots & \langle \phi_2 | \phi_m \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \phi_m | \phi_1 \rangle & \langle \phi_m | \phi_2 \rangle & \dots & \langle \phi_m | \phi_m \rangle \end{pmatrix} \,. \tag{2.11.7}$$

Again applying the variational principle and the Rayleigh-Ritz method in section 2.7, we arrive at (see exercise 2.10) the Roothaan-Hall equations (Roothan 1951, Hall 1951)

$$\mathbf{F}\mathbf{c}_i = \epsilon_i \mathbf{S}\mathbf{c}_i \qquad \text{or} \qquad \mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon} \,, \tag{2.11.8}$$

where $\boldsymbol{\epsilon}$ is a diagonal matrix with the orbital energies ϵ_i. We have thus converted the Hartree-Fock equations in eq. (2.10.18), which are a set of coupled integro-differential equations, to finding the eigenvalues and eigenvectors of the Fock matrix. The overlap matrix $\mathbf{S}$ is regarded as the metric of the Fock matrix $\mathbf{F}$ since it reduces to the unity matrix $\mathbf{1}$ for an orthonormal basis. As for the Hartree-Fock equations in eq. (2.10.18), the Roothaan-Hall equation in eq. (2.11.8) is solved by an iterative method since the Fock matrix $\mathbf{F}$ depends on the eigenvectors, i.e. the orbital coefficients, in $\mathbf{C}$, which we also here refer to as the self-consistent field (SCF) method.

2.11.1 Density matrices

To introduce density matrices, we regard an element of the Fock matrix F_{pq} in eq. (2.11.6),

$$
\begin{aligned}
F_{pq} &= \langle \phi_p | \hat{f} | \phi_q \rangle \\
&= \langle \phi_p | \hat{h} | \phi_q \rangle + \sum_{j=1}^{n} \langle \phi_p | \hat{\mathcal{J}}_j - \hat{\mathcal{K}}_j | \phi_q \rangle \\
&= \langle \phi_p | \hat{h} | \phi_q \rangle + \sum_{j=1}^{n} \langle \phi_p \chi_j | \hat{g} | \phi_q \chi_j \rangle - \langle \phi_p \chi_j | \hat{g} | \chi_j \phi_q \rangle \\
&= \langle \phi_p | \hat{h} | \phi_q \rangle + \sum_{j=1}^{n} \sum_{r,s=1}^{m} c_{jr} c_{js} \Big(\langle \phi_p \phi_r | \hat{g} | \phi_q \phi_s \rangle - \langle \phi_p \phi_r | \hat{g} | \phi_s \phi_q \rangle \Big) \\
&= \langle \phi_p | \hat{h} | \phi_q \rangle + \sum_{r,s=1}^{m} D_{rs} \Big(\langle \phi_p \phi_r | \hat{g} | \phi_q \phi_s \rangle - \langle \phi_p \phi_r | \hat{g} | \phi_s \phi_q \rangle \Big) \,,
\end{aligned}
\tag{2.11.9}
$$

where we have defined the density matrix as

$$D_{rs} = \sum_{j=1}^{n} c_{jr} c_{js} . \tag{2.11.10}$$

We also introduce the following notation for the two-electron integrals,

$$G_{prqs} = \langle \phi_p \phi_r | \hat{g} | \phi_q \phi_s \rangle - \langle \phi_p \phi_r | \hat{g} | \phi_s \phi_q \rangle \tag{2.11.11}$$

so that

$$F_{pq} = h_{pq} + \sum_{r,s=1}^{m} D_{rs} G_{prqs} . \tag{2.11.12}$$

The energy for a Slater determinant in eq. (2.10.1) is recalled and rephrased in terms of density matrices,

$$
\begin{aligned}
E_0 &= \sum_{i=1}^{n} \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{n} \left(\langle \chi_i \chi_j | \hat{g} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \hat{g} | \chi_j \chi_i \rangle \right) + V_{nn} \\
&= \sum_{i=1}^{n} \sum_{p,q=1}^{m} c_{ip} c_{iq} \langle \phi_p | \hat{h} | \phi_q \rangle + \frac{1}{2} \sum_{i,j=1}^{n} \sum_{p,q,r,s=1}^{m} c_{ip} c_{iq} c_{jr} c_{js} \left(\langle \phi_p \phi_r | \hat{g} | \phi_q \phi_s \rangle - \langle \phi_p \phi_r | \hat{g} | \phi_s \phi_q \rangle \right) \\
&= \sum_{p,q=1}^{m} D_{pq} h_{pq} + \frac{1}{2} \sum_{p,q,r,s=1}^{m} D_{pq} D_{rs} G_{prqs} + V_{nn} .
\end{aligned} \tag{2.11.13}
$$

2.11.2 Basis sets

We need to have a mathematical representation of the basis functions $\phi_p(i)$ in eq. (2.11.1). Traditionally there are two approaches, either plane waves are used which is suitable when applying periodic boundary conditions in solid-state chemistry or as a linear combination of atomic orbitals (although these "atomic orbitals" may not be a solution to the Schrödinger equation in eq. (2.5.2)). Two types of atomic orbitals are commonly employed, Slater-type orbitals (STOs) that decay exponentially with the distance from the nuclei, and Gaussian-type orbitals (GTOs) which adopt Gaussian functions.

The choice of GTOs versus STOs as the functions in the basis set is still the subject of a vivic discussion, although GTOs dominate today in the commonly employed quantum chemical software. An STO is indeed the exact solution to the one-electron problem as the hydrogen atom, but on the other hand, we do not know how the exact solution looks like for a many-electron problem. STOs have a more long-range decay than GTOs, and describes the cusp at the nucleus. GTOs were originally introduced to describe one STO by several GTOs (Boys 1950) since the two-electron integrals in eq. (2.11.11) are much easier to calculate by using GTOs as compared to STOs.

A useful relation for a Gaussian function positioned at nucleus I, $\phi_{i,I}(r)$,

$$\phi_{i,I}(r) = \left(\frac{2\alpha_i}{\pi}\right)^{\frac{3}{4}} e^{-\alpha_i(\vec{r}-\vec{R}_I)^2} \tag{2.11.14}$$

is its product rule (see exercise 2.11 for a derivation),

$$\phi_{i,I}\phi_{j,J} = C e^{-\beta(\vec{r}-\vec{R}_K)^2} \tag{2.11.15}$$

where

$$\beta = \alpha_i + \alpha_h, \qquad \vec{R}_K = \frac{\alpha_i\vec{R}_I + \alpha_j\vec{R}_J}{\alpha_i + \alpha_j} \quad \text{and} \qquad C = \left(\frac{2}{\pi}\right)^2 \left(\alpha_i\alpha_j\right)^{\frac{3}{4}} e^{\frac{\alpha_i\alpha_j}{\alpha_i+\alpha_j}(\vec{R}_I-\vec{R}_J)^2} \tag{2.11.16}$$

which simplifies the integral calculations greatly for GTOs.

In general we write a Gaussian basis function in Cartesian coordinates as

$$\phi_i(x,y,z) = x^a y^b z^c e^{-\alpha_i r^2}, \quad a,b,c \geq 0, \tag{2.11.17}$$

where a, b and c are integers and an s-function thus corresponds to $a+b+c = 0$, a p-function to $a+b+c = 1$, a d-function to $a+b+c = 2$, etc.

There is a huge amount of basis sets available in the literature and accessible by simple keywords in quantum chemical software. Here we will only discuss some general principles and we will use the correlation-consistent basis sets (Dunning Jr. 1989, Woon and Dunning Jr. 1993) as an example. If we first assign the number of basis functions to each atom so that the GTOs can contain all the electrons of the neutral atom, e.g. for C with 6 electrons we need two s-functions and one p-function (which indeed is three basis functions, p_x, p_y and p_z) denoted [2s1p]. We denote the GTO describing the $1s$ electrons of C for a core function and the GTOs describing the $2s$ and $2p$ electrons for valence functions. A double-ζ basis set

	H-He	Li-Ne	Na-Ar
cc-pVDZ	[2s1p]	[3s2p1d]	[4s3p2d]
cc-pVTZ	[3s2p1d]	[4s3p2d1f]	[5s4p3d1f]
cc-pVQZ	[4s3p2d1f]	[5s4p3d2f1g]	[6s5p4d2f1g]

Table 2.3: The number of basis functions in some of the correlation-consistent basis sets, cc-pVXZ, X={D, T, Q}.

for the C atom contains one additional *s*- and *p*-function and in addition one *d*-function, denoted [3s2p1d]. A table for the correlation-consistent basis sets, cc-pVZX, X={D, T, Q} including also the number of basis functions for triple-ζ and quadruple-ζ basis sets is given in table 2.3.

In this type of hierarchy of basis sets, double-ζ, triple-ζ, etc., we add what is called *polarization functions* for each level in the hierarchy with the purpose to improve the description of covalent bonds. The calculated accuracy of many molecular properties depends strongly on the description of the covalent bonds in the molecule, where the molecular geometry is a typical example. It is also beneficial to have a family of basis sets where the hierarchy converges towards the basis set limit, so that we can control the error introduced in a truncated basis set expansion. The cc-pVXZ basis sets is an example of such a family of basis sets that converges smoothly to the basis set limit when the basis set is increased in a systematic way.

Also *diffuse functions* are often added to a basis set to improve the description of the electron charge distribution far away from the nuclei, which is important for example for the calculation of molecular polarizabilities in eq. (2.9.62). Correlation-consistent basis sets with diffuse functions are denoted "augmented" basis sets, aug-cc-pVXZ, where for example for C the cc-pVDZ basis set consisting of [3s2p1d] are extended to [4s3p2d] for aug-cc-pVDZ. Further augmentation with diffuse functions are denoted doubly augmented, d-aug-cc-pVXZ, triply augmented, t-aug-cc-pVZX, etc. In comparison to adding polarization functions, no higher angular-momentum functions are added to the diffuse basis set and obviously the exponent α_i in eq. (2.11.17) are very different when adding polarization or diffuse functions. There are also other extensions of basis sets, for example in the cc-pCVXZ basis sets extra core functions are added to improve the description of the electron distribution close to the nuclei which for example is important in the calculation of the Fermi-contact term in spin-spin coupling constants.

Example 2.2: Basis set limit of the HF molecule at the Hartree-Fock level.

Hartree-Fock calculations on the HF molecule are presented in table 2.4 using the NWChem software (Valiev et al. 2010), where molecular properties as the dipole moment,quadrupole moment, polarizability as well as the equilibrium bond length are presented for three hierarchies of basis sets: cc-pVXZ, aug-cc-pVXZ and d-aug-cc-pVXZ with X={D, T, Q, 5} (Dunning Jr. 1989, Kendall et al. 1992, Woon and Dunning Jr. 1994). Since the basis set is increased systematically, we should be able to deduce a suitable basis set for each property at the Hartree-Fock level.

We define the *z*-axis along the dipole moment axis of the HF molecule so that

basis set	E/hartree	μ/D	Θ_{zz}/B	α_{xx}/Å^3	α_{zz}/Å^3	R_e/Å
cc-pVDZ	-100.019419	1.94920	2.03526	0.22905	0.59513	0.90148
cc-pVTZ	-100.058021	1.94077	2.09725	0.38085	0.73062	0.89794
cc-pVQZ	-100.067695	1.93330	2.11739	0.48097	0.78760	0.89685
cc-pV5Z	-100.070440	1.93189	2.13462	0.54619	0.81708	0.89685
aug-cc-pVDZ	-100.033474	1.93076	2.15627	0.56147	0.82766	0.90019
aug-cc-pVTZ	-100.061078	1.92502	2.15742	0.63241	0.84625	0.89912
aug-cc-pVQZ	-100.068568	1.92206	2.15772	0.65580	0.85106	0.89772
aug-cc-pV5Z	-100.070583	1.92163	2.15486	0.66118	0.85191	0.89595
d-aug-cc-pVDZ	-100.033649	1.92112	2.18807	0.66093	0.84559	0.89992
d-aug-cc-pVTZ	-100.061177	1.92134	2.16222	0.66619	0.85126	0.89916
d-aug-cc-pVQZ	-100.068605	1.92128	2.15656	0.66575	0.85235	0.89727
d-aug-cc-pV5Z	-100.070587	1.92153	2.15440	0.66512	0.85237	0.89694

Table 2.4: Basis set convergence for the bond length R_e, dipole moment μ_z, quadrupole moment Θ_{zz}, and the polarizability, α_{xx} and α_{zz}, for the HF molecule at the Hartree-Fock level. See example 2.2 for a discussion.

$\alpha_{yy} = \alpha_{xx}$ and $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\Theta_{zz}$ (since the quadrupole moment is traceless, see eq. (2.9.32)). All off-diagonal tensor elements, $\alpha_{\alpha\beta}$ and $\Theta_{\alpha\beta}$ for $\alpha \neq \beta$, are 0 because of symmetry reasons. All the properties (obviously apart from R_e) are calculated at an experimental geometry, $R_e = 0.9168$ Å. Thus we look at the basis set dependence of a property separately from the basis set dependence of the molecular geometry. (It is, however, common to do the opposite and calculate the properties at the optimized geometry for each basis set, but then we mix the basis set dependence of the property and the molecular geometry in the same calculations.)

The total energy, E, cannot be measured experimentally, and its inclusion in the table only serves as a consistency check. Since the variational principle in section 2.7 is used in the Hartree-Fock approximation, the energy must be lowered if the size of the basis set is increased. That is true both for the sequence D→T→Q→5 as well as for cc→aug-cc→d-aug-cc, and as can be seen in table 2.4 these conditions are fulfilled. If not, it would be a clear sign of that something is wrong with the calculation, and since human errors are prone also among computational chemists, it is a good advice to inlude as many consistency checks as possible. We also see for example that improving the basis set from aug-cc-pVTZ to d-aug-cc-pVTZ lowers the energy by only 99 μhartree, whereas it has a relatively large effect on the polarizability. In general, diffuse functions do not decrease the total energy, E, by a lot if the basis set is well converged with respect to polarization functions, whereas diffuse functions may have a crucial effect on for example the polarizability where the tail of the orbitals needs to be described accurately.

The bond length, R_e, is well described by the cc-pVTZ basis set and additional diffuse functions have very little effect. In contrast, the polarizability is well described by the d-aug-cc-pVDZ basis set, and addition of extra polarization functions have a minor effect. The dipole and quadrupole moments are somewhere in between and in this example (the HF molecule using the Hartree-Fock approximation) an aug-cc-pVTZ

> basis set gives a good description.
>
> Normally, we do not present results for the Hartree-Fock approximation and basis sets are designed to include also what we are missing in the Hartree-Fock approximation, namely electron correlation (see section 2.12). The requirements on the basis set will change depending on the computational method, the molecule and the property, and we will discuss more examples when we have established more accurate computational methods including also electron correlation. That is also the reason why we do not include a comparison to experimental results in this example. We demonstrate, however, that it is important to have hierarchies of basis sets approaching the basis set limit. The actual basis set used in a study will be a compromise between accuracy and computational efficiency but the choice of basis set should be based on a systematic study of the basis set dependence.

A large amount of various basis sets are normally included in a database within the quantum chemical software, and the user normally only has to provide a simple keyword to use a basis set in a calculation. However, many software adopting Gaussian basis sets rely on a common basis set exchange (BSE) server where most basis sets can be obtained (Feller 1996, Schuchardt et al. 2007).

2.12   Electron correlation

The electron correlation energy of state i, E_i^{corr}, is pragmatically defined as (Löwdin 1955)

$$E_i^{\text{corr}} = E_i^{\text{exact}} - E_i^{\text{HF}} \, , \tag{2.12.1}$$

i.e. the energy not included in the Hartree-Fock approximation, E_i^{HF}. The exact energy E_i^{exact} here refers to the "exact" solution of the Schrödinger equation within the molecular orbital ansatz for a *given* basis set, so the "true" solution to the problem would be to include all electron correlation as well as an infinitely large basis set (see figure 2.7). Since the molecular Hamiltonian in eq. (2.4.2) commutes with the Fock operator in eq. (2.10.9) (see exercise 2.12), the "exact" wavefunction ψ_i^{exact} can be expressed as a linear combination of the states to the solution to the Hartree-Fock approximation, ψ_μ^{HF},

$$\psi_i^{\text{exact}} = \sum_\mu C_{i\mu} \psi_\mu^{\text{HF}} \tag{2.12.2}$$

where $C_{i\mu}$ are expansion coefficients to be determined. Within molecular orbital theory, we thus focus on which Hartree-Fock states ψ_μ^{HF} to include and how to determine their respective coefficients $C_{i\mu}$. All methods discussed in this section are based on the restricted Hartree-Fock method, i.e. a closed-shell system with two electrons in each occupied orbital (see eq. (2.6.39)). We can therefore depict the methods by using figure 2.8 where we in the Hartree-Fock ground state have put two electrons in each orbital filling the orbitals with the lowest orbital energies (see figure 2.8a). The Hartree-Fock states included in eq. (2.12.3) can be depicted as single excitations (see figure 2.8b), double excitations (see figure 2.8c), etc. out of the Hartree-Fock ground state.
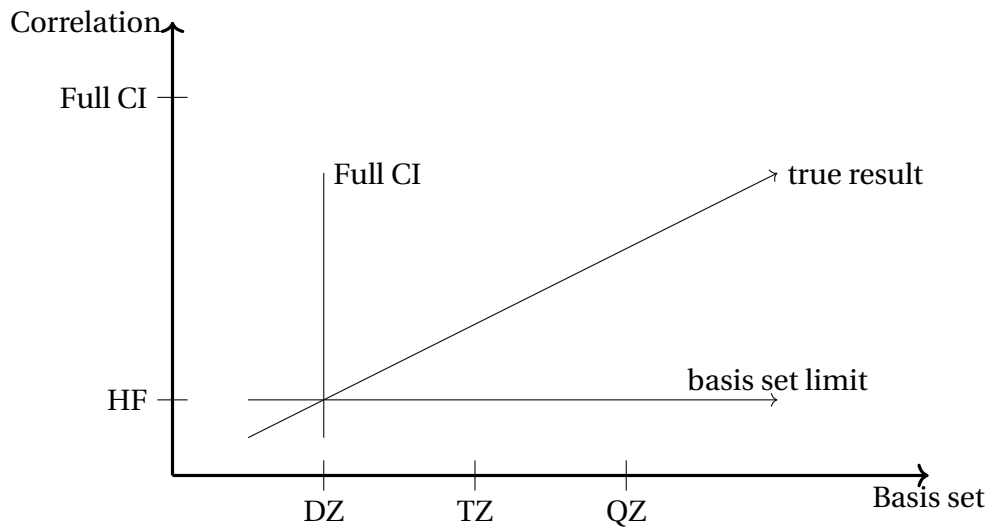
Figure 2.7: Illustration of that we need both electron correlation, ideally in the full CI limit, *and* very large basis sets to get the "true result".

2.12.1   Configuration interaction (CI) methods

In configuration interaction (CI) methods, we rewrite the expansion in eq. (2.12.3) as

$$\psi_0^{\text{CI}} = C_0\psi_0^{\text{HF}} + \sum_\mu C_\mu\psi_\mu^{(1)} + \sum_\mu C_\mu\psi_\mu^{(2)} + \ldots = C_0\psi_0^{\text{HF}} + \sum_i \sum_a C_i^a\psi_i^a + \sum_{\substack{i,\\j>i}}\sum_{\substack{a,\\b>a}} C_{ij}^{ab}\psi_{ij}^{ab} + \ldots, \quad (2.12.3)$$

where ψ_i^{HF} is the Hartree-Fock ground state (see figure 2.8a), $\psi_\mu^{(1)}$ denotes a single excitation of the Hartree-Fock wavefunction (see figure 2.8b) and $\psi_\mu^{(2)}$ is a double excitation of the Hartree-Fock wavefunction (see figure 2.8c). In the last part of eq. (2.12.3), i and j refers to occupied orbitals and a and b to virtual orbitals, respectively, so that ψ_i^a and ψ_{ij}^{ab} are singly and doubly excited states with the Hartree-Fock ground state as the reference state. Normally we truncate after single and double excitations and this method is termed CISD (CI with singles and doubles excitations). The coefficients C_μ are determined variationally. The orbital coefficients c_{ij} in the LCAO approximation in eq. (2.6.1) are not reoptimized, and therefore a truncated CI method relies on that the Hartree-Fock approximation is a good starting point.

2.12.1.1   Brillouin's theorem

We look at one of the energy contributions, the coupling between the Hartree-Fock state and all single excitations. Adopting the notation in eq. (2.10.1),

$$\begin{aligned} \sum_i \sum_a \langle\psi_0^{\text{HF}}|\hat{\mathcal{H}}^{\text{el}}|\psi_i^a\rangle &= \sum_i \sum_a \left(\langle\chi_i|\hat{h}|\chi_a\rangle + \frac{1}{2}\sum_j\left(\langle\chi_i\chi_j|\hat{g}|\chi_a\chi_j\rangle - \langle\chi_i\chi_j|\hat{g}|\chi_j\chi_a\rangle\right)\right) \\ &= \sum_i \sum_a \langle\chi_i|\hat{f}|\chi_a\rangle = \sum_i \sum_a \epsilon_i\langle\chi_i|\chi_a\rangle = \sum_i \sum_a \epsilon_i\delta_{ia} = 0, \quad (2.12.4) \end{aligned}$$

(a) Ground state

(b) Examples of single excitations

(c) Examples of double excitations
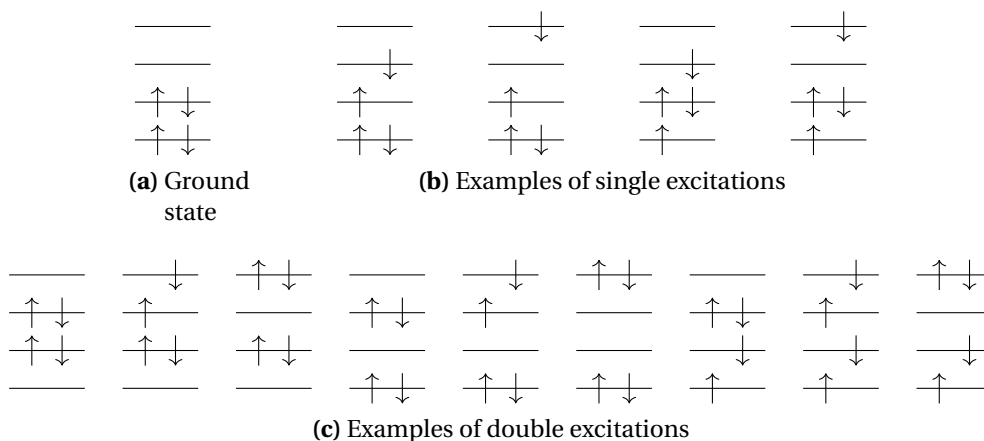
Figure 2.8: Illustration of (a) the Hartree-Fock ground state, (b) single excitations, and (c) double excitations for a system of 4 electrons in 4 orbitals.

where we first have used the definition of the Fock operator in eq. (2.10.9) and the Coulomb and exchange operators in eqs. (2.10.6) and (2.10.7), and then we have used that the canonical orbitals are eigenfunctions of the Fock operator $\hat{f}$ (see eq. (2.10.18)) as well as that the orbitals form an orthonormal set. The relation in eq. (2.12.4) is the Brillouin's theorem.

	n	cc-pVDZ		cc-pVTZ		cc-pVQZ	
	n	m	N_{FCI}	m	N_{FCI}	m	N_{FCI}
H_2O	10	24	$6.5 \cdot 10^{9}$	58	$8.2 \cdot 10^{13}$	115	$9.4 \cdot 10^{16}$
CO_2	22	42	$9.4 \cdot 10^{19}$	90	$9.6 \cdot 10^{27}$	165	$1.1 \cdot 10^{34}$
C_6H_6	42	114	$1.4 \cdot 10^{46}$	264	$3.0 \cdot 10^{62}$	510	$6.9 \cdot 10^{74}$

Table 2.5: Examples of the number of Hartree-Fock states included in a full CI calculation for some typical molecules and basis sets. n is the number of electrons in the molecule, m is the number of basis functions for the given basis set and molecule, and N_{FCI} is the number of Hartree-Fock states included according to eq. (2.12.5).

2.12.1.2 Full CI

In full CI all possible excitations in eq. (2.12.3) are included. The number of ways, N_{FCI}, n electrons can be distributed in m orbitals (where we can put two electrons in each orbital) is given by the binomial coefficient,

$$N_{\text{FCI}} = \frac{(2m)!}{n!(2m-n)!} \tag{2.12.5}$$

which is a factorial scaling with the size of the problem and makes full CI a very expensive method also for relatively small systems (see table 2.5 for some examples). So full CI is limited by both the number of electrons in the molecule as well as the size of the basis set (m basis functions give m orbitals). For a given basis set, however, full CI gives the exact solution and is therefore valuable for validating other methods for including electron correlation.

2.12.2 Møller-Plesset perturbation theory

We introduced perturbation theory as a general tool in section 2.8 and here we will use it for including electron correlation according to Møller-Plesset (MP) perturbation theory (Møller and Plesset 1934). In this method, we assume that $\hat{\mathcal{H}}_0$ in eq. (2.8.1) is simply operator given for the Hartree-Fock approximation in eq. (2.10.10),

$$\hat{\mathcal{H}}_{\text{HF}} = \sum_{i=1}^{n} \hat{f}_i = \sum_{i=1}^{n} \left(\hat{h}_i + \sum_{j=1}^{n} \left(\hat{\mathcal{J}}_j - \hat{\mathcal{K}}_j \right) \right), \tag{2.12.6}$$

where it is noted that the Coulomb, $\hat{\mathcal{J}}_j$, and exchange, $\hat{\mathcal{K}}_j$, terms are counted twice for each electron pair i and j, which is also reflected in the Hartree-Fock energy in eq. (2.10.21). The perturbation operator in eq. (2.8.1), $\hat{\mathcal{H}}_1$, becomes

$$\hat{\mathcal{H}}_1 = \hat{\mathcal{H}}^{\text{el}} - \hat{\mathcal{H}}_{\text{HF}} = \hat{V}_{ee} - \sum_{i,j=1}^{n} \left(\hat{\mathcal{J}}_j - \hat{\mathcal{K}}_j \right), \tag{2.12.7}$$

where $\hat{\mathcal{H}}^{\text{el}}$ is the molecular Hamiltonian in eq. (2.4.2). A rather peculiar fact about $\hat{\mathcal{H}}_1$ is that the second term on the right-hand side of eq. (2.12.7) is around twice the size of the first

term, whereas one in general in perturbation theory should expect the perturbation $\hat{\mathcal{H}}_1$ to be as small as possible. The zeroth-order energy, $\varepsilon_0^{(0)}$, becomes

$$\varepsilon_0^{(0)} = \sum_{i=1}^{n} \epsilon_i \tag{2.12.8}$$

by simply using eq. (2.10.18). The first-order correction to the energy $\varepsilon_0^{(1)}$ is according to eq. (2.8.9) the expectation value of the perturbation operator $\hat{\mathcal{H}}_1$ which leads to

$$\varepsilon_0^{(1)} = -\frac{1}{2} \sum_{i,j=1}^{n} \left(J_{ij} - K_{ij} \right) \tag{2.12.9}$$

where the integration over the first term on the right-hand side of eq. (2.12.7) cancels exactly half of the integration over the second term. The Hartree-Fock energy E_0 in eq. (2.10.21) is thus retained as

$$E_0 = \varepsilon_0^{(0)} + \varepsilon_0^{(1)} + V_{nn} \,, \tag{2.12.10}$$

where we also added the classical nuclear repulsion energy. Electron correlation, as defined in eq. (2.12.1), thus enters first in the second-order contribution to the energy in Møller-Plesset perturbation theory since the sum of the zeroth-order contribution and first-order correction gives the Hartree-Fock energy.

To get the second-order energy, the MP2 energy, we recapitulate the second-order energy from RSPT in eq. (2.8.18),

$$\varepsilon_0^{(2)} = \sum_{j=1}^{\infty} \frac{\langle \psi_0^{(0)} | \hat{\mathcal{H}}_1 | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | \hat{\mathcal{H}}_1 | \psi_0^{(0)} \rangle}{\varepsilon_0^{(0)} - \varepsilon_j^{(0)}} \tag{2.12.11}$$

where we here regard a correction to the ground-state energy. As for the CI method in section 2.12.1, we write the excited states, $\psi_j^{(0)}$, as a sum of single excitations ψ_i^a, double excitations ψ_{ij}^{ab}, etc. Because of the Slater-Condon rules discussed in section 2.6.2, higher excitations than double excitations do not contribute to eq. (2.12.11) for an orthogonal set of states. Furthermore, for the single excitations we can utilize Brillouin's theorem in section 2.12.1.1 on one of the terms,

$$\sum_i \sum_a \langle \psi_0^{\mathrm{HF}} | \hat{\mathcal{H}}^{\mathrm{el}} - \sum_j \hat{f}_j | \psi_i^a \rangle = \sum_i \sum_a \underbrace{\langle \psi_0^{\mathrm{HF}} | \hat{\mathcal{H}}^{\mathrm{el}} | \psi_i^a \rangle}_{\substack{=0 \\ \text{Brillouin's theorem}}} - \left(\sum_j \epsilon_j \right) \underbrace{\langle \psi_0^{\mathrm{HF}} | \psi_i^a \rangle}_{\substack{=0 \\ \text{orthogonal states}}} \,, \tag{2.12.12}$$

so neither the single excitations contribute to the MP2 energy. Finally, the double excitations give the following term

$$
\begin{aligned}
\sum_{\substack{i \\ j>i}} \sum_{\substack{a \\ b>a}} \langle \psi_0^{\mathrm{HF}} | \hat{\mathcal{H}}^{\mathrm{el}} - \sum_k \hat{f}_k | \psi_{ij}^{ab} \rangle &= \sum_{\substack{i \\ j>i}} \sum_{\substack{a \\ b>a}} \langle \psi_0^{\mathrm{HF}} | \hat{V}_{ee} | \psi_{ij}^{ab} \rangle \\
&= \sum_{\substack{i \\ j>i}} \sum_{\substack{a \\ b>a}} \langle \chi_i \chi_j | \hat{g} | \chi_a \chi_b \rangle - \langle \chi_i \chi_j | \hat{g} | \chi_b \chi_a \rangle \,,
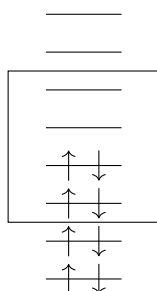\end{aligned}
\tag{2.12.13}
$$

Figure 2.9: Illustration of the CASSCF method for a system of 8 electrons in 8 orbitals. The active space consists of 4 electrons in 4 orbitals, and in a CASSCF calculation we include all states where the 4 electrons are distributed over the 4 orbitals. According to eq. (2.12.5) this leads to $N_{\text{CASSCF}} = 8!/(4!)^2 = 70$ in a CASSCF calculation whereas $N_{\text{FCI}} = 16!/(8!)^2 = 12870$ for a full CI calculation.

so the MP2 energy becomes

$$\varepsilon_0^{(2)} = \sum_{\substack{i \\ j>i}} \sum_{\substack{a \\ b>a}} \frac{\left| \langle \chi_i \chi_j | \hat{g} | \chi_a \chi_b \rangle - \langle \chi_i \chi_j | \hat{g} | \chi_b \chi_a \rangle \right|^2}{(\epsilon_i - \epsilon_a) + (\epsilon_j - \epsilon_b)} \, , \qquad (2.12.14)$$

where we in the denominator have used that the excitation energies for the unperturbed wavefunction is simply given as orbital energy differences. This can be simplified for a closed-shell system along the route taken to obtain eq. (2.6.39).

2.12.3   Multiconfigurational SCF

We introduce multiconfigurational SCF (MCSCF) methods by describing the complete active space SCF (CASSCF) method (Roos 1987). Based on a Hartree-Fock calculation, we select an active space and within this active space we allow for *all* excitations from the occupied states (see figure 2.9 for an example). As for the CI method, the coefficients C_μ in eq. (2.12.3) are determined variationally but in contrast to the CI method, also the orbital coefficients c_{ij} in eq. (2.6.1) are reoptimized so the molecular orbitals are actually modified in an MCSCF method as compared to the Hartree-Fock method. MCSCF methods are thus suitable for molecules where the Hartree-Fock approximation is poor, for example for molecules with a nearly degenerate ground state or for describing the breaking of chemical bonds. However, a CASSCF calculation is by no means a black-box calculation. The selection of the active space requires a detailed insight about the molecular system and the cost of the calculation scales factorially with the size of the active space.

2.13   Density functional theory

Through the Hohenberg-Kohn theorem (Hohenberg and Kohn 1964), density functional theory (DFT) provides an alternative foundation to electronic structure theory as compared to the Schrödinger equation. DFT gives also a theoretical foundation to concepts of the electronic structure of molecular systems as electronegativity and chemical hardness. In

addition, DFT based on the Kohn-Sham approach (KS-DFT) (Kohn and Sham 1965) has, essentially since the work by Becke (Becke 1993), become the main tool in computational quantum chemistry. The reason for its success is that KS-DFT includes electron correlation, and for many properties KS-DFT gives experimental accuracy, with a computational cost comparable to a Hartree-Fock calculation.

The Hohenberg-Kohn existence theorem states that the *ground-state* energy and all other ground-state properties are uniquely defined by the electron density. That, for example, implies that the Hamiltonian in principle can be derived from the electron density. Mathematically this is expressed as an energy functional[3] of the electron density, $E[\rho(\vec{r})]$,

$$E[\rho(\vec{r})] = \int V_{\text{ext}}(\vec{r})\rho(\vec{r})\,d\vec{r} + F[\rho(\vec{r})] \, , \tag{2.13.1}$$

where $V_{\text{ext}}(\vec{r})$ is the external electrostatic potential where the most important term normally arises from the nuclei of the molecular system, and $F[\rho(\vec{r})]$ is a so far unknown energy functional containing the remaining energy terms as the kinetic energy of the electrons and the electron-electron interactions.

The number of electrons, n, is conserved,

$$\int \rho(\vec{r})\,d\vec{r} = n \, , \tag{2.13.2}$$

and by applying the variational principle in section 2.7, the energy functional, $E[\rho(\vec{r})]$, is minimized with respect to the electron density with the constraint that the number of electrons is kept constant as

$$\frac{\delta}{\delta\rho(\vec{r})}\left(E[\rho(\vec{r})] - \mu\int\rho(\vec{r})\,d\vec{r}\right) = 0 \, , \tag{2.13.3}$$

where δ denotes a *functional derivative* and μ is a Lagrangian multiplier for the constraint in eq. (2.13.2). Eq. (2.13.3) is rewritten as

$$\left(\frac{\delta E[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right)_{V_{\text{ext}}} = \mu \, , \tag{2.13.4}$$

which may be regarded as the DFT equivalent to the Schrödinger equation. We put V_{ext} as a subscript to denote that it is kept constant (c.f. how we write partial derivatives in thermodynamics), e.g. the nuclear positions are kept fixed in the clamped-nucleus approximation as described in section 2.4.

2.13.1   Electronegativity

We identify μ in eq. (2.13.4) as the chemical potential for electrons, and it also provides a definition for the electronegativity ξ of the entire system (with a minus sign),

$$-\xi = \mu = \left(\frac{\partial E}{\partial n}\right)_{V_{\text{ext}}} \, . \tag{2.13.5}$$

---

[3]A simple example of a functional: $g[f(x)] = \int_{-\infty}^{\infty} f(x)\,dx$, i.e. we provide a function as the argument and the functional returns a value, e.g. an energy.

The electronegativity is a concept used for a long time (Jensen 1996) and extensively in for example organic chemistry based on e.g. the electronegativity scales by Pauling (Pauling 1932) and Mulliken (Mulliken 1935) to discuss reactivity in molecules, but it is first with DFT that the electronegativity obtained a proper definition (Parr and Yang 1989). Similarly, DFT provides the foundation for other concepts like the chemical hardness, Fukui indexes for reactivity in molecules, etc. (Parr and Yang 1989, Pearson 1997). We also use these concepts in the construction of a force field model based on electronegativity equalization in section 3.3.1.1.

2.13.2   Kohn-Sham approach

DFT has become the workhorse in computational quantum chemistry, and it is the Kohn-Sham approach that is used in the actual DFT calculations. In KS-DFT (Kohn and Sham 1965), the energy functional $F[\rho(\vec{r})]$ in eq. (2.13.1) is partitioned as

$$E[\rho(\vec{r})] = \int V_{\text{ext}}(\vec{r})\rho(\vec{r})\,\mathrm{d}\vec{r} + E_{\text{KE}}[\rho(\vec{r})] + E_{\text{H}}[\rho(\vec{r})] + E_{\text{XC}}[\rho(\vec{r})] \,, \qquad (2.13.6)$$

where $E_{\text{KE}}[\rho(\vec{r})]$ is the kinetic energy for an electron gas (ideal gas) but with the correct density, $E_{\text{H}}[\rho(\vec{r})]$ is the Hartree term which corresponds to classical electrostatics and the Coulomb term in the Hartree-Fock approximation in section 2.10., and, finally, $E_{\text{XC}}[\rho(\vec{r})]$

is the exchange-correlation functional and contains the remaining terms. We need a mathematical representation of the electron density, and the choice in the Kohn-Sham approach is to use orbitals, $\varphi(\vec{r}_i)$,

$$\rho(\vec{r}) = \sum_{i=1}^{n} |\varphi(\vec{r}_i)|^2 \,. \tag{2.13.7}$$

We have thus left a 3-variable representation, as in $\rho(\vec{r})$, and returned to a $3n$-variable representation as in the molecular orbital approach. Furthermore, we can now use the same basis sets (see section 2.11.2) as in molecular orbital theory. Following eq. (2.13.4) for each term in eq. (2.13.6), we have for example,

$$V_{\mathrm{XC}} = \left(\frac{\delta E_{\mathrm{XC}}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \right)_{V_{\mathrm{ext}}} , \tag{2.13.8}$$

where V_{XC} is the exchange-correlation functional. In the Kohn-Sham approach, eq. (2.13.4) leads to

$$\left(V_{\mathrm{KE}} + V_{\mathrm{ext}} + V_{\mathrm{H}} + V_{\mathrm{XC}} \right) \varphi_i = \varepsilon_i \varphi_i \,. \tag{2.13.9}$$

Recall the Fock operator in eq. (2.10.9)

$$\hat{f}_i = \hat{h}_i + \sum_{j=1}^{n} \left(\hat{\mathscr{J}}_j - \hat{\mathscr{K}}_j \right) , \tag{2.13.10}$$

where $\hat{h}_i$ is the one-electron term here corresponding to V_{KE} and V_{ext}, $\hat{\mathscr{J}}_j$ is the Coulomb term which here corresponds to V_{H}, and the exchange term $\hat{\mathscr{K}}_j$ is replaced by the exchange-correlation functional V_{XC}. Thus it is reasonable to regard the terms in the Kohn-Sham approach in eq. (2.13.9) as a modified Fock operator,

$$\hat{f}_i^{\mathrm{DFT}} = V_{\mathrm{KE}} + V_{\mathrm{ext}} + V_{\mathrm{H}} + V_{\mathrm{XC}} \,, \tag{2.13.11}$$

which includes an *ad hoc* correction for electron correlation in the exchange-correlation functional V_{XC}. The exact form of V_{XC} is unknown, but many functionals (and with a *functional*, we mean the choice of V_{XC}) have been suggested. Many of these functionals have been developed to describe certain properties and many functionals even contain empirical parameters fitted to experiments, so the choice of a functional in an actual calculation have to be based on a thorough literature study on DFT calculations on similar molecular systems. The success of computational DFT is, however, indisputable. With the proper choice of functional and basis set, results can be obtained that rivals experiments and with a computational cost that is considerably less expensive than other methods to include electron correlation.

Exercises

Ex. 2.1 — Show that the eigenvalues are real and that the eigenfunctions are orthogonal for a Hermitian operator.

Ex. 2.2 — Show that the normalization factor for an n-electron Slater determinant is $1/\sqrt{n!}$.

Ex. 2.3 — The energy of the hydrogen molecule in the molecular-orbital model (LCAO approximation) is regarded. (a) Give an expression for the energy of the ground state. (b) Give an expression for the triplet state with the lowest energy.

Ex. 2.4 — Show the relations for the antisymmetrizing operator $\hat{\mathscr{A}}$ in eqs. (2.6.25) and (2.6.26).

Ex. 2.5 — Given the exact solution, $\hat{\mathscr{H}}\psi_i = E_i\psi_i$, show that for a trial function, $\tilde{\psi}_i$, the *variation theorem* is fulfilled, i.e., $\tilde{E}_0 \geq E_0$ where the equal sign holds when the trial function is identical to the exact solution.

Ex. 2.6 — Show the Rayleigh-Ritz method, i.e., apply the variational theorem on a trial function,

$$\tilde{\psi}_0 = \sum_i c_i \phi_i$$

expanded in a set of functions ϕ_i. (a) Show first that the Rayleigh-Ritz method leads to the secular equation

$$\sum_i c_i \left(H_{ik} - \tilde{E}_0 S_{ik} \right) = 0$$

where $H_{ik} = \langle \phi_i | \hat{\mathscr{H}} | \phi_k \rangle$ and $S_{ik} = \langle \phi_i | \phi_k \rangle$. (b) Rewrite this equation in terms of a secular

determinant

$$|\mathbf{H} - \tilde{E}_0 \mathbf{S}| = 0$$

where H_{ik} is a matrix element of $\mathbf{H}$, and similarly, S_{ik} is a matrix element of $\mathbf{S}$.

Ex. 2.7 — What is the dependence of the choice of origin on the molecular dipole moment for

  a) a neutral molecule ?

  b) a charged molecule ?

Ex. 2.8 — What is the dependence of the choice of origin on the molecular second moment for

  a) an uncharged and unpolar molecule ?

  b) an uncharged and polar molecule ?

  c) a charged molecule ?

Ex. 2.9 — Show eq. (2.9.40) by using integration by parts (partial integration).

Ex. 2.10 — Show the Roothaan-Hall equations in eq. (2.11.8).

Ex. 2.11 — Show the Gaussian product rule in eqs. (2.11.15) and (2.11.16).

Ex. 2.12 — Show that the molecular Hamiltonian in eq. (2.4.2) commutes with the Fock operator in eq. (2.10.9).

Ex. 2.13 — Show eq. (2.8.37).

Ex. 2.14 — Show eq. (2.8.38).

Ex. 2.15 — Solve the Schrödinger equation in eq. (2.A.40),

$$\frac{\partial^2 \psi}{\partial \varphi^2} = -m_l^2 \psi \, ,$$

and normalize it.

2.A   Quantum-mechanical model systems

We here present some model systems in quantum mechanics which can be solved exactly. The selection is limited to model systems used in subsequent chapters.

2.A.1   Translation - Particle in a one-dimensional box

The model system is described in figure 2.10. It is a one-dimensional system where we in one region, $0 < x < a$, have a potential energy that is zero, $V = 0$. In the remaining part, $x \leq 0$
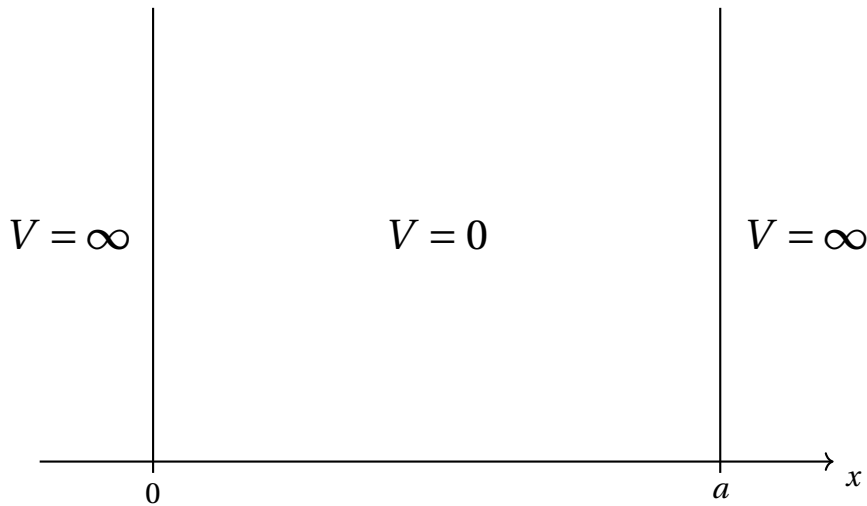
Figure 2.10: The one-dimensional box.

and $x \geq a$, we have an infinite potential energy, $V = \infty$,

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & x \leq 0 \text{ or } x \geq a \end{cases} . \qquad (2.A.1)$$

The Schrödinger equation in one dimension is

$$\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \hat{V}\psi = E\psi . \qquad (2.A.2)$$

In the region outside the box, $x \leq 0$ and $x \geq a$, the potential energy is infinitely high and it is therefore not possible for the particle to be in this region. The probability to find the particle is therefore zero in this region, $\psi^2 = 0$, and thus also the wavefunction is zero, $\psi = 0$. It gives two boundary conditions, $\psi(0) = 0$ and $\psi(a) = 0$, that is used to solve the Schrödinger equation for the central region. For the central region, $0 < x < a$, where $V = 0$, the Schrödinger equation becomes,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{-2mE}{\hbar^2}\psi . \qquad (2.A.3)$$

This differential equation has a solution of the form,

$$\psi(x) = A\sin(ax) + B\cos(bx) . \qquad (2.A.4)$$

If the trial solution in eq. (2.A.4) is put into the Schrödinger equation in eq. (2.A.3),

$$- Aa^2\sin(ax) - Bb^2\cos(bx) = \frac{-2mE}{\hbar^2}\left(A\sin(ax) + B\cos(bx)\right) , \qquad (2.A.5)$$

it leads to

$$a^2 = b^2 = \frac{2mE}{\hbar^2} . \qquad (2.A.6)$$

Furthermore, using the boundary condition, $\psi(0) = 0$, and that the wavefunction is continuous leads to that $B = 0$ since $\cos(0) \neq 0$. So far, we have achieved,

$$\psi(x) = A \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right) . \tag{2.A.7}$$

Using the second boundary condition, $\psi(a) = 0$, gives

$$A \sin\left(\frac{\sqrt{2mE}}{\hbar} a\right) = 0 , \tag{2.A.8}$$

and using

$$\sin(u) = 0 \quad \Rightarrow \quad u = \pm n\pi , \quad n = 0, 1, 2, \ldots, \infty , \tag{2.A.9}$$

so that

$$\frac{\sqrt{2mE}}{\hbar} a = \pm n\pi , \quad n = 0, 1, 2, \ldots, \infty , \tag{2.A.10}$$

gives

$$\psi(x) = A \sin\left(\pm \frac{n\pi}{a} x\right) = \pm A \sin\left(\frac{n\pi}{a} x\right) , \quad n = 0, 1, 2, \ldots, \infty , \tag{2.A.11}$$

since $\sin(-x) = -\sin(x)$. A is a constant with arbitrary sign, so we can simply replace $\pm A$ with A. For $n = 0$, we note that $\psi(x) = 0$. This solution is not allowed since the probability to find
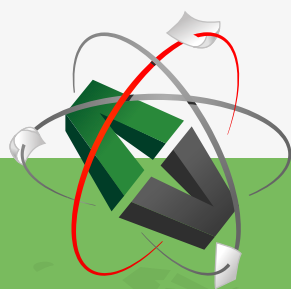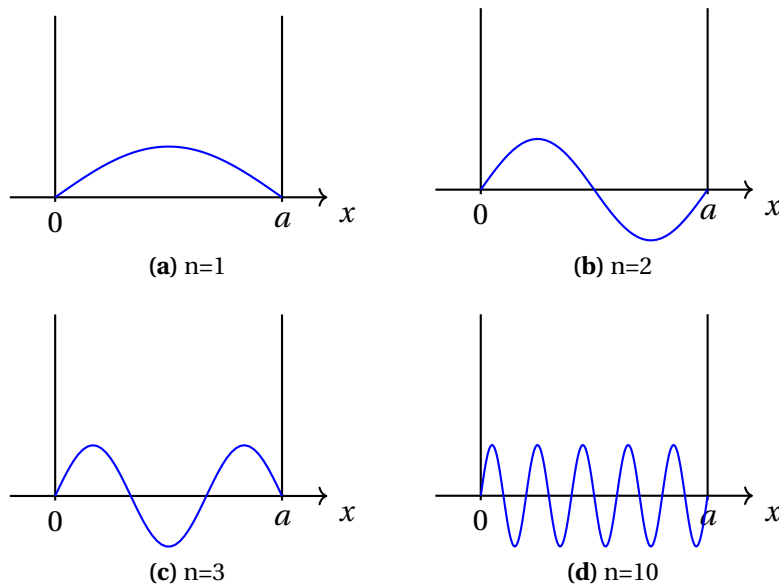
Figure 2.11: The wavefunctions, $\psi_n(x)$, (in blue) for the one-dimensional box

the particle, $\psi^2(x)$, becomes zero in the entire space, and the particle has to be somewhere. For the region, $0 < x < a$, the wavefunction thus becomes

$$\psi(x) = A\sin\left(\frac{n\pi}{a}x\right), \qquad n = 1, 2, \dots, \infty. \tag{2.A.12}$$

Normally, we assume that the wavefunction is normalized,

$$\int_0^a \psi^2(x)\,\mathrm{d}x = 1 \qquad \Rightarrow \qquad \psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right), \quad n = 1, 2, \dots, \infty. \tag{2.A.13}$$

Using eq. (2.A.10), the energies are obtained as

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}, \qquad n = 1, 2, \dots, \infty. \tag{2.A.14}$$

The excitation energies, ΔE_n, are thus given as

$$\Delta E_n = E_{n+1} - E_n = (2n + 1)\frac{h^2}{8ma^2}. \tag{2.A.15}$$

The wavefunctions for a few n are shown in figure 2.11 and the corresponding probabilities are shown in figure 2.12.

2.A.1.1   Particle in a two- and three-dimensional box

The model system for a two-dimensional box (can be used as a model for a surface) is a trivial extension of the one-dimensional box in section 2.A.1. The box has two side lengths, a and

(a) n=1

(b) n=2

(c) n=3

(d) n=10
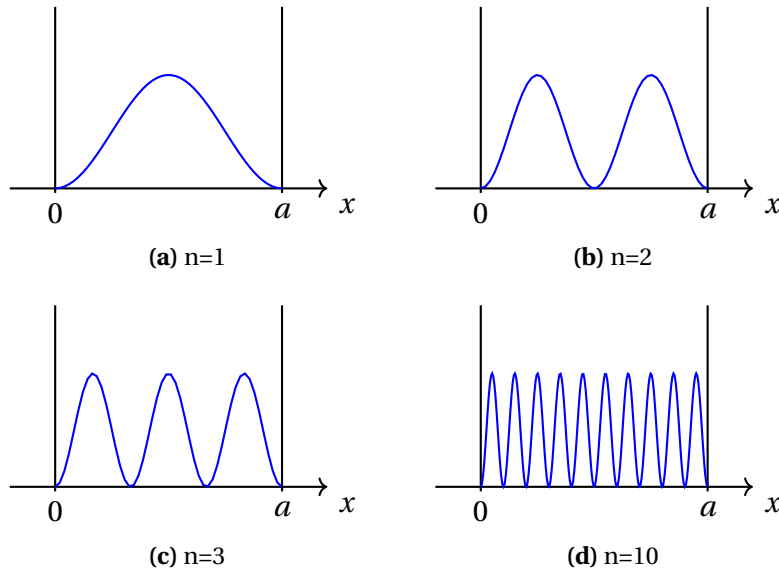
Figure 2.12: The probabilities, $\psi_n^2(x)$, (in blue) for the one-dimensional box

b, and the potential energy, V, is given as

$$V(x, y) = \begin{cases} 0 & 0 < x < a \text{ and } 0 < y < b \\ \infty & \text{elsewhere} \end{cases} . \tag{2.A.16}$$

As for the one-dimensional box, the wavefunction, $\psi(x, y) = 0$, is zero in the region where $V = \infty$. For the region within the box, $0 < x < a$ and $0 < y < b$, the Schrödinger equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{-2mE}{\hbar^2}\psi . \tag{2.A.17}$$

As in eq.2.1.5, we can use separation of variables and the wavefunction is given as the product of two one-dimensional functions,

$$\psi(x, y) = \psi_x(x)\psi_y(y) \tag{2.A.18}$$

Using the solutions of the one-dimensional box in eqs. (2.A.13) and (2.A.14), the wavefunction becomes

$$\psi(x, y) = \frac{2}{\sqrt{ab}} \sin\left(\frac{n_x \pi}{a}x\right)\sin\left(\frac{n_y \pi}{b}y\right) , \quad n_x = 1, 2, \ldots, \infty, n_y = 1, 2, \ldots \infty , \tag{2.A.19}$$

and the energy is

$$E_{n_x n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right) . \tag{2.A.20}$$

A further generalization to three dimensions where

$$V(x, y, z) = \begin{cases} 0 & 0 < x < a \text{ and } 0 < y < b \text{ and } 0 < z < c \\ \infty & \text{elsewhere} \end{cases} , \tag{2.A.21}$$

gives the wavefunction

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{b} y\right) \sin\left(\frac{n_z \pi}{c} z\right) , \tag{2.A.22}$$

which has the following possible quantum numbers: $n_x = 1, 2, \ldots, \infty$, $n_y = 1, 2, \ldots \infty$, and $n_z = 1, 2, \ldots \infty$. The energy becomes

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) . \tag{2.A.23}$$

2.A.2   Vibrations - Harmonic oscillator

The harmonic oscillator may be regarded as a simple model for the vibration of a diatomic molecule around the equilibrium bond length, R_e, where $q = R - R_e$ is thus the deviation from R_e. The Hamiltonian is given as

$$\hat{\mathcal{H}} = \frac{-\hbar^2}{2\mu} \frac{\partial}{\partial q^2} + \frac{1}{2} k q^2 , \tag{2.A.24}$$

Figure 2.13: Particle on a ring with a radius **r**. The particle has the momentum **p** and the angular momentum **l**.

where μ is the reduced mass for a diatomic molecule,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \ , \tag{2.A.25}$$

and k is the force constant obtained as the second derivative of $V(q)$ calculated in $q = 0$. In eq. (2.A.25), m_I is the mass of atom I. The solutions for the Schrödinger equation are known

$$\psi_n(q) = A_n H_n(y) e^{\frac{-y^2}{2}} \ , \tag{2.A.26}$$

where $e^{\frac{-y^2}{2}}$ is a Gaussian function, $H_n(y)$ are the Hermite polynomials, and

$$y = \frac{q}{\alpha} \ , \quad \alpha = \left(\frac{\hbar^2}{\mu k} \right)^{\frac{1}{4}} \ , \quad A_n = \left(\alpha \pi^{\frac{1}{2}} 2^n n! \right)^{-\frac{1}{2}} \ . \tag{2.A.27}$$

The energies, ε_n, are given as

$$\varepsilon_n = \left(n + \frac{1}{2} \right) h\nu = \left(n + \frac{1}{2} \right) \hbar\omega = \left(n + \frac{1}{2} \right) \frac{hc}{\lambda} \tag{2.A.28}$$

which is expressed either with the frequency, ν, the angular frequency, ω, or the wavelength, λ.

2.A.3   Rotation - Particle on a ring

First we regard classical mechanics for a particle moving on a ring with a radius $r = |\mathbf{r}|$, see figure 2.13. The particle has a momentum $\mathbf{p} = m\mathbf{v}$, where m is the mass of the particle and $\mathbf{v}$ is its velocity, and we define the angular momentum $\mathbf{l}$ as

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} \ . \tag{2.A.29}$$

The velocity $v = |\mathbf{v}|$ can be written as

$$v = 2\pi r \nu = r\omega \ , \tag{2.A.30}$$

where ν is the frequency (number of rotations per time unit) and $\omega = 2\pi\nu$ is the angular velocity (radians per time unit). For $l = |\mathbf{l}|$ and $p = |\mathbf{p}|$, we get from eq. (2.A.29) that $l = rp$. Since $p = mv = mr\omega$, we get $l = mr^2\omega = I\omega$ where we define the moment of inertia I of the particle as

$$I = mr^2 \ . \tag{2.A.31}$$

The kinetic energy K, as well as the total energy E since the potential energy is 0, can thus be written as

$$E = K = \frac{1}{2}mv^2 = \frac{1}{2}I\omega^2 = \frac{l^2}{2I} \ . \tag{2.A.32}$$

We will now demonstrate that the angular momentum $\mathbf{l}$ is quantized. A particle can rotate both ways, $\pm\mathbf{p}$, thus $\mathbf{l}$ in figure 2.13 can be directed both upwards and downwards,

$$l_z = \pm pr \ . \tag{2.A.33}$$

According to de Broglie each particle behave like a wave as

$$\lambda = \frac{h}{p} \ , \tag{2.A.34}$$

where λ is the wavelength. Thus the angular momentum becomes

$$l_z = \pm\frac{hr}{\lambda} \ . \tag{2.A.35}$$

If we rotate the angle 2π, we need to get the same l_z, thus the number of wavelengths per full rotation have to be an integer m_l, i.e. $m_l\lambda = 2\pi r$, leading to

$$l_z = \pm\frac{hr}{\lambda} = \hbar m_l \ , \qquad m_l = 0, \pm 1, \pm 2, \dots \ , \tag{2.A.36}$$

where as before $\hbar = h/2\pi$ and the $\pm$ is included in m_l. Note that $m_l = 0$ corresponds to an infinitely large wavelength λ. The energy of the system in eq. (2.A.32) becomes

$$E = \frac{l^2}{2I} = \frac{m_l^2\hbar^2}{2I} \ , \tag{2.A.37}$$

where we have degeneracy for all m_l apart from $m_l = 0$. The Schrödinger equation for the motion in the xy-plane (no z component) is given as

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi = E\psi \tag{2.A.38}$$

for the case when the potential energy is zero. For a particle on a ring, we use cylindrical coordinate, r and φ, where the radius r is fixed (see figure 2.14), leading to the Schrödinger equation,

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial^2\psi}{\partial\varphi^2} = E\psi \ . \tag{2.A.39}$$

Using eq. (2.A.37) for the energy and the definition of the moment of inertia in eq. (2.A.31) leads to

$$\frac{\partial^2\psi}{\partial\varphi^2} = -m_l^2\psi \ . \tag{2.A.40}$$

Thus the wavefunction becomes

$$\psi_{m_l}(\varphi) = \frac{e^{i m_l \varphi}}{\sqrt{2\pi}} \ , \tag{2.A.41}$$

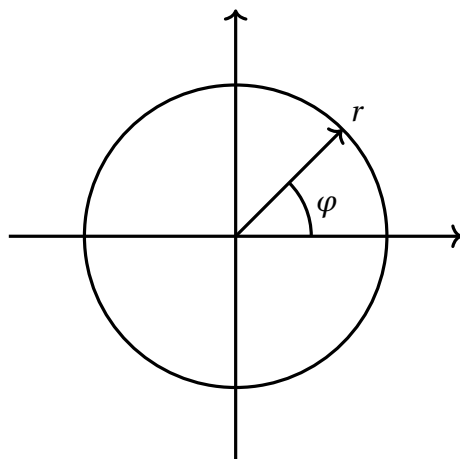which is normalized (see exercise 2.15).

Figure 2.14: Coordinate system for cylindrical coordinates

2.A.4   Particle on a sphere

For a particle on a sphere, we adopt spherical polar coordinates, r, θ and φ (Arfken et al. 2013, ch. 3),

$$
\begin{aligned}
x &= r\sin(\theta)\cos(\varphi) & 0 \leq \theta \leq \pi \\
y &= r\sin(\theta)\sin(\varphi) & 0 \leq \varphi \leq 2\pi \\
z &= r\cos(\theta) & r \text{ is a constant}
\end{aligned}
$$

As for a particle on a ring, the potential energy is zero resulting in the following Schrödinger equation,

$$
\frac{-\hbar^2}{2m}\nabla^2\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{2.A.42}
$$

For spherical polar coordinates,

$$
\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2 \;, \tag{2.A.43}
$$

where Λ^2 is the Legendrian,

$$
\Lambda^2 = \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} \;. \tag{2.A.44}
$$

The Legendrian has known eigenfunctions and eigenvalues a

$$
\Lambda^2 Y_{lm_l}(\theta,\varphi) = -l(l+1)Y_{lm_l}(\theta,\varphi) \;, \tag{2.A.45}
$$

where $Y_{lm_l}(\theta,\varphi)$ is a spherical harmonics which are tabulated (see e.g. (Arfken et al. 2013, ch. 15)). The eigenvalues l and m_l are quantized as,

- $l = 0, 1, 2, \ldots, \infty$
- $m_l = 0, \pm 1, \ldots \pm l$.

Note that the allowed values of m_l depends on l, which is the reason for its notation (used also in the previous section). For a particle on a sphere, r is constant, so we get for the Schrödinger equation,

$$\frac{-\hbar}{2I}\Lambda^2\psi_{lm_l} = l(l+1)\frac{\hbar}{2I}\psi_{lm_l} , \qquad (2.A.46)$$

so that

$$E_{lm_l} = l(l+1)\frac{\hbar}{2I} . \qquad (2.A.47)$$

The energy E_{lm_l} depends only on l so we have a degeneracy factor $g = 2l+1$, i.e. the number of degenerate states.

2.A.5 One-electron atom

We will here solve the Schrödinger equation for the one-electron atom discussed in section 2.5.1 where atomic orbitals were introduced. Within the Born-Oppenheimer approximation (see section 2.4) we regard a nucleus at rest in a fixed position. The potential energy operator $\hat{V}$ is given from eq. (2.5.1) as the Coulomb interaction between the nucleus and the electron,

$$\hat{V} = \frac{-Ze^2}{4\pi\varepsilon_0 r} . \qquad (2.A.48)$$

Since $\hat{V}$ only depends on one variable, the distance between the nucleus and the electron r, it is tempting to use spherical polar coordinates (r, θ, φ) as in appendix 2.A.4 instead of Cartesian coordinates (x, y, z). The Schrödinger equation becomes

$$\frac{-\hbar^2}{2m_e}\nabla^2\psi + \hat{V}\psi = E\psi \qquad (2.A.49)$$

where m_e is the mass of the electron and ∇^2 in spherical polar coordinates was given in eq. (2.A.43). The wavefunction $\psi(r, \theta, \varphi)$ is separable as

$$\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi) . \qquad (2.A.50)$$

Thus the Schrödinger equation in spherical polar coordinates becomes

$$\frac{-\hbar^2}{2m_e}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(rR(r)Y(\theta,\varphi)\right)\right) + \frac{1}{r^2}\Lambda^2 R(r)Y(\theta,\varphi) - \frac{-Ze^2}{4\pi\varepsilon_0 r}R(r)Y(\theta,\varphi) = ER(r)Y(\theta,\varphi) . \quad (2.A.51)$$

The angular part is identical to the solution for a particle on a sphere in eq. (2.A.45),

$$\Lambda^2 Y_{lm_l}(\theta, \varphi) = -l(l+1)Y_{lm_l}(\theta, \varphi) , \qquad (2.A.52)$$

where $Y_{lm_l}(\theta, \varphi)$ were the spherical harmonics. For the radial part, we get the following equation

$$\frac{-\hbar^2}{2m_e}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(rR(r)\right)\right) + \frac{1}{r^2}\left(-l(l+1)\right)R(r) - \frac{-Ze^2}{4\pi\varepsilon_0 r}R(r) = ER(r) , \qquad (2.A.53)$$

for which the solutions are the associated Laguerre functions, $R_{nl}(r)$ (see e.g. (Arfken et al. 2013, ch. 18)). The wavefunction thus becomes

$$\psi_{nlm_l}(r, \theta, \varphi) = R_{nl}(r)Y_{lm_l}(\theta, \varphi) , \qquad (2.A.54)$$

which is the result used in eq. (2.5.2).

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FORCE FIELDS

3.1 Introduction to force fields

In a force field, the potential energy surface of a molecule or a system of molecules is described with a relatively simple model based on atom-type parameters and approximate analytical expressions for a set of energy terms where each energy term has a physical interpretation. The motivation for constructing a force field is in particular that we in molecular dynamics (MD) simulations need to calculate the forces between a large amount of particles (perhaps 10.000 atoms) repeatedly. A typical time-step in an MD simulation is 1 fs so for an MD simulation of 100 ns we need to calculate all the interatomic forces 10^8 times. A standard force field for the potential energy surface, $V(R^{3N})$, may look like

$$
V\left(R^{3N}\right) = \underbrace{\sum_i^{\text{bonds}} \frac{k_i}{2}\left(l_i - l_{i,0}\right)^2}_{\text{bond stretches}} + \underbrace{\sum_i^{\text{angles}} \frac{k_i}{2}\left(\theta_i - \theta_{i,0}\right)^2}_{\text{angle bends}} + \underbrace{\sum_i^{\text{torsions}} \frac{V_i}{2}\left(1 + \cos\left(n_i\omega_i - \gamma_i\right)\right)}_{\text{torsional motion}}
$$
$$
+ \underbrace{\sum_{i,j>i} \underbrace{4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^6\right)}_{\text{Lennard-Jones term}} + \underbrace{\frac{q_i q_j}{4\pi\varepsilon_0 R_{ij}}}_{\text{Coulomb term}}}_{\text{intermolecular interactions}} , \tag{3.1.1}
$$

where each energy term will be described in some detail below. Each energy term has a physical meaning, but is in this chapter introduced in a phenomenological way based on empirical experience. Each term contains variables related to the molecular geometry, e.g. the bond length l_i, the bond angle, θ_i, the torsional angle, ω_i, and the interatomic distance, R_{ij}. In addition, each energy term contains atom-type parameters, e.g. the force constant, k_i, and the equilibrium bond length, $l_{i,0}$, for the bond stretching term. Even if it is desirable to have only one value of each atom-type parameter for each element, it is in many cases not possible as for example for the carbon atom since a carbon atom in a methyl group, $-CH_3$, and in a carbonyl group, $>C=O$, has quite different properties (e.g. the carbon atomic charges, q_i, have different sign). The transferability of atom-type parameters, i.e. the applicability of the same set of values of the atom-type parameters to a variety of different types of molecular systems (e.g. proteins, nonpolar polymers, ionic crystals, etc.) is thus a central issue when discussing force fields.

In the construction of a force field, we have to make a choice of which energy terms to include, the functional form of each energy term and how to obtain the values of the atom-type parameters. Historically, force fields have been parametrized against experimental data, termed *empirical* force fields, as for example structural and thermodynamic data. *Semi-empirical* force fields are still common, where usually the atomic charges in the Coulomb term in eq. (3.1.1) are obtianed from quantum chemical calculations and the remaining energy terms are parametrized from experimental data. Finally, a force field can be parametrized from a set of quantum chemical calculations on model systems.

Quantum chemical data is in principle preferred since it provides a consistent data set on the microscopic level, whereas most available experimental data are on the macroscopic level, i.e. measured at a given temperature and pressure. The limitation of the data set used in the parametrization limits the applicabililty of the force field, e.g. if only data at room temperature and ambient pressure are included in the parametrization it cannot be expected to be applicable at other thermodynamic states.

We will in this chapter give an introduction to various force field terms based on a phenomenological approach, i.e. the energy terms are introduced in *ad hoc* manor and not derived from an underying and more fundamental theory. However, in section 3.4 some of the contributions will be derived from quantum mechanics. We divide the force field into two types of terms, *bonded* and *non-bonded* interactions. With bonded interactions, we refer to terms that describe covalent bonding, whereas non-bonded interactions describe relatively weak through-space interactions. Non-bonded interactions are not restricted to intermolecular interactions, but also includes interactions in relatively large molecules between atoms in different parts of the molecule. For example, atom 1 in the larger of the two molecules in figure 3.1 cannot see the difference between the interaction with atom N in the same molecule and the interaction with the atoms in the small molecule, so these interactions need to be treated on an equal footing in a force field model.
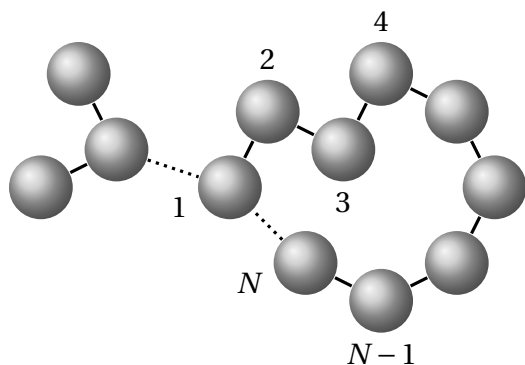
Figure 3.1: Sketch to illustrate that the interactions between atoms of different parts of the molecule, in this case atom 1 and atom N, are essentially the same as the interaction between atom 1 and the atoms in the small molecule.
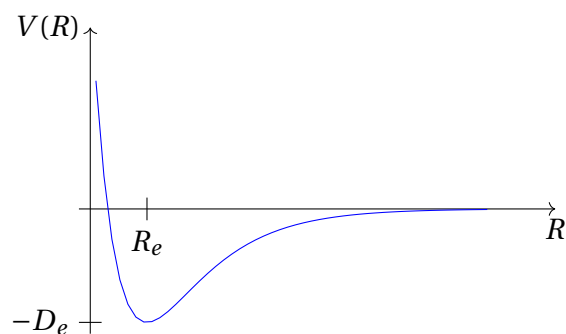
Figure 3.2: The Morse potential for a diatomic molecule. D_e is the dissociation energy and R_e is the bond distance at the energy minimum, respectively.

3.2 Force-field terms for covalent bonding

We will here introduce the most common force-field terms for describing covalent bonding: bond stretching, angle bending and torsional motion.

3.2.1 Bond stretching

Let us regard the potential energy, $V(R)$, as a function of the bond distance, R, of a diatomic molecule which often can be represented accurately with a Morse potential (see figure 3.2) (Morse 1929),

$$V(R) = D_e \left(e^{-2a(R-R_e)} - 2e^{-a(R-R_e)} \right), \tag{3.2.1}$$

where R_e is the equilibrium distance, i.e. the bond distance at the minimum of the potential well, D_e is the depth of the potential surface (dissociation energy), i.e. minus the potential energy at R_e, and a is a parameter describing the width of the potential well. The Morse potential can be written in different ways and is here given so that the potential energy approaches zero at infinite separation.

As a first approximation, we represent a covalent bond with a classical harmonic oscillator, i.e. two atoms are connected with a spring with a force constant, k. We make a Taylor expansion of the potential energy, $V(R)$, around the equilibrium geometry, R_e. If we introduce the Dunham expansion parameter $Q = (R - R_e)/R_e$ (Dunham 1932a;b), the Taylor expansion around $R = R_e$, i.e. $Q = 0$ becomes

$$V(Q) = \underbrace{V(0)}_{\text{zero level}} + \underbrace{V'(0)\,Q}_{V'(0)=0 \text{ in the minimum}} + \underbrace{\frac{1}{2}V''(0)\,Q^2}_{\text{Harmonic term}} + \underbrace{\frac{1}{6}V^{(3)}(0)\,Q^3}_{\text{Anharmonicity}} + \underbrace{\frac{1}{24}V^{(4)}(0)\,Q^4}_{\text{Quartic term}} \ldots, \tag{3.2.2}$$

where the zero level, $V(0)$, can be ignored (the potential energy surface can always be shifted with a constant energy). The linear term in Q is 0 since the gradient is 0 at the minimum. The
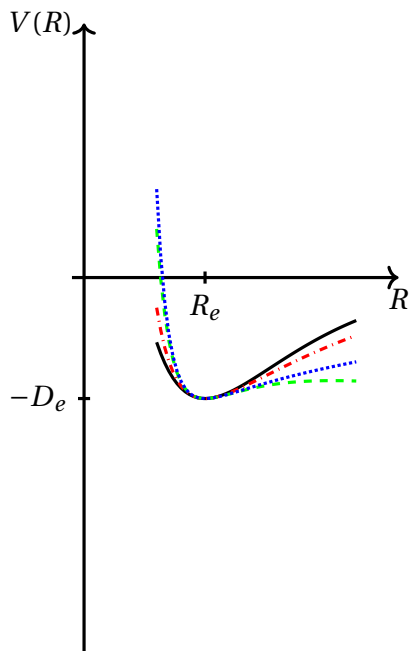
Figure 3.3: A diatomic molecule represented as two atoms connected with a spring. According to Hooke's law, the force as a function of the bond distance, $F(R)$, is given as $F(R) = -k(R - R_e)$, where k is the force constant and R_e is the equilibrium bond length.
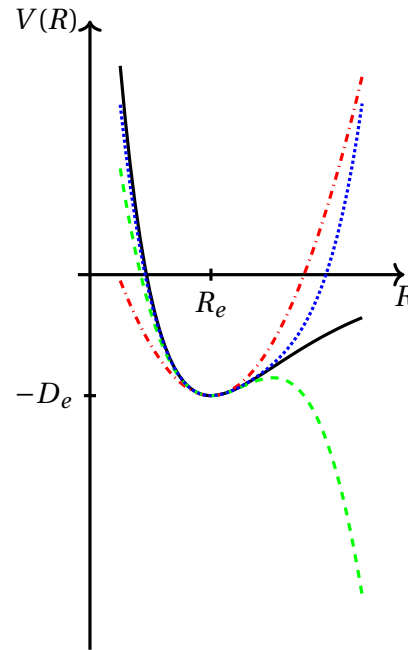
Figure 3.4: A Taylor expansion of the Morse potential. The full line denotes the Morse potential, whereas the dash-dotted (red) line shows a truncation after the harmonic term, the dashed line (green) shows a truncation after the anharmonic (cubic) term, and the dotted line (blue) shows a truncation after the quartic term, respectively.

quadratic term in Q is the harmonic term, we denote the cubic term in Q the anharmonicity of the potential energy, and we finally have the quartic term. If the anharmonicity and other higher order terms in the Taylor expansion are ignored, we get the classical harmonic oscillator,

$$V(Q) = \frac{k}{2}Q^2 \quad \text{with } k \equiv V''(0) \ . \tag{3.2.3}$$

A Taylor expansion of the Morse potential in eq. (3.2.1) is shown in figure 3.4. Truncation after the harmonic term gives a reasonable description around the minimum. At large separation between the atoms, $Q \to \infty$, also $V(Q) \to \infty$, so the dissociation limit is not described correctly. If the model, however, is restricted to describing non-reacting molecules where the bond length always is expected to be close to R_e, truncation after the harmonic term is a reasonable approximation. Truncation after the anharmonic term (again see figure 3.4) leads to that the energy $V(Q) \to -\infty$ for large Q. Whereas a harmonic approximation may be useful in the sense that it keeps the molecules in a stable configuration, a truncation after the anharmonic term may be disastrous in an energy minimization scheme or in a molecular dynamics simulation where the energy cannot diverge towards $-\infty$. A truncation after the quartic term has essentially the same features as a truncation after the harmonic term but it resembles the Morse potential more accurately at slightly larger Q than the harmonic approximation.

The Simons-Parr-Finlan (SPF) expansion, where the expansion parameter Q is chosen as $Q = (R - R_e)/R$ (Simons et al. 1973) is shown in figure xx and it has a superior performance with respect to convergence as compared to the Dunham expansion essentially since $Q \to 1$ when $R \to \infty$ for this choice of Q. A generalization is given by the Thakkar expansion (Thakkar 1975),

$$V(R) = c_0(p)\lambda^2 \left(1 + \sum_{n=1}^{\infty} c_n(p)\lambda^n\right), \tag{3.2.4}$$

where

$$\lambda(R, p) = \text{sgn}(p)\left(1 - \left(\frac{R_e}{R}\right)^p\right) \quad \text{where} \quad \text{sgn}(p) = \begin{cases} 1 & p > 0 \\ 0 & p = 0 \\ -1 & p < 0 \end{cases}. \tag{3.2.5}$$

In eq. (3.2.4), p is a nonzero real number. The Thakkar expansion reduces to the Dunham expansion for $p = -1$, to the SPF expansion for $p = 1$, and to the Lennard-Jones potential that will be discussed in eq. (3.3.53) for $p = 6$ and $c_n(p) = 0$ for $n \geq 1$.

3.2.2   Angle bending

We use the water molecule as a typical example of an angle bending term (see figure 3.5), where the equilibrium angle, θ_e, between the O-H bonds is 104.5°. As for bond stretching,

Figure 3.5: Definition of the internal co-ordinates, the bond lengths, R_1 and R_2 and the bond angle θ, for the water molecule.
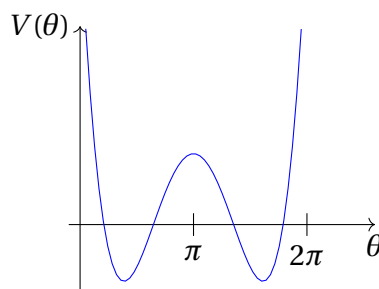
Figure 3.6: A double minimum potential for the angle bending term, e.g. for the water molecule.

we normally use a harmonic oscillator approximation for the angle bending term,

$$V(\theta) = \frac{k_\theta}{2}\left(\theta - \theta_e\right)^2 \tag{3.2.6}$$

which is an approximation that is valid when the angle θ is close to the equilibrium angle θ_e. A better model is given in figure 3.6 for the water molecule. However, for example for the water molecule at $\theta = \pi$, which corresponds to a linear water molecule, the potential energy barrier is so high that the linear molecule will not exist unless we are at extremely high temperatures. It is therefore in most cases sufficient to adopt a Taylor expansion around one of the minima as in eq. (3.2.6). For ammonia, on the other hand, the umbrella motion that inverts the molecule cannot be ignored at ambient conditions and eq. (3.2.6) would be a severe approximation.

3.2.3   Dihedral terms

A dihedral angle is defined as the angle between two planes as illustrated in figure 3.7. If the atoms 1, 2 and 3 define one plane, and the atoms 2, 3 and 4 define the second plane, the dihedral angle ω is the angle between these two planes. The dihedral (or torsional) energy is given as a periodic function

$$V(\omega) = \sum_n \frac{V_n}{2}\left(1 + \cos(n\omega - \gamma)\right) \tag{3.2.7}$$

where n gives the periodicity (e.g. $n = 2$ for 180° periodicity and $n = 3$ for 120° periodiicy, respectively), V_n is the rotational energy barrier and γ defines where the dihedral angle is 0. The energy term can also be written as the real part of a Fourier series,

$$V(\omega) = \sum_n C_n \cos(\omega)^n \tag{3.2.8}$$

Some molecules, as for example benzene, are expected to be planar, and often we would like to add a constraint to keep the molecule planar. If we add constraints, for example by adding Lagrangian multipliers in a constrained energy minimization, the molecule is kept planar all
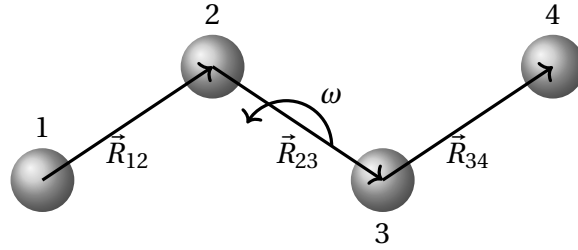
Figure 3.7: Definition of dihedral angle.

the time. Alternatively, we can add an extra energy term, referred to as an energy restraint or an improper torsion term,

$$V(\omega) = k_\omega \left(1 - \cos 2\omega\right) \tag{3.2.9}$$

where the molecule is kept *almost* planar if k_ω has a very large value.

3.2.4 Cross terms

Sometimes cross terms are included describing the coupling between e.g. two bond stretches or a bond stretch and an angle bending term. Let us take the water molecule in figure 3.5 as an example where the intramolecular motion is described by two bond lengths R_1 and R_2 and a bond angle θ. We carry out a Taylor expansion around $R_{1,0}$, $R_{2,0}$ and θ_0,

$$
\begin{aligned}
V(R_1, R_2, \theta) \;=\; & V(R_{1,0}, R_{2,0}, \theta_0) + \left(R_1 - R_{1,0}\right) \left.\frac{\partial V}{\partial R_1}\right|_{R_{1,0}, R_{2,0}, \theta_0} + \left(R_2 - R_{2,0}\right) \left.\frac{\partial V}{\partial R_2}\right|_{R_{1,0}, R_{2,0}, \theta_0} \\
+ \; & \left(\theta - \theta_0\right) \left.\frac{\partial V}{\partial \theta}\right|_{R_{1,0}, R_{2,0}, \theta_0} + \frac{1}{2} \left(R_1 - R_{1,0}\right)^2 \left.\frac{\partial^2 V}{\partial R_1^2}\right|_{R_{1,0}, R_{2,0}, \theta_0} \\
+ \; & \frac{1}{2} \left(R_2 - R_{2,0}\right)^2 \left.\frac{\partial^2 V}{\partial R_2^2}\right|_{R_{1,0}, R_{2,0}, \theta_0} + \frac{1}{2} \left(\theta - \theta_0\right)^2 \left.\frac{\partial^2 V}{\partial \theta^2}\right|_{R_{1,0}, R_{2,0}, \theta_0} \\
+ \; & \left(R_1 - R_{1,0}\right) \left(R_2 - R_{2,0}\right) \left.\frac{\partial^2 V}{\partial R_1 \partial R_2}\right|_{R_{1,0}, R_{2,0}, \theta_0} + \left(R_1 - R_{1,0}\right) \left(\theta - \theta_0\right) \left.\frac{\partial^2 V}{\partial R_1 \partial \theta}\right|_{R_{1,0}, R_{2,0}, \theta_0} \\
+ \; & \left(R_2 - R_{2,0}\right) \left(\theta - \theta_0\right) \left.\frac{\partial^2 V}{\partial R_2 \partial \theta}\right|_{R_{1,0}, R_{2,0}, \theta_0} + \ldots \tag{3.2.10}
\end{aligned}
$$

where the last three terms are coupling terms. It is common that only a few of the coupling terms are important. For water it is suitable to introduce a symmetric stretch coordinate,

$$Q_1 - Q_{1,0} = \left(R_1 - R_{1,0}\right) + \left(R_2 - R_{2,0}\right) \tag{3.2.11}$$

and an antisymmetric stretch coordinate,

$$Q_2 - Q_{2,0} = \left(R_1 - R_{1,0}\right) - \left(R_2 - R_{2,0}\right) \tag{3.2.12}$$

where it turns out that only one of the cross terms,

$$V(Q_1, Q_2, \theta) = \ldots + \left(Q_1 - Q_{1,0}\right)\left(\theta - \theta_0\right) \left.\frac{\partial^2 V}{\partial Q_1 \partial \theta}\right|_{Q_{1,0}, Q_{2,0}, \theta_0} + \ldots \qquad (3.2.13)$$

is of importance. When including cross terms, the atom-type parameters $R_{1,0}$, $R_{2,0}$ and θ_0 (or $Q_{1,0}$, $Q_{2,0}$ and θ_0) do not correspond to the equilibrium geometry, which is realized by minimizing the potential energy surface in eq. (3.2.10).

3.2.5 Summary of bonding terms

We have from a phenomenological standpoint discussed the regular energy terms included in a force field to describe covalent bonds: bond stretching, angle terms and torsional motion, sometimes extended by coupling terms and additional terms for example describing hyperconjugation (how π-conjugation affects bond stretching in neighbouring groups). Sometimes the following classification is used (Maple et al. 1994, Hwang et al. 1994, Allinger et al. 1996):

- Class I: only harmonic terms, not any cross terms

- Class II: anharmonic terms and cross terms

- Class III: also additional terms, e.g. to describe hyperconjugation

3.3 Intermolecular interactions

In section 3.2, we discussed interactions mainly describing covalent bonds referred to as bonded interactions. In this section, we discuss intermolecular interactions, i.e. weak interactions as compared to covalent forces, as for example dispersion interactions in liquid argon, hydrogen bonding in liquid water and ion-ion interactions in electrolytes. Furthermore, the energy terms used to describe intermolecular interactions are also adopted for long-range interactions within the same molecule, as the energy terms discussed in the previous section are restricted to interactions between an atom and atoms up to three atoms away within the same molecule (see figure 3.1, i.e. the bonded terms include interactions between atom 1 and atoms 2, 3 and 4).

As is in the previous section, we will introduce the energy terms for intermolecular interactions in a phenomenological way, whereas the connection to quantum mechanics is treated in section 3.4. The four most important intermolecular interaction energies are:

- electrostatic energy: interactions between ions and/or polar systems using classical electrostatics.

- induction energy: arising from that the electron density of a molecule is polarized by an electric field from the surrounding molecules resulting in induced electric moments (e.g. induced dipole moments).

- short-range repulsion energy: essentially arising from that the Pauli exclusion principle needs to be fulfilled.

- dispersion energy: arising from that the motion of the electrons is correlated.

3.3.1 Electrostatic interactions

In quantum chemistry, the charge distribution of a molecule with N atoms is represented by a set of nuclear charges, $\{Z_I, I = 1, 2, \ldots, N\}$, and an electron density, $\rho(\vec{r})$, so that

$$\int \rho(\vec{r}) \, \mathrm{d}\tau = n \, , \tag{3.3.1}$$

where n is the number of electrons in the molecule. In a force field, the most simple way to represent the molecular charge distribution is by a set of atomic charges, $\{q_I, I = 1, 2, \ldots, N\}$, in conjunction with Coulomb's law for the interaction between atomic charges,

$$V = \sum_{I=1}^{N} \sum_{J=I+1}^{N} \frac{q_I q_J}{4\pi\varepsilon_0 R_{IJ}} \, , \tag{3.3.2}$$

where R_{IJ} is the distance between atoms I and J. The key problem in obtaining atomic charges is therefore how to partition the electron density into atomic contributions. An atomic charge therefore consists of the part of the electron density assigned to the atom plus the nuclear charge of the atom. Also, an atomic charge does not have a unique definition since it is not a measurable quantity, and in the literature we find literally hundreds of approaches to calculate atomic charges.

It is reasonable to expect that the atomic charges of a molecule should reproduce the molecular electric moments discussed in section 2.9.1. It is always imposed that the molecule has the correct total charge,

$$q^{\mathrm{mol}} = \sum_{I=1}^{N} q_I \, . \tag{3.3.3}$$

For a neutral molecule, $q^{\mathrm{mol}} = 0$, even round-off errors giving a small molecular charge different from zero would give large errors in the electrostatic energy because of the long-range $1/R$ distance dependence for charge-charge interactions. For small molecules, it is reasonable that the molecular dipole moment,

$$\mu_\alpha^{\mathrm{mol}} = \sum_{I=1}^{N} q_I R_{I,\alpha} \, , \tag{3.3.4}$$

and the molecular quadrupole moment (see eq. (2.9.32)),

$$\Theta_{\alpha\beta}^{\mathrm{mol}} = \sum_{I=1}^{N} q_I \left(\frac{3}{2} R_{I,\alpha} R_{I,\beta} - \frac{1}{2} R_{I,\gamma} R_{I,\gamma} \delta_{\alpha\beta} \right) \, , \tag{3.3.5}$$

are well described by the atomic charges q_I.

If atomic charges are not sufficient to represent the molecular charge distribution, there are several ways to improve the model. A systematic way would be to add atomic dipole moments, $\mu_{I,\alpha}$, and atomic second moments, $Q_{I,\alpha\beta}$, (or alternatively atomic quadrupole moments, $\Theta_{I,\alpha\beta}$) which would improve the corresponding molecular moments as

$$\mu_\alpha^{\text{mol}} = \sum_{I=1}^{N} q_I R_{I,\alpha} + \mu_{I,\alpha} \, , \qquad (3.3.6)$$

and

$$Q_{\alpha\beta}^{\text{mol}} = \sum_{I=1}^{N} q_I R_{I,\alpha} R_{I,\beta} + \mu_{I,\alpha} R_{I,\beta} + R_{I,\alpha} \mu_{I,\beta} + Q_{I,\alpha\beta} \, , \qquad (3.3.7)$$

where the latter can be converted to the quadrupole moment by eq. (2.9.32).

Alternatively, extra charges placed outside the atoms, so-called virtual charges, may be added for describing lone-pairs, e.g. in water, or π-systems, e.g. in benzene. Again, the representation of the electrostatics in a force field in terms of distributed charges, dipole moments, etc. is not unique and many models exist in the literature, but it appears like atomic charges extended by atomic dipole moments and sometimes atomic quadrupole moments is a more general and systematic approach.

Atomic charges are often obtained from quantum chemical calculations using various partition techniques of the electronic charge distribution as for example Mulliken charges (Mul-

liken 1955), Hirshfeld charges (Hirshfeld 1977), etc., which traditionally often has been combined with experimental data to obtain atom-type parameters for the other energy terms in a semi-empirical force field. For small molecules, atomic charges may be parametrized from quantum-chemically derived molecular dipole moments and quadrupole moments (eqs. (3.3.4) and (3.3.5)), but the dipole moment for larger molecules is not a very meaningful property since it is a sum of numerous important contributions where each contribution describes the local electrostatics around e.g. a binding site and needs to be modelled accurately.

One way to address this is to parametrize the electrostatic potential on a set of lattice points $\{a_j, j = 1, \ldots, m\}$ around a molecule,

$$\varphi_{a_j} = \sum_{I=1}^{N} \frac{q_I}{R_{Ia_j}} , \tag{3.3.8}$$

against a quantum-chemically derived electrostatic potential. It is an attractive approach since the electrostatic potential is probed locally around all important interaction sites of the molecule. One potential problem is that the electrostatic potential calculated close to the molecule does not follow the classical behaviour for point charges in eq. (3.3.8) since at short distances, the quantum-chemically derived electrostatic potential is calculated within the molecular charge distribution and short-range damping terms are required. In general, parametrizations like this are tricky because of redundant data and over-fitting so expertise in multivariate data analysis and chemometrics is highly demanded.

Example 3.1: The dipole moment of HCN.

We can in principle get the correct dipole moment of HCN by using partial atomic charges in two different ways as illustrated in figure 3.8, i.e. either by a charge transfer between C and N or between H and C. With the choice of $\delta = 0.5$ e, both possibilities give approximately the correct dipole moment by using eq. 3.3.4, $\mu_z^{\text{mol}} = -2.81$ D for the "CN" case and $\mu_z^{\text{mol}} = -2.61$ D for the "CH" case, respectively, compared to the quantum chemical value of $\mu_z^{\text{mol}} = -2.70$ D, but the two cases can, for this example, easily be distinguished by calculating the quadrupole moment. The quadrupole moments calculated by eq. (3.3.5), Θ_{zz}^{mol}, become -0.44 B for the "CN" case and 5.47 B for the "CH" case, respectively, compared to the quantum chemical value of 1.92 B.

A reasonable distribution of the partial atomic charges for HCN obtained from fitting the electrostatic potential around the molecule is given in figure 3.9. These partial atomic charges give a dipole moment $\mu_z^{\text{mol}} = -2.67$ D and a quadrupole moment $\Theta_{zz}^{\text{mol}} = 1.80$ B again using eqs. (3.3.4) and (3.3.5), both in good agreement with the respective quantum chemical value.

The quantum chemical calculations have been carried out with the NWChem package (Valiev et al. 2010) adopting the PBE functional (Perdew et al. 1996) and the cc-pVDZ basis set (Dunning Jr. 1989), resulting in the bond lengths $R_{CN} = 1.170$ Å and $R_{CH} = 1.085$ Å, respectively, in addition to the quantum chemical values given above.

Atomic partial charges are to a very small degree transferable, e.g. there is not one set of carbon atomic charges that can be used for all types of carbon atoms in e.g. methyl groups,
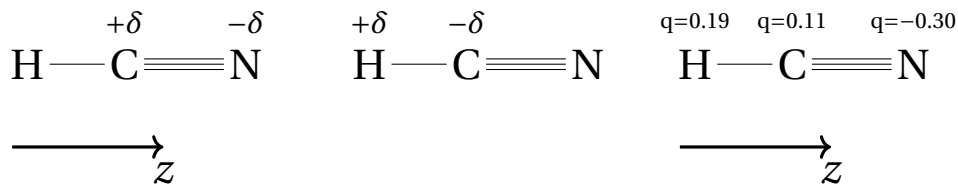
Figure 3.8: Two possible distributions of partial atomic charges in HCN.

Figure 3.9: Partial atomic charges of HCN obtained from fitting the electrostatic potential around the molecule.

aromatic rings, carbonyl groups, etc. Let us consider a simple example, F_2 and HF. The atomic charges in F_2, $q_F = 0$, because of symmetry reasons whereas HF is highly polar with a dipole moment of 1.8265 D (Muenter and Klemperer 1970) described by the partial charges $q_F = -q_H = -0.41$ e for the bond length 0.9168 Å (Mann et al. 1961). Another example is to consider the carbon partial charges in benzene and formaldehyde. In benzene, $q_C \approx -0.05$ e wheras $q_C \approx 0.40$ e in formaldehyde, again demonstrating the lack of transferability of atomic partial charges.

3.3.1.1 Electronegativity equalization model

In the electronegativity equalization model (EEM), it is assumed that each atom in a molecule can be described by an atomic electronegativity, ξ_I, and an atomic chemical hardness, η_I (Mortier et al. 1985). If the electronegativities of two atoms are different, charge will flow from one atom the other until the molecular electronegativity (chemical potential) is the same everywhere (equalized). In addition, a work is required to charge an atom, which is determined by the chemical hardness (or capacitance) of the atom. Electronegativity and chemical hardness are central concepts in density functional theory and has been discussed thoroughly (Parr and Yang 1989, Geerlings et al. 2003). The molecular energy, V, for a molecule with N atoms becomes

$$V = \sum_I^N \xi_I q_I + \frac{1}{2} \sum_I^N \eta_I q_I^2 + \frac{1}{2} \sum_{I,J \neq I}^N q_I T_{IJ}^{(0)} q_J + \mu \left(q^{\text{mol}} - \sum_I^N q_I \right), \qquad (3.3.9)$$

where the third term is the regular Coulomb interaction between two atomic charges, q_I and q_J. The last term is a constraint that preserves the molecular charge, q^{mol}, where μ is a Lagrangian multiplier. The atomic charges are obtained by minimizing the molecular energy in eq. (3.3.9) with respect to the atomic charges and the Lagrangian multiplier. We thus obtain

$$\frac{\partial V}{\partial q_K} = 0 = \xi_K + \eta_K q_K + \sum_{L \neq K}^N T_{KL}^{(0)} q_L - \mu, \qquad (3.3.10)$$

and

$$\frac{\partial V}{\partial \mu} = 0 = q^{\text{mol}} - \sum_I^N q_I, \qquad (3.3.11)$$

where the last term is simply the applied constraint. A set of $N + 1$ coupled linear equations is obtained which can be solved by standard numerical techniques

$$
\begin{pmatrix}
\eta_1 & T_{12}^{(0)} & \cdots & T_{1N}^{(0)} & 1 \\
T_{21}^{(0)} & \eta_2 & \cdots & T_{2N}^{(0)} & 1 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
T_{N1}^{(0)} & T_{N2}^{(0)} & \cdots & \eta_N & 1 \\
1 & 1 & \cdots & 1 & 0
\end{pmatrix}
\begin{pmatrix}
q_1 \\ q_2 \\ \vdots \\ q_N \\ \mu
\end{pmatrix}
=
\begin{pmatrix}
\xi_1 \\ \xi_2 \\ \vdots \\ \xi_N \\ q^{\mathrm{mol}}
\end{pmatrix},
\tag{3.3.12}
$$

or alternatively the atomic charges are calculated as

$$
\begin{pmatrix}
q_1 \\ q_2 \\ \vdots \\ q_N \\ \mu
\end{pmatrix}
=
\begin{pmatrix}
\eta_1 & T_{12}^{(0)} & \cdots & T_{1N}^{(0)} & 1 \\
T_{21}^{(0)} & \eta_2 & \cdots & T_{2N}^{(0)} & 1 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
T_{N1}^{(0)} & T_{N2}^{(0)} & \cdots & \eta_N & 1 \\
1 & 1 & \cdots & 1 & 0
\end{pmatrix}^{-1}
\begin{pmatrix}
\xi_1 \\ \xi_2 \\ \vdots \\ \xi_N \\ q^{\mathrm{mol}}
\end{pmatrix}.
\tag{3.3.13}
$$

Thus, the atomic electronegativity, ξ_I, and chemical hardness, η_I, are atom-type parameters that has to be determined. The method has been parametrized in different ways, e.g. the Delft molecular mechanics (DMM) force field has been developed for hydrocarbons by

Donor   Acceptor
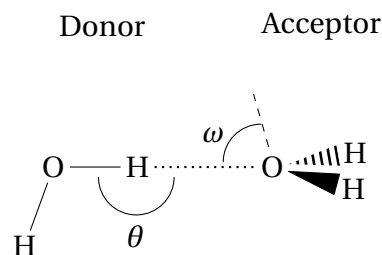
Figure 3.10: Water dimer. The angles θ and ω refer to the notation in eq. (3.3.15), where the dashed line indicates the direction of an oxygen lone-pair orbital. The distance $R_{\text{H}\cdots\text{O}}$ in eq. (3.3.15) refers to the distance between the H atom in the hydrogen donor molecule and the O atom in the hydrogen acceptor molecule.

parametrizing experimental data (van Duin et al. 1994). Electronegativity equalization is useful in organic chemistry to determine where it is likely that electrophilic and nucleophilic attacks occur in a molecule since these types of reactions highly depend on the local differences in the electrostatic potential around the molecule.

For a diatomic molecule, using the constraint $q_I + q_J = 0$, we get the solution (see exercise 3.1),

$$- q_J = q_I = \frac{\xi_J - \xi_I}{\eta_I + \eta_J - 2 T_{IJ}^{(0)}} \; . \tag{3.3.14}$$

The sign of the partial charge is thus determined by the difference in electronegativity between the two atom-types in the dimer. Consequently, the model works for the example discussed above, F_2 and HF. The atomic partial charges q_F in F_2 are zero by cancellation of $\xi_F - \xi_F$ in eq. (3.3.14), wheras they are non-zero in HF since $\xi_H - \xi_F \neq 0$. The magnitude of the atomic charges depends on all atom-type parameters as well as the bond distance in $T_{IJ}^{(0)}$, so the EEM also includes a geometry dependence of the atomic charges important in e.g. modeling conformational energies in molecules.

3.3.1.2 Hydrogen bonding

Hydrogen bonds are in general difficult to model in a force field and extra terms are sometimes added to the force field as in the YETI force field (Vedani 1988),

$$V_{\text{YETI}} = \left(\frac{A}{R_{\text{H}\cdots\text{O}}^{12}} - \frac{C}{R_{\text{H}\cdots\text{O}}^{10}} \right) \cos^2 \theta \cos^4 \omega \tag{3.3.15}$$

where A and C are parameters and the notation is explained for the water dimer in figure 3.10. This energy term is highly dependent on the angles θ and ω with the purpose to model that hydrogen bonds are strongly orientation dependent.

Since hydrogen bonds are to a large extent electrostatic interactions (Stone et al. 1997), a more systematic way is to include atomic dipole moments in the model. A dipole-dipole

interaction can according to eq. (2.9.35) be written as

$$V_{\mu\mu} = -\frac{3\left(\vec{\mu}_I \cdot \vec{R}_{IJ}\right)\left(\vec{R}_{IJ} \cdot \vec{\mu}_J\right) - \left(\vec{\mu}_I \cdot \vec{\mu}_J\right)}{R_{IJ}^5} \tag{3.3.16}$$

gives an appropriate dependence on the mutual molecular orientation as seen from the vector scalar products in eq. (3.3.16).

3.3.2 Electronic polarization

The electronic density of a molecule is polarized by an electric field from the electric moments of the surrounding molecules, normally referred to as the induction energy in a force field. We recall from section 2.9.2 that the polarizability $\alpha_{\alpha\beta}$ is defined as the linear response to an electric field, E_β,

$$\mu_\alpha^{\text{ind}} = \alpha_{\alpha\beta}E_\beta \tag{3.3.17}$$

where μ_α^{ind} is the induced dipole moment. We generalize eq. (3.3.17) to atomic polarizabilities, $\alpha_{I,\alpha\beta}$, as

$$\mu_{I,\alpha}^{\text{ind}} = \alpha_{I,\alpha\beta}E_{I,\beta}^{\text{tot}} \tag{3.3.18}$$

where $\mu_{I,\alpha}^{\text{ind}}$ is the atomic induced dipole moment and $E_{I,\beta}^{\text{tot}}$ is the total electric field at atom I, i.e. it includes for example the electric field from an applied external field and the atomic charges of the surrounding molecules as well as the electric field from all surrounding atomic induced dipole moments.

The discussion in section 2.9.2 for a classical polarizability in an external field is extended to a system of many polarizable particles. In addition to the electrostatic energy and self-energy given in eq. (2.9.41) for a single particle, a dipole-dipole interaction energy (see eq. (3.4.8)) is also included. The induction energy V_{ind} of a system of polarizable particles in an external electric field, $E_{I,\alpha}^{\text{ext}}$, is given as (Vesely 1977)

$$V_{\text{ind}} = -\frac{1}{2}\sum_{I,J\neq I}^{N}\mu_{I,\alpha}^{\text{ind}}T_{IJ,\alpha\beta}^{(2)}\mu_{J,\beta}^{\text{ind}} + \sum_{I}^{N}V_{I,\text{self}} - \sum_{I}^{N}\mu_{I,\alpha}^{\text{ind}}E_{I,\alpha}^{\text{ext}} \tag{3.3.19}$$

where $\mu_{I,\alpha}^{\text{ind}}$ is the induced dipole moment of particle I, $T_{IJ,\alpha\beta}^{(2)}$, is the interaction tensor of rank 2 defined in eq. (2.9.22), and $V_{I,\text{self}}$ is the self-energy of particle I as defined in eq. (2.9.40),

$$V_{I,\text{self}} = \frac{1}{2}\left(\alpha_{I,\alpha\beta}\right)^{-1}\mu_{I,\alpha}^{\text{ind}}\mu_{I,\beta}^{\text{ind}} . \tag{3.3.20}$$

The external electric field may arise from permanent electric moments of the surrounding particles of the system or other external sources. The system is polarized in such a way that the induction energy is minimized,

$$\frac{\partial V_{\text{ind}}}{\partial \mu_{K,\gamma}^{\text{ind}}} = 0 = -\left(\sum_{J\neq K}^{N}T_{KJ,\gamma\beta}^{(2)}\mu_{J,\beta}^{\text{ind}}\right) + \left(\alpha_{K,\beta\gamma}\right)^{-1}\mu_{K,\beta}^{\text{ind}} - E_{K,\gamma}^{\text{ext}} \tag{3.3.21}$$

which gives

$$\mu_{K,\beta}^{\text{ind}} = \alpha_{K,\beta\gamma}\left(E_{K,\gamma}^{\text{ext}} + \sum_{J\neq K}^{N} T_{KJ,\gamma\beta}^{(2)}\mu_{J,\beta}^{\text{ind}}\right) \tag{3.3.22}$$

The atomic induced dipole moments are thus given from a set of $3N$ coupled equations and is a true many-body term. If polarizabilities are included in a force field, the calculation of induced dipole moments will be relatively time-consuming as compared to other energy terms. The expression of the potential energy in eq. (3.3.19) may be simplified by using eq. (3.3.22) as

$$
\begin{aligned}
V_{\text{ind}} &= -\frac{1}{2}\sum_{I,J\neq I}^{N}\mu_{I,\alpha}^{\text{ind}}T_{IJ,\alpha\beta}^{(2)}\mu_{J,\beta}^{\text{ind}} + \frac{1}{2}\sum_{I}^{N}\mu_{I,\alpha}^{\text{ind}}\left(E_{I,\alpha}^{\text{ext}} + \sum_{J\neq I}^{N}T_{IJ,\alpha\beta}^{(2)}\mu_{J,\beta}^{\text{ind}}\right) - \sum_{I}^{N}\mu_{I,\alpha}^{\text{ind}}E_{I,\alpha}^{\text{ext}} \\
&= -\frac{1}{2}\sum_{I}^{N}\mu_{I,\alpha}^{\text{ind}}E_{I,\alpha}^{\text{ext}}
\end{aligned}
\tag{3.3.23}
$$

The self-energy thus cancels the induced dipole-induced dipole interaction and half of the interaction between the induced dipoles and the external electric field. By inserting eq. (3.3.22), eq. (3.3.23) may be rewritten as

$$V_{\text{ind}} = -\frac{1}{2}\sum_{I}^{N}\alpha_{I,\alpha\beta}\left(E_{I,\beta}^{\text{ext}} + \sum_{J\neq I}^{N}T_{IJ,\beta\gamma}^{(2)}\mu_{J,\gamma}^{\text{ind}}\right)E_{I,\alpha}^{\text{ext}} \tag{3.3.24}$$
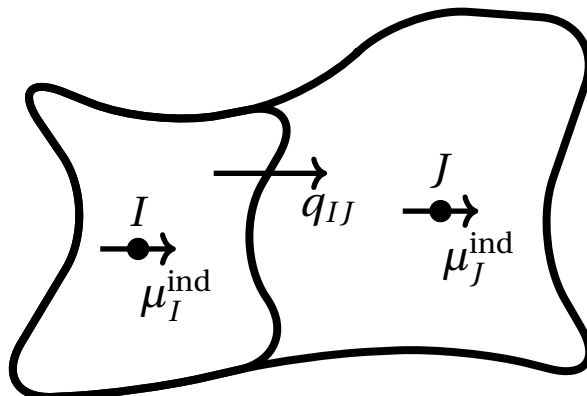
Figure 3.11: Polarization in a system divided into two subsystems.

Although the induction energy in eq. (3.3.19) is quadratic in the induced dipole moment, the final result in eq. (3.3.23) is only linear in $\mu_{I,\alpha}^{\text{ind}}$. The result in eq. (3.3.23) is, however, only valid for the optimum $\mu_{I,\alpha}^{\text{ind}}$ fulfilling the requirement in eq. (3.3.21), $\partial V_{\text{ind}}/\partial \mu_{K,\gamma}^{\text{ind}} = 0$. Eq. (3.3.24) can therefore, for example, not be used to calculate the gradient of the induction energy.

3.3.2.1 Distributed polarizabilities

If a system is divided into subsystems (see figure 3.11 for an illustration), as for example a molecular polarizability into atomic contributions, there are two major contributions to the polarizability. We have a monopole contribution arising from charge transfter between the subsystems as a response to the difference in electrostatic potential between the subsystems, which we will describe by an extension of the electronegativity equalization method in section 3.3.1.1. Secondly, we have a local polarization within each subsystem where the leading term is described by an atomic induced dipole moment.

3.3.2.2 Electronegativity equalization methods

The electronegativity equalization method (EEM) for calculating atomic charges in section 3.3.1.1 is extended with the interaction with an external potential, φ_I^{ext}. The molecular energy V in eq. (3.3.9) becomes thus

$$V = \sum_I^N \left(\xi_I + \varphi_I^{\text{ext}} \right) q_I^{\text{tot}} + \frac{1}{2} \sum_I^N \eta_I (q_I^{\text{tot}})^2 + \frac{1}{2} \sum_{I,J \neq I}^N q_I^{\text{tot}} T_{IJ}^{(0)} q_J^{\text{tot}} + \mu \left(q^{\text{mol}} - \sum_I^N q_I^{\text{tot}} \right) \qquad (3.3.25)$$

Following the same procedure as in section 3.3.1.1, eq. (3.3.12) becomes

$$\begin{pmatrix} \eta_1 & T_{12}^{(0)} & \dots & T_{1N}^{(0)} & 1 \\ T_{21}^{(0)} & \eta_2 & \dots & T_{2N}^{(0)} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ T_{N1}^{(0)} & T_{N2}^{(0)} & \dots & \eta_N & 1 \\ 1 & 1 & \dots & 1 & 0 \end{pmatrix} \begin{pmatrix} q_1^{\text{tot}} \\ q_2^{\text{tot}} \\ \vdots \\ q_N^{\text{tot}} \\ \mu \end{pmatrix} = \begin{pmatrix} \xi_1 + \varphi_1^{\text{ext}} \\ \xi_2 + \varphi_2^{\text{ext}} \\ \vdots \\ \xi_N + \varphi_N^{\text{ext}} \\ q^{\text{mol}} \end{pmatrix} \qquad (3.3.26)$$

Dividing q^{tot} into the atomic charges defined in section 3.3.1.1 and induced atomic charges, q_I^{ind}, arising from the response to external electrostatic potential gives for q_I^{ind},

$$
\begin{pmatrix} q_1^{\text{ind}} \\ q_2^{\text{ind}} \\ \vdots \\ q_N^{\text{ind}} \\ 0 \end{pmatrix} = \begin{pmatrix} \eta_1 & T_{12}^{(0)} & \dots & T_{1N}^{(0)} & 1 \\ T_{21}^{(0)} & \eta_2 & \dots & T_{2N}^{(0)} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ T_{N1}^{(0)} & T_{N2}^{(0)} & \dots & \eta_N & 1 \\ 1 & 1 & \dots & 1 & 0 \end{pmatrix}^{-1} \begin{pmatrix} \varphi_1^{\text{ext}} \\ \varphi_2^{\text{ext}} \\ \vdots \\ \varphi_N^{\text{ext}} \\ 0 \end{pmatrix}
\tag{3.3.27}
$$

or

$$
q_I^{\text{ind}} = \sum_{J=1}^{N} A_{IJ} \varphi_J^{\text{ext}}
\tag{3.3.28}
$$

where A_{IJ} is a relay matrix determining charge flow to atom I from an external electrostatic potential at atom J.

If a homogeneous external electric field, E_β^{ext}, is regarded, its electrostatic potential at atom J, φ_J^{ext} is

$$
\varphi_J^{\text{ext}} = -R_{J,\beta} E_\beta^{\text{ext}} .
\tag{3.3.29}
$$

The response to E_β^{ext} thus becomes

$$
\frac{\partial q_I^{\text{ind}}}{\partial E_\beta^{\text{ext}}} = -\sum_{J=1}^{N} A_{IJ} R_{J,\beta} .
\tag{3.3.30}
$$

We recall from eq. (2.9.36) that the molecular polarizability is defined as

$$
\alpha_{\alpha\beta} = \frac{\partial \mu_\alpha^{\text{ind}}}{\partial E_\beta^{\text{ext}}} ,
\tag{3.3.31}
$$

and since

$$
\mu_\alpha^{\text{ind}} = \sum_{I=1}^{N} q_I^{\text{ind}} R_{I,\alpha} ,
\tag{3.3.32}
$$

we get

$$
\alpha_{\alpha\beta} = -\sum_{I,J=1}^{N} R_{I,\alpha} A_{IJ} R_{J,\beta} .
\tag{3.3.33}
$$

For planar molecules, however, only an in-plane polarizability is obtained, and EEM can thus only give a part of the molecular polarizability.

3.3.2.3   Point-dipole interaction model

The point-dipole interaction model (PDI) model has many similarities with the electronegativity equalization model in the previous section 3.3.2.2 in the sense that it relies on a set of native atom-type parameters that couple with each other through electrostatic interactions to give the molecular property. If we have a molecule of N atoms in an external electric field,

E_β^{ext}, and an atom-type polarizability, α_P, is assigned to each atom, an atomic induced dipole moment, μ_α^{ind}, is given as

$$\mu_{I,\alpha}^{\text{ind}} = \alpha_{I,\alpha\beta}\left(E_{I,\beta}^{\text{ext}} + \sum_{J \neq I}^{N} T_{IJ,\alpha\beta}^{(2)} \mu_{J,\beta}^{\text{ind}} \right) \tag{3.3.34}$$

where the last term is the electric field from all other atomic induced dipole moments in the molecule. Since we have $3N$ coupled equations, the set of equations can be written in matrix form as

$$\boldsymbol{\mu}^{\text{ind}} = \boldsymbol{\alpha}\left(\mathbf{E}^{\text{ext}} + \mathbf{T}^{(2)}\boldsymbol{\mu}^{\text{ind}} \right) \tag{3.3.35}$$

which may be rearranged as

$$\boldsymbol{\mu}^{\text{ind}} = \left(\boldsymbol{\alpha}^{-1} - \mathbf{T}^{(2)} \right)^{-1} \mathbf{E}^{\text{ext}} = \mathbf{B}\mathbf{E}^{\text{ext}} \tag{3.3.36}$$

where $\mathbf{B}$ is the relay tensor defined as

$$\mathbf{B} = \left(\boldsymbol{\alpha}^{-1} - \mathbf{T}^{(2)} \right)^{-1} \tag{3.3.37}$$

The atomic induced dipole moment is given in terms of the relay tensor as

$$\mu_{I,\alpha}^{\text{ind}} = \sum_{J=1}^{N} B_{IJ,\alpha\beta} E_{J,\beta}^{\text{ext}} \tag{3.3.38}$$

It is noted that the molecular induced dipole moment is simply the sum of the atomic induced dipole moments,

$$\mu_\alpha^{\text{ind}} = \sum_{I=1}^{N} \mu_{I,\alpha}^{\text{ind}} \tag{3.3.39}$$

In addition, if a homogeneous electric field, $E_{J,\beta}^{\text{ext}} = E_\beta^{\text{ext}}$, is assumed, the molecular induced dipole moment is given as

$$\mu_\alpha^{\text{ind}} = \left(\sum_{I,J=1}^{N} B_{IJ,\alpha\beta} \right) E_\beta^{\text{ext}} \tag{3.3.40}$$

From its definition in eq. (2.9.36),

$$\mu_\alpha^{\text{ind}} = \alpha_{\alpha\beta}^{\text{mol}} E_\beta^{\text{ext}} \tag{3.3.41}$$

the molecular polariazability is obtained as

$$\alpha_{\alpha\beta}^{\text{mol}} = \sum_{I,J=1}^{N} B_{IJ,\alpha\beta} \tag{3.3.42}$$

The definition of atomic polarizabilities is not unique, but one way to define it is as

$$\mu_{I,\alpha}^{\text{ind}} = \alpha_{I,\alpha\beta}^{\text{atom}} E_\beta^{\text{ext}} \tag{3.3.43}$$

which results in

$$\alpha_{I,\alpha\beta}^{\text{atom}} = \sum_{J}^{N} B_{IJ,\alpha\beta} \tag{3.3.44}$$

Even if the atom-type parameter, α_P, is isotropic,

$$\alpha_{P,\alpha\beta} = \alpha_P \delta_{\alpha\beta} \tag{3.3.45}$$

the resulting molecular polarizability includes the anisotropy because of the intramolecular electric fields.

The PDI model thus gives a distributed representation of the molecular polarizability in terms of the relay tensor $B_{IJ,\alpha\beta}$. The relay tensor is interpreted as the response in terms of an atomic induced dipole moment at atom I, $\mu_{I,\alpha}^{\text{ind}}$, arising from a perturbation by an electric field at atom J, $E_{J,\beta}$. The PDI model may also be regarded as a correction to an additive model by carrying out a Taylor expansion of the $\mathbf{B}$ tensor in eq. (3.3.37) around $\boldsymbol{\alpha}\mathbf{T}^{(2)} = 0$,

$$\mathbf{B} = \left(\boldsymbol{\alpha}^{-1} - \mathbf{T}^{(2)} \right)^{-1} = \left(\mathbf{1} - \boldsymbol{\alpha}\mathbf{T}^{(2)} \right)^{-1} \boldsymbol{\alpha} = \left(\mathbf{1} + \boldsymbol{\alpha}\mathbf{T}^{(2)} + \left(\boldsymbol{\alpha}\mathbf{T}^{(2)} \right)^2 + \ldots \right) \boldsymbol{\alpha} \tag{3.3.46}$$

which converges if $\boldsymbol{\alpha}\mathbf{T}^{(2)} < \mathbf{1}$. It is also instructive to solve the two-atom problem, which results in (Silberstein 1917a;b)

$$\alpha_\parallel = \frac{\alpha_i + \alpha_j + 4\alpha_i\alpha_j/R^3}{1 - 4\alpha_i\alpha_j/R^6} \tag{3.3.47}$$

for the component parallel to the diatomic bond $\alpha_\parallel$, and

$$\alpha_\perp = \frac{\alpha_i + \alpha_j - 2\alpha_i\alpha_j/R^3}{1 - \alpha_i\alpha_j/R^6} \tag{3.3.48}$$

for the component perpendicular to the bond $\alpha_\perp$. If R^{-6}-term is neglected, the isotropic part of the molecular polarizability is additive

$$\alpha^{\mathrm{mol}} = \frac{1}{3}\left(\alpha_\parallel + 2\alpha_\perp\right) = \alpha_i + \alpha_j \tag{3.3.49}$$

which indicates that the isotropic part of the polarizability is easier to model than the individual tensor components and thereby also the anisotropy of the polarizability tensor.

3.3.3 Dispersion and short-range repulsion

If we consider the interactions in e.g. liquid argon, where electrostatic and polarization (in the absence of an external electric field) interactions are not present, the dominating interactions consist of attractive dispersion interactions and short-range repulsion.

3.3.3.1 Dispersion

Dispersion interactions arises from that the motion of the electrons are correlated, and London derived an equation for the dispersion energy from second-order perturbation

theory (see section 3.4.2 for details) resulting in (London 1930)

$$V_{\text{disp}} = \frac{-C_6}{R^6} \, , \tag{3.3.50}$$

where C_6 is a parameter with a postive value since the dispersion energy is always attractive. Higher-order terms in the perturbation expansion may be included,

$$V_{\text{disp}} = \frac{-C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} + \dots \, , \tag{3.3.51}$$

but normally only the R^{-6}-term is included.

3.3.3.2 Repulsion

The physical origin of the exchange-repulsion energy is the Pauli exclusion principle, i.e. that two electrons cannot be in the same quantum mechanical state. So when two closed-shell, e.g. two argon atoms, come close to each other they will repell each other just to fulfil the Pauli exclusion principle. The other energy terms commonly included to describe intermolecular forces (electrostatics, induction and dispersion), normally have quite significant approximations at short interatomic distances whereas the long-range behaviour is more or less correct. It is therefore common to define the repulsion energy V_{rep} more pragmatically as (Engkvist et al. 2000)

$$V_{\text{rep}} = V_{\text{int}} - V_{\text{ele}} - V_{\text{ind}} - V_{\text{disp}} \, , \tag{3.3.52}$$

so that it contains also short-range errors in the other energy terms as well as higher-order energy terms that often are short-range, as e.g. for the dispersion energy in eq. (3.3.51). The repulsion energy V_{rep} is therefore often parametrized from a set of quantum chemical calculations of the interaction energy V_{int} on molecular dimers and clusters and subtracting the other energy terms.

3.3.3.3 Lennard-Jones potential

Lennard-Jones suggested the following model for the interaction between two rare-gas atoms (Lennard-Jones 1931),

$$V_{\text{LJ}} = 4\epsilon \left(\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right) = \frac{A}{R^{12}} - \frac{C_6}{R^6} \, , \tag{3.3.53}$$

which consists of a short-range repulsion energy with an R^{-12}-dependence and a more long-range attractive London dispersion energy as in eq. (3.3.50). We express the atom-type parameters either as ϵ and σ or as A and C_6. The reason for the choice of the R^{-12}-dependence is that the repulsive $(\sigma/R)^{12}$ term is the square of the attractive $(\sigma/R)^6$ term, which Lennard-Jones took advantage of in solving some statistical mechanical model systems analytically.[1] In a molecular force field, the Lennard-Jones potential is generalized

---

[1] The choice of the R^{-12}-dependence is often attributed to computational efficiency. It is indeed computationally efficient, which may explain its present popularity, but Lennard-Jones presented his work in 1931 long before the first computers in the 1950's.

to a pair-wise additive force field,

$$V_{\text{LJ}} = \sum_{I=1}^{N_A} \sum_{J=1}^{N_B} 4\epsilon_{IJ} \left(\left(\frac{\sigma_{IJ}}{R_{IJ}} \right)^{12} - \left(\frac{\sigma_{IJ}}{R_{IJ}} \right)^6 \right) \tag{3.3.54}$$

where N_A and N_B are the number of atoms in molecules A and B, respectively. Eq. (3.3.54) contains atom-pair parameters, ϵ_{IJ} and σ_{IJ}, which leads to $M(M+1)/2$ number of parameters for M atom types. It is favourable to reduce the number of parameters in the model to M parameters by applying the Lorentz-Berthelot mixing rules,

$$\sigma_{IJ} = \frac{1}{2} \left(\sigma_{II} + \sigma_{JJ} \right) ; \qquad \epsilon_{IJ} = \sqrt{\epsilon_{II} \epsilon_{JJ}} \tag{3.3.55}$$

Example 3.2: Interaction between an Ar atom and an ion.

Is the leading interaction energy between an Ar atom and an ion a dispersion energy or an induction energy? It is an induction energy, and the argument is as follows. The ion with a charge q gives an electric field at the Ar atom,

$$E_\alpha = -\nabla_\alpha \left(\frac{1}{R} \right) = \frac{R_\alpha}{R^3} = \frac{1}{R^2}$$

where we in the last step have assumed that both particles have been placed along one of the coordinate axis x, y or z. The Ar atom is polarized by the field and gets an induced dipole moment,

$$\mu_\alpha^{\text{ind}} = \alpha_{\alpha\beta} E_\beta$$

We recall the induction energy in eq. (3.3.23)

$$V_{\text{ind}} = -\frac{1}{2} \mu_\alpha^{\text{ind}} E_\alpha = -\frac{1}{2} \alpha_{\alpha\beta} E_\beta E_\alpha$$

The electric field from a charge has an R^{-2}-dependence so the induction energy has an R^{-4}-dependence as compared to an R^{-6}-dependence for the dispersion energy.

3.3.3.4 Many-body interactions

A pair-wise additive force field is of the form

$$V = \sum_{I=1}^{N} \sum_{J=I+1}^{N} V_{IJ} \tag{3.3.56}$$

where V_{IJ} is the pair-interaction energy. The electrostatic energy discussed in section 3.3.1 is a true pair-wise additive energy term (see Coulomb's law in eq. (3.3.2)). This pair-wise additivity is, however, lost if the atomic charges are calculated by the EEM in section 3.3.1.1 since the values of the atomic charges depend on the surroundings. The induction energy in section 3.3.2 is a true N-body term in the sense that the induced dipole moment in

eq. (3.3.22) depends on the electric field of the induced dipole moments of *all* surrounding molecules leading to a set of coupled equations.

The repulsion and dispersion energies are in the Lennard-Jones potential in section 3.3.3.3 given as a pair-wise additive energy. The repulsion and dispersion energies are, however, only approximately pair-wise additive and corrections can be included as three-body, four-body, etc. energy terms,

$$V = \sum_{I=1}^{N} \sum_{J=I+1}^{N} V_{IJ} + \sum_{I=1}^{N} \sum_{J=I+1}^{N} \sum_{K=J+1}^{N} V_{IJK} + \sum_{I=1}^{N} \sum_{J=I+1}^{N} \sum_{K=J+1}^{N} \sum_{L=K+1}^{N} V_{IJKL} + \ldots \qquad (3.3.57)$$

A famous example is the three-body dispersion (Axilrod-Teller) term given here for a system of three identical particles as (Axilrod and Teller 1943)

$$V_{AT} = C \frac{3 \cos \gamma_1 \cos \gamma_2 \cos \gamma_3 + 1}{R_{12}^3 R_{23}^3 R_{31}^3} , \qquad (3.3.58)$$

where the angles and distances are defined in figure 3.12 and C is a positive number proportional to $V_{IP} \alpha^3$ where V_{IP} is the ionization potential and α is the polarizability. The Axilrod-Teller term, V_{AT}, is for a system of rare-gas atoms around 8% of the London dispersion term in eq. (3.3.50) and should not be ignored in a study of e.g. liquid argon. For a system of polar molecules, e.g. liquid water, the London dispersion energy is only around 10% of the electrostatic energy so the Axilrod-Teller term can in this case to a good
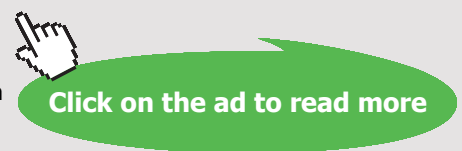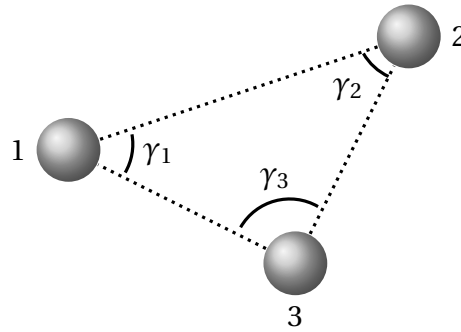
Figure 3.12: Three-atom system with the notation for the Axilrod-Teller term. R_{IJ} in eq. (3.3.58) are the distances between the atoms.

approximation be ignored since it contributes with less than 1% of the total interaction energy.

It is a poor idea to approximate the induction energy in section 3.3.2 with three-body and possibly four-body terms as demonstrated in exercise 3.4, instead one should rely on the expression based on classical electrostatics discussed in section 3.3.2.

3.3.4 Effective force fields

With effective force fields, we mean force fields that effectively include some energy terms into some of the other energy terms simplifying the force field further. Effective force fields thus include the essence of the interactions needed for modeling a particular type of systems but their applicability area will be rather restricted. As discussed in eq. (3.3.56), a pair-wise additive force field is of the form

$$V = \sum_{I=1}^{N} \sum_{J=I+1}^{N} V_{IJ} \tag{3.3.59}$$

where V_{IJ} is the pair-interaction energy between atoms I and J. For N atoms, we thus have to compute $N(N-1)/2$ pair energies V_{IJ}, and a major saving in computational time may be achieved from reducing the number of interaction sites N rather than simplifying V_{IJ}. This is particularly true if the most expensive term in the calculation of V_{IJ} is to calculate

$$\frac{1}{R_{IJ}} = \frac{1}{\sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2}} \tag{3.3.60}$$

where the divide and square-root operations are computationally expensive.

An important example is electrolytes where it is common to replace the solvent molecules by a dielectric constant (relative permittivity), ε, that shields the interactions between the ions in the calculation of the electrostatic energy, V_{ele},

$$V_{\text{ele}} = \sum_{I=1}^{M} \sum_{J=I+1}^{M} \frac{q_I q_J}{4\pi\varepsilon_0\varepsilon R_{IJ}} \tag{3.3.61}$$

where M is the number of ions in the solution. Typical values for ε is $\varepsilon \approx 2$ for unpolar hydrocarbons and $\varepsilon \approx 78$ for liquid water.

A common example is effective pair potentials where all many-body terms, including also electronic polarization discussed in section 3.3.2, are described by a pair-wise additive atomistic force field,

$$V = V_{\text{ele}} + V_{LJ} \, , \tag{3.3.62}$$

consisting of an electrostatic term V_{ele} in eq. (3.3.2) and a Lennard-Jones term V_{LJ} in eq. (3.3.54). For example for a pair potential of water, the atomic charges should for an effective pair potentential not reflect the gas-phase dipole moment of 1.85 D (Clough et al. 1973, Dyke and Muenter 1973), but rather the dipole moment of the water molecule in the liquid phase of around 2.9 ± 0.6 D (Badyal et al. 2000). The difference of around 1.1 ± 0.6 D is thus an average induced dipole moment typical for liquid water. This approach works well for homogeneous surroundings, e.g. liquid water, but is less accurate for heterogeneous surroundings, e.g. interactions with ions or at surfaces, where the molecular induced dipole moment will be significantly different from the average value.

Another example of effective force fields is united atom force fields, where functional groups are represented as pseudo-atoms. Most commonly, hydrogen atoms are suppressed in unpolar system, e.g. some polymers like polyethylene, where for example the methyl group -CH_3 is reduced to a one-centre Me group normally placed at the position of the C atom. Suppressing all hydrogen atoms will drastically reduce the number of interactions to calculate in eq. (3.3.59), and will speed up the calculation dramatically.

Inorganic systems are in principle more complicated since they include heavier elements and d- and f-electrons would require higher order atomic multipoles as quadrupole and possibly octupole moments to describe the electrostatics. Many solid-state systems have, however, ionic bonds leading to that charge-charge interactions dominate. A simple example is the Born model for ionic solids,

$$V = \sum_{I=1}^{N} \sum_{J=I+1}^{N} = \underbrace{\frac{q_I q_J}{4\pi\varepsilon_0 R_{IJ}}}_{\text{electrostatics}} + \underbrace{\frac{A_{IJ}}{R_{IJ}^n}}_{\text{repulsion}} \, . \tag{3.3.63}$$

3.3.5   Summary of nonbonding terms

The most important non-bonding energy terms in a force field for modeling intermolecular interactions as well as long-range interactions within molecules are

- electrostatics
- induction
- dispersion
- short-range repulsion

In general for a force field, each energy term relies on a choice of a function form which in the best case are derived from quantum mechanics. Force fields also rely heavily on a set of atom-type parameters which needs to be parametrized from e.g. a set of atom-type parameters. So far we have given a more or less phenomenological introduction to force

fields. In section 3.4, the force field terms for intermolecular interactions are derived from quantum mechanical perturbation theory putting this section on a more firm basis.

The advantage of force fields is that they present a rapid way of calculating interaction energies as well as the force acting on each particle in the system, and force fields are therefore used extensively in molecular dynamics and Monte Carlo simulations pf liquids where the interaction between many particles need to be calculated repeatedly.

3.4   Intermolecular forces from quantum mechanics

Perturbation theory may be adopted to link the force field approach to quantum mechanics (Buckingham 1967, Margenau and Kestner 1969, Stone 1996, Engkvist et al. 2000). For two molecules, A and B, where molecule A has n_A electrons and N_A nuclei and molecule B has n_B electrons and N_B nuclei, respectively, the Hamiltonian may be divided into three contributions as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_A + \hat{\mathcal{H}}_B + \hat{V}_{AB} \, . \tag{3.4.1}$$

The molecular Hamiltonian of a molecule A is given from eq. (2.4.2) as

$$\hat{\mathcal{H}}_A = \sum_{i=1}^{n_A} \frac{-1}{2}\nabla_i^2 + \sum_{i=1}^{n_A}\sum_{I=1}^{N_A} \frac{-Z_I}{r_{iI}} + \sum_{\substack{i=1,\\j=i+1}}^{n_A} \frac{1}{r_{ij}} + \sum_{\substack{I=1,\\J=I+1}}^{N_A} \frac{Z_I Z_J}{R_{IJ}} \, , \tag{3.4.2}$$

and the part describing the interaction between the two molecules, $\hat{\mathcal{V}}_{AB}$, is given as

$$\hat{\mathcal{V}}_{AB} = \sum_{i=1}^{n_A}\sum_{J=1}^{N_B} \frac{-Z_J}{r_{iJ}} + \sum_{I=1}^{N_A}\sum_{j=1}^{n_B} \frac{-Z_I}{r_{Ij}} + \sum_{i=1}^{n_A}\sum_{j=1}^{n_B} \frac{1}{r_{ij}} + \sum_{I=1}^{N_A}\sum_{J=1}^{N_B} \frac{Z_I Z_J}{R_{IJ}} \, . \tag{3.4.3}$$

It is noted that we in eqs. (3.4.1)-(3.4.3) have assigned some nuclei and electrons to molecule A and the remaining nuclei and electrons to molecule B, and as compared to eq. (2.4.2) the only difference is that the summations have been restricted. Within the Born-Oppenheimer approximation the positions of the nuclei are known and it is in most cases trivial to assign a nucleus to a molecule. For the electrons, on the other hand, we have stated that n_A electrons belong to molecule A and n_B electrons belong to molecule B, which is an approximation.

Regular Rayleigh-Schrödinger perturbation theory in section 2.8.1 is adopted on the interaction between two molecules. Using multipole expansions (see section 2.9.1) and the long-range approximation for intermolecular interactions, it is demonstrated that second-order perturbation theory gives an electrostatic energy, an induction energy and the dispersion energy.

3.4.1   The first-order energy

Using the multipole expansion in eq. (2.9.35) leads to that the interaction operator in eq. (3.4.3) is given as

$$\hat{\mathcal{V}}_{AB} = \sum_{m,n=0}^{\infty} \frac{(-1)^m}{m!n!} \hat{\mathcal{M}}_{A,\alpha_1\ldots\alpha_m}^{(m)} T_{AB,\alpha_1\ldots\alpha_{m+n}}^{(m+n)} \hat{\mathcal{M}}_{B,\alpha_{m+1}\ldots\alpha_{m+n}}^{(n)} \, . \tag{3.4.4}$$

Adopting Rayleigh-Schrödinger perturbation theory, where $\hat{\mathcal{V}}_{AB}$ is regarded as a perturbation to the molecular Hamiltonians, $\hat{\mathcal{H}}_A$ and $\hat{\mathcal{H}}_B$, in eq. (3.4.1), the first order correction to the energy becomes according to eq. (2.8.9),

$$\varepsilon_0^{(1)} = \langle \psi_0^{(0)} | \hat{\mathcal{V}}_{AB} | \psi_0^{(0)} \rangle \, , \tag{3.4.5}$$

where the ground state is considered. The molecular wavefunctions are supposed to be known, e.g. $\hat{\mathcal{H}}_A|\psi_{A,i}\rangle = \varepsilon_{A,i}|\psi_{A,i}\rangle$, and the molecular wavefunction $\psi_{A,i}$ is correctly antisymmetrized with respect to the n_A electrons of molecule A. The wavefunction of two molecules may be written in terms of the molecular wave functions as a generalized Heitler-London wavefunction (Margenau and Kestner 1969),

$$|\psi_0^{(0)}\rangle = \hat{\mathscr{A}}_{AB} |\psi_{A,0}\psi_{B,0}\rangle \, , \tag{3.4.6}$$

where $\hat{\mathscr{A}}_{AB}$ is an operator that ensures that the total wavefunction is correctly antisymmetrized. In the long-range approximation, it is assumed, however, that the zeroth-order wavefunction is given as a direct product of the two molecular wavefunctions,

$$|\psi_0^{(0)}\rangle \approx |\psi_{A,0}\psi_{B,0}\rangle \, . \tag{3.4.7}$$

The operator, $\hat{\mathscr{A}}_{AB}$, will construct a set of correctly anti-symmetrized orbitals for the entire complex. This effect will only be substantial if the wavefunctions for the separate molecules

overlap, $S_{AB} = \langle \psi_{A,0} | \psi_{B,0} \rangle$, which declines exponentially with the distance between the two molecules. Since $\psi_{A,0}$ is a function of only the electronic coordinates of molecule A, and likewise $\psi_{B,0}$ is a function of only the electronic coordinates of molecule B, the first-order energy becomes by using eq. (3.4.4),

$$
\begin{aligned}
\varepsilon_0^{(1)} &= \sum_{m,n=0}^{\infty} \left(\frac{(-1)^m}{m! n!} \langle \psi_{A,0} | \hat{\mathcal{M}}_{A,\alpha_1 \dots \alpha_m}^{(m)} | \psi_{A,0} \rangle \, T_{AB,\alpha_1 \dots \alpha_{m+n}}^{(m+n)} \langle \psi_{B,0} | \hat{\mathcal{M}}_{B,\alpha_{m+1} \dots \alpha_{m+n}}^{(n)} | \psi_{B,0} \rangle \right) \\
&= \sum_{m,n=0}^{\infty} \frac{(-1)^m}{m! n!} M_{A,\alpha_1 \dots \alpha_m}^{(m)} T_{AB,\alpha_1 \dots \alpha_{m+n}}^{(m+n)} M_{B,\alpha_{m+1} \dots \alpha_{m+n}}^{(n)} \\
&= q_A T_{AB}^{(0)} q_B + q_A T_{AB,\alpha}^{(1)} \mu_{B,\alpha} + \frac{1}{2} q_A T_{AB,\alpha\beta}^{(2)} Q_{B,\alpha\beta} + \dots \\
&\quad - \mu_{A,\alpha} T_{AB,\alpha}^{(1)} q_B - \mu_{A,\alpha} T_{AB,\alpha\beta}^{(2)} \mu_{B,\beta} - \frac{1}{2} \mu_{A,\alpha} T_{AB,\alpha\beta\gamma}^{(3)} Q_{B,\beta\gamma} + \dots \\
&\quad + \frac{1}{2} Q_{A,\alpha\beta} T_{AB,\alpha\beta}^{(2)} q_B + \frac{1}{2} Q_{A,\alpha\beta} T_{AB,\alpha\beta\gamma}^{(3)} \mu_{B,\gamma} + \frac{1}{4} Q_{A,\alpha\beta} T_{AB,\alpha\beta\gamma\delta}^{(4)} Q_{B,\gamma\delta} + \dots \,,
\end{aligned}
\tag{3.4.8}
$$

where a molecular moment, $M_{A,\alpha_1 \dots \alpha_m}^{(m)}$, is defined in eq. (2.9.50). The electrostatic energy in eq. (3.4.8) may be rewritten in terms of the quadrupole moment in eq. (2.9.32) as

$$
\begin{aligned}
\varepsilon_0^{(1)} &= q_A T_{AB}^{(0)} q_B + q_A T_{AB,\alpha}^{(1)} \mu_{B,\alpha} + \frac{1}{3} q_A T_{AB,\alpha\beta}^{(2)} \theta_{B,\alpha\beta} + \dots \\
&\quad - \mu_{A,\alpha} T_{AB,\alpha}^{(1)} q_B - \mu_{A,\alpha} T_{AB,\alpha\beta}^{(2)} \mu_{B,\beta} - \frac{1}{3} \mu_{A,\alpha} T_{AB,\alpha\beta\gamma}^{(3)} \theta_{B,\beta\gamma} + \dots \\
&\quad + \frac{1}{3} \theta_{A,\alpha\beta} T_{AB,\alpha\beta}^{(2)} q_B + \frac{1}{3} \theta_{A,\alpha\beta} T_{AB,\alpha\beta\gamma}^{(3)} \mu_{B,\gamma} + \frac{1}{9} \theta_{A,\alpha\beta} T_{AB,\alpha\beta\gamma\delta}^{(4)} \theta_{B,\gamma\delta} + \dots \,.
\end{aligned}
\tag{3.4.9}
$$

In figure 2.6, it is noted that the molecular electric moments are calculated around the local origin of each molecule. Adopting the definition of the electrostatic potential in eq. (2.9.1), the electrostatic potential at molecule A becomes

$$
\begin{aligned}
\varphi_A &= T_{AB}^{(0)} q_B + T_{AB,\alpha}^{(1)} \mu_{B,\alpha} + \frac{1}{2} T_{AB,\alpha\beta}^{(2)} Q_{B,\alpha\beta} + \dots \\
&= \sum_{n=0}^{\infty} \frac{1}{n!} T_{AB,\alpha_1 \dots \alpha_n}^{(n)} M_{B,\alpha_1 \dots \alpha_n}^{(n)}
\end{aligned}
\tag{3.4.10}
$$

and the electrostatic potential at molecule B becomes,

$$
\begin{aligned}
\varphi_B &= q_A T_{AB}^{(0)} - \mu_{A,\alpha} T_{AB,\alpha}^{(1)} + \frac{1}{2} Q_{A,\alpha\beta} T_{AB,\alpha\beta}^{(2)} + \dots \\
&= \sum_{n=0}^{\infty} \frac{-1^n}{n!} M_{A,\alpha_1 \dots \alpha_n}^{(n)} T_{AB,\alpha_1 \dots \alpha_n}^{(n)}
\end{aligned}
\tag{3.4.11}
$$

where the difference in sign for the dipole moment terms again arises from the definition of the distance vector $\vec{R}_{AB}$ in figure 2.6. The mth derivative of the electrostatic potential at molecule A with respect to a displacement is given as

$$
\varphi_{A,\alpha_1 \dots \alpha_m}^{(m)} = \sum_{n=0}^{\infty} \frac{1}{n!} T_{AB,\alpha_1 \dots \alpha_{m+n}}^{(m+n)} M_{B,\alpha_{m+1} \dots \alpha_{m+n}}^{(n)}
\tag{3.4.12}
$$

and correspondingly

$$\varphi_{B,\alpha_1\ldots\alpha_m}^{(m)} = \sum_{n=0}^{\infty} \frac{-1^n}{n!} M_{A,\alpha_{m+1}\ldots\alpha_{m+n}}^{(n)} T_{AB,\alpha_1\ldots\alpha_{m+n}}^{(m+n)} \tag{3.4.13}$$

The first-order energy may thus be written as

$$\begin{aligned}
\varepsilon_0^{(1)} &= \sum_{m=0}^{\infty} \frac{-1^m}{m!} M_{A,\alpha_1\ldots\alpha_m}^{(m)} \varphi_{A,\alpha_1\ldots\alpha_m}^{(m)} \\
&= \sum_{m=0}^{\infty} \frac{1}{m!} \varphi_{B,\alpha_1\ldots\alpha_m}^{(m)} M_{B,\alpha_1\ldots\alpha_m}^{(m)}
\end{aligned} \tag{3.4.14}$$

The electrostatic energy may thus be calculated either as the interaction between the electric moments at the molecules or as the interaction between the electric moment and the Taylor expansion of the electrostatic potential at one of the molecules.

3.4.2 The second-order energy

For the interaction between two molecules in the long-range limit, where it is again assumed that the zeroth-order wave function is given as the direct product of two molecular

wavefunctions as in eq. (3.4.7), the second-order energy in eq. (2.8.18) becomes

$$\varepsilon_0^{(2)} = \sum_{u+v=1}^{\infty} \frac{\langle \psi_{A,0}\psi_{B,0}|\hat{V}_{AB}|\psi_{A,u}\psi_{B,v}\rangle \langle \psi_{A,u}\psi_{B,v}|\hat{V}_{AB}|\psi_{A,0}\psi_{B,0}\rangle}{\varepsilon_{A,0} - \varepsilon_{A,u} + \varepsilon_{B,0} - \varepsilon_{B,v}} \tag{3.4.15}$$

where the notation $|\psi_p^{(0)}\rangle = |\psi_{A,0}\psi_{B,0}\rangle$, $\varepsilon_0^{(0)} = \varepsilon_{A,0} + \varepsilon_{B,0}$ and $\varepsilon_p^{(0)} = \varepsilon_{A,u} + \varepsilon_{B,v}$ have been adopted. Using the multipole expansion of $\hat{V}_{AB}$ in eq. (3.4.4), the second-order energy becomes,

$$
\begin{aligned}
\varepsilon_0^{(2)} =\ & \sum_{m,n,p,q=0}^{\infty} \left(\frac{(-1)^{m+p}}{m!n!p!q!} \sum_{u+v=1}^{\infty} \left(\frac{1}{\varepsilon_{A,0} - \varepsilon_{A,u} + \varepsilon_{B,0} - \varepsilon_{B,v}} \right. \right. \\
& \times\ \langle \psi_{A,0}|\hat{\mathcal{M}}_{A,\alpha_1\ldots\alpha_m}^{(m)}|\psi_{A,u}\rangle T_{AB,\alpha_1\ldots\alpha_{m+n}}^{(m+n)} \langle \psi_{B,0}|\hat{\mathcal{M}}_{B,\alpha_1\ldots\alpha_n}^{(n)}|\psi_{B,v}\rangle \\
& \times\ \left. \left. \langle \psi_{A,u}|\hat{\mathcal{M}}_{A,\beta_1\ldots\beta_p}^{(p)}|\psi_{A,0}\rangle T_{AB,\beta_1\ldots\beta_{p+q}}^{(p+q)} \langle \psi_{B,v}|\hat{\mathcal{M}}_{B,\beta_1\ldots\beta_q}^{(q)}|\psi_{B,0}\rangle \right) \right)
\end{aligned}
\tag{3.4.16}
$$

This energy is divided into three terms that are treated separately: a) $u = 0$, $v = 1,\ldots,\infty$, b) $u = 1,\ldots,\infty$, $v = 0$, c) $u = 1,\ldots,\infty$, $v = 1,\ldots,\infty$. The first term ($u = 0$, $v = 1,\ldots,\infty$) becomes

$$
\begin{aligned}
\varepsilon_{0,a}^{(2)} =\ & \sum_{m,n,p,q=0}^{\infty} \left(\frac{(-1)^{m+p}}{m!n!p!q!} \sum_{v=1}^{\infty} \left(\frac{1}{\varepsilon_{B,0} - \varepsilon_{B,v}} \right. \right. \\
& \times\ \langle \psi_{A,0}|\hat{\mathcal{M}}_{A,\alpha_1\ldots\alpha_m}^{(m)}|\psi_{A,0}\rangle T_{AB,\alpha_1\ldots\alpha_{m+n}}^{(m+n)} \langle \psi_{B,0}|\hat{\mathcal{M}}_{B,\alpha_1\ldots\alpha_n}^{(n)}|\psi_{B,v}\rangle \\
& \times\ \left. \left. \langle \psi_{A,0}|\hat{\mathcal{M}}_{A,\beta_1\ldots\beta_p}^{(p)}|\psi_{A,0}\rangle T_{AB,\beta_1\ldots\beta_{p+q}}^{(p+q)} \langle \psi_{B,v}|\hat{\mathcal{M}}_{B,\beta_1\ldots\beta_q}^{(q)}|\psi_{B,0}\rangle \right) \right) \\
=\ & \sum_{n,q=1}^{\infty} \frac{1}{n!q!} P_{B,\alpha_1\ldots\alpha_n,\beta_1\ldots\beta_q}^{(n,q)} \varphi_{B,\alpha_1\ldots\alpha_n}^{(n)} \varphi_{B,\beta_1\ldots\beta_n}^{(q)}
\end{aligned}
\tag{3.4.17}
$$

which is analogous to the expression obtained in eq. (2.9.60) for a molecule in an external electrostatic potential. The leading term ($n = 1$, $q = 1$) becomes

$$\varepsilon_{0,a}^{(2)} = -\frac{1}{2}\alpha_{B,\alpha\beta} E_{B,\beta} E_{B,\alpha} \tag{3.4.18}$$

which as in eq. (2.9.63) is identified as a induction energy. The second term, ($u = 1,\ldots,\infty$, $v = 0$), becomes

$$
\begin{aligned}
\varepsilon_{0,b}^{(2)} =\ & \sum_{m,n,p,q=0}^{\infty} \left(\frac{(-1)^{m+p}}{m!n!p!q!} \sum_{u=1}^{\infty} \left(\frac{1}{\varepsilon_{A,0} - \varepsilon_{A,u}} \right. \right. \\
& \times\ \langle \psi_{A,0}|\hat{\mathcal{M}}_{A,\alpha_1\ldots\alpha_m}^{(m)}|\psi_{A,u}\rangle T_{AB,\alpha_1\ldots\alpha_{m+n}}^{(m+n)} \langle \psi_{B,0}|\hat{\mathcal{M}}_{B,\alpha_1\ldots\alpha_n}^{(n)}|\psi_{B,0}\rangle \\
& \times\ \left. \left. \langle \psi_{A,u}|\hat{\mathcal{M}}_{A,\beta_1\ldots\beta_p}^{(p)}|\psi_{A,0}\rangle T_{AB,\beta_1\ldots\beta_{p+q}}^{(p+q)} \langle \psi_{B,0}|\hat{\mathcal{M}}_{B,\beta_1\ldots\beta_q}^{(q)}|\psi_{B,0}\rangle \right) \right) \\
=\ & \sum_{m,p=1}^{\infty} \frac{1}{m!p!} P_{A,\alpha_1\ldots\alpha_m,\beta_1\ldots\beta_p}^{(m,p)} \varphi_{A,\alpha_1\ldots\alpha_m}^{(m)} \varphi_{A,\beta_1\ldots\beta_p}^{(p)}
\end{aligned}
\tag{3.4.19}
$$

If eq. (3.4.17) gives the energy of the polarization of particle B, eq. (3.4.19) gives the contribution to the polarization of particle A. Again the leading term ($m = 1$, $p = 1$) is given as

$$\varepsilon_{0,b}^{(2)} = -\frac{1}{2}\alpha_{A,\alpha\beta}E_{A,\beta}E_{A,\alpha} \qquad (3.4.20)$$

and the total induction energy, $\varepsilon_{0,a+b}^{(2)}$, becomes

$$\varepsilon_{0,a+b}^{(2)} = \varepsilon_{0,a}^{(2)} + \varepsilon_{0,b}^{(2)} = -\frac{1}{2}\sum_{I=A}^{B}\alpha_{I,\alpha\beta}E_{I,\beta}E_{I,\alpha} \qquad (3.4.21)$$

The result obtained in eq. (3.4.21) is not consistent with the classical expression for the induction energy given in eq. (3.3.24) since the contribution to the electric field from the induced dipole moments is missing in eq. (3.4.21). It has been demonstrated that the additional term in eq. (3.3.24) may be obtained from higher order energy terms in the perturbation expansion (Stone 1989).

The third term ($u = 1,\ldots,\infty$, $v = 1,\ldots,\infty$), which will be identified as the dispersion energy,

$$
\begin{aligned}
\varepsilon_{0,c}^{(2)} \;=\; & \sum_{m,n,p,q=0}^{\infty} \left(\frac{(-1)^{m+p}}{m!\,n!\,p!\,q!} \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} \left(\frac{1}{\varepsilon_{A,0} - \varepsilon_{A,u} + \varepsilon_{B,0} - \varepsilon_{B,v}} \right. \right. \\
& \times \;\; \langle \psi_{A,0} | \hat{\mathcal{M}}_{A,\alpha_1\ldots\alpha_m}^{(m)} | \psi_{A,u} \rangle \, T_{AB,\alpha_1\ldots\alpha_{m+n}}^{(m+n)} \, \langle \psi_{B,0} | \hat{\mathcal{M}}_{B,\alpha_1\ldots\alpha_n}^{(n)} | \psi_{B,v} \rangle \\
& \times \;\; \left. \left. \langle \psi_{A,u} | \hat{\mathcal{M}}_{A,\beta_1\ldots\beta_p}^{(p)} | \psi_{A,0} \rangle \, T_{AB,\beta_1\ldots\beta_{p+q}}^{(p+q)} \, \langle \psi_{B,v} | \hat{\mathcal{M}}_{B,\beta_1\ldots\beta_q}^{(q)} | \psi_{B,0} \rangle \right) \right) \quad (3.4.22)
\end{aligned}
$$

is not as straightforward as the induction energy to separate into term that are dependent on the properties of the separate molecules. The nominator is readily separated into a product of molecular properties, but in order to resolve the denominator, the following identity is used,

$$
\begin{aligned}
\frac{1}{a+b} \;=\; & \frac{2}{\pi} \int_0^{\infty} \frac{ab}{\left(a^2+\omega^2\right)\left(b^2+\omega^2\right)} d\omega \\
\;=\; & \frac{2}{\pi} \int_0^{\infty} \left(\frac{1}{a+i\omega} + \frac{1}{a-i\omega} \right)\left(\frac{1}{b+i\omega} + \frac{1}{b-i\omega} \right) d\omega, \qquad a,b>0 \quad (3.4.23)
\end{aligned}
$$

The dispersion energy is thus rewritten as

$$
\begin{aligned}
\varepsilon_{0,c}^{(2)} \;=\; & \frac{-2}{\pi} \sum_{m,n,p,q=0}^{\infty} \int_0^{\infty} \left(\frac{(-1)^{m+p}}{m!\,n!\,p!\,q!} \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} \right. \\
& \left(\left(\frac{1}{\omega_{A,p}+i\omega} + \frac{1}{\omega_{A,p}-i\omega} \right)\left(\frac{1}{\omega_{B,q}+i\omega} + \frac{1}{\omega_{B,q}-i\omega} \right) \right) \\
& \times \;\; \langle \psi_{A,0} | \hat{\mathcal{M}}_{A,\alpha_1\ldots\alpha_m}^{(m)} | \psi_{A,u} \rangle \, T_{AB,\alpha_1\ldots\alpha_{m+n}}^{(m+n)} \, \langle \psi_{B,0} | \hat{\mathcal{M}}_{B,\alpha_1\ldots\alpha_n}^{(n)} | \psi_{B,v} \rangle \\
& \times \;\; \left. \langle \psi_{A,u} | \hat{\mathcal{M}}_{A,\beta_1\ldots\beta_p}^{(p)} | \psi_{A,0} \rangle \, T_{AB,\beta_1\ldots\beta_{p+q}}^{(p+q)} \, \langle \psi_{B,v} | \hat{\mathcal{M}}_{B,\beta_1\ldots\beta_q}^{(q)} | \psi_{B,0} \rangle \right) d\omega \quad (3.4.24)
\end{aligned}
$$

where the notation $\omega_{I,n} = \varepsilon_{I,n} - \varepsilon_{I,0}$ has been introduced. The frequency-dependent dipole-dipole polarizability, $\alpha_{\alpha\beta}(\omega)$, is defined in eq. (2.9.75) leading to

$$
\alpha_{\alpha\beta}^{\mathrm{mol}}(i\omega) = \sum_{p=1}^{\infty} \left(\frac{1}{\omega_p+i\omega} + \frac{1}{\omega_p-i\omega} \right) \langle \psi_0^{(0)} | -\sum_i r_{i,\alpha} | \psi_p^{(0)} \rangle \langle \psi_p^{(0)} | -\sum_i r_{i,\beta} | \psi_0^{(0)} \rangle \quad (3.4.25)
$$

If again, only the leading term in the second order energy, ($m=1$, $n=1$, $p=1$, $q=1$), is included, the dispersion energy is given as

$$
\varepsilon_{0,c}^{(2)} = \frac{-2}{\pi} \int_0^{\infty} \alpha_{A,\alpha\beta}(i\omega)\, T_{AB,\alpha\gamma}^{(2)}\, T_{AB,\beta\delta}^{(2)}\, \alpha_{B,\gamma\delta}(i\omega)\, d\omega \quad (3.4.26)
$$

If the frequency-dependent polarizability is approximated according to the Unsöld approximation (Unsöld 1927)

$$
\alpha_{\alpha\beta}(\omega) = \alpha_{\alpha\beta} \frac{\overline{\omega}^2}{\overline{\omega}^2 - \omega^2} \; ; \quad \alpha_{\alpha\beta}(i\omega) = \alpha_{\alpha\beta} \frac{\overline{\omega}^2}{\overline{\omega}^2 + \omega^2} \quad (3.4.27)
$$

where $\overline{\omega}$ is a kind of average excitation energy of the molecule, the dispersion energy becomes

$$\varepsilon_{0,c}^{(2)} = -\frac{1}{4}\frac{\overline{\omega}_A\overline{\omega}_B}{\overline{\omega}_A + \overline{\omega}_B}\alpha_{A,\alpha\beta}T_{AB,\alpha\gamma}^{(2)}T_{AB,\beta\delta}^{(2)}\alpha_{B,\gamma\delta} \qquad (3.4.28)$$

Finally, if isotropic polarizabilities, $\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}$, are regarded, the expression for the dispersion energy is reduced to the well-known London formula,

$$\varepsilon_{0,c}^{(2)} = -\frac{C_{6,AB}}{R_{AB}^6}, \qquad (3.4.29)$$

where $C_{6,AB}$ is an atom-pair parameter depending on the polarizabilities.

To conclude, the second order energy provides both the induction and dispersion energies. Both of these energies describes a response to the presence of the other molecule. Since a system always responds such as the energy is minimized, both the induction and dispersion energies give attractive contributions to the interaction energy.

Exercises

Ex. 3.1 — Derive the result for the two-particle system of the EEM in eq. (3.3.14) and from its general equations in eq. (3.3.10) and (3.3.11),

$$-q_J = q_I = \frac{\xi_J - \xi_I}{\eta_I + \eta_J - 2T_{IJ}^{(0)}}$$

Also explain why this is a reasonable model for

i) having one set of atom-type parameters for each element describing the atomic charges in both e.g. CO and O_2.

ii) describing the geometry-dependence of atomic charges.

Finally, what is the fundamental flaw in the EEM (seen from inspection of the two-particle equation at $R \to \infty$)?

Ex. 3.2 — With a self-energy, $T_{II}^{(0)} = \eta_I$, the Coulomb interaction energy for a set of N atoms may be written as

$$V = \frac{1}{2} \sum_{I,K}^{N} q_I T_{IK}^{(0)} q_K$$

including also the $I = K$ term. We change to charge-transfer variables,

$$q_I = \sum_{J}^{N} q_{IJ} \qquad \text{and} \qquad q_K = \sum_{L}^{N} q_{KL}$$

where we imply that $q_{II} = 0$ (i.e. there is no charge transfer to "itself") and that charge conservation is imposed by $q_{IJ} = -q_{JI}$. Show that V can be rewritten in terms of the charge-transfer variables q_{IJ} in a "symmetrized" way (i.e. with respect to the subscripts I and J as well as K and L, respectively) so that

$$V = \frac{1}{8} \sum_{I,J,K,L}^{N} q_{IJ} \left(T_{IK}^{(0)} + T_{JL}^{(0)} - T_{IL}^{(0)} - T_{JK}^{(0)} \right) q_{KL}$$

Ex. 3.3 — Consider the interaction energy between methane and the fluorine ion, F^-. In terms of a one-centre multipole expansion for each molecule (ion), which is the leading term? (Hint: model methane with atomic charges and use carbon as the local origin in methane for the calculation of its electric moments)

Ex. 3.4 — Consider a system with two atomic charges with magnitude $+q$ placed in $(0, 0, \pm z)$ and an isotropic point polarizability α placed in $(0, 0, 0)$. What is the interaction energy (electrostatics and polarization)? Is the interaction energy pair-wise additive?

Recommended literature

- A. J. Stone, *The Theory of Intermolecular Forces*, Oxford University Press, 1996.

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