

Molecular Quantum Dynamics

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We provide a brief introduction to some basic ideas of Molecular Quantum Dynamics. We discuss the scope, strengths and main applications of this field of science. Finally, we also mention open problems of current interest in this exciting subject.

1 Introduction: classical and quantum physics

1.1 Classical physics

In classical mechanics, one can use Newton's three laws to translate a classical physics problem into a mathematical one.^[1] Roughly speaking, the first and third laws concern the allowed reference frames, which means they are concerned with the relationships between the ways different physical observers describe mathematically the same physical phenomena. The celebrated second law, which reads $F = ma$, describes the *dynamics*. Dynamics is the area of science concerned with the forces that cause motion and changes of state of objects. In this context, F is the magnitude of the force applied, m is the mass of the object subject to the force and a is the magnitude of the acceleration that the object has.^[2] The equation $F = ma$ leads naturally to a system of ordinary differential equations for the positions of particles as a function of time.

[1] An introduction on Newton's famous laws can be found in [10].

[2] This simple version of the formula applies to the case of forces F that are constant in time and act on pointlike objects of mass m .

1.2 Quantum physics

In the most common formulation of quantum mechanics, the central object is not a particle, or a collection of particles, but it is the *wave function*.^[3] The wave function $\psi(\mathbf{x}, t)$ is a complex valued function of the variables $\mathbf{x} = (x, y, z)$ and t , and it is used to give the (clearly non-negative) probability density $p(\mathbf{x}, t) := |\psi(\mathbf{x}, t)|^2$ for finding the particle(s) at the point \mathbf{x} in space at time t . It is clear that, if the particles exist, at any time t they must be somewhere, and we deduce that

$$\int |\psi(\mathbf{x}, t)|^2 d^3x = 1.$$

Notice that the fact that the total probability adds up to 1 is the mathematical way of stating that the object *must* be somewhere. The connection between wave function and probability densities was established mainly by the Nobel Prize awardee Max Born. An introduction on this interesting topic can be found in [7].

The dynamics of quantum particles are governed by the analogue of Newton's second law, which is known as the time-dependent *Schrödinger equation*, which we print here

$$i \hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}, t) + V(\mathbf{x}, t) \psi(\mathbf{x}, t). \quad (1)$$

In the Schrödinger equation we used $\nabla^2 := \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, the external potential $V(\mathbf{x}, t)$ that affects the quantum systems and the famous Planck constant \hbar . The Planck constant measures the “quantumness” of physical effects. If an aspect of a physical effect vanishes for $\hbar = 0$, then it can be somehow regarded as the “quantum part” of the effect.

The Schrödinger equation describes how the wave function $\psi(\mathbf{x}, t)$ changes with time under the effect of an external potential $V(\mathbf{x}, t)$, such as the electrical potential generated by an electrically charged source. It is a partial differential equation,^[4] whose solution is mathematically far more complicated than that of an ordinary differential equation.

We note in passing that it is a long-standing problem to determine if the wave function is a real object, in the sense of an object with a physical reality in its own right, or just a mathematical tool used by scientists to describe real objects. This question led to many exciting philosophical and scientific debates already at the times of very famous scientists such as E. Schrödinger, A. Einstein and N. Bohr, and it is still ongoing today [9].

^[3] For a simple introduction to the wave function and its role and interpretation in quantum mechanics, see [3].

^[4] That is, a differential equation in more than one variable.

1.3 Many body quantum physics and computational problems

So far we have introduced the main object that describes a single quantum particle.

If a quantum system consists of N identical particles moving in d dimensions, then the vector \mathbf{x} belongs to the $(N \cdot d)$ -dimensional space $\mathbb{R}^{N \cdot d}$. This means that, in order to describe the dynamics of N identical quantum particles that propagate in d dimensions, one needs a wave function $\psi(\mathbf{x}, t)$ that depends on $N \cdot d + 1$ variables.

This is a significant problem in molecular quantum mechanics. For example, the small carbon dioxide molecule CO_2 has three atomic nuclei (one carbon and two oxygens) and 22 electrons, all moving in 3-dimensional space. In Figure 1 we present a simple image of the CO_2 molecule.

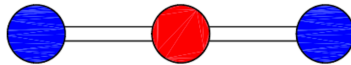


Figure 1: In the figure we have the generic structure of the CO_2 molecule. The two blue spheres represent the Oxygen atoms, while the central red one represents the Carbon atom. Oxygen is element 8 on the periodic table, while Carbon is element 6 on the periodic table [11]. The lines in between represent the exchange valence electrons, that roughly means the electrons responsible for the binding of the molecule. Although the carbon and Oxygens “share” few electrons, the Oxygens carry 8 electrons each while the Carbon only 6. All of these electrons move around the much heavier nuclei, forming the so-called *electron cloud*.

It follows from what we discussed above that the Schrödinger equation for the carbon dioxide molecule is a partial differential equation in 76 dimensions!^[5] Often this situation is called the “curse of dimensionality”, see [8].

^[5] This number can be obtained as follows: We have three nuclei and 22 electrons, for a total of 25 particles. Therefore, $(22 + 3) \times 3 + 1 = 76$, where the time t is 1-dimensional, while the vector of space variables \mathbf{x} has 75 components (space dimensions).

There are well developed numerical techniques, see for example [2], [4] or [6] for finding approximate solutions to partial differential equations in a few dimensions. However, already for simple molecules like CO_2 , we have to work with 76 dimensions which is definitely off scale. In fact, even just storing information of a function of 75 dimensions on a computer for one fixed point in time can be a serious challenge.

2 Quantum Molecular Dynamics: Foundations

What distinguishes molecular quantum mechanics from “standard” quantum mechanics?

Molecules have atoms with nuclei and electrons. All electrons are identical, while atomic nuclei have masses that are drastically larger than that of the electrons (even if combined together). Typical nuclei are made up of roughly equal numbers of protons and neutrons, and each proton or neutron has mass roughly 1836 times larger than that of an electron.

In a truly brilliant 1927 paper, the Nobel Prize awardee Max Born and J. Robert Oppenheimer argued that, because of this great disparity of electron and nuclei masses, one could “separate” the motion of the electrons from the motion of the nuclei within molecules that were in *stationary states*, see the original and translated articles [1]. Stationary states are “static”, in the sense that they do not have any interesting dynamics (or, in other words, their time evolution does not carry any interesting physical information). As a simple pictorial representation of a steady state, one can imagine opening the water tap in a sink. After an initial convulse transitional moment, the water flow settles to *steady state*, where the configuration is the same at any instant in time (until the user changes something by altering the dynamics, that is, turns the tap). In this sense, we have uninteresting dynamics, since nothing changes. In our case steady states have the form $\psi_{\text{steady}}(t, x) = e^{-itE/\hbar} \Phi(x)$, where E is the energy of the state. The probability density $|\Phi(x)|^2$ does not depend on time.

A few years after the pioneering paper of Born and Oppenheimer, scientists realized that the same ideas could be applied to molecular systems in typical chemical reactions. That led to what is often now called the time-dependent Born–Oppenheimer approximation [7]. Intuitively, given the same available energy in the molecules, the large-mass nuclei move much more slowly than the low-mass electrons. Therefore, the difference between the two time scales (the time it takes electrons or nuclei to cross the same distance) is what allows to separate and identify the two types of motions.

Roughly speaking, the time-dependent Born–Oppenheimer approximation states that the electrons in a molecular system stay in one steady state, such as

their “ground state”, which is the configuration of electrons that has the lowest possible energy, while the nuclei move. This is also known as the “adiabatic approximation”. This means that, to the approximation at which scientists mostly consider these systems, it is sufficient to consider the electrostatic potential that repels the nuclei (which all carry positive charges) and an effective external potential generated by the negatively charged “cloud” of electrons. That such a cloud is a good model for electrons is justified by the fact that they move so fast compared to the nuclei, that they can be thought of being effectively “smeared out” over some volume of space, together with their charge. Furthermore, since the nuclei are so massive with respect to the electrons, the nuclei dynamics obey a *semiclassical approximation* in an effective potential generated by the electrons and the nuclear-nuclear electrostatic repulsion. The semiclassical approximation involves mathematical efforts that are just slightly more complicated than those employed for studies in classical mechanics. Therefore, one can think of the nuclear motion as being close to classical motion, while the electrons are found and remain in one steady state.

3 Modern work and open questions

The main task of interest undertaken by most computational chemists is to determine the electrons’ steady state, and therefore the effective potential felt by the nuclei. This is usually called the *electron structure problem*, and there are several very sophisticated computer programs one can use to generate approximate solutions, see for example [5]. Decades of work by thousands of theoretical chemists have gone into the development of these programs.

The 2015 Oberwolfach Workshop on Quantum Molecular Dynamics sought to bring together mathematicians and scientists from chemistry and physics to discuss this subject for mutual benefit. There are many issues and open questions of current research interest. Here we list a few:

- How should one deal with the curse of dimension?
- Molecules have positions of the nuclei called *level crossings*, where the time-dependent Born–Oppenheimer approximation is not applicable. Level crossings are points where two (or more) electronic energy levels are equal. The Born–Oppenheimer approximation does not deal with these points because it functions on the basic working assumption that the electronic level of interest is isolated from all other electronic energy levels (that is, it does not cross with others). How should one deal with them?
- How can one describe a molecule in a complex environment, such as a solution, since solutions are very complicated because they involve many more nuclei and electrons than just a single molecule?

We end this snapshot by noting that theoretical chemists will almost certainly develop new techniques for approximately solving the electron structure problem. Therefore, current and novel challenges for mathematicians will include dealing with level crossings (and the failure of the Born-Oppenheimer approximation), as well as with ways to finding more accurate numerical solutions of the time-dependent Schrödinger equation for the nuclei.

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Fig. 1 was created by the authors.

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