The Meaning of Time in Quantum Mechanics

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1   Abstract

We propose a research program to investigate the role of time in non-relativistic quantum mechanics. Although our proposal is of general relevance, we will specialize our applications to the field of quantum chemistry. We will begin by discussing the meaning of a "chemical event" and the importance of constructing time operators to understand the nature of chemical events. We formulate a novel set of non-linear eigenvalue equations, which can be solved numerically to construct time operators for different many-body Hamiltonians. Next, we discuss quantum clocks and the conditions an ideal clock must satisfy. We introduce the adiabatic time approximation (ATA), which provides a rigorous criterion for time to be regarded as a parameter rather than an operator. Finally, we discuss the effects of decoherence on quantum clocks, within the framework of the theory of open quantum systems.

2   Project Summary

Since the early days of quantum theory, time has played a special role. While the spatial location of quantum objects can be easily manipulated, time appears to continuously and uncontrollably move forward. Therefore, the special role of time in quantum mechanics is often taken for granted, particularly in the field of quantum chemistry.

In our proposed research, we reexamine the meaning of time in quantum mechanics and question whether it truly deserves a special role. We look at the conditions under which time must be treated as a dynamical variable like space, and when it can in fact be treated as a special parameter. This naturally leads us to investigate the nature of "quantum clocks," which are devices used to keep

track of time. This research is significant, because it will raise and answer new questions about the meaning of time, which are not often addressed in current research.

3   Proposed Research

3.1   Introduction

The wave function of a quantum system describes the probability amplitude for different events to occur at points in space-time. However, the traditional formulation of quantum theory treats space and time on a completely different footing. In non-relativistic quantum mechanics, and chemistry in particular, it is often taken for granted that time is a continuous parameter and not a dynamical variable. If we think of space on the other hand, we know that position is treated as a dynamical variable represented by an operator.

The unequal treatment of space and time in quantum mechanics has many ramifications, particularly when we begin to ask questions about *when* and *where* a particular event occurs. The implications of this have been explored extensively in the quantum gravity literature and in fields related to the foundations of quantum mechanics. However, the unequal treatment of space and time in the microscopic realms of quantum chemistry and condensed matter physics has hardly been explored to date.

I propose a FQXI-supported research program that will explore the meaning of time in chemical systems. My group will explore questions such as: *What is a chemical event? How can we define a clock to measure when a chemical event occurs? What are the conditions under which it is valid to treat time as a parameter and not a dynamical variable? Can the role of time in chemistry teach us about the meaning of time in other fields such as quantum gravity?* To better understand these questions, we will explore three broad areas of research, outlined in the sections below.

3.2   Time Operators in Chemistry and the Meaning of "Chemical Events"

Time-dependent processes in chemistry are ubiquitous. Chemical reactions occur as molecules collide with one another, exchanging kinetic and potential energy as chemical bonds are formed and broken. Similarly, in photochemical processes photons are absorbed and emitted as energy is channeled into different degrees of freedom (electronic, rotational and vibrational). For instance, the formation of a chemical bond or photodissociation of a molecule can be regarded as a *chemical event* and it is natural to ask not only where this event occurs, but also *when*. In order to address this question, time must be regarded as an observable quantity, i.e. a dynamical variable represented by an operator and not a parameter.

Mathematically, the problem of constructing time operators is formulated as follows: Given a Hamiltonian $\hat{H}$, its associated time operator $\hat{t}$, is constructed by imposing the canonical commutation relation:

$$\left[\hat{t}, \hat{H}\right]|\psi_n\rangle = i\hbar|\psi_n\rangle, \tag{1}$$

over a certain domain of the Hilbert space spanned by the states $\{|\psi_n\rangle\}$. Note that eq. 3.2 is a non-linear eigenvalue problem, as one must find both the operator $\hat{t}$ and the eigenvectors $\{|\psi_n\rangle\}$. Solving eq. 3.2 for single particle quantum systems is often a fairly straight forward task. For example, consider the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} - qE\hat{x}, \tag{2}$$

which describes a particle of charge q in one-dimension subjected to a constant electric field E. By solving eq 3.2, one finds that the time operator is:

$$\hat{t} = -\frac{\hat{p}}{qE}, \tag{3}$$

and the states $\{|\psi_n\rangle\}$ span the entire Hilbert space. The eigenstates of $\hat{t}$ describe states that arrive at the origin $(x = 0)$ at a definite time. Thus the event defined by the time operator for the linear potential is arrival at the origin.

Solving eq. 3.2 for many-body systems is far less trivial. We must take into account correlations between different particles as well as Fermionic or Bosonic statistics. We propose to extend the above analysis to **construct time operators for chemical systems and study the chemical events they describe**. As a starting point, one might begin with the full Hamiltonian operator of non-relativistic electrons and nuclei, interacting with the quantized electromagnetic field:

$$\hat{H} = \hat{H}_{el} + \hat{H}_n + \hat{H}_{em} + \hat{H}_{el-n} + \hat{H}_{el-em} + \hat{H}_{n-em}, \tag{4}$$

where the first three terms represent free electrons, nuclei and photons, while the last three are their respective interactions. We can construct a time operator by solving the non-linear eigenvalue problem posed in eq. 3.2. Unlike the single particle case, which can be solved exactly, solving the non-linear eigenvalue problem in eq. 3.2 must be done numerically for the Hamiltonian in eq. 3.2. Non-linear eigenvalue problems are common in computational chemistry and many highly efficient numerical algorithms exist. My group has vast computational resources, as well as the domain expertise available to accomplish this task. **We will numerically construct time operators for a variety of chemical systems and investigate their spectra to answer questions about chemical events such as: When does a molecule absorb or emit a phonton? When does the absorbed energy fully dissipate into nuclear vibrational energy? How long does it take for a chemical reaction between two molecules to occur?**

The task of constructing a time operator for the full Hamiltonian in eq. 3.2 will be computationally demanding. Approximate and model Hamiltonians are

often used to simply quantum many-body calculations. Each model Hamiltonian gives rise to a corresponding model time operator through the solution to eq. 3.2. **Another area of research will be to construct and classify time operators for different model Hamiltonians of varying degrees of complexity.** For example, in chemistry it is often possible to make approximations to simplify eq. 3.2. By invoking the Born-Oppenheimer approximation (BO), one can treat the nuclei classically as well as the electromagnetic field and arrive at the electronic Hamiltonian:

$$\hat{H} = \int d^3r \Psi^+(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(\mathbf{r},t) \right] \Psi(\mathbf{r}) + \int d^3r \int d^3r' \Psi^+(\mathbf{r}')\Psi^+(\mathbf{r}) \left[\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \right] \Psi(\mathbf{r})\Psi(\mathbf{r}'),$$
(5)

where $\Psi^+(\mathbf{r})$ and $\Psi(\mathbf{r})$ are field operators, respectively creating and destroying an electron at position $\mathbf{r}$. The *external potential*, $v_{ext}(\mathbf{r},t)$, is the potential external to the electrons, which incorporates the nuclear Coulomb potential and the interaction between electrons and the electromagnetic field. The Hamiltonian in eq. 3.2 is often used as the starting point in chemistry and many-body physics. Therefore much of our research will focus on constructing time operators for this Hamiltonian with different external potentials, $v_{ext}(\mathbf{r},t)$.

In addition, it is often insightful to make further approximations and construct model Hamiltonians with discrete Hilbert spaces. One widely used example is the Hubbard model Hamiltonian:

$$\hat{H} = \sum_{i,j,\sigma} \left[T_{ij} + v_{ext,i,j} \right] \hat{c}_{i,\sigma}^+ \hat{c}_{j,\sigma} + \sum_i U_i \hat{c}_{i,\uparrow}^+ \hat{c}_{i,\uparrow} \hat{c}_{i,\downarrow}^+ \hat{c}_{j,\downarrow},$$
(6)

where $\hat{c}_{i,\sigma}^+$ and $\hat{c}_{i,\sigma}$ respectively create and destroy and electron with spin $\sigma = \uparrow, \downarrow$ on the ith site. Another example is the Heisenberg Hamiltonian:

$$\hat{H} = \sum_{i,j} J_{ij}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \sum_i \mathbf{B}_i(t) \cdot \hat{\mathbf{S}}_i,$$
(7)

which exclusively treats the spin degrees of freedom $\hat{\mathbf{S}}_i$, on the ith site in the presence of a local magnetic field $\mathbf{B}_i(t)$. Studying and classifying the time operators for these different Hamiltonians will be an important component of our research.

3.3 Quantum Clocks and the Adiabatic Time Approximation

In chemistry, the Newtonian concept of time as a continuous parameter is so deeply ingrained, that one almost never questions how time is actually measured. It is tacitly assumed that time can be measured with respect to some degree of freedom (a *clock*), with perfect accuracy and minimal disturbance to the system. However, if we begin to investigate when chemical events occur or how long they take, we must use a clock that probes the system and therefore disturbs it to some extent. For instance, if we want to know when two molecules

have reacted, we might use a beam of photons as a probe, which will inherently influence the dynamics of the reaction through electron-photon scattering. **We are interested in understanding how different degrees of freedom can be used as clocks to measure the time and duration of chemical events and how they influence those events.**

As a first step, it helps to consider two limiting cases. At one extreme, we might use a degree of freedom, which is entirely classical and isolated from the chemical event, such as a clock on the wall of the laboratory. We may measure this clock as accurately as we wish with absolutely no influence over the chemical system. However, measuring this clock provides absolutely no information about events occurring within the system. Consequently, the time measured by a clock on the laboratory wall is simply a parameter, identical to the parametric time appearing in the time-dependent Schrodinger equation. At the other extreme, we might use the quantum system itself as a clock. In this case, time becomes a quantum observable represented by the operator $\hat{t}$ satisfying the canonical commutation relation with the system Hamiltonian $\hat{H}_s$. As a result, the uncertainty in $\hat{t}$, Δt and the uncertainty in $\hat{H}_s$, ΔE must always satisfy the Heisenberg uncertainty relation:

$$\Delta t \Delta E \geq \frac{\hbar}{2}. \tag{8}$$

This implies that if we use the system itself as a clock, we must completely sacrifice knowledge of the energy of the system ($\Delta E = \infty$) in order to make a precise measurement of the time of an event ($\Delta t = 0$). Unfortunately, if we have no knowledge of the energy of the system, we can't actually say whether or not a chemical event has occurred. Clearly, an ideal clock for chemical events must lie somewhere between these two extremes, i.e. it is neither the clock on the laboratory wall nor the system itself, but rather some external apparatus that is coupled to the system.

Understanding the conditions on an ideal clock to measure when chemical events occur and how long they take is the subject of our future investigation. To date, my research group has made important first steps in this direction. We have succeeded in deducing the conditions under which the time measured on a clock coupled to the system of interest can be regarded as a parameter, rather than a dynamical variable. It turns out that these conditions are very similar to the Born-Oppenheimer approximation, used to separate the time scales for electronic and nuclear motion.

To make the discussion mathematically precise, we partition into the system, the clock and the remainder of the universe, external to the system and the clock. The universe is taken to be essentially classical, evolving with a time parameter t_u. The clock and system have respective Hamiltonians denoted $\hat{H}_c(\hat{c})$, $\hat{H}_s(\hat{s})$ and time operators denoted $\hat{t}_c(\hat{c})$ and $\hat{t}_s(\hat{s})$. $\hat{s}$ and $\hat{c}$ denote a complete set of operators acting in the system and clock Hilbert spaces, such as the momentum, position and/or spin degrees of freedom. The full Hamiltonian of the system and clock is:

$$\hat{H}_{s-c}(t_u) = \hat{H}_s + \hat{H}_c + \hat{V}(\hat{s}, \hat{c}, t_u), \tag{9}$$

where $\hat{V}$ is the interaction between the system and the clock, which we allow to depend on the parametric time of the universe t_u, for complete generality. The time operator for the clock, $\hat{t}_c$, is a hermitian operator and admits a complete spectrum of eigenstates satisfying the eigenvalue equation:

$$\hat{t}_c|t_c\rangle = t_c|t_c\rangle. \tag{10}$$

The question we will ask is the following: *Under what conditions are the values of t_c identical to t_u from the point of view of the system?* Once a suitable clock satisfying these conditions has been found, we are free to set $t_c = t_u$ and use the states of the clock to measure parametric time in place of the time of the universe.

We now proceed to deduce these conditions. An arbitrary initial state of the system and clock, $|\Psi_{s-c}(t_u = 0)\rangle$, admits a decomposition into eigenstates of the clock's time operator according to:

$$|\Psi_{s-c}(t_u = 0)\rangle = \sum_{t_c} a(t_u, t_c)|\psi_s(t_u = 0, t_c)\rangle \otimes |t_c\rangle. \tag{11}$$

By placing the clock in an appropriate position, we can prepare the initial state:

$$|\Psi_{s-c}(t_u = 0)\rangle = |\psi_s(t_u = 0, t_c)\rangle \otimes |t_c\rangle, \tag{12}$$

in which the clock is in a definite eigenstate of the time operator. The combined clock-system wave function evolves according to the time-dependent Schrodinger equation:

$$i\hbar \frac{d}{dt_u}|\Psi_{s-c}(t_u)\rangle = \hat{H}_{s-c}(t_u)|\Psi_{s-c}(t_u)\rangle, \tag{13}$$

with the parametric time of the universe. The solution to eq. 3.3 is:

$$|\Psi_{s-c}(t_u)\rangle = \mathcal{T}Exp\left[\int_0^{t_u} dt'_u \hat{H}_{s-c}(t'_u)\right]|\Psi_{s-c}(0)\rangle = \mathcal{T}Exp\left[\int_0^{t_u} dt'_u(\hat{H}_s + \hat{H}_c + \hat{V}(\hat{s}, \hat{c}, t'_u))\right]|\psi_s(t_u = 0, t_c)\rangle \otimes |t \tag{14}$$

where $\mathcal{T}$ denotes the time ordering operator. Using the Baker-Campbell-Hausdorff formula, we can replace the above expression by the tensor product expression:

$$|\Psi_{s-c}(t_u)\rangle \approx \left[\mathcal{T}Exp\left[\int_0^{t_u} dt'_u\left[\hat{H}_s + \hat{V}(\hat{s}, c, t'_u)\right]\right]|\psi_s(t_u = 0, t_c)\rangle\right] \otimes \left[e^{-i\hat{H}_c t_u}|t_c\rangle\right], \tag{15}$$

under the condition $t_u||[\hat{H}_c, \int_0^{t_u} dt'_u \hat{V}(\hat{s}, c, t'_u)]|| \ll 1$. Since $||\int_0^{t_u} dt'_u \hat{V}(\hat{s}, c, t'_u)|| \leq ||\hat{V}(\hat{s}, c, t_u)||t_u$, we can write this condition as:

$$t_u^2||[\hat{H}_c, \hat{V}(\hat{s}, c, t_u)]|| \ll 1. \tag{16}$$

Due to the canonical commutation relation, $[\hat{t}_c, \hat{H}_c] = i\hbar$, the Hamiltonian generates translations on the time states according to:

$$e^{-i\hat{H}_c t_u}|t_c\rangle = |t_c + t_u\rangle, \tag{17}$$

which allows us to write eq. 3.3 as:

$$|\Psi_{s-c}(t_u)\rangle \approx \left[\mathcal{T}Exp\left[\int_0^{t_u} dt'_u \left[\hat{H}_s + \hat{V}(\hat{s}, c, t'_u)\right]\right] |\psi_s(t_u = 0, t_c)\rangle\right] \otimes |t_c + t_u\rangle.$$

(18)

By choosing $t_c = 0$, we arrive at the important result that if the condition in eq. 3.3 is satisfied,

$$|\Psi_{s-c}(t_u)\rangle \approx \left[\mathcal{T}Exp\left[\int_0^{t_u} dt'_u \left[\hat{H}_s + \hat{V}(\hat{s}, c, t'_u)\right]\right] |\psi_s(t_u = 0)\rangle\right] \otimes |t_u\rangle \equiv |\psi_s(t_u)\rangle \otimes |t_u\rangle.$$

(19)

As a result of eq. 3.3, the clock degree of freedom is simply a parameter with regard to the wave function of the system, which we refer to as the **adiabatic time approximation** (ATA). The ATA is analogous to the Born-Oppenheimer approximation, in which the nuclear degrees of freedom are regarded as parameters with respect to the electronic wave function. Investigating this analogy fully will be the subject of future research.

3.4 Time Operators for Open Quantum Systems

Most of the literature on time operators has focused on isolated quantum systems, evolving according to the time-dependent Schrodinger equation. However, many quantum systems are not isolated but instead undergo relaxation and decoherence due to interaction with an external environment. Such systems are no longer described by a wave function, but instead by a statistical density matrix $\hat{\rho}(t)$, evolving according to a quantum master equation:

$$i\hbar \frac{d}{dt}\hat{\rho}(t) = [\hat{H}_s, \hat{\rho}(t)] + \mathcal{D}\left[\hat{\rho}(t)\right],$$

(20)

where the first term on the right hand side describes unitary evolution of the system and the second term gives rise to relaxation and decoherence due to the environment. We are interested in how the environment affects the time and duration of events occurring within the system. To answer this question, we will solve eq. 3.4 to obtain $\hat{\rho}(t)$ for different systems. We can then investigate quantities such as the expectation value of the system time operator:

$$\langle \hat{t}_s \rangle = Tr\left[\hat{t}_s \hat{\rho}(t)\right],$$

(21)

and the two-time correlation function:

$$\langle \hat{t}_s(t)\hat{t}_s(t') \rangle = Tr\left[\hat{t}_s(t)\hat{t}_s(t')\hat{\rho}(0)\right],$$

(22)

where the Heisenberg operator $\hat{t}_s(t)$ satisfies:

$$-i\hbar \frac{d}{dt}\hat{t}_s(t) = [\hat{H}_s, \hat{t}_s(t)] + \mathcal{D}\left[\hat{t}_s(t)\right].$$

(23)

Another approach will be to use non-hermitian Hamiltonians to represent open quantum systems. Non-Hermitian Hamiltonians are widely used in the atomic

and molecular physics literature, to describe the resonant decay of excited states. In this formalism, the system Hamiltonian $\hat{H}_s$ is replaced by the non-Hermitian Hamiltonian:

$$\hat{H}'_s = \hat{H}_s + i\hat{V}, \tag{24}$$

where $\hat{V}$ is a Hermitian operator describing coupling of the system to the environment. Clearly, in order to maintain the canonical commutation relation, we must find a non-Hermitian time operator

$$\hat{t}'_s = \hat{t}_s + i\hat{T}, \tag{25}$$

where $\hat{T}$ is a Hermitian operator describing the effects of the environment on the time of processes within the system. The exact meaning of this non-hermitian time operator is a new direction we will explore in my group.

Lastly, we are interested in understanding the related question of how decoherence effects clock degrees of freedom used to measure events. It is well appreciated that decoherence is responsible for the quantum-classical transition as one moves from microscopic to macroscopic scales. This means that decoherence is also responsible for the difference between macroscopic (classical) clocks and atomic-scale (quantum) clocks. We will investigate how different types of environmental noise affect different clocks and how the quantum-classical transition is manifest.

3.5 Context Within My Present Research Program

A large segment of my group works at the intersection of quantum chemistry with quantum computation and information theory as well as open quantum systems. Our research addresses how quantum systems can be used to simulate other quantum systems (the field of quantum simualtion) and the effects of decoherence. We have also worked in fields related to chemical dynamics and time-dependent processes in chemistry, as well as spectroscopy. A unifying theme of all this research is that it involves understanding how quantum many-body systems evolve in time.

Working in time-dependent quantum mechanics has led my group to ask the deep questions about the fundamental nature of time outlined in this proposal. I have a large interdisciplinary group with diverse backgrounds in physics and chemistry, well equipped to address both the computational and conceptual aspects of the proposed work. However, we do not yet have funding available to work exclusively on the fundamental role of time. The FQXI grant will be essential in enabling us to devote proper resources to answer these fundamental questions.

3.6 Communicating Results to a Wider Audience

The work outlined in this proposal is of broad interest to many scientific communities, ranging from applied chemists to theoretical physicists. The work is also of high impact as it addresses problems that have remained unanswered

since the early days of quantum theory. As a result, we believe that the results of our work will be suitable for journals such as Science and Nature, which are read by a large and diverse readership. Also, because the proposed work is of interest to chemists and physicists alike, we intend to present it at conferences involving many different scientific communities.

I have been involved in developing online course material though the HarvardX platform, with open-access to non-experts and lay people throughout the world. The results of our proposed research are sufficiently fundamental that they can be presented as part of my introductory online quantum mechanics course.

4   References

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