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Introduction

Chemistry is the science dealing with construction, transformation and properties of molecules. Theoretical chemistry is the subfield where mathematical methods are combined with fundamental laws of physics to study processes of chemical relevance.[1–7]

Molecules are traditionally considered as "composed" of atoms or, in a more general sense, as a collection of charged particles, positive nuclei and negative electrons. The only important physical force for chemical phenomena is the Coulomb interaction between these charged particles. Molecules differ because they contain different nuclei and numbers of electrons, or because the nuclear centers are at different geometrical positions. The latter may be "chemically different" molecules such as ethanol and dimethyl ether or different "conformations" of, for example, butane.

Given a set of nuclei and electrons, theoretical chemistry can attempt to calculate things such as:

- Which geometrical arrangements of the nuclei correspond to stable molecules?
- What are their relative energies?
- What are their properties (dipole moment, polarizability, NMR coupling constants, etc.)?
- What is the rate at which one stable molecule can transform into another?
- What is the time dependence of molecular structures and properties?
- How do different molecules interact?

The only systems that can be solved exactly are those composed of only one or two particles, where the latter can be separated into two pseudo one-particle problems by introducing a "center of mass" coordinate system. Numerical solutions to a given accuracy (which may be so high that the solutions are essentially "exact") can be generated for many-body systems, by performing a very large number of mathematical operations. Prior to the advent of electronic computers (i.e. before 1950), the number of systems that could be treated with a high accuracy was thus very limited. During the 1960s and 1970s, electronic computers evolved from a few very expensive, difficult to use, machines to become generally available for researchers all over the world. The performance for a given price has been steadily increasing since and the use of computers is now widespread in many branches of science. This has spawned a new field in chemistry, *computational chemistry*, where the computer is used as an "experimental" tool, much like, for example, an NMR (nuclear magnetic resonance) spectrometer.

Computational chemistry is focused on obtaining results relevant to chemical problems, not directly at developing new theoretical methods. There is of course a strong interplay between traditional theoretical chemistry and computational chemistry. Developing new theoretical models may

enable new problems to be studied, and results from calculations may reveal limitations and suggest improvements in the underlying theory. Depending on the accuracy wanted, and the nature of the system at hand, one can today obtain useful information for systems containing up to several thousand particles. One of the main problems in computational chemistry is selecting a suitable level of theory for a given problem and to be able to evaluate the quality of the obtained results. The present book will try to put the variety of modern computational methods into perspective, hopefully giving the reader a chance of estimating which types of problems can benefit from calculations.

1.1 Fundamental Issues

Before embarking on a detailed description of the theoretical methods in computational chemistry, it may be useful to take a wider look at the background for the theoretical models and how they relate to methods in other parts of science, such as physics and astronomy.

A very large fraction of the computational resources in chemistry and physics is used in solving the so-called *many-body problem*. The essence of the problem is that two-particle systems can in many cases be solved exactly by mathematical methods, producing solutions in terms of analytical functions. Systems composed of more than two particles cannot be solved by analytical methods. Computational methods can, however, produce approximate solutions, which in principle may be refined to any desired degree of accuracy.

Computers are not smart – at the core level they are in fact very primitive. Smart programmers, however, can make sophisticated computer programs, which may make the computer appear smart, or even intelligent. However, the basics of any computer program consist of doing a few simple tasks such as:

- Performing a mathematical operation (adding, multiplying, square root, cosine, etc.) on one or two numbers.
- Determining the relationship (equal to, greater than, less than or equal to, etc.) between two numbers.
- Branching depending on a decision (add two numbers if $N > 10$, else subtract one number from the other).
- Looping (performing the same operation a number of times, perhaps on a set of data).
- Reading and writing data from and to external files.

These tasks are the essence of any programming language, although the syntax, data handling and efficiency depend on the language. The main reason why computers are so useful is the sheer speed with which they can perform these operations. Even a cheap off-the-shelf personal computer can perform billions (10^9) of operations per second.

Within the scientific world, computers are used for two main tasks: performing numerically intensive calculations and analyzing large amounts of data. The latter can, for example, be pictures generated by astronomical telescopes or gene sequences in the bioinformatics area that need to be compared. The numerically intensive tasks are typically related to simulating the behavior of the real world, by a more or less sophisticated computational model. The main problem in simulations is the multiscale nature of real-world problems, often spanning from subnanometers to millimeters (10^{-10}–10^{-3}) in spatial dimensions and from femtoseconds to milliseconds (10^{-15}–10^{-3}) in the time domain.
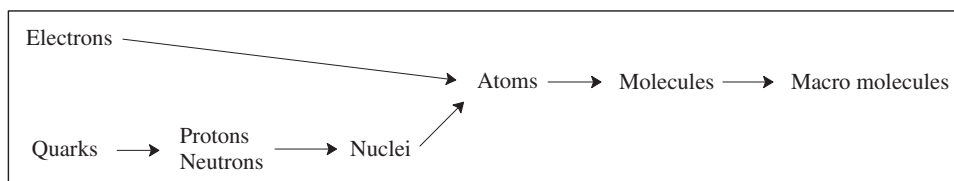
Figure 1.1 Hierarchy of building blocks for describing a chemical system.

1.2 Describing the System

In order to describe a system we need four fundamental features:

- System description. What are the fundamental units or "particles" and how many are there?
- Starting condition. Where are the particles and what are their velocities?
- Interaction. What is the mathematical form for the forces acting between the particles?
- Dynamical equation. What is the mathematical form for evolving the system in time?

The choice of "particles" puts limitations on what we are ultimately able to describe. If we choose atomic nuclei and electrons as our building blocks, we can describe atoms and molecules, but not the internal structure of the atomic nucleus. If we choose atoms as the building blocks, we can describe molecular structures, but not the details of the electron distribution. If we choose amino acids as the building blocks, we may be able to describe the overall structure of a protein, but not the details of atomic movements (see Figure 1.1).

The choice of starting conditions effectively determines what we are trying to describe. The complete phase space (i.e. all possible values of positions and velocities for all particles) is huge and we will only be able to describe a small part of it. Our choice of starting conditions determines which part of the phase space we sample, for example which (structural or conformational) isomer or chemical reaction we can describe. There are many structural isomers with the molecular formula C_6H_6, but if we want to study benzene, we should place the nuclei in a hexagonal pattern and start them with relatively low velocities.

The interaction between particles in combination with the dynamical equation determines how the system evolves in time. At the fundamental level, the only important force at the atomic level is the electromagnetic interaction. Depending on the choice of system description (particles), however, this may result in different effective forces. In force field methods, for example, the interactions are parameterized as stretch, bend, torsional, van der Waals, etc., interactions.

The dynamical equation describes the time evolution of the system. It is given as a differential equation involving both time and space derivatives, with the exact form depending on the particle masses and velocities. By solving the dynamical equation the particles' position and velocity can be predicted at later (or earlier) times relative to the starting conditions, that is how the system evolves in the phase space.

1.3 Fundamental Forces

The interaction between particles can be described in terms of either a force ($\mathbf{F}$) or a potential ($\mathbf{V}$). These are equivalent, as the force is the derivative of the potential with respect to the position $\mathbf{r}$:

$$\mathbf{F}(\mathbf{r}) = -\frac{\partial \mathbf{V}}{\partial \mathbf{r}} \tag{1.1}$$

Table 1.1 Fundamental interactions.

Name	Particles	Range (m)	Relative strength
Strong interaction	Quarks	$<10^{-15}$	100
Weak interaction	Quarks, leptons	$<10^{-15}$	0.001
Electromagnetic	Charged particles	∞	1
Gravitational	Mass particles	∞	10^{-40}

Current knowledge indicates that there are four fundamental interactions, at least under normal conditions, as listed in Table 1.1.

Quarks are the building blocks of protons and neutrons, and lepton is a common name for a group of particles including the electron and the neutrino. The strong interaction is the force holding the atomic nucleus together, despite the repulsion between the positively charged protons. The weak interaction is responsible for radioactive decay of nuclei by conversion of neutrons to protons (β decay). The strong and weak interactions are short-ranged and are only important within the atomic nucleus.

Both the electromagnetic and gravitational interactions depend on the inverse distance between the particles and are therefore of infinite range. The electromagnetic interaction occurs between all charged particles, while the gravitational interaction occurs between all particles with a mass, and they have the same overall functional form:

$$\mathbf{V}_{elec}(\mathbf{r}_{ij}) = C_{elec} \frac{q_i q_j}{r_{ij}}$$
$$\mathbf{V}_{grav}(\mathbf{r}_{ij}) = -C_{grav} \frac{m_i m_j}{r_{ij}}$$

(1.2)

In SI units $C_{elec} = 9.0 \times 10^9$ N m^2/C^2 and $C_{grav} = 6.7 \times 10^{-11}$ N m^2/kg^2, while in atomic units $C_{elec} = 1$ and $C_{grav} = 2.4 \times 10^{-43}$. On an atomic scale, the gravitational interaction is completely negligible compared with the electromagnetic interaction. For the interaction between a proton and an electron, for example, the ratio between $\mathbf{V}_{elec}$ and $\mathbf{V}_{grav}$ is 10^{39}. On a large macroscopic scale, such as planets, the situation is reversed. Here the gravitational interaction completely dominates and the electromagnetic interaction is absent.

On a more fundamental level, it is believed that the four forces are really just different manifestations of a single common interaction, because of the relatively low energy regime we are living in. It has been shown that the weak and electromagnetic forces can be combined into a single unified theory, called *quantum electrodynamics* (QED). Similarly, the strong interaction can be coupled with QED into what is known as the *standard model*. Much effort is being devoted to also include the gravitational interaction into a grand unified theory, and *string theory* is currently believed to hold the greatest promise for such a unification.

Only the electromagnetic interaction is important at the atomic and molecular level, and in the large majority of cases, the simple Coulomb form (in atomic units) is sufficient:

$$\mathbf{V}_{Coulomb}(\mathbf{r}_{ij}) = \frac{q_i q_j}{r_{ij}}$$

(1.3)

Within QED, the Coulomb interaction is only the zeroth-order term and the complete interaction can be written as an expansion in terms of the (inverse) velocity of light, *c*. For systems where relativistic effects are important (i.e. containing elements from the lower part of the periodic table) or when

high accuracy is required, the first-order correction (corresponding to an expansion up to $1/c^2$) for the electron–electron interaction may be included:

$$\mathbf{V}_{\text{elec}}(\mathbf{r}_{12}) = \frac{1}{r_{12}} \left[1 - \frac{1}{2} \left(\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right) \right] \tag{1.4}$$

The first-order correction is known as the *Breit* term, and $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$ represent velocity operators. The first term in Equation (1.4) can be considered as a magnetic interaction between two electrons, but the whole Breit correction describes a "retardation" effect, since the interaction between distant particles is "delayed" relative to interactions between close particles, owing to the finite value of c (in atomic units, $c \sim 137$).

1.4 The Dynamical Equation

The mathematical form for the dynamical equation depends on the mass and velocity of the particles and can be divided into four regimes (see Figure 1.2).

Newtonian mechanics, exemplified by Newton's second law ($\mathbf{F} = m\mathbf{a}$), applies for "heavy", "slow-moving" particles. Relativistic effects become important when the velocity is comparable to the speed of light, causing an increase in the particle mass m relative to the rest mass m_0. A pragmatic borderline between Newtonian and relativistic (Einstein) mechanics is $\sim 1/3 c$, corresponding to a relativistic correction of a few percent.

Light particles display both wave and particle characteristics and must be described by quantum mechanics, with the borderline being approximately the mass of a proton. Electrons are much lighter and can only be described by quantum mechanics, while atoms and molecules, with a few exceptions, behave essentially as classical particles. Hydrogen (protons), being the lightest nucleus, represents a borderline case, which means that quantum corrections in some cases are essential. A prime example is the tunnelling of hydrogen through barriers, allowing reactions involving hydrogen to occur faster than expected from transition state theory.
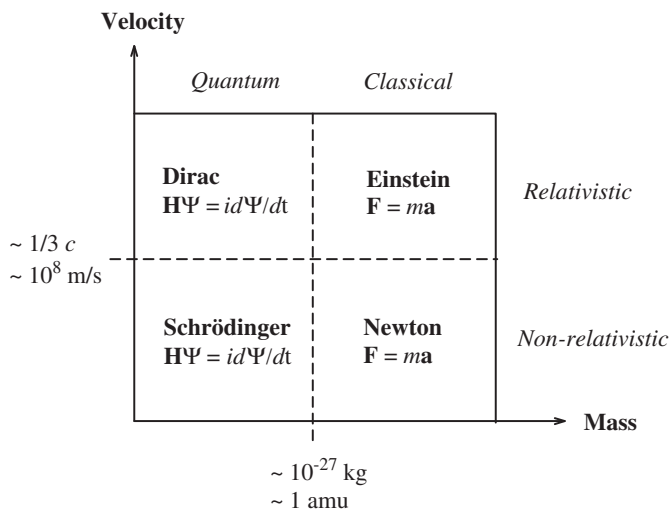

Figure 1.2 Domains of dynamical equations.

A major difference between quantum and classical mechanics is that classical mechanics is *deterministic* while quantum mechanics is *probabilistic* (more correctly, quantum mechanics is also deterministic, but the interpretation is probabilistic). Deterministic means that Newton's equation can be integrated over time (forward or backward) and can predict where the particles are at a certain time. This, for example, allows prediction of where and when solar eclipses will occur many thousands of years in advance, with an accuracy of meters and seconds. Quantum mechanics, on the other hand, only allows calculation of the *probability* of a particle being at a certain place at a certain time. The probability function is given as the square of a wave function, $P(\mathbf{r},t) = \Psi^2(\mathbf{r},t)$, where the wave function Ψ is obtained by solving either the Schrödinger (non-relativistic) or Dirac (relativistic) equation. Although they appear to be the same in Figure 1.2, they differ considerably in the form of the operator $\mathbf{H}$.

For classical mechanics at low velocities compared with the speed of light, Newton's second law applies:

$$\mathbf{F} = \frac{d\mathbf{p}}{dt} \tag{1.5}$$

If the particle mass is constant, the derivative of the momentum $\mathbf{p}$ is the mass times the acceleration:

$$\mathbf{p} = m\mathbf{v}$$
$$\mathbf{F} = \frac{d\mathbf{p}}{dt} = m\frac{d\mathbf{v}}{dt} = m\mathbf{a} \tag{1.6}$$

Since the force is the derivative of the potential (Equation (1.1)) and the acceleration is the second derivative of the position $\mathbf{r}$ with respect to time, it may also be written in a differential form:

$$-\frac{\partial \mathbf{V}}{\partial \mathbf{r}} = m\frac{\partial^2 \mathbf{r}}{\partial t^2} \tag{1.7}$$

Solving this equation gives the position of each particle as a function of time, that is $\mathbf{r}(t)$.

At velocities comparable to the speed of light, Newton's equation is formally unchanged, but the particle mass becomes a function of the velocity, and the force is therefore not simply a constant (mass) times the acceleration:

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}} \tag{1.8}$$

For particles with small masses, primarily electrons, quantum mechanics must be employed. At low velocities, the relevant equation is the time-dependent Schrödinger equation:

$$\mathbf{H}\Psi = i\frac{\partial \Psi}{\partial t} \tag{1.9}$$

The Hamiltonian operator is given as a sum of kinetic and potential energy operators:

$$\mathbf{H}_{\text{Schrödinger}} = \mathbf{T} + \mathbf{V}$$
$$\mathbf{T} = \frac{\mathbf{p}^2}{2m} = -\frac{1}{2m}\nabla^2 \tag{1.10}$$

Solving the Schrödinger equation gives the wave function as a function of time, and the probability of observing a particle at a position $\mathbf{r}$ and time t is given as the square of the wave function:

$$P(\mathbf{r}, t) = \Psi^2(\mathbf{r}, t) \tag{1.11}$$

For light particles moving at a significant fraction of the speed of light, the Schrödinger equation is replaced by the Dirac equation:

$$\mathbf{H}\Psi = i\frac{\partial \Psi}{\partial t} \tag{1.12}$$

Although it is formally identical to the Schrödinger equation, the Hamiltonian operator is significantly more complicated:

$$\mathbf{H}_{\text{Dirac}} = (c\boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta}mc^2) + \mathbf{V} \tag{1.13}$$

The $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are 4×4 matrices and the relativistic wave function consequently has four components. Traditionally, these are labelled the *large* and *small* components, each having an α and β spin function (note the difference between the $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ matrices and α and β spin functions). The large component describes the electronic part of the wave function, while the small component describes the positronic (electron antiparticle) part of the wave function, and the $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ matrices couple these components. In the limit of $c \to \infty$, the Dirac equation reduces to the Schrödinger equation, and the two large components of the wave function reduce to the α and β spin-orbitals in the Schrödinger picture.

1.5 Solving the Dynamical Equation

Both the Newton/Einstein and Schrödinger/Dirac dynamical equations are differential equations involving the derivative of either the position vector or wave function with respect to time. For two-particle systems with simple interaction potentials $\mathbf{V}$, these can be solved analytically, giving $\mathbf{r}(t)$ or $\Psi(\mathbf{r},t)$ in terms of mathematical functions. For systems with more than two particles, the differential equation must be solved by numerical techniques involving a sequence of small finite time steps.

Consider a set of particles described by a position vector $\mathbf{r}_i$ at a given time t_i. A small time step Δt later, the positions can be calculated from the velocities, acceleration, hyperaccelerations, etc., corresponding to a Taylor expansion with time as the variable

$$\mathbf{r}_{i+1} = \mathbf{r}_i + \mathbf{v}_i(\Delta t) + \tfrac{1}{2}\mathbf{a}_i(\Delta t)^2 + \tfrac{1}{6}\mathbf{b}_i(\Delta t)^3 + \cdots \tag{1.14}$$

The positions a small time step Δt earlier were (replacing Δt with $-\Delta t$)

$$\mathbf{r}_{i-1} = \mathbf{r}_i - \mathbf{v}_i(\Delta t) + \tfrac{1}{2}\mathbf{a}_i(\Delta t)^2 - \tfrac{1}{6}\mathbf{b}_i(\Delta t)^3 + \cdots \tag{1.15}$$

Addition of these two equations gives a recipe for predicting the positions a time step Δt later from the current and previous positions, and the current acceleration, a method known as the *Verlet* algorithm:

$$\mathbf{r}_{i+1} = (2\mathbf{r}_i - \mathbf{r}_{i-1}) + \mathbf{a}_i(\Delta t)^2 + \cdots \tag{1.16}$$

Note that all odd terms in the Verlet algorithm disappear, that is the algorithm is correct to third order in the time step. The acceleration can be calculated from the force or, equivalently, the potential:

$$\mathbf{a} = \frac{\mathbf{F}}{m} = -\frac{1}{m}\frac{\partial \mathbf{V}}{\partial \mathbf{r}} \tag{1.17}$$

The time step Δt is an important control parameter for a simulation. The *largest* value of Δt is determined by the *fastest* process occurring in the system, typically being an order of magnitude smaller than the fastest process. For simulating nuclear motions, the fastest process is the motion of hydrogens, being the lightest particles. Hydrogen vibrations occur with a typical frequency of 3000 cm^{-1},

corresponding to $\sim 10^{14}$ s^{-1}, and therefore necessitating time steps of the order of one femtosecond (10^{-15} s).

1.6 Separation of Variables

As discussed in the previous section, the central problem is solving a differential equation with respect to either the position (classical) or wave function (quantum) for the particles in the system. The standard method of solving differential equations is to find a set of coordinates where the differential equation can be separated into less complicated equations. The first step is to introduce a *center of mass* coordinate system, defined as the mass-weighted sum of the coordinates of all particles, which allows the translation of the combined system with respect to a fixed coordinate system to be separated from the internal motion. For a two-particle system, the internal motion is then described in terms of a reduced mass moving relative to the center of mass, and this can be further transformed by introducing a coordinate system that reflects the symmetry of the interaction between the two particles. If the interaction only depends on the interparticle distance (e.g. Coulomb or gravitational interaction), the coordinate system of choice is normally a polar (two-dimensional) or spherical polar (three-dimensional) system. In these coordinate systems, the dynamical equation can be transformed into solving one-dimensional differential equations.

For more than two particles, it is still possible to make the transformation to the center of mass system. However, it is no longer possible to find a set of coordinates that allows a separation of the degrees of freedom for the internal motion, thus preventing an analytical solution. For many-body ($N > 2$) systems, the dynamical equation must therefore be solved by computational (numerical) methods. Nevertheless, it is often possible to achieve an approximate separation of variables based on physical properties, for example particles differing considerably in mass (such as nuclei and electrons). A two-particle system consisting of one nucleus and one electron can be solved exactly by introducing a center of mass system, thereby transforming the problem into a pseudo-particle with a reduced mass ($\mu = m_1 m_2 / (m_1 + m_2)$) moving relative to the center of mass. In the limit of the nucleus being infinitely heavier than the electron, the center of mass system becomes identical to that of the nucleus. In this limit, the reduced mass becomes equal to that of the electron, which moves relative to the (stationary) nucleus. For large, but finite, mass ratios, the approximation $\mu \approx m_e$ is unnecessary but may be convenient for interpretative purposes. For many-particle systems, an exact separation is not possible, and the *Born–Oppenheimer* approximation corresponds to assuming that the nuclei are infinitely heavier than the electrons. This allows the electronic problem to be solved for a given set of stationary nuclei. Assuming that the electronic problem can be solved for a large set of nuclear coordinates, the electronic energy forms a parametric hypersurface as a function of the nuclear coordinates, and the motion of the nuclei on this surface can then be solved subsequently.

If an approximate separation is not possible, the many-body problem can often be transformed into a pseudo one-particle system by taking the average interaction into account. For quantum mechanics, this corresponds to the Hartree–Fock approximation, where the average electron–electron repulsion is incorporated. Such pseudo one-particle solutions often form the conceptual understanding of the system and provide the basis for more refined computational methods.

Molecules are sufficiently heavy that their motions can be described quite accurately by classical mechanics. In condensed phases (solution or solid state), there is a strong interaction between molecules, and a reasonable description can only be attained by having a large number of individual molecules moving under the influence of each other's repulsive and attractive forces. The forces in this case are complex and cannot be written in a simple form such as the Coulomb or gravitational

interaction. No analytical solutions can be found in this case, even for a two-particle (molecular) system. Similarly, no approximate solution corresponding to a Hartree–Fock model can be constructed. The only method in this case is direct simulation of the full dynamical equation.

1.6.1 Separating Space and Time Variables

The time-dependent Schrödinger equation involves differentiation with respect to both time and position, the latter contained in the kinetic energy of the Hamiltonian operator:

$$\mathbf{H}(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$
$$\mathbf{H}(\mathbf{r}, t) = \mathbf{T}(\mathbf{r}) + \mathbf{V}(\mathbf{r}, t) \tag{1.18}$$

For (bound) systems where the potential energy operator is time-independent ($\mathbf{V}(\mathbf{r},t) = \mathbf{V}(\mathbf{r})$), the Hamiltonian operator becomes time-independent and yields the total energy when acting on the wave function. The energy is a constant, independent of time, but depends on the space variables.

$$\mathbf{H}(\mathbf{r}, t) = \mathbf{H}(\mathbf{r}) = \mathbf{T}(\mathbf{r}) + \mathbf{V}(\mathbf{r})$$
$$\mathbf{H}(\mathbf{r})\Psi(\mathbf{r}, t) = E(\mathbf{r})\Psi(\mathbf{r}, t) \tag{1.19}$$

Inserting this in the time-dependent Schrödinger equation shows that the time and space variables of the wave function can be separated:

$$\mathbf{H}(\mathbf{r})\Psi(\mathbf{r}, t) = E(\mathbf{r})\Psi(\mathbf{r}, t) = i\frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$
$$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r})\mathrm{e}^{-iEt} \tag{1.20}$$

The latter follows from solving the first-order differential equation with respect to time, and shows that the time dependence can be written as a simple phase factor multiplied by the spatial wave function. For time-*in*dependent problems, this phase factor is normally neglected, and the starting point is taken as the time-independent Schrödinger equation:

$$\mathbf{H}(\mathbf{r})\Psi(\mathbf{r}) = E(\mathbf{r})\Psi(\mathbf{r}) \tag{1.21}$$

1.6.2 Separating Nuclear and Electronic Variables

Electrons are very light particles and cannot be described by classical mechanics, while nuclei are sufficiently heavy that they display only small quantum effects. The large mass difference indicates that the nuclear velocities are much smaller than the electron velocities, and the electrons therefore adjust very fast to a change in the nuclear geometry.

For a general *N*-particle system, the Hamiltonian operator contains kinetic ($\mathbf{T}$) and potential ($\mathbf{V}$) energy for all particles:

$$\mathbf{H} = \mathbf{T} + \mathbf{V}$$
$$\mathbf{T} = \sum_{i=1}^{N} \mathbf{T}_i \quad ; \quad \mathbf{V} = \sum_{i>j}^{N} \mathbf{V}_{ij} \tag{1.22}$$

The potential energy operator is the Coulomb potential (Equation (1.3)). Denoting nuclear coordinates with $\mathbf{R}$ and subscript n, and electron coordinates with $\mathbf{r}$ and subscript e, this can be expressed as follows:

$$
\begin{aligned}
\mathbf{H}_{\text{tot}}\Psi_{\text{tot}}(\mathbf{R}, \mathbf{r}) &= E_{\text{tot}}\Psi_{\text{tot}}(\mathbf{R}, \mathbf{r}) \\
\mathbf{H}_{\text{tot}} = \mathbf{H}_e + \mathbf{T}_n \quad &; \quad \mathbf{H}_e = \mathbf{T}_e + \mathbf{V}_{\text{ne}} + \mathbf{V}_{\text{ee}} + \mathbf{V}_{\text{nn}} \\
\Psi_{\text{tot}}(\mathbf{R}, \mathbf{r}) &= \Psi_n(\mathbf{R})\Psi_e(\mathbf{R}, \mathbf{r}) \\
\mathbf{H}_e\Psi_e(\mathbf{R}, \mathbf{r}) &= E_e(\mathbf{R})\Psi_e(\mathbf{R}, \mathbf{r}) \\
(\mathbf{T}_n + E_e(\mathbf{R}))\Psi_n(\mathbf{R}) &= E_{\text{tot}}\Psi_n(\mathbf{R})
\end{aligned}
\tag{1.23}
$$

The above approximation corresponds to neglecting the coupling between the nuclear and electronic velocities, that is the nuclei are stationary from the electronic point of view. The electronic wave function thus depends *parametrically* on the nuclear coordinates, since it only depends on the *position* of the nuclei, not on their *momentum.* To a good approximation, the electronic wave function thus provides a *potential energy surface* upon which the nuclei move, and this separation is known as the *Born–Oppenheimer* approximation.

The Born–Oppenheimer approximation is usually very good. For the hydrogen molecule (H_2) the error is of the order of 10^{-4} au, and for systems with heavier nuclei the approximation becomes better. As we shall see later, it is possible only in a few cases to solve the electronic part of the Schrödinger equation to an accuracy of 10^{-4} au, that is neglect of the nuclear–electron coupling is usually only a minor approximation compared with other errors.

1.6.3 Separating Variables in General

Assume that a set of variables can be found where the Hamiltonian operator $\mathbf{H}$ for two particles/variables can be separated into two independent terms, with each only depending on one particle/variable:

$$
\mathbf{H} = \mathbf{h}_1 + \mathbf{h}_2
\tag{1.24}
$$

Assume furthermore that the Schrödinger equation for one particle/variable can be solved (exactly or approximately):

$$
\mathbf{h}_i\phi_i = \varepsilon_i\phi_i
\tag{1.25}
$$

The solution to the two-particle problem can then be composed of solutions of one-variable Schrödinger equations:

$$
\Psi = \phi_1\phi_2 \quad ; \quad E = \varepsilon_1 + \varepsilon_2
\tag{1.26}
$$

This can be generalized to the case of N particles/variables:

$$
\begin{aligned}
\mathbf{H} &= \sum_i \mathbf{h}_i \\
\Psi = \prod_i \phi_i \quad &; \quad E = \sum_i \varepsilon_i
\end{aligned}
\tag{1.27}
$$

The properties in Equation (1.27) may be verified by inserting the entities in the Schrödinger Equation (1.21).

1.7 Classical Mechanics

1.7.1 The Sun–Earth System

The motion of the Earth around the Sun is an example of a two-body system that can be treated by classical mechanics. The interaction between the two "particles" is the gravitational force:

$$\mathbf{V}\left(\mathbf{r}_{12}\right) = -C_{\mathrm{grav}}\frac{m_1 m_2}{r_{12}} \tag{1.28}$$

The dynamical equation is Newton's second law, which in differential form can be written as

$$-\frac{\partial \mathbf{V}}{\partial \mathbf{r}} = m\frac{\partial^2 \mathbf{r}}{\partial t^2} \tag{1.29}$$

The first step is to introduce a center of mass system, and the internal motion becomes motion of a "particle" with a reduced mass given by

$$\mu = \frac{M_{\mathrm{Sun}} m_{\mathrm{Earth}}}{M_{\mathrm{Sun}} + m_{\mathrm{Earth}}} = \frac{m_{\mathrm{Earth}}}{(1 + m_{\mathrm{Earth}}/M_{\mathrm{Sun}})} \cong m_{\mathrm{Earth}} \tag{1.30}$$

Since the mass of the Sun is 3×10^5 times larger than that of the Earth, the reduced mass is essentially identical to the Earth's mass ($\mu = 0.999997 m_{\mathrm{Earth}}$). To a very good approximation, the system can therefore be described as the Earth moving around the Sun, which remains stationary.

The motion of the Earth around the Sun occurs in a plane, and a suitable coordinate system is a polar coordinate system (two-dimensional) consisting of r and θ (Figure 1.3).

The interaction depends only on the distance r, and the differential equation (Newton's equation) can be solved analytically. The bound solutions are elliptical orbits with the Sun (more precisely, the center of mass) at one of the foci, but for most of the planets, the actual orbits are close to circular. Unbound solutions corresponding to hyperbolas also exist and could, for example, describe the path of a (non-returning) comet (see Figure 1.4).

Each bound orbit can be classified in terms of the dimensions (largest and smallest distance to the Sun), with an associated total energy. In classical mechanics, there are no constraints on the energy and all sizes of orbits are allowed. If the zero point for the energy is taken as the two particles at rest infinitely far apart, positive values of the total energy correspond to unbound solutions (hyperbolas, with the kinetic energy being larger than the potential energy) while negative values correspond to bound orbits (ellipsoids, with the kinetic energy being less than the potential energy). Bound solutions are also called *stationary* orbits, as the particle position returns to the same value with well-defined time intervals.
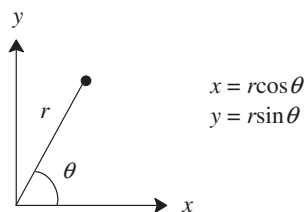

$$x = r\cos\theta$$
$$y = r\sin\theta$$
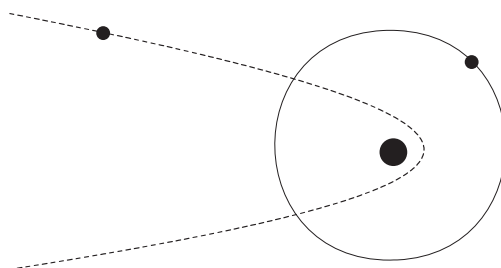
Figure 1.3 A polar coordinate system.

Figure 1.4 Bound and unbound solutions to the classical two-body problem.

1.7.2   The Solar System

Once we introduce additional planets in the Sun–Earth system, an analytical solution for the motions of all the planets can no longer be obtained. Since the mass of the Sun is so much larger than the remaining planets (the Sun is 1000 times heavier than Jupiter, the largest planet), the interactions between the planets can to a good approximation be neglected. For the Earth, for example, the second most important force is from the Moon, with a contribution that is 180 times smaller than that from the Sun. The next largest contribution is from Jupiter, being approximately 30 000 times smaller (on average) than the gravitational force from the Sun. In this *central field model*, the orbit of each planet is determined as if it was the only planet in the solar system, and the resulting computational task is a two-particle problem, that is elliptical orbits with the Sun at one of the foci. The complete solar system is the unification of eight such orbits and the total energy is the sum of all eight individual energies.

A formal refinement can be done by taking the *average* interaction between the planets into account, that is a Hartree–Fock type approximation. In this model, the orbit of one planet (e.g. the Earth) is determined by taking the average interaction with all the other planets into account. The average effect corresponds to spreading the mass of the other planets evenly along their orbits.

The Hartree–Fock model (Figure 1.5) represents only a very minute improvement over the independent orbit model for the solar system, since the planetary orbits do not cross. The effect of a planet inside the Earth's orbit corresponds to adding its mass to the Sun, while the effect of the spread-out mass of a planet outside the Earth's orbit is zero. The Hartree–Fock model for the Earth thus consists of increasing the Sun's effective mass with that of Mercury and Venus, that is a change of only 0.0003%. For the solar system there is thus very little difference between totally neglecting the planetary interactions and taking the average effect into account.
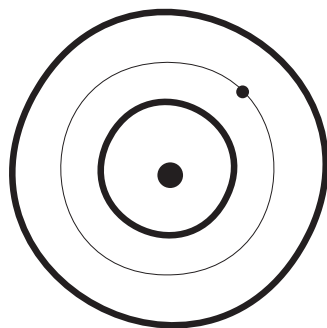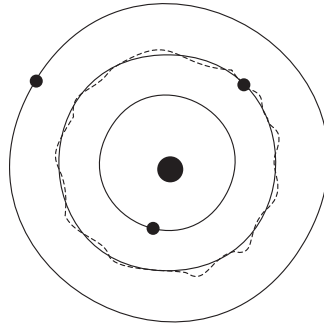

Figure 1.5 A Hartree–Fock model for the solar system.

Figure 1.6 Modeling the solar system with actual interactions.

The real system, of course, includes all interactions, where each pair interaction depends on the actual distance between the planets (Figure 1.6). The resulting planetary motions cannot be solved analytically, but can be simulated numerically. From a given starting condition, the system is allowed to evolve for many small time steps, and all interactions are considered constant within each time step. By sufficiently small time steps, this yields a very accurate model of the real many-particle dynamics, and will display small wiggles of the planetary motion around the elliptical orbits calculated by either of the two independent-particle models.

Since the perturbations due to the other planets are significantly smaller than the interaction with the Sun, the "wiggles" are small compared with the overall orbital motion, and a description of the solar system as planets orbiting the Sun in elliptical orbits is a very good approximation to the true dynamics of the system.

1.8 Quantum Mechanics

1.8.1 A Hydrogen-Like Atom

A quantum analog of the Sun–Earth system is a nucleus and one electron, that is a hydrogen-like atom. The force holding the nucleus and electron together is the Coulomb interaction:

$$\mathbf{V}(\mathbf{r}_{12}) = \frac{q_1 q_2}{r_{12}} \tag{1.31}$$

The interaction again only depends on the distance, but owing to the small mass of the electron, Newton's equation must be replaced with the Schrödinger equation. For bound states, the time-dependence can be separated out, as shown in Section 1.6.1, giving the time-independent Schrödinger equation:

$$\mathbf{H}\Psi = E\Psi \tag{1.32}$$

The Hamiltonian operator for a hydrogen-like atom (nuclear charge of Z) can in Cartesian coordinates and atomic units be written as follows, with M being the nuclear and m the electron mass ($m = 1$ in atomic units):

$$\mathbf{H} = -\frac{1}{2M}\nabla_1^2 - \frac{1}{2m}\nabla_2^2 - \frac{Z}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}} \tag{1.33}$$

The Laplace operator is given by

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \tag{1.34}$$

The two kinetic energy operators are already separated, since each only depends on the three coordinates for one particle. The potential energy operator, however, involves all six coordinates. The center of mass system is introduced by the following six coordinates:

$$X = \frac{(Mx_1 + mx_2)}{(M + m)} \quad ; \quad x = x_1 - x_2$$

$$Y = \frac{(My_1 + my_2)}{(M + m)} \quad ; \quad y = y_1 - y_2 \tag{1.35}$$

$$Z = \frac{(Mz_1 + mz_2)}{(M + m)} \quad ; \quad z = z_1 - z_2$$

Here the X, Y, Z coordinates define the center of mass system and the x, y, z coordinates specify the relative position of the two particles. In these coordinates the Hamiltonian operator can be rewritten as

$$\mathbf{H} = -\frac{1}{2}\nabla_{XYZ}^2 - \frac{1}{2\mu}\nabla_{xyz}^2 - \frac{Z}{\sqrt{x^2 + y^2 + z^2}} \tag{1.36}$$

The first term only involves the X, Y and Z coordinates, and the ∇^2_{XYZ} operator is obviously separable in terms of X, Y and Z. Solution of the XYZ part gives translation of the whole system in three dimensions relative to the laboratory-fixed coordinate system. The xyz coordinates describe the relative motion of the two particles in terms of a pseudo-particle with a reduced mass μ relative to the center of mass:

$$\mu = \frac{M_{\text{nuc}}m_{\text{elec}}}{M_{\text{nuc}} + m_{\text{elec}}} = \frac{m_{\text{elec}}}{\left(1 + m_{\text{elec}}/M_{\text{nuc}}\right)} \cong m_{\text{elec}} \tag{1.37}$$

For the hydrogen atom, the nucleus is approximately 1800 times heavier than the electron, giving a reduced mass of $0.9995m_{\text{elec}}$. Similar to the Sun–Earth system, the hydrogen atom can therefore to a good approximation be considered as an electron moving around a stationary nucleus, and for heavier elements the approximation becomes better (with a uranium nucleus, for example, the nucleus/electron mass ratio is ~430 000). Setting the reduced mass equal to the electron mass corresponds to making the assumption that the nucleus is infinitely heavy and therefore stationary.

The potential energy again only depends on the distance between the two particles, but in contrast to the Sun–Earth system, the motion occurs in three dimensions, and it is therefore advantageous to transform the Schrödinger equation into a spherical polar set of coordinates (Figure 1.7).
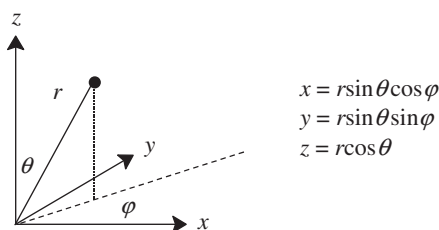

$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$

Figure 1.7 A spherical polar coordinate system.

The potential energy becomes very simple, but the kinetic energy operator becomes complicated:

$$\mathbf{H} = -\frac{1}{2\mu}\nabla^2_{r\theta\varphi} - \frac{Z}{r}$$

$$\nabla^2_{r\theta\varphi} = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

(1.38)

The kinetic energy operator, however, is almost separable in spherical polar coordinates, and the actual method of solving the differential equation can be found in a number of textbooks. The bound solutions (negative total energy) are called orbitals and can be classified in terms of three *quantum numbers*, n, l and m, corresponding to the three spatial variables r, θ and φ. The quantum numbers arise from the boundary conditions on the wave function, that is it must be periodic in the θ and φ variables and must decay to zero as $r \to \infty$. Since the Schrödinger equation is not completely separable in spherical polar coordinates, there exist the restrictions $n > l \geq |m|$. The n quantum number describes the *size* of the orbital, the l quantum number describes the *shape* of the orbital, while the m quantum number describes the *orientation* of the orbital relative to a fixed coordinate system. The l quantum number translates into names for the orbitals:

- $l = 0$: s-orbital
- $l = 1$: p-orbital
- $l = 2$: d-orbital
- $l = 3$: f-orbital, etc.

The orbitals can be written as a product of a *radial* function, describing the behavior in terms of the distance r between the nucleus and electron, and *spherical harmonic* functions Y_{lm}, representing the angular part in terms of the angles θ and φ. The orbitals can be visualized by plotting three-dimensional objects corresponding to the wave function having a specific value (e.g. $\Psi^2 = 0.10$) (see Table 1.2).

The orbitals for different quantum numbers are orthogonal and can be chosen to be normalized:

$$\left\langle \Psi_{n,l,m} \middle| \Psi_{n',l',m'} \right\rangle = \delta_{n,n'}\delta_{l,l'}\delta_{m,m'}$$

(1.39)

Table 1.2 Hydrogenic orbitals obtained from solving the Schrödinger equation.

n	l	m	$\Psi_{n,l,m}(r,\theta,\varphi)$	Shape and size
1	0	0	$Y_{0,0}(\theta,\varphi)e^{-Zr}$	
2	0	0	$Y_{0,0}(\theta,\varphi)(2 - Zr)e^{-Zr/2}$	
	1	$\pm 1, 0$	$Y_{1,m}(\theta,\varphi)Zre^{-Zr/2}$	
3	0	0	$Y_{0,0}(\theta,\varphi)(27 - 18Zr + 2Z^2r^2)e^{-Zr/3}$	
	1	$\pm 1, 0$	$Y_{1,m}(\theta,\varphi)Zr(6 - Zr)e^{-Zr/3}$	
	2	$\pm 2, \pm 1, 0$	$Y_{2,m}(\theta,\varphi)Z^2r^2e^{-Zr/3}$	

The orthogonality of the orbitals in the angular part (l and m quantum numbers) follows from the shape of the spherical harmonic functions, as these have l nodal planes (points where the wave function is zero). The orthogonality in the radial part (n quantum number) is due to the presence of $(n–l–1)$ radial nodes in the wave function.

In contrast to classical mechanics, where all energies are allowed, wave functions and associated energies are quantized, that is only certain values are allowed. The energy only depends on n for a given nuclear charge Z and is given by

$$E = -\frac{Z^2}{2n^2} \tag{1.40}$$

Unbound solutions have a positive total energy and correspond to scattering of an electron by the nucleus.

1.8.2   The Helium Atom

Like the solar system, it is not possible to find a set of coordinates where the Schrödinger equation can be solved analytically for more than two particles (i.e. for many-electron atoms). Owing to the dominance of the Sun's gravitational field, a central field approximation provides a good description of the actual solar system, but this is not the case for an atomic system. The main differences between the solar system and an atom such as helium are:

1. The interaction between the electrons is only a factor of two smaller than between the nucleus and electrons, compared with a ratio of at least 1000 for the solar system.
2. The electron–electron interaction is repulsive, compared with the attraction between planets.
3. The motion of the electrons must be described by quantum mechanics owing to the small electron mass, and the particle position is determined by an orbital, the square of which gives the probability of finding the electron at a given position.
4. Electrons are indistinguishable particles having a spin of $^1/_2$. This fermion character requires the total wave function to be antisymmetric, that is it must change sign when interchanging two electrons. The antisymmetry results in the so-called exchange energy, which is a non-classical correction to the Coulomb interaction.

The simplest atomic model would be to neglect the electron–electron interaction and only take the nucleus–electron attraction into account. In this model each orbital for the helium atom is determined by solving a hydrogen-like system with a nucleus and one electron, yielding hydrogen-like orbitals, 1s, 2s, 2p, 3s, 3p, 3d, etc., with $Z = 2$. The total wave function is obtained from the resulting orbitals subject to the aufbau and Pauli principles. These principles say that the lowest energy orbitals should be filled first and only two electrons (with different spin) can occupy each orbital, that is the electron configuration becomes 1s^2. The antisymmetry condition is conveniently fulfilled by writing the total wave function as a Slater determinant, since interchanging any two rows or columns changes the sign of the determinant. For a helium atom, this would give the following (unnormalized) wave function, with the orbitals given in Table 1.2 with $Z = 2$:

$$\Phi = \begin{vmatrix} \phi_{1s\alpha}(1) & \phi_{1s\beta}(1) \\ \phi_{1s\alpha}(2) & \phi_{1s\beta}(2) \end{vmatrix} = \phi_{1s\alpha}(1)\phi_{1s\beta}(2) - \phi_{1s\beta}(1)\phi_{1s\alpha}(2) \tag{1.41}$$

The total energy calculated by this wave function is simply twice the orbital energy, −4.000 au, which is in error by 38% compared with the experimental value of −2.904 au. Alternatively, we can use the

wave function given by Equation (1.41), but include the electron–electron interaction in the energy calculation, giving a value of −2.750 au.

A better approximation can be obtained by taking the *average* repulsion between the electrons into account when determining the orbitals, a procedure known as the Hartree–Fock approximation. If the orbital for one of the electrons was somehow known, the orbital for the second electron could be calculated in the electric field of the nucleus and the first electron, described by its orbital. This argument could just as well be used for the *second* electron with respect to the *first* electron. The goal is therefore to calculate a set of self-consistent orbitals, and this can be done by iterative methods.

For the solar system, the non-crossing of the planetary orbitals makes the Hartree–Fock approximation only a very minor improvement over a central field model. For a many-electron atom, however, the situation is different since the position of the electrons is described by three-dimensional probability functions (square of the orbitals), that is the electron "orbits" "cross". The average nucleus–electron distance for an electron in a 2s-orbital is larger than for one in a 1s-orbital, but there is a finite probability that a 2s-electron is closer to the nucleus than a 1s-electron. If the 1s-electrons in lithium were completely inside the 2s-orbital, the latter would experience an effective nuclear charge of 1.00, but owing to the 2s-electron penetrating the 1s-orbital, the effective nuclear charge for an electron in a 2s-orbital is 1.26. The 2s-electron in return screens the nuclear charge felt by the 1s-electrons, making the effective nuclear charge felt by the 1s-electrons less than 3.00. The mutual screening of the two 1s-electrons in helium produces an effective nuclear charge of 1.69, yielding a total energy of −2.848 au, which is a significant improvement relative to the model with orbitals employing a fixed nuclear charge of 2.00.

Although the effective nuclear charge of 1.69 represents the lowest possible energy with the functional form of the orbitals in Table 1.2, it is possible to further refine the model by relaxing the functional form of the orbitals from a strict exponential. Although the exponential form is the exact solution for a hydrogen-like system, this is not the case for a many-electron atom. Allowing the orbitals to adopt best possible form, and simultaneously optimizing the exponents ("effective nuclear charge"), gives an energy of −2.862 au. This represents the best possible independent-particle model for the helium atom, and any further refinement must include the instantaneous correlation between the electrons. By using the electron correlation methods described in Chapter 4, it is possible to reproduce the experimental energy of −2.904 au (see Table 1.3).

The equal mass of all the electrons and the strong interaction between them makes the Hartree–Fock model less accurate than desirable, but it is still a big improvement over an independent orbital model. The Hartree–Fock model typically accounts for ∼99% of the total energy, but the remaining *correlation energy* is usually very important for chemical purposes. The correlation between the electrons describes the "wiggles" relative to the Hartree–Fock orbitals due to the instantaneous interaction between the electrons, rather than just the average repulsion. The goal of correlated methods

Table 1.3 Helium atomic energies in various approximations.

Wave function	Z_{eff}	Energy (au)
He$^+$ exponential orbital, no electron–electron repulsion	2.00	−4.000
He$^+$ exponential orbital, including electron–electron repulsion	2.00	−2.750
Optimum single exponential orbital	1.69	−2.848
Best orbital, Hartree–Fock limit		−2.862
Experimental		−2.904

for solving the Schrödinger equation is to calculate the remaining correction due to the electron–electron interaction.

1.9 Chemistry

The Born–Oppenheimer separation of the electronic and nuclear motions is a cornerstone in computational chemistry. Once the electronic Schrödinger equation has been solved for a large number of nuclear geometries (and possibly also for several electronic states), the *potential energy surface* (PES) is known. The motion of the nuclei on the PES can then be solved either classically (Newton) or by quantum (Schrödinger) methods. If there are N nuclei, the dimensionality of the PES is $3N$, that is there are $3N$ nuclear coordinates that define the geometry. Of these coordinates, three describe the overall translation of the molecule and three describe the overall rotation of the molecule with respect to three axes. For a linear molecule, only two coordinates are necessary for describing the rotation. This leaves $3N − 6(5)$ coordinates to describe the internal movement of the nuclei, which for small displacements may be chosen as "vibrational normal coordinates".

It should be stressed that nuclei are heavy enough that quantum effects are almost negligible, that is they behave to a good approximation as classical particles. Indeed, if nuclei showed significant quantum aspects, the concept of molecular structure (i.e. different configurations and conformations) would not have any meaning, since the nuclei would simply tunnel through barriers and end up in the global minimum. Dimethyl ether, for example, would spontaneously transform into ethanol. Furthermore, it would not be possible to speak of a molecular geometry, since the Heisenberg uncertainty principle would not permit a measure of nuclear positions with an accuracy smaller than the molecular dimension.

Methods aimed at solving the electronic Schrödinger equation are broadly referred to as "electronic structure calculations". An accurate determination of the electronic wave function is very demanding. Constructing a complete PES for molecules containing more than three or four atoms is virtually impossible. Consider, for example, mapping the PES by calculating the electronic energy for every 0.1 Å over, say, a 1 Å range (a very coarse mapping). With three atoms, there are three internal coordinates, giving 10^3 points to be calculated. Four atoms already produce six internal coordinates, giving 10^6 points, which is possible to calculate, but only with a determined effort. Larger systems are out of reach. Constructing global PESs for all but the smallest molecules is thus impossible. By restricting the calculations to the "chemically interesting" part of the PES, however, it is possible to obtain useful information. The interesting parts of a PES are usually nuclear arrangements that have low energies. For example, nuclear movements near a minimum on the PES, which corresponds to a stable molecule, are molecular vibrations. Chemical reactions correspond to larger movements, and may in the simplest approximation be described by locating the lowest energy path leading from one minimum on the PES to another.

These considerations lead to the following definition:

Chemistry is knowing the energy as a function of the nuclear coordinates.

The large majority of what are commonly referred to as molecular properties may similarly be defined as:

Properties are knowing how the energy changes upon adding a perturbation.

In the following chapters we will look at some aspects of solving the electronic Schrödinger equation or otherwise construct a PES, how to deal with the movement of nuclei on the PES and various

technical points of commonly used methods. A word of caution here: although it is the nuclei that move, and the electrons follow "instantly" (according to the Born–Oppenheimer approximation), it is common also to speak of "atoms" moving. An isolated atom consists of a nucleus and some electrons, but in a molecule the concept of an atom is not well defined. Analogously to the isolated atom, an atom in a molecule should consist of a nucleus and some electrons. But how does one partition the total electron distribution in a molecule such that a given portion belongs to a given nucleus? Nevertheless, the words nucleus and atom are often used interchangeably.

Much of the following will concentrate on describing individual molecules. Experiments are rarely done on a single molecule; rather they are performed on macroscopic samples with perhaps 10^{20} molecules. The link between the properties of a single molecule, or a small collection of molecules, and the macroscopic observable is statistical mechanics. Briefly, macroscopic properties, such as temperature, heat capacity, entropy, etc., are the net effect of a very large number of molecules having a certain distribution of energies. If all the possible energy states can be determined for an individual molecule or a small collection of molecules, statistical mechanics can be used for calculating macroscopic properties.

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