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Recent Advances in Computational Methods for Modelling Photocatalytic Reactions: Insights into Quantum Mechanisms, Materials, and Applications

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Abstract

Review Article

Photocatalysis, particularly in energy conversion and environmental remediation, has become a significant technology due to its ability to utilise solar energy to degrade pollutants and produce clean energy. At the core of developing effective photocatalysts are quantum chemistry methods, most notably Density Functional Theory (DFT), which can be employed to simulate electronic structures and predict catalytic behaviour. This review paper discusses the theoretical methods used in photocatalysis, focusing on DFT and its developments, including hybrid functionals, meta-GGA, and their range-separated hybrid models. Furthermore, we discuss multi-configurational and perturbation theory methods, which are used for systems with strong electron correlations, and integrating DFT with machine learning to accelerate the discovery of new photocatalytic materials. The paper focuses on DFT's role in synthesising new materials, notably metal-organic frameworks (MOFS). It presents their applications in water-splitting photocatalysis, CO_2 reduction, and the degradation of organic pollutants. Finally, we review recent developments in computational methods used to model the mechanisms and reactions of photocatalysis, focusing on the need to optimise the light-matter interface. Despite the immense promise, challenges persist in accurately modelling complex photocatalysis systems, necessitating ongoing advances in computational methods. The advancement of photocatalysis will depend on aligning theory and experiment and refining computational models to optimise the efficiency and scalability of catalysis processes.

Keywords: Photocatalysis, Density Functional Theory (DFT), Hybrid Functionals, Metal-Organic Frameworks (MOFs), Photocatalytic Water Splitting, CO_2 Reduction, Computational Chemistry, Machine Learning, Photodegradation, Quantum Chemistry.

1. INTRODUCTION

Photocatalysis is an emerging area of research that focuses on optimising and controlling chemical reactions using radiant energy, especially light. The acceleration of these reactions is achieved either by direct light interaction or by inducing excitation in a substance that catalytically facilitates the primary response [1, 2]. This dynamic field holds great promise in addressing energy-related challenges [3], and environmental concerns [4–6], by mimicking complex processes in natural photochemistry and incorporating sustainable materials.

Photocatalysts are molecular systems, including nanoparticles, surfaces, or organic/inorganic molecules, with specific semiconducting properties such as light absorption, charge transfer, and particular electronic and geometric characteristics. Researchers are making notable strides in developing innovative light-responsive materials and gaining a deeper understanding of their mechanisms. These materials can potentially

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revolutionise the photocatalysis field by enhancing the efficiency of processes and broadening their range of applications [7, 8]. Photocatalysis holds considerable promise in various scientific fields, including energy, environmental solutions, and advancements in health and materials. A key application is its ability to utilise sunlight to produce hydrogen fuel. This clean and renewable energy source is essential for reducing pollution and decreasing dependence on non-renewable fossil fuels.

In addition to its energy-related applications, photocatalysis also holds significant potential for light signal detection, which could lead to enhanced communication and security technologies. By detecting light intensity, wavelength, or colour, photocatalysis can support optical communication, imaging, and encryption, enhancing information and security systems. Furthermore, photocatalysis plays a significant role in environmental preservation, mainly through its ability to purify water [9], and air [10], removing pollutants and pathogens. This capability directly improves environmental quality and human health, making it an essential tool for achieving the global goal of clean and safe resources. Additionally, photocatalysis makes significant contributions to materials science by enabling the creation of innovative compounds and materials, ranging from pharmaceuticals and polymers to nanomaterials and catalysts [7]. These advancements have applications across industrial [11], and biomedical sectors [12], highlighting the broad impact of photocatalysis.

Moreover, photocatalysis can modify surface or interface properties, directly impacting the functionality and performance of devices such as batteries [13], capacitors, and solar cells [14]. This capability not only drives technological progress but also boosts the efficiency and sustainability of these devices, ultimately improving their overall reliability. A key area of focus within photocatalysis is the enhancement of solar cells [15], with researchers working to improve the efficiency and stability of converting solar energy into electrical energy, aiming for significant advancements in the development of sustainable and efficient energy solutions [16]. In summary, photocatalysis stands out as a versatile and promising field, poised to address complex global challenges across a wide range of scientific and technological sectors.

In photocatalysis, computational modelling plays a crucial role, providing a foundation for understanding the complex mechanisms underlying photocatalysis and facilitating the design of semiconductor photocatalyst systems [17]. Simulations that capture the dynamics of numerous electrons, nuclei, and molecules within condensed matter [18], facilitate in-depth studies of atomic and electronic structures, along with the associated properties of nanostructures at sub-nanometer scales [19]. This capability enables the development of innovative theoretical models for photocatalyst materials and interfaces, which are crucial for the strategic design and engineering of semiconductor photocatalyst systems [20, 21].

Quantum chemical methods, such as ab initio and semi-empirical approaches, play a vital role in photocatalysis modeling [22–26]. These methods are essential for capturing and representing various chemical properties at the quantum level. By utilising these techniques, researchers gain valuable insights into the intricate processes of photocatalysis. First-principles calculations on high-performance computing platforms can establish a virtual laboratory to explore the nuanced interactions between physical properties, such as atomic structures, defects, interfaces, and the electronic structure of materials. This approach is crucial for testing new concepts and ideas in the development of efficient photocatalyst materials and devices. Additionally, computational modeling helps in the design and optimisation of metal–organic frameworks (MOFs) for photocatalysis [27, 28], focusing on tailoring band edge positions to achieve optimal photocatalytic performance. Moreover, computational fluid dynamics (CFD) modelling plays a crucial role in designing and optimising microreactors used in photoredox catalysis [29,30], thereby deepening our understanding of reagent interactions and the impact of light on the reaction medium. In summary, computational modeling is an indispensable tool that drives the advancement of photocatalysis, offering comprehensive insights into light–matter interactions and facilitating the discovery of novel materials and devices with broad applications.

Chemical kinetics methods [31, 32], are also crucial in photocatalysis, where multiple simultaneous reactions frequently occur. These simulations rely on the energetics of intermediate compounds, which can be calculated using quantum mechanics. The complexities of photocatalytic reaction kinetics are influenced by various factors, including the nature of the catalyst, the reactants involved, and the intensity of light. External factors, such as impurities, temperature, and the pH of the reaction medium, can also influence the kinetics of photocatalytic reactions. Studying chemical kinetics within the context of photocatalysis is vital for understanding reaction mechanisms and optimising the performance of photocatalytic systems.

Although conventional computational methods have proven helpful in modelling photocatalytic processes, their effectiveness is constrained by the inherent complexity of the studied reactions. Overcoming these challenges requires primarily refining the precision and applicability of these methods [33]. Precision is crucial due to the intricate nature of photocatalysis, which involves complex molecular-level interactions [34]. Traditional computational techniques often struggle to capture these intricate dynamics, necessitating improvements to more accurately represent the interplay among electrons, nuclei, and molecules within photocatalytic systems. Simultaneously, it is essential to enhance the applicability of computational methods, given the diverse and dynamic characteristics of photocatalytic processes. Researchers are developing methodologies that can accommodate various conditions, materials, and environmental factors, making the models more versatile and applicable to real-world scenarios [35–37]. In essence, the challenge lies not only in improving the accuracy of these methods but also in increasing their adaptability to effectively address the wide range of scenarios encountered in photocatalysis research.

This review concludes by examining the promising future of modelling in photocatalysis research, with a primary focus on the potential of multiscale modelling approaches [38, 39], as well as advancements in machine learning [40, 41], and innovative quantum algorithms [42], that aim to overcome existing challenges. In this context, multiscale modeling is a vital tool for bridging different levels of description, capturing both interactions and feedback mechanisms. For example, it integrates quantum mechanical calculations of the electronic structure and optical properties of photocatalytic materials with kinetic models of reaction pathways and rates. Additionally, it accounts for environmental factors such as temperature, pressure, and solvent effects, providing a comprehensive understanding of photocatalytic processes and guiding the rational design of materials and systems. Meanwhile, machine learning and artificial intelligence are making significant contributions to the field by facilitating the discovery of new photocatalytic materials, optimising reaction conditions, and extracting meaningful patterns from large and noisy datasets. By leveraging existing experimental and simulation data, predictive models could potentially accelerate material screening and evaluation while identifying key factors that influence photocatalytic activity and selectivity. Quantum computing offers a paradigm shift, providing exceptional accuracy and speed in solving quantum mechanical equations related to electronic and optical properties. By overcoming the scalability and complexity limitations of classical computing, quantum computing enables the simulation of large, realistic photocatalytic systems and explores quantum phenomena like entanglement, superposition, and tunneling. This opens new possibilities beyond traditional tools, thereby expanding the horizons of photocatalysis research.

Although multiscale modelling is an extensively used technique, ML/AI models are still developing significantly, and quantum computing is in its early stages. Despite their varying levels of maturity, these techniques collectively drive advancements in photocatalysis research. By enhancing clarity and coherence, this review examines how modelling methods [43, 44] influence the photocatalysis field.

2. Basics of Photocatalysis

The fundamental principles of photocatalysis involve the interaction of light with matter, the creation of electron–hole pairs, and the subsequent redox reactions that occur on the photocatalyst surface. The foundation of photocatalytic process modeling is rooted in band structure theory [45]. This concept, derived from solid-state physics, explains the distribution of electron energy levels within solids. According to band theory, these energy levels are organised into bands, separated by "band gaps"—regions that lack electron states.

The photocatalytic process begins with the generation of an electron–hole pair, induced by light (a photogenerated exciton) within the catalyst (e.g., a molecule, nanoparticle, or surface). If the photon energy is equal to or greater than the photocatalyst's bandgap, an electron from the catalyst's valence band is excited and moved to the unoccupied conduction band, creating a positive hole in the valence band. This separation of charges generates a potential that facilitates redox reactions on the surface of the photocatalyst. The electrons in the conduction band can be transferred to an electron acceptor (1), while the hole can either oxidise a donor molecule or reduce an oxidant (2):

$e^- + A \rightarrow A^{-}\cdot$ (1)
$h^+ + H\cdot D \rightarrow H^+ + D$ (2)

This process generates highly reactive intermediate radicals that react with reactant molecules on the photocatalyst surface, leading to the formation of the desired products [46–48]. The band gap of the material influences the efficiency of photocatalytic processes. A smaller band gap allows the absorption of a broader spectrum of light; however, the band gap must be large enough to provide the energy required for the reactions. Bandgap engineering is a strategy used to optimise the band gap for enhanced light absorption and charge carrier dynamics [49].

Two of the most well-known photocatalytic processes under active research and development are water splitting (3) [50, 51], and the reduction of carbon dioxide (6) [52]:

$H_2O + h\nu \rightarrow 2H_2 + ½O_2$ (3)
$2H^+ + 2e^- \rightarrow 2H_2$ (4)
$H_2O + 2h^+ \rightarrow 2H^+ + ½O_2$ (5)
$CO_2 + 2H + h\nu \rightarrow 2H_2 + O_2$ (6)
$CO_2 + 2H + h\nu \rightarrow CO + H_2O$ (7)
$CO_2 + 4H + h\nu \rightarrow C + 2H_2O$ (8)

Water cannot directly absorb sunlight in the first reaction [53], as it is transparent across the entire spectrum. The photon energy is transferred to water molecules via the initial absorption of sunlight by the catalyst, which is then transferred to H_2O [54]. This leads to a four-step process: first, the absorption of a photon with energy more significant than the band gap of the photocatalyst, resulting in the generation of an electron–hole pair; second, the separation of the photoexcited electron and hole; third, their reaction with water molecules to yield hydrogen (reduction, (4)) and oxygen (oxidation, (5)); and finally, the release of the produced hydrogen and oxygen from the photocatalyst surface. The photocatalyst must have a wide band gap (greater than 1.23 ev) to split water efficiently. However, factors such as internal material resistance and the overpotential of the water-splitting reaction increase the necessary band gap, which can range from 1.6 to 2.4 eV [55, 56]. It is also important to note that water splitting is an energy-demanding process with $\Delta H > 0$.

Titanium dioxide (TiO_2) is an example of a semiconductor with an appropriate band structure. Its bandgap of 3.2 eV enables it to absorb ultraviolet light and generate electron–hole pairs. When irradiated with light, electrons are excited from the valence band to the conduction band, leaving behind positive holes. These electrons and holes then migrate to the surface of TiO_2 and react with water molecules [57]. Natural photosynthesis in plants and certain bacteria also involves water splitting, facilitated by absorbing energy from four photons, which is converted into chemical energy through a complex biochemical pathway [58]. This process requires higher energy input from photons, making it more challenging to achieve compared to photochemical splitting.

The second reaction in photocatalysis is a multistep process that involves several intermediates and products, depending on the catalyst's properties and the reaction conditions [6-8]. The pathways and mechanisms involved in CO_2 reduction are influenced by various factors, including the type of catalyst material, its structure, morphology, composition, surface area, defect density, and the applied potential, ph, temperature, pressure, solvent, electrolyte, and gas diffusion [52, 59]. To analyse such reactions, energy diagrams for possible intermediates are helpful, as they aid in predicting the most promising pathways among parallel processes [60]. Modifying the catalytic surface, through defects, vacancies, or additives, can optimise and control the reaction. Such modifications can alter the electronic structure, adsorption properties, and catalytic activity of the catalyst [61].

➢ Key Steps in the Photocatalytic Reaction Process

The photocatalytic reaction process can generally be divided into the following significant steps [62–64]:

- **Adsorption**:

  The reactant molecule adsorbs onto the semiconductor surface, forming a physical or chemical bond with the catalyst. This step is crucial as it facilitates the subsequent interactions between the molecule and the catalyst. The adsorption process is influenced by the catalyst's surface area, charge, and affinity for the reactant.

- **Exciton Formation**:

  When the catalyst absorbs light, typically in the UV or visible spectrum, it generates electron–hole pairs through a process called exciton formation. The excited electrons transition from the valence band to the conduction band, leaving behind positive holes in the valence band. These electron–hole pairs, also known as excitons, are highly reactive but have a short lifetime.

- **Reaction**:

  The excited electrons or holes react with the adsorbed molecule, either directly or indirectly. In direct reactions, electrons or holes transfer from the catalyst to the molecule, causing oxidation or reduction. Indirect reactions generate reactive oxygen species (ROS), such as hydroxyl radicals, superoxide anions, or hydrogen peroxide, by reacting excited particles with water or oxygen. These ROS then attack the adsorbed molecule, leading to its degradation or mineralisation.

- **Over-Reaction**:

  The reaction continues until the molecule is completely broken down into simple and harmless products, such as water, carbon dioxide, or inorganic ions. This step, known as mineralisation or complete oxidation, ensures that no toxic intermediates remain in the solution, thereby making the process environmentally safe.

- **Desorption**:

  The final step involves releasing reaction products from the catalyst surface. This desorption frees up the active sites on the catalyst for new adsorption and reaction cycles. The efficiency of desorption depends on several factors, including the concentration of reactants, temperature, and ph.

Recent years have seen significant progress in photocatalysis, particularly in enhancing the performance and efficiency of photocatalysts. Researchers have focused on modifying the structure of photocatalysts by exploring new materials, including perovskites [67,68], metal–organic frameworks [69], and nanomaterials [70]. The development of hybrid systems, such as coupling photocatalysts with electrocatalysts [71], or photoelectrocatalysts, has also been a promising avenue for improving overall photocatalytic performance. These innovations are paving the way for more efficient applications in environmental remediation [65], energy production [66], and chemical synthesis.

3. Quantum Chemical Methods in Photocatalysis: Ab Initio, DFT, Semi-Empirical

Ab initio quantum chemical methods offer significant advantages in understanding and enhancing photocatalytic processes. These methods enable the analysis of precursor characteristics, such as catalyst bandgaps, the density of states, and adsorption spectra. These provide initial insights that can later be used in machine learning models. Additionally, these methods allow for a detailed examination of the entire photocatalytic process [72, 73].

➢ Overview of Ab Initio Methods

Ab initio quantum chemical methods involve solving the electronic Schrödinger equation from first principles, without relying on experimental data. This enables the accurate prediction of various properties and behaviors in photocatalytic reactions. Several ways in which these methods contribute to the field include:

- **Detailed Electronic Structure Analysis**:

Ab initio methods provide precise descriptions of the electronic structure of molecules involved in photocatalysis. This information is crucial for predicting absorption energy, charge transfer, and the dynamics of intermediate compounds during photochemical reactions [74–76].

- **Mechanistic Insight**:

These methods enable an in-depth understanding of the step-by-step mechanisms of photocatalytic reactions, including light absorption, charge transfer, and bond breaking. This insight enhances our understanding of the complex processes at play [24–80].

- **Prediction of Excited States**:

Ab initio methods can predict the properties of excited electronic states. This is crucial for understanding how light energy is converted into chemical reactions—a key aspect of photocatalysis [81–83].

- **Screening and Design of Catalysts**:

Ab initio methods can calculate properties such as reaction barriers and energetics, helping to identify optimal catalyst structures that enhance photocatalytic activity and efficiency. This capability is instrumental in the rational design of catalysts [84–86].

- **Quantitative Prediction of Reaction Rates**:

By combining first-principles methods with kinetic models, ab initio methods enable the prediction of reaction rates, facilitating the design of photocatalysts with enhanced performance [87].

- **Insights into Reaction Mechanism Dynamics**:

Ab initio molecular dynamics simulations offer real-time insights into the movement of atoms and electrons during photocatalytic reactions. This dynamic view helps understand how the photocatalytic processes unfold at the atomic scale [88–90].

- **Tailoring Material Properties**:

These methods facilitate the optimisation of material properties, such as band gaps and surface reactivity, which are essential for designing materials that efficiently promote the desired photochemical reactions [91–94].

➢ Rational Design of Photocatalysts

Ab initio modeling ultimately enables the rational design of photocatalysts with enhanced efficiency and selectivity. By providing a comprehensive understanding of reaction mechanisms and guiding catalyst selection, these methods offer a complete picture of the electronic and dynamic properties of photocatalysts. Quantum chemical methods provide a comprehensive toolkit for modeling photocatalytic systems, thereby advancing sustainable energy and environmental solutions. They encompass a wide range of phenomena, including chemical reactions, excited-state dynamics, and light absorption and emission. Despite the advantages, modeling photocatalytic processes presents significant challenges due to their complex and multiscale nature. Wave function (WF) methods, although accurate and robust, are often impractical for large and complex systems due to their high computational cost and low scalability. As a result, methods utilising Density Functional Theory (DFT) have become more favorable alternatives.

While DFT is computationally more feasible for studying larger systems, it is still an approximation. Modern DFT functionals, although widely used, must be tailored to specific molecular systems and processes to ensure accuracy. These approximations should be used cautiously, especially when high precision is required.

➢ Variational and Perturbation Methods in Photocatalysis

The Schrödinger equation, in its simplest, time-independent form, has various solutions based on different methods and approximations. These methods can be divided into two main categories:

- **Variational Methods**:

These methods are based on the principle of minimising the energy of a trial wave function (represented in one determinant form in the case of DFT). They are commonly used to study the electronic structure and properties of photoactive materials, including absorption spectra, excited states, and reaction pathways in photocatalysis.

- **Perturbation Methods**:

Perturbation methods assume that the system’s Hamiltonian can be divided into a solvable part and a perturbation term, which is treated as a minor correction to the solvable part. While these methods are also used in photocatalysis, they are less commonly employed compared to variational methods.

Ab initio quantum chemical methods, including DFT, play a crucial role in advancing photocatalysis by providing insights into reaction mechanisms, excited states, and catalyst design. These methods enable the development of photocatalysts with improved efficiency and selectivity. While they face challenges, such as high computational costs and the need for approximations, they remain a powerful tool for modeling and optimising photocatalytic systems in sustainable energy and environmental applications.

- **Variational and Perturbation Methods in Photocatalysis Modeling**

In photocatalysis modeling, variational methods offer invaluable insights into photoactive materials' electronic structure and properties. These methods facilitate the exploration of aspects such as excited states and the effects of environmental factors on photoinduced processes, which are often difficult to observe experimentally. Variational methods are instrumental in approximating the ground state of a quantum system and can, in some cases, also be used to calculate excited states. The wave function, which mathematically represents the quantum state of a system, can be expressed in various forms, each differing in the number of configurations and their specific representation.

The simplest form of wave function is the single-configuration wave function, which is used in methods such as Hartree–Fock and some variants of Density Functional Theory (DFT) [97]. In these methods, the wave function is approximated by a single Slater determinant, which represents a specific configuration of electrons. However, the single-configuration approximation often fails to provide an accurate representation of complex electron correlation effects, electron transfer, and other crucial processes in photocatalysis. This limitation arises because the single-configuration approximation cannot capture multi-electronic phenomena that play a vital role in the efficiency of photocatalytic reactions.

For instance, when conducting computational analysis on metal–organic frameworks (MOFs), which are commonly used in photocatalysis, the single-configuration approximation proves inadequate. MOFs contain transition metals that serve as active sites within their structure, often leading to nearly degenerate electron configurations. These metals give rise to multi-configurational wave functions for excited states, making accurate predictions more challenging [98, 99]. This complexity requires methods that consider different molecular configurations and optimise them accordingly.

- **Multi-Configurational Methods**

To address these challenges, multi-configurational methods represent the molecular wave function as a combination of different configurations, which are then optimised. One such method is Configuration Interaction (CI), which uses a predefined set of orbitals and determines the configuration coefficients through variational procedures. However, the Complete Active Space Self-Consistent Field (CASSCF) method is considered a more advanced multi-configurational approach. This method optimises both the orbitals and CI coefficients' self-consistency, generating an entire CI wavefunction within the selected active space. CASSCF is particularly useful for analysing systems with multi-reference character or non-dynamical, static, or strong correlation, such as photocatalytic MOFs with tunable optical properties [106].

Although CASSCF is highly effective, it is computationally demanding for large systems. To mitigate this issue, approximations like restricting the active space or employing the Density Matrix Renormalization Group (DMRG) technique [108], are often used to enhance its efficiency. These methods enable researchers to explore complex photocatalytic systems more efficiently, although they require substantial computational resources.

- **Coupled Cluster (CC) Methods**

Another powerful approach is the Coupled Cluster (CC) method, which accounts for electron correlations by systematically including clusters of excitations based on a Hartree–Fock (HF) reference function. The accuracy of CC improves by including higher-order excitations, such as CCSD (Coupled Cluster Singles and Doubles) and CCSDT (Coupled Cluster Singles, Doubles, and Triples). This method offers a more realistic representation of quantum systems and is particularly useful in studying the energetics and reaction pathways in photocatalysis [110].

While CC methods are computationally expensive, they hold great potential for improving the understanding of photocatalytic processes. The resolution of identity technique [111], has been proposed to enhance the scalability of CC methods. This method significantly enhances computational efficiency, enabling researchers to model larger systems without compromising the accuracy of their results.

In photocatalysis, variational and perturbation methods are essential for accurately modeling complex quantum systems. Variational methods, such as those employed in density functional theory (DFT) and the Hartree–Fock method, provide a foundation for understanding electronic structure, excited states, and reaction pathways. However, to capture the complexities of electron correlation and multi-electronic phenomena, more advanced methods, such as CI, CASSCF, and CC, are necessary. While these methods are computationally intensive, they are crucial for advancing our understanding of photocatalytic processes and optimising catalyst design. Through ongoing research and the development of improved computational techniques, these methods continue to provide deeper insights into the mechanisms of photocatalysis.

➢ Perturbation Theory and Its Applications in Photocatalysis

Perturbation theory (PT)-based techniques are highly valued for incorporating electronic correlation into low-level approximations and modeling the response of molecular systems to external perturbations, such as light radiation. However, even the simplest post-Hartree-Fock method, Møller–Plesset Perturbation Theory (MP2), is not commonly used for medium-to-large-sized systems due to its computational complexity. Despite this limitation, MP2 can still accurately predict fundamental properties, such as electronic structure, dipole moments, vibration frequencies, and polarizability, for specific molecular systems like C–NO_2 clusters. These properties are crucial for understanding the optical response of molecules in excited states, including fluorescence decay and second-harmonic generation, both of which are essential for investigating photoinduced processes and excited-state dynamics.

To incorporate the effects of external fields, MP2 can be integrated with more precise methods, such as response theory and time-dependent density functional theory (TD-DFT) [112].

➢ Multiconfigurational Systems and CASPT2

Many molecular systems exhibit multiconfigurational character, meaning their electronic structure cannot be described by a single Slater determinant. This is especially true for organic, inorganic, ligand-field, and conjugated systems, which exhibit rich photophysical behavior, including absorption spectra, excitation energies, potential energy surfaces, and photochemical processes such as photoisomerisation, photodissociation, and photoreduction.

To capture the multiconfigurational nature of these systems, perturbation theory methods can be applied to the wave function obtained from the CASSCF method [113]. This approach, known as complete active space perturbation theory (CASPT2) [114], is one of the most successful methods for studying the spectroscopy of multiconfigurational systems. However, it does come with some theoretical challenges.

➢ Perturbation Methods in Transition Metal Compounds

Perturbation methods are also widely applied to study the electronic structure and magnetic properties of transition metal compounds, which exhibit phenomena such as spin-crossover, exchange coupling, and magnetic anisotropy. These phenomena depend on the balance between electron–electron interactions and crystal field effects, which can be tuned using perturbation theory methods.

➢ Time-Dependent Computational Methods for Photocatalysis

For studying the dynamic properties crucial to photocatalysis, such as charge carrier dynamics and recombination phenomena, sophisticated time-dependent computational methodologies are required. One approach involves solving the time-dependent Schrödinger equation, which provides insights into the quantum mechanical behavior of electrons within a material under investigation. Alternatively, ab initio molecular dynamics (AIMD) [115], simulations can be used to trace the temporal evolution of atomic positions and velocities within a molecular framework, accounting for quantum mechanical effects on the electronic subsystem. These methods provide a comprehensive understanding of the photocatalytic process, enabling the incorporation of external variables, such as temperature variations, to optimise process parameters for improved efficiency.

➢ Challenges in Time-Dependent Schrödinger Equation Solving

Solving the exact time-dependent Schrödinger equation for systems with complex Hamiltonians, subject to time-dependent external perturbations, is a computationally demanding task. As a result, various methods have been developed to simplify the problem. One such approach is Floquet theory, which is particularly useful for systems with time-periodic Hamiltonians. Floquet theory enables the derivation of quasi-stationary states, which represent eigenstates of an effective, time-independent Hamiltonian known as the Floquet Hamiltonian. Using the Floquet–Magnus expansion or the rotating wave approximation, these states can be used to calculate optical properties, including polarizability and harmonic generation [116]. This method is also adaptable to different switching functions of external perturbations, making it versatile for analysing and modeling complex systems [117].

➢ Time-Dependent Density Functional Theory (TDDFT)

Another widely used method is time-dependent density functional theory (TDDFT), a special case of response theory that characterises how a system responds to time-dependent external perturbations [118,119]. TDDFT can simulate the dynamics of electronic density and effective potential under arbitrary time-dependent external potentials. It can be implemented in various forms, such as linear response theory, nonlinear response theory, and real-time response theory. TDDFT is more general and versatile than perturbation theory as it can capture non-perturbative phenomena, such as strong-field ionisation and high-harmonic generation, making it a powerful tool for studying photocatalytic systems.

In summary, perturbation theory and its various applications, including MP2, CASPT2, and TDDFT, are crucial for understanding and modeling the complex dynamics involved in photocatalysis. These methods help elucidate the electronic structure, magnetic properties, and photochemical behaviors of molecular systems under external perturbations such as light, temperature, and electric fields. As computational methods continue to evolve, the combination of perturbation theory with time-dependent approaches, such as TDDFT, will provide increasingly detailed insights into photocatalytic processes, aiding in the design and optimisation of photocatalysts for energy and environmental applications.

4. Example: Fundamental Properties Using Density Functional Theory

Density Functional Theory (DFT) remains the primary method for investigating the chemical properties of photocatalysts. The core of DFT lies in the concept of an energy functional that depends on the electron density of the system. The minimum of this functional provides the ground-state energy and electron density of the system [120]. By using electron density as the primary variable, DFT significantly simplifies the problem compared to wave functions, which require 3N coordinates, where N is the number of electrons.

However, the exact form of the energy functional is unknown, and only approximate expressions are available. These approximations are based on assumptions about the energy functional's dependence on electron density, and they may incorporate additional variables, such as kinetic energy density (τ), exchange potential (ε_x), and other non-local interactions. By introducing these variables, the functional becomes more adept at capturing the intricate interplay of electronic behaviors, though it also increases the computational challenges involved in the calculations.

The general form of the energy functional in DFT is represented as:

$$E_\rho = E(\rho_{LDA}) \cdot \nabla\rho \cdot [\varepsilon_x(\varphi_i)] \dots ..$$

Where:

- **LDA**: Local Density Approximation
- **GGA**: Gradient-Corrected Approximation
- **Hybrid**: Combines features of ab initio methods and DFT

➢ Types of DFT Functionals

There are several types of DFT functionals, each with its advantages and limitations:

- **Local Density Approximation (LDA)**:
  - This function depends only on the local density ρ(r) at a given point in space.
  - It is the simplest and computationally cheapest approximation, but it is often inaccurate for systems with strong electron–electron interactions or spatial variations in density.
  - Examples of LDA functionals include VWN [121] and PWC [122].
- **Gradient-Corrected Approximation (GGA)**:
  - This functional depends on both the local density ρ(r) and its gradient ∇ρ(r), improving upon LDA by accounting for the non-uniformity of the electron density.
  - It enhances accuracy but still fails to capture some essential effects like dispersion or self-interaction.
  - Commonly used GGA functionals include PW91 [123], BLYP [124], and PBEsol [125].

- **Hybrid Functionals**:
  - These functionals combine features of ab initio methods, such as Hartree–Fock, with features of DFT. They improve the accuracy of GGA by incorporating exact exchange and correlation effects $\varepsilon_x\rho_i$.
  - However, they increase computational cost and complexity because a large number of two-electron integrals need to be constructed from orbitals.
  - Examples include B3LYP [126] and PBE0 [127].

- **Meta-GGA**:
  - This functional depends on the local density, its gradient, and the kinetic energy density τ(r), improving the accuracy of GGA by accounting for non-local effects of exchange and correlation.
  - Meta-GGA functionals introduce new parameters and challenges for functional design but offer greater functionality. Some of these functionals, like SCAN [130], satisfy all constraints, making them attractive candidates for electronic structure calculations.
  - Examples include M11-L [128] and revTPSS [129].

- **Range-Separated Hybrid**:
  - This functional separates the exchange and correlation into short-range and long-range components, applying different approximations for each.
  - It improves the accuracy of hybrid methods by reducing the self-interaction and delocalisation errors. However, it requires the choice of a range-separation parameter, which may depend on the system under study [132].

- **Double Hybrid**:
  - This functional combines a hybrid functional with a perturbative correction based on methods like MP2.
  - It improves the accuracy of hybrid methods by incorporating dynamic correlation effects, but it also increases the computational expense and sensitivity to the choice of the basis set [133].

DFT remains a crucial method for investigating the fundamental properties of photocatalysts, enabling the understanding of their electronic structure, reactivity, and interactions. By utilising different types of functionals, ranging from simpler approximations, such as LDA, to more complex ones, like double hybrid functionals, DFT provides a flexible and robust framework for studying photocatalytic materials. Each functional offers a balance between computational cost and accuracy, making it essential for researchers to select the most appropriate functional depending on the system and properties they are investigating.

The functionals are listed in order of increasing complexity and the non-locality of density dependence. In general, this leads to better accuracy, but not always. For example, LDA is more straightforward and faster than GGA, but GGA is more accurate and flexible for most systems. However, there are some cases where LDA performs better than GGA, such as the following:

- **Elastic Constants of Some Crystals**:

LDA tends to overbind atoms and predict stiffer bonds, which results in better agreement with experimental values of elastic constants for some materials, such as diamond or silicon. GGA, on the other hand, tends to underestimate elastic constants due to softer bonds and the use of gradient corrections.

- **Phase Transitions of Some Metals**:

The LDA is more accurate than the GGA for predicting the critical pressures of structural phase transitions in some group IV, V, and VI elements, such as C, Si, Ge, Sn, S, Se, and Te. This is because LDA is exact for a uniform gas and works better for simple metals. At the same time, GGA introduces errors due to gradient corrections and the over-delocalization of the electrons.

These examples illustrate where LDA is more accurate than GGA; however, they are not general rules. In most cases, GGA is preferred over LDA for studying the electronic structure and properties of many-body systems. However, even GGA may not be sufficient for some systems that require more advanced functionals, such as hybrid, meta-GGA, range-separated hybrid, or double-hybrid.

The photocatalytic properties and performance of catalysts depend strongly on the supporting surfaces on which they are situated. In some cases, the support surface can even act as a photocatalyst itself. These surfaces can be engineered to enhance chemical efficiency by creating defects and vacancies, as well as modifying their geometry. For instance, adjusting the HOMO–LUMO gap of a catalyst by altering the support surface can facilitate the charge separation process and improve the electron–hole transfer efficiency, thereby affecting the reaction rate [134, 135].

However, such systems are too large and complicated to be explicitly modeled by DFT at the molecular level. Therefore, a specific version of DFT combined with periodic boundary conditions (PBC DFT) is employed to simulate catalysts deposited on periodic systems, such as crystals, surfaces, and nanotubes [136]. It uses Bloch's theorem, which states that the eigenfunction of an electron in a periodic potential is. $\psi nk(r)$ can be written as the product of a plane wave e^{ikr} and a periodic function $unk(r)$. Mathematically, the Bloch theorem can be expressed as follows:

$$\psi nk(r) = e^{ikr}u_{nk}(r)$$

Where n is the band index, and k is the wave vector [137]. PBC DFT solves the Schrödinger or, more precisely, Kohn–Sham equation for the Bloch wave function using a self-consistent approach that involves the electron density, the exchange-correlation energy, and the effective potential. PBC DFT can compute the energy band structure, the density of states, optical properties (reflectivity, absorption, refractive index, dielectric function, etc.), and other electronic properties of periodic materials.

This method not only lowers the computational cost but also enables the investigation of the electronic structure and other essential properties of periodic systems, offering valuable insights into the photocatalytic behavior of materials, especially those supported on complex surfaces. In Figures 1 and 2, examples of calculated absorption curves and electronic properties (the band structure and density of states) of several common catalytic materials (CdS, CeO2, Fe2O3, Si, TiO2, WO3, ZrO2) are presented. These calculations were conducted using the HSE06 density functional theory (DFT) functional, as implemented in the CASTEP software package (version 24.1, Castep Developers Group, UK).

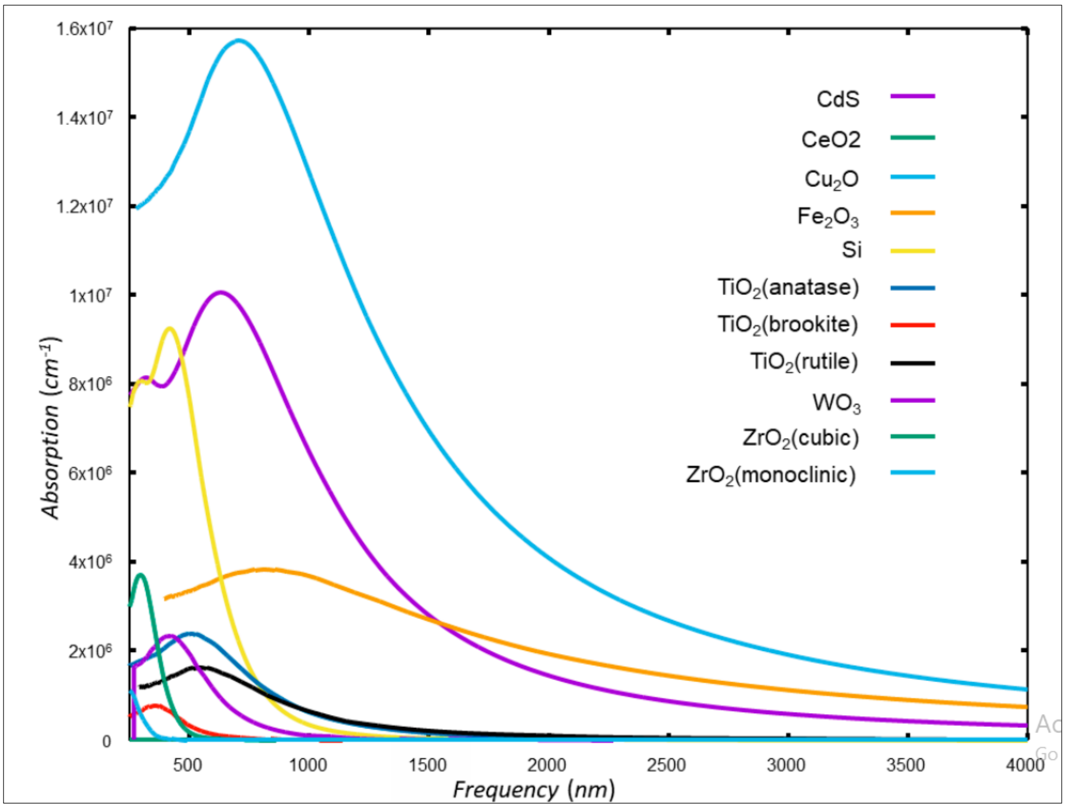

Figure 1: Absorption Coefficients for Typical Photocatalysts

This figure presents the absorption coefficients of various photocatalysts, showcasing how their absorption characteristics vary across different wavelengths. The data highlights the significant role of these materials in photocatalytic processes, with varying efficiency based on their light absorption properties. The plot includes several typical photocatalysts, such as CdS, CeO_2, Fe_2O_3, TiO_2 (in different phases), WO_3, and ZrO_2. The absorption data are crucial for understanding their effectiveness in applications such as water splitting, CO_2 reduction, and other photocatalytic reactions.

Due to periodic symmetry, using plane wave basis sets is more appropriate for PBC DFT [138]. This symmetry implies that the potential energy and the electron density are invariant under a discrete set of lattice translations, allowing us to define a primitive unit cell that can be repeated infinitely in all directions to form the crystal. The wavefunctions of the electrons in the crystal can then be written as Bloch functions, which are the product of a plane wave and a periodic function with the same periodicity as the crystal. This simplifies the computation of electronic properties, such as the band structure and the density of states, by reducing the problem to a finite number of k-points in the Brillouin zone. One can also reduce the computational cost by using pseudopotentials to replace the atomic cores and account for their effect on the valence electrons.

Pseudopotentials are effective potentials that smooth out the oscillations of the wavefunctions near the nuclei and remove the core electrons from the simulation. This avoids the singularities of the Coulomb potential and reduces the number of plane waves required to represent the wavefunctions accurately. Pseudopotentials also reduce the size of the basis set needed for complete system convergence, significantly lowering the computational effort for periodic boundary condition (PBC) density functional theory (DFT) calculations.

Unfortunately, in addition to the computational cost and the basis set dependence, there is an additional difficulty in using hybrid DFT functionals for periodic systems, associated with the treatment of long-range interactions. Hybrid functionals are designed to enhance the treatment of long-range electrostatic interactions. However, the non-local character of these contributions means that they can be computationally expensive and difficult to apply accurately in periodic systems [139]. Additionally, they often fail to describe dispersion forces, which are crucial for weakly bound systems, such as molecular crystals, van der Waals solids, and layered materials.

To account for these effects, one may need to use empirical corrections or more sophisticated methods such as range-separated hybrids or self-interaction corrections. However, these approaches also introduce new parameters and approximations that may affect the accuracy and transferability of the results. Therefore, choosing the appropriate hybrid functional for periodic systems is not a trivial task and requires careful validation and comparison with experimental data or higher-level methods.

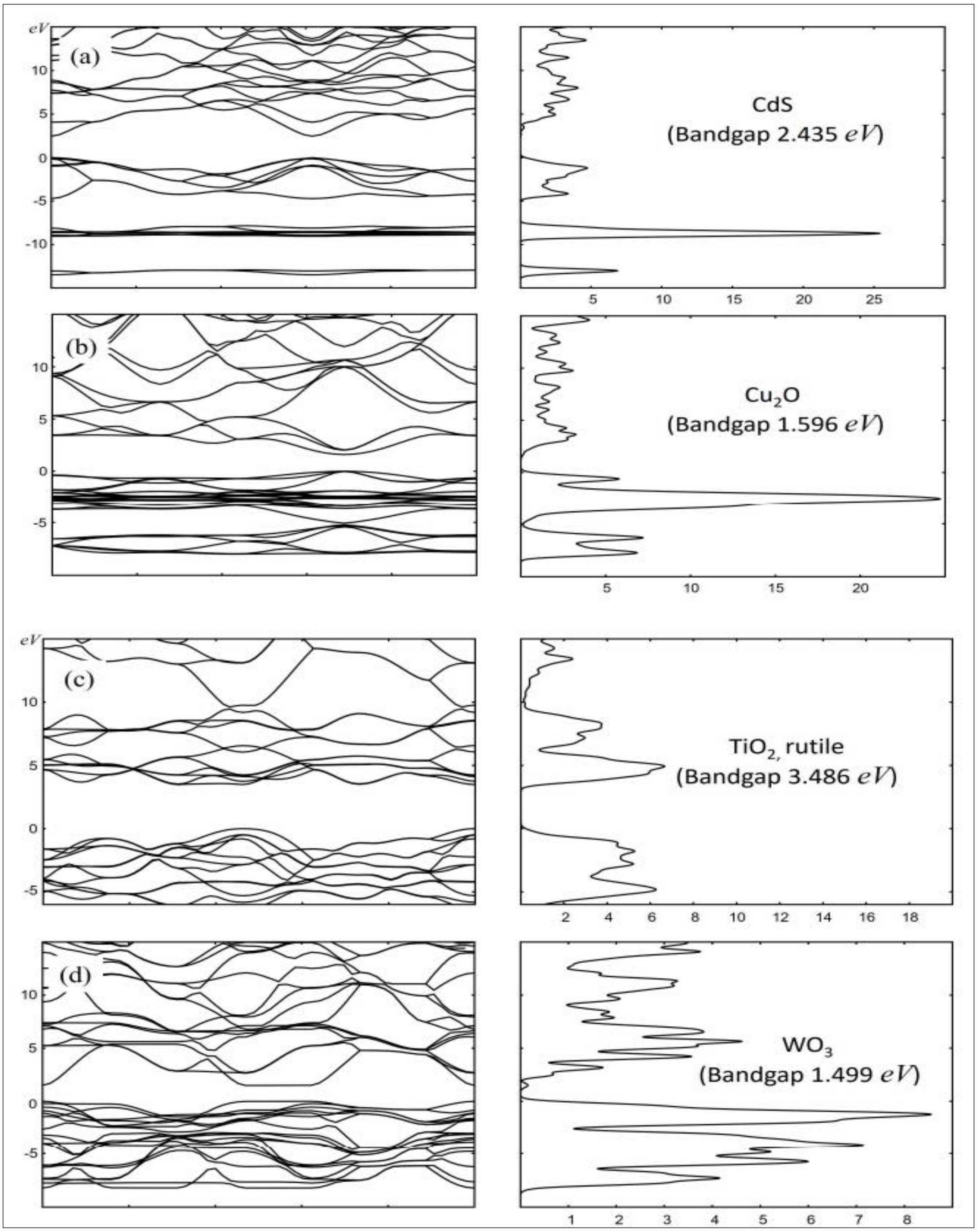

Figure 2: Band Structures and Density of States for Various Photocatalysts

This figure illustrates the band structures and density of states (DOS) for four different photocatalytic materials: (a) CdS, (b) Cu_2O, (c) TiO_2 (rutile phase), and (d) WO_3. The band structures show the electronic energy levels, while the density of states provides insight into the distribution of these energy levels. This information is crucial for understanding the electronic properties of these materials and their potential effectiveness in photocatalytic applications such as solar energy conversion and environmental remediation.

To model a semi-infinite slab using PBC DFT, one should employ a primitive unit cell of the bulk crystal and then cut it along a desired surface plane to create the slab. The thickness of the slab must be carefully chosen to avoid artificial interactions between the top and bottom surfaces. This is important because these interactions can skew the simulation's results, rendering them unrealistic. Additionally, a vacuum layer should be incorporated within the system to separate the slab from its periodic images in the direction normal to the surface. The thickness of this vacuum layer should be sufficient to prevent spurious interactions between the slabs while minimising computational costs.

A typical approach to modeling the photocatalytic process on a surface involves various strategies. These range from assuming that the surface atoms are arranged the same way as the bulk atoms, with surface energy proportional to the number of dangling bonds, to considering the rearrangement and relaxation of surface atomic positions due to the lower coordination number and higher reactivity of surface atoms. This is important because surface atoms are more reactive than bulk atoms, resulting in distinct behavior in catalysis. Furthermore, introducing various types of defects, such as vacancies, adatoms, steps, kinks, impurities, and the interaction between the surface and adsorbed molecules (e.g., water, oxygen, hydrogen, and hydroxyl groups), helps replicate a realistic photocatalytic environment. This often requires optimising multiple adsorption sites and configurations [140].

DFT is now widely applied to analyse the electronic structure of photocatalysts (see Section 3), including the localisation of critical orbitals, the redistribution of electronic density upon excitation, and the formation of electron-hole pairs during photocatalysis. Researchers utilise DFT for materials screening and design, making it an indispensable tool for advancing our understanding of photocatalysis and sustainable energy conversion. Numerous studies have reviewed the importance of DFT calculations in this field. For instance, Butera [141], provides practical guidance on using DFT in both homogeneous and heterogeneous catalysis, covering atomic-centered basis sets, plane waves, and the evaluation of energy barriers. The study discusses transition state theory (TST) and the energetic span model (ESM) in the context of understanding chemical reaction kinetics in catalysis. TST explains how chemical reactions occur and their rate determination, while ESM focuses on energy differences between intermediates and transition states, defining the turnover frequency (TOF) of catalytic events.

Another study [142], investigates the multifunctional properties of XO_2 monolayers (where X = Ti, Ni, Ge) using DFT. The research explores the structural, electronic, optical, and photocatalytic properties of these materials, emphasising the influence of strain and stacking on their characteristics. This offers valuable insights into the materials' potential applications across various fields. Additionally, the study by Wenzhi Yao [143], examines the g-C_3N_4/BiOBr (001) heterostructure via DFT, exploring its geometric and electronic structures and their influence on photocatalytic activity. The study reveals that the heterojunction functions as a type-II heterojunction, which facilitates effective electron-hole separation at the interface. It also shows that applying an external electric field can tune the electronic structure and enhance optical absorption in the visible region, potentially improving photocatalytic performance.

However, conventional descriptors such as HOMO-LUMO, (p)DOS, and band structure may not fully capture the electronic structure of photocatalysts, especially in systems with strong electron correlation or when studying excited states [1-144]. More advanced techniques are often required to address these limitations and accurately examine the electronic properties of photocatalysts.

For systems with strong electron correlation, such as transition metal complexes and rare-earth compounds, single-determinant approximations like DFT may fail [145], and the energy gap between frontier orbitals may not be sufficient for an accurate analysis. In these cases, multi-reference methods are necessary, where the focus shifts to the wave function, and natural orbitals can be derived post-processing. For excited states and electronic density redistribution, Dyson and Brueckner orbitals offer valuable insights [146]. Dyson orbitals describe the excited states of molecules, while Brueckner orbitals correct for electron-electron repulsion in ground-state calculations.

To explore nonlinear optical properties and their relevance to photocatalysis [148], studies on the absorption of two photons, a critical nonlinear phenomenon, have been conducted. These insights are crucial for understanding light absorption and charge transfer processes in photocatalysis. Nonlinear optical activity in organic and inorganic materials is widely studied for enhancing photocatalytic properties, particularly in applications such as water splitting and CO_2 reduction.

Finally, the Fukui function can be used to analyse the reactivity of molecules, identifying potential sites where electrons are likely to be accepted or donated during chemical reactions [151]. This tool is essential for predicting interactions between photocatalysts and reactants in photocatalysis. For even greater accuracy, the dual descriptor can be employed, as it offers more reliable identification of nucleophilic and electrophilic regions than the Fukui function, making it a more trustworthy measure of local reactivity [153,154].

To gain deeper insights into chemical bonding, the Crystal Orbital Overlap Population (COOP) is a powerful tool in quantum chemistry [155]. In the context of photocatalysis, the orbital overlap population measures the electron density shared between overlapping orbitals, indicating the strength of bonding interactions between atoms. Two primary methods used in this analysis are the COOP [156], and Crystal Orbital Hamilton Population (COHP) [157], which focus on different aspects of bonding.

- COOP divides the electron density between atoms, indicating whether interactions are bonding or antibonding. By integrating the COOP curve, one can obtain the electron count, similar to the Mulliken population analysis. This gives insight into how the electron density is distributed in the system.

- COHP, on the other hand, dissects the band structure energy into bonding and antibonding contributions. By integrating the COHP curve, one can obtain an energy value that reflects the strength of the bond, showing how stable the bond is in terms of energy.

While COOP provides information on the distribution of electrons between atoms, COHP reveals the energetic implications of bonding. Both analyses are valuable in studying photocatalysis as they offer insights into the electronic structure and stability of catalysts involved in light-induced chemical reactions. Understanding these interactions is essential for optimising the design and efficiency of photocatalytic materials.

In practical photocatalytic studies, analysing the orbital overlap population can provide critical information on the electronic structure of catalysts and the interactions between catalysts and reactants [158]. This understanding is crucial for modeling the processes involved in photocatalysis, such as light absorption, charge separation, and transfer, as well as the reactivity of the catalyst. By analysing orbital overlap populations, researchers can predict and optimise the efficiency of photocatalytic reactions, ultimately leading to the development of more effective photocatalysts for applications such as water splitting and CO_2 reduction.

Figure 3 illustrates an example of such an analysis for carbon and copper atoms when a carbon dioxide molecule is bonded to the (111) surface of a copper oxide. The partial density of states (pDOS) would show the contribution of these atoms to the electronic states of the system. In a bonded system, shifts in the pDOS are expected due to the interaction between CO_2 and the Cu_2O surface, indicating charge transfer and bonding characteristics. In this example, the analysis suggests that CO_2 binds as a tilted linear molecule coordinated to an unsaturated surface cation, and the presence of surface vacancies can influence the adsorption and activation of the CO_2 molecule. These interactions would be reflected in both the COOP and COHP analyses, as well as in the partial DOS for the carbon and copper atoms.

In photocatalysis, precise energies and accurate electronic density redistributions are crucial, and sometimes these can exceed the capabilities of even the most advanced DFT methods. In such cases, multireference methods and many-body perturbation theory [159, 160], can significantly enhance the quality of modeling photocatalytic reactions. These methods are beneficial for capturing the complex electronic interactions in photocatalytic systems, especially when dealing with excited states or systems where electron correlation is non-negligible. By incorporating multireference approaches, researchers can achieve a more nuanced understanding of photocatalytic processes, potentially leading to breakthroughs in the efficiency and effectiveness of photocatalysts.

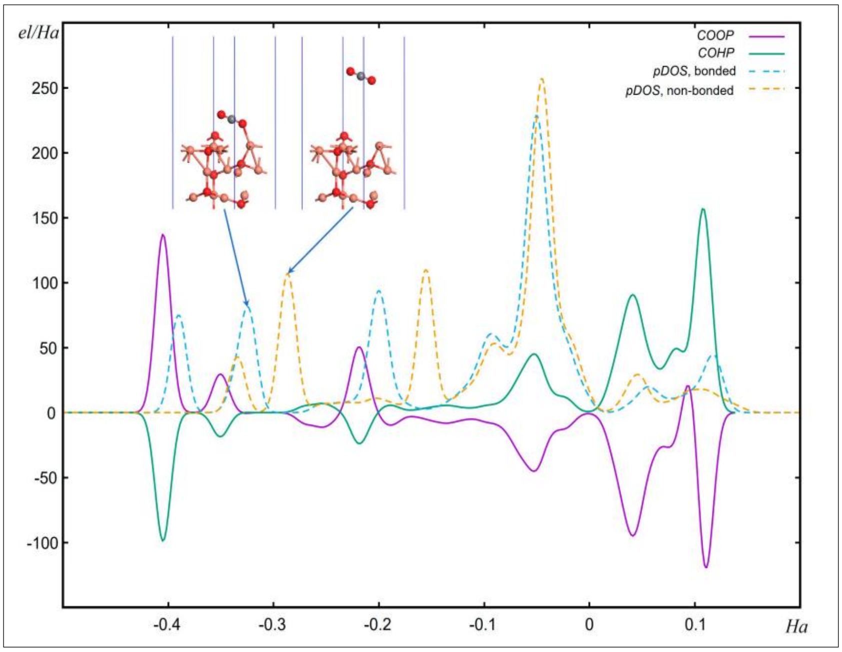

Figure 3: Crystal Orbital Overlap and Hamilton Populations for Carbon and Copper Atoms in CO_2 Molecule Bonded to a $Cu_2O(111)$ Surface.

This figure presents the crystal orbital overlap population (COOP) and crystal orbital Hamilton population (COHP) for the carbon and copper atoms in a CO_2 molecule that is bonded to the $Cu_2O(111)$ surface. Additionally, the partial density of states (DOS) is included for both the bonded and non-bonded systems, showing the contribution of these atoms to the electronic states of the system. The analysis highlights the charge transfer and bonding characteristics between the CO_2 molecule and the Cu_2O surface.

5. Software

The landscape of quantum chemistry software packages is diverse, offering both commercial and free options to cater to various molecular and periodic boundary condition applications, as well as density functional theory (DFT) and wave function-based methods. Different software packages offer distinct advantages and disadvantages depending on the research objectives, methodology, parallelisation, and accessibility. This section introduces some of the most widely used quantum chemistry software packages, highlighting their key features and capabilities.

For molecular quantum chemistry, Gaussian 16 is one of the most comprehensive software packages. It supports a range of molecular methods, including Hartree-Fock (HF) and density functional theory (DFT), as well as multiconfigurational models such as complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI). It includes an extensive library of density functionals and various basis sets, such as Gaussian-type orbitals (GTOs) and effective core potentials (ECPs) [161]. Gaussian 16 can calculate excited states, transition states, and reaction paths, and its parallelisation capabilities are optimised for SMP workstations and single-node clusters. However, it requires the additional Linda parallel library for multiple cluster nodes.

Another widely used commercial software for molecular quantum chemistry is Amsterdam Density Functional (ADF), which specialises in density functional theory (DFT) calculations for molecular systems. ADF supports various DFT methods, including generalised gradient approximations (GGAs), hybrid functionals, meta-GGAs, and range-separated functionals. It can account for relativistic and spin-orbit coupling effects and calculate excited states, transition states, and reaction paths using methods such as TDDFT, constrained DFT, and transition state search [162]. ADF is particularly well-suited for large and complex systems, such as transition metal complexes and biomolecules.

For a free-for-academia option, Orca is a versatile software that excels in coupled cluster, multi-reference, semi-empirical, and DFT methods. Orca can perform various coupled cluster methods, such as CCSD and CCSD(T), as well as multi-reference methods like CASSCF and MRCI with DMRG. It also supports a variety of DFT functionals and can calculate excited states and transition states using techniques such as CIS, TDDFT, and IRC [163, 164]. Orca is highly scalable and optimised for complex quantum chemistry simulations.

For periodic boundary condition (PBC) quantum chemistry, Vienna Ab initio Simulation Package (VASP) is a leading commercial software. VASP supports PBC DFT and various many-body perturbation theory methods, including the GW approximation, the Bethe-Salpeter equation (BSE), and the random phase approximation (RPA). It offers flexibility in choosing functionals and basis sets, including plane waves, projector augmented wave (PAW) methods, and ultrasoft pseudopotentials (USPPs) [165]. VASP is renowned for its ability to handle large-scale calculations and offers excellent flexibility in selecting functional and basis sets.

Another open-source alternative for PBC DFT is Quantum Espresso, which is highly valued for its open-source nature, allowing rapid adaptation and innovation. It supports a range of DFT functionals and many-body perturbation theory methods, including the GW approximation, BSE, and RPA. Quantum Espresso is capable of calculating band structures, density of states, optical properties, and surface reactions using methods such as k-point sampling. It can handle large systems, including nanomaterials and biomolecules [166].

CASTEP is a powerful tool for computational materials science, available as part of the Material Studio suite for commercial use or free for academic use. CASTEP supports a range of PBC functionals, including LDA, GGA, hybrid, and meta-GGA, and offers a highly efficient plane-wave basis set. It includes a built-in pseudopotential generator, enabling users to create custom pseudopotentials for any element. Although CASTEP does not support many-body perturbation methods like GW and BSE, it offers a range of spectroscopic features, including IR, Raman, and NMR spectra, which are directly related to experimental data [167, 168].

The landscape of quantum chemistry software is vast, offering both commercial and free software options tailored to various molecular and periodic boundary condition applications, as well as density functional theory (DFT) and wave function-based methods. Depending on the research goals, different software packages offer unique advantages in terms of methodology, parallelisation, and accessibility. Below is an overview of some popular quantum chemistry software packages.

DMol3 (version 2024, BIOVIA Inc., San Diego, CA, USA) [169], is a versatile software package for DFT calculations across various systems, including molecules, clusters, surfaces, and solids. It employs a numerical radial function basis set, which is space-saving and efficient compared to the plane-wave basis set used in programs like CASTEP. DMol3 also supports the conductor-like screening model (COSMO) for simulating solvation effects and offers enhanced parallelisation using MPI/OpenMP for large systems. Additionally, it calculates electron transport properties using non-equilibrium Green's function theory.

OpenMX (version 2023, Northwestern University, Illinois) [170], utilises a linear combination of pseudoatomic orbitals (LCPAO) basis set, offering greater flexibility and transferability compared to traditional basis sets. It supports advanced features such as spin–orbit coupling, non-collinear magnetism, and spin-polarised DFT+U. OpenMX is well-parallelized using both OpenMP and MPI, resulting in high efficiency. As an open-source software, it can be configured with various compilers and numerical libraries.

OpenMolcas (version 23, Lund University, Sweden) [171], specialises in multiconfigurational methods, making it ideal for accurately describing complex electron correlation. It includes core methods such as CASSCF and CASPT2, which aid in predicting spectral properties and studying the electronic and optical behavior of molecules. OpenMolcas is open-source, allowing for community-driven development and the integration of new features.

DFTB+ (version 24) [172], is the most widely used implementation of the DFTB approach, available as a standalone program or integrated into other software packages. It employs a minimal basis set of valence orbitals and a parametrised Hamiltonian derived from the Slater–Koster model. DFTB+ supports various methods for spin effects, time-dependent DFTB, excited states, and transport calculations. It also provides advanced features, such as LDA+U, spin–orbit coupling, and pseudo-self-interaction correction. DFTB+ offers a range of techniques for calculating electronic properties, including band structures and optical spectra, and is highly efficient with MPI, OpenMP, and GPU support.

6. CONCLUSIONS AND PERSPECTIVES

Computational modeling in photocatalysis has become a crucial and powerful tool in various fields, particularly in energy and materials science. Over the past few decades, advancements in computational and quantum chemistry have allowed for a more detailed understanding of photocatalytic processes. However, to stay aligned with the rapid progress in experimental techniques and meet industrial demands, modeling must continuously evolve. This can be achieved through several factors.

➢ Key Factors for Progress

- **Quantum Chemical Algorithms Development**

Advancements in quantum chemical algorithms are essential for improving the accuracy and efficiency of simulations. The continuous evolution of algorithms enables researchers to handle increasingly complex systems and refine predictions in fields such as photocatalysis. However, improving algorithms alone may not be sufficient if hardware and computational techniques don't keep pace.

- **Development of Numerical Algorithms**

The development of numerical algorithms aims to enhance the efficiency of quantum chemical calculations by optimising computational methods and addressing challenges such as scaling and convergence issues. Nonetheless, while linearisation techniques (such as clustering) offer improvements, they may not be enough to handle the increasing complexity of real-world systems.

- **Exploitation of Molecular System Structures**

Using the structure of molecular systems is another crucial factor for improving simulations. By incorporating features like clustering and the intrinsic symmetry of systems, computational models can be optimised. However, achieving the speed required for large systems remains a significant challenge, and the efficiency gained by these methods is still limited.

- **Parallelization and Computational Hardware**

The advances in parallel computing have significantly accelerated computational chemistry. However, the increased number of processing units often leads to increased overhead, as described by Amdahl's law. Despite the exponential growth in computational power, primarily driven by Moore's Law, the scaling of methods and the need for high-speed computations in large systems remain significant hurdles to overcome.

- **New Paradigms in Computational Modeling**

New approaches, such as multiscale modeling, offer the potential to overcome limitations associated with single-scale models. Multiscale models combine different levels of detail, or "sub-models," to simulate systems more accurately and efficiently. This approach is widely used in material science, fluid dynamics, and other engineering disciplines. However, the lack of a general theory for multiscale modeling has limited its widespread application in photocatalysis.

➢ Challenges and Future Directions

The combination of quantum chemical algorithms, numerical techniques, molecular system structures, and parallelisation offers the best prospects for addressing the increasing demands in photocatalysis research. However, while multiscale modeling provides great potential, its development has been slow due to a lack of general theory and a universally accepted framework. The interdisciplinary nature of multiscale modeling has led to inconsistent terminology and frameworks, complicating collaboration between researchers from different fields. For example, in physics, "scale" refers to the length, time, or energy scales of a system. In contrast, in biology, it refers to the level of organisation of an organism, such as molecular, cellular, or higher levels.

A significant challenge in multiscale modeling is establishing methods for validation and verification. Validation ensures that a model aligns with empirical data, while verification verifies that the model is implemented correctly. Both processes are critical for ensuring the reliability of multiscale models, but they are complex due to the many sources of uncertainty, such as model assumptions, parameter estimation, and data quality, that must be considered.

- **New Paradigms: Machine Learning and Quantum Computing**

In addition to algorithmic and hardware advancements, new paradigms such as machine learning (ML) and quantum computing (QC) hold immense promise for the future of quantum chemistry. ML and AI can greatly enhance quantum chemistry by improving data analysis, model development, and predictions. Specifically, ML can help design new molecules, optimize reaction conditions, and discover new chemical phenomena. In quantum chemistry, machine learning (ML) can enhance the accuracy and efficiency of quantum methods, including density functional theory (DFT), configuration interaction (CI), quantum Monte Carlo (QMC), and multiconfigurational approaches such as complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI). For example, ML can help design new exchange-correlation functionals for DFT, reducing computational costs while maintaining accuracy. It can also help refine the convergence of quantum methods and guide the search for optimal solutions.

The second application of ML involves bypassing traditional quantum methods to directly predict properties and behaviors of molecules and materials based on existing data. Machine learning (ML) can construct interatomic potentials, enabling efficient molecular dynamics simulations. It can predict molecular properties such as energies, forces, dipole moments, polarizabilities, and spectra from descriptors like atomic coordinates and chemical compositions. Furthermore, ML can analyse large data sets from experiments or simulations to discover new chemical phenomena, reaction pathways, and catalytic mechanisms.

- **Quantum Computing: A New Frontier**

On the other hand, quantum computing (QC) presents a new frontier for simulating quantum systems. QC can revolutionise quantum chemistry by providing robust solutions to simulate molecular properties, explore potential energy surfaces, and perform quantum dynamics. Although QC has enormous potential, it faces challenges such as data quality, algorithm development, and hardware limitations.

Computational modeling in photocatalysis holds great potential for advancing the field, but significant challenges remain. The combination of improving quantum chemical algorithms, developing new numerical techniques, exploiting molecular system structures, enhancing parallelisation, and embracing emerging paradigms such as machine learning and quantum computing offers the best prospects for overcoming these challenges. Multiscale modeling, although still in its infancy, represents the most promising direction for addressing the complex demands of photocatalysis research, but it requires further development in theory and methodology to achieve its full potential.

A promising application of machine learning (ML) in photocatalysis is the use of chemical descriptors derived from quantum chemistry calculations to characterise the catalytic activity of materials. ML frameworks have demonstrated exceptional capabilities in predicting material properties by establishing a nonlinear relationship between input and output data corresponding to catalytic properties. Unlike traditional computational methods, which require computationally expensive quantum chemical calculations, ML methods can provide fast and cost-efficient predictions of catalytic properties. The success of these ML models depends heavily on designing descriptors that uniquely represent materials, are computationally inexpensive to calculate, and accurately reflect the nature of the targeted properties.

Researchers have developed various descriptors to capture the key characteristics of materials, including local geometric features, individual atomic properties at potential active sites, and generalised coordination descriptors (e.g., valence, free bonds, and ionic radius). However, modeling catalytic reactions remains a challenging task, as it involves following complex reaction pathways. Although atomic fingerprints can effectively predict bulk properties (e.g., thermodynamics, viscosity, boiling point, fracture toughness), they are not well-suited for predicting catalytic reaction paths. Thus, ongoing research to develop new catalytic descriptors and their integration with ML techniques is vital for advancing this field.

- **Challenges of Applying ML in Computational Chemistry**

One of the significant challenges in applying ML in computational chemistry is its lack of interpretability. ML models are often regarded as "black boxes", meaning that their internal workings and reasoning processes are not transparent to users. This presents a significant challenge in computational chemistry, where the goal is not only to predict outcomes but also to understand the underlying mechanisms that govern chemical phenomena. For instance, while ML models can predict reaction rates, selectivity, and reaction pathways for catalytic reactions, they fail to explain why specific catalysts are more effective or selective than others. Understanding these underlying factors is essential for the rational design and optimisation of catalysts and reactions.

➢ Quantum Computing: The Future of Photocatalysis Modeling

Another promising solution for advancing photocatalysis modeling is quantum computing (QC) [173]. Initially proposed by Richard Feynman to solve complex Schrödinger equations for large systems, quantum computing now holds immense potential to improve various scientific fields, including machine learning, artificial intelligence, and cryptography. Recent progress in quantum computing has led to the development of new quantum algorithms, which have already shown remarkable success in predicting molecular electronic structures. Examples include the qubit coupled cluster method [174], the multireference quantum Krylov algorithm for strongly correlated electrons [175], and the quantum imaginary time evolution algorithm [176]. These innovations have opened the door for simulating chemical dynamics [177,178] with impressive accuracy and computational speed.

Quantum computing has also demonstrated practical applicability in fields such as determining the excited state energies of small molecules [179], simulating molecular electronics [180], and tracking Diels–Alder reaction pathways [181]. Notably, researchers have successfully utilized quantum computers to design novel catalysts for CO_2 reduction, a crucial process in combating climate change and producing renewable fuels.

➢ Challenges Facing Quantum Computing

Despite its potential, quantum computing faces substantial challenges related to scalability, noise, error correction, and the development of new algorithms. Current quantum computing hardware is limited by the number of qubits, which restricts the complexity and size of molecular systems that can be simulated. Furthermore, high noise and error rates are standard, which impact the accuracy and reliability of quantum computations. Efficient error-correction schemes are essential, but these require additional qubits and computational resources. Despite these hurdles, the demand for robust quantum computing methods presents opportunities to harness quantum advantages, spurring interdisciplinary collaboration and innovations in photocatalysis and chemistry.

➢ Future Prospects

The future of quantum computing in computational chemistry holds immense potential, particularly for overcoming the limitations of classical computers. As quantum computing continues to evolve, it promises to transform the modeling of photocatalytic reactions and accelerate the discovery of novel photocatalysts. The continued development of quantum algorithms and machine learning methods will be pivotal in addressing challenges and optimising photocatalysis for real-world applications.

This review highlights the significant strides in computational modeling techniques for photocatalysis, with a focus on molecular and periodic boundary condition (PBC) density functional theory (DFT) approaches. These methods have shown considerable success in various photocatalytic systems, including metal oxides, metal chalcogenides, carbon-based materials, metal halide perovskites, and metal–organic frameworks. We have also reviewed and compared the most widely used computational chemistry software, providing practical tips for researchers to select the appropriate tools for their specific research needs. Furthermore, the review explores the challenges and perspectives for future developments in quantum chemistry methods, emphasising the potential of machine learning and quantum computing to revolutionise the modeling of photocatalytic reactions.

Table 1: Comparative Analysis of Methods Regarding Photocatalytic Systems

Method	Description	Strengths	Limitations	Extensions	Applications in Photocatalysis
Density Functional Theory (DFT)	Minimises a functional of electronic density, for which only approximate expressions are available.	Widely used for its efficiency and a good balance between accuracy and computational cost.	May struggle with systems that have strong correlation effects or require accurate descriptions of excited states.	New functionals (SCAN, Double hybrid, range-separated, etc.), CASDFT, density fitting	Geometry optimisation, orbital energies, transition states (TS), reaction barriers, DOS, band structure
Multiconfigurational and Multireference Methods (MRCI,	Consider multi-configurational states for a	Provide a better treatment of systems with	Computationally intensive and may not be	Combination with DFT (CASDFT),	Excitations, spectroscopy, and accurate

CASSCF, RASSCF, etc.)	more accurate description of systems with significant electron correlation.	near-degeneracy and strong static correlation.	suitable for extensive systems.	AI/ML, DMRG, resolution of identity	electronic density distributions
Perturbation Theory (MP2, MBPT)	Account for electron correlation beyond the mean-field approximation by using perturbative corrections.	Can accurately describe quasiparticle excitations and excited states.	Requires high computational resources and expertise to apply correctly.	New GW and Green function approximations, in combination with CAS (CASPT2)	Excitations, accurate adsorption energies, quasiparticle and exciton binding modeling
Semiempirical Methods (MNDO, AM3, PM6, PM7, DFTB, etc.)	Utilise empirical parameters obtained from experimental data or high-level calculations to account for electron correlation effects.	Less computationally demanding, suitable for large systems and long time-scale simulations.	Less accurate than ab initio methods; may not capture all relevant physical interactions; requires parametrisation.	New Hamiltonians, combinations with more accurate methods in QM/MM, ONIOM, etc.	Preliminary geometry optimisation, modeling large systems, and properties

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