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Designing Smarter Hole Transport Materials: A Review of Theory-Driven Molecular Strategies for Next-Generation Solar Cells

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Abstract: Hole transport materials (HTMs) play a pivotal role in determining the efficiency, operational stability, and overall performance of both organic and perovskite solar cells. As the demand for high-efficiency and cost-effective solar energy technologies grows, the rational design of HTMs has become increasingly critical. Density Functional Theory (DFT) has emerged as a powerful and predictive computational approach for guiding the molecular design of HTMs, offering insights into critical parameters such as frontier molecular orbital (HOMO-LUMO) energies, reorganization energy, ionization potential, and thermal stability. This review summarizes the theoretical foundation of DFT as applied to HTM development, focusing on widely used functionals (e.g., B3LYP, CAM-B3LYP) and basis sets, and discussing performance descriptors that influence charge transport and film formation. Representative case studies, including benchmark materials such as Spiro-OMeTAD, P3HT, and novel derivatives like P3CPenT, illustrate how DFT can reduce experimental trial-and-error and accelerate the screening of promising candidates. Additionally, the review explores emerging strategies, such as the development of dopant-free HTMs, sustainable and lead-free material systems, and the integration of machine learning with quantum chemical calculations for high-throughput material discovery. These approaches highlight the evolving synergy between computational modeling and experimental synthesis. Overall, DFT continues to be instrumental in the next-generation design of HTMs, offering a roadmap for tailoring molecular properties to meet the stringent demands of modern photovoltaic applications.

Keywords: Hole transport materials (HTMs), Next-Generation Solar Cells, Density Functional Theory, Global Energy.

INTRODUCTION

The significant rise in global energy use has intensified concerns about pollution, resource depletion and the need for long-term energy solutions driven by population growth and industrialization in developing countries (Kannan, N., & Vakeesan, D. 2016; Mudakkar, S. R. *et al.*, 2013). This has increased demand for sustainable and clean energy which resulted in fast improvement in solar cell technology (jin Kim, C. 2024; Bouich, A. *et al.*, 2023; Syahirah, N. *et al.*, 2022; Maka, A. O. M., & Alabid, J. M. 2022). A solar cell is a type of photovoltaic device that uses solar energy to generate electricity (Kumar, N. S., & Naidu, K. C. B. *et al.*, 2021). Recent improvements in organic solar cells (OSCs) that have reached over 18% efficiency can be traced back to better active layer materials, better interfaces and better bulk-heterojunction film morphology (Li, C. *et al.*, 2022; Huang, J. *et al.*, 2017) and need encapsulation, control over their shape and engineering at the interface to stay stable. They are inexpensive to manufacture using roll-to-roll methods and they can function more effectively when paired with lithium-ion batteries. Donor and acceptor materials need to have well-aligned energy levels, high extinction coefficients, nanoscale phase separation and high charge carrier mobility for high power conversion efficiency (PCE) (Clarke, T. M., & Durrant, J. R. 2010; Lu, L., & Ya, M. E. 2020). Perovskite solar cells (PSCs) have achieved an efficiency increase from around 10% to over 22% since 2012, surpassing other technologies (Djurišić, A. B., *et al.*, 2017). Perovskites have contributed to the development of perovskite solar cells since 1839. In 2009, the efficiency these cells was 3.81% and it ranges from 25% to 29% at present. They make use of hybrid organic-inorganic compounds with ABX_3 crystal structures (Jiang, F. *et al.*, 2016).

Organic and perovskite solar cells stand out among all because they are lightweight, can be made on flexible surfaces and at low temperatures (Sun, Y. *et al.*, 2021; Yang, D. *et al.*, 2019). However to turn these benefits into long-term business success, the devices need to be more stable and efficient, and a lot of these advantages depend on the quality of the materials being used in the cell (Li, N. *et al.*, 2020). The hole transport material (HTM) plays an important role in both OSCs and PSCs which is located between the light-absorbing layer and the anode and serve an important function in extracting and transferring positive charge carriers

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(holes) as well as acting as an energy barrier to prevent undesired electron flow (Bui, V. K. H., & Nguyen, T. P. 2023). Their efficacy has a direct impact on power conversion efficiency (PCE), device lifespan and manufacturing cost. Numerous obstacles still exist despite advancements in the development of different HTMs including mismatched energy levels, instability in the presence of environmental stress and intricate or costly synthesis pathways (Jahantigh, F., & Safikhani, M. J. 2019). A good HTM for perovskite solar cells needs to have energy levels that work well together, be stable and mobile, and be processable in a solution so that it can be scaled up, made cheaper and easier to manufacture. In the past few years, new avenues for creating more stable and effective HTMs have been made possible by molecular engineering aided by computational techniques particularly Density Functional Theory (DFT) (Tsuneda, T. 2013; Burke, K., & Wagner, L. O. 2013; Schleder, G. R., *et al.,* 2019). Researchers can use DFT to predict and assess crucial molecular characteristics such as reorganization energy, energy levels, dipole moment and charge transport parameters, before beginning experimental synthesis. This theoretical discovery dramatically minimizes the trial-and-error process, making material creation cost-effective, faster and more targeted (de Proft, F., & Geerlings, P. 2001).

The main topic of this review is the strategic fusion of theory and molecular design in the creation of hole transport materials (HTMs). It demonstrates how DFT-based methods may forecast stability under operational conditions, inform molecular structure and guide energy level alignment. We intend to demonstrate how theoretical modeling is speeding up the discovery of next-generation HTMs by looking at recent developments and a few chosen cases including information from our own computational work. The review also covers the present real-world difficulties, restrictions and new developments like green synthesis methods and AI-assisted material screening. This paper offers valuable insights for both theorists and experimentalists working to design advanced HTMs that can address the rising demands of contemporary solar energy technology.

Fundamentals of Hole Transport Materials in Solar Cells

In both organic solar cells (OSCs) and perovskite solar cells (PSCs), the hole transport material (HTM) plays a critical role in determining the efficiency and stability of the device (Snaith, H. J. 2013; Shariatinia, Z. 2020; Yin, X. *et al.,* 2020). It serves as a selective contact layer that prevents electrons from recombining at the interface. At the same time, it facilitates the movement of positive charge carriers which are also known as holes, from the active layer to the anode (Alkarsifi, R. *et al.,* 2022). HTMs influence interfacial contact quality, the long-term durability, charge extraction and energy level alignment of the device (Bui, V. K. H., & Nguyen, T. P. 2023). The HTM is typically deposited on the perovskite absorber's top in n-i-p structured PSCs (Kim, G. W., *et al.,* 2022) while it serves as the bottom contact layer in p-i-n structures. In any case, ensure effective carrier transport, lowering charge recombination and raising the overall power conversion efficiency (PCE) depend on its careful selection and optimization (Ameen, S., *et al.,* 2016; Völker, S. F. *et al.,* 2015).

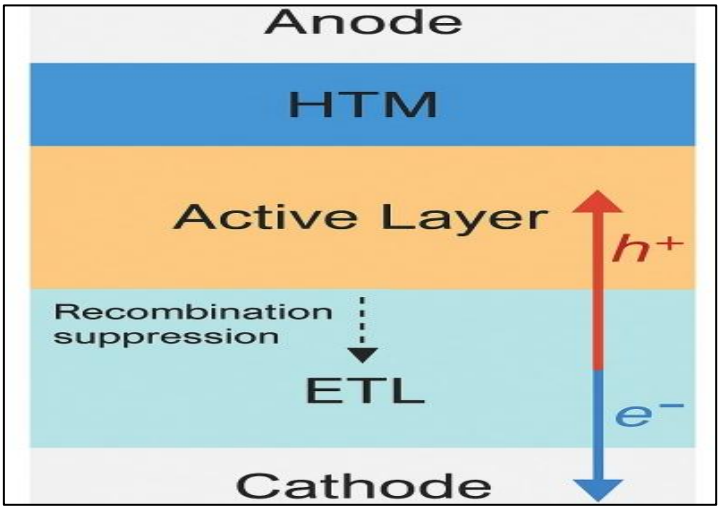

Figure 1. Role of the hole transport material (HTM) in charge extraction and selective hole transport in a typical solar cell architecture

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The efficacy of an HTM hinges on a combination of physical, chemical and electrical properties. An ideal HTM should exhibit high intrinsic hole mobility to effectively carry charges (Pham, H. D., *et al.*, 2020). This is particularly crucial in thick layers or large-area devices where transport bottlenecks can significantly hinder performance. In organic solar cells (OSCs), the HOMO level of the hole transport material (HTM) must align well with the valance band of either the donor polymer or the perovskite (Desoky, M. M. H. *et al.*, 2021; Desoky, M. M. H., *et al.*, 2021). This alignment minimizes energy loss and enhances charge transfer efficiency during hole extraction. HTMs should exhibit minimal structural rearrangement during charge transfer for effective hole hopping. Reorganization energy is often evaluated in DFT-based studies to identify suitable molecular candidates (Hannappel, T., *et al.*, 2024). HTMs must remain stable under operating conditions such as high temperatures, moisture, exposure to light and oxygen (Shahinuzzaman, M., *et al.*, 2024; Raza, E., Aziz, F., & Ahmad, Z. 2018). The lifespan of the device is often reduced by material deterioration at the interface. Dopants like Li-TFSI and tBP have traditionally been used to increase the conductivity of hole transport materials (HTMs) such as Spiro-OMeTAD. However, there is an increasing trend toward using dopant-free materials as they help mitigate problems associated with instability and moisture absorption (Ren, G., *et al.*, 2021; Guo, Y. 2022). The ability to process materials efficiently is essential for mass production. HTMs must create uniform, defect-free films and should function effectively during low-temperature solution processing (Vivo, P. *et al.*, 2017).

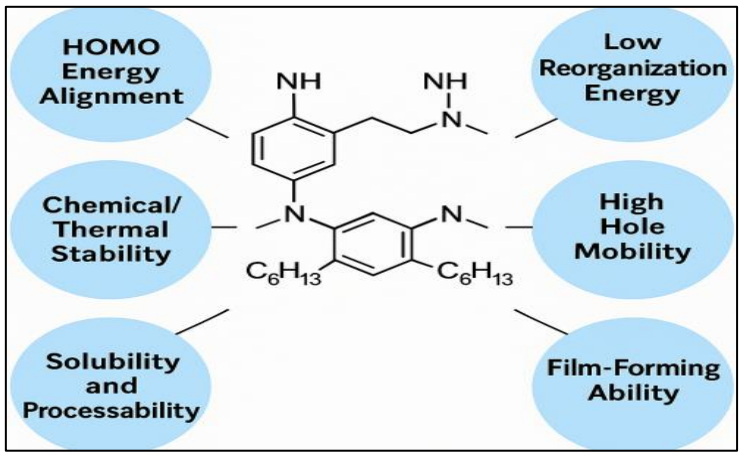

Figure 2. Design requirements for high-performance hole transport materials (HTMs) in organic and perovskite solar cells

Classification of Hole Transport Materials

Hole Transport Materials (HTMs) can be categorized based on their processing requirements, chemical nature and device configuration compatibility. The classification is carried out based on material type to ensure accurate comparison of their structural and electronic properties. Molecules should be small to achieve precision in molecular design and ensure reproducibility is crucial in this field. Prominent examples of such compounds include Spiro-OMeTAD and various derivatives of TPD (Nakka, L. *et al.*, 2022). However, it is important to note that some of these materials necessitate doping to attain sufficient conductivity. Polymeric HTMs such as P3HT and PTAA provide excellent mechanical flexibility and film-forming properties. Their performance can vary based on synthesis conditions and molecular weight (Synthesis of organic materials for optoelectronic applications, 2024). Inorganic HTMs such as CuSCN and NiOx have gained interest due to their intrinsic stability and affordability. They work particularly well for long-term and large-scale applications (Mbese, J. Z. 2025; Matebese, F. *et al.*, 2018). Hybrid HTMs balance robustness and tunability by combining inorganic and organic components and represent a new class in both OSCs and PSCs (Palilis, L. C., *et al.*, 2020). The analysis categorizes the materials based on device architecture to highlight performance variations across different configurations. Different hole transport materials (HTMs) are tailored to suit specific architectural designs. For example, Spiro-OMeTAD is highly effective in normal (n-i-p) perovskite solar cells (PSCs) while inverted structures more commonly utilize PTAA or NiOx (Rombach, F. M. *et al.*, 2021; Burschka, J., *et al.*, 2013). Some HTMs

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function effectively without additives, enhancing stability and simplifying fabrication (Li, S. *et al.*, 2021; Deng, Z., *et al.*, 2021) while others require dopants to improve conductivity (Manzhos, S., *et al.*, 2021). In the past decade, many hole transport materials (HTMs) have been researched but only a few have consistently met performance standards. Table 1 summarizes the materials that are frequently used.

Table 1. Comparative properties of widely used hole transport materials in solar cells

HTM Type	Example	HOMO Level (eV)	Hole Mobility ($cm^2/V.s$)	Stability	Doping Required	Scientific Evaluation
Small molecule	Spiro-OMeTAD	~-5.2	10^{-5}–10^{-4}	Moderate	Yes	High efficiency but costly and moisture sensitive
Polymeric	PTAA	~-5.2	~10^{-3}	High	No	Stable but expensive; variable quality
Conductive polymer	PEDOT:PSS	~-5.1	~10^{-3}	Low	No	Acidic and hygroscopic; easy to process
Inorganic	NiOx	~-5.3	10^{-2}–10^{-3}	High	No	Low-cost and stable but interface issues
Inorganic	CuSCN	~-5.3	~10^{-4}	High	No	High transparency; crystallinity control needed
Organic	P3CPenT	~-5.3	~10^{-5}–10^{-4}	Moderate	No	Moderate efficiency, dopant-free stability

MOLECULAR DESIGN STRATEGIES FOR HOLE TRANSPORT MATERIALS

A DFT Perspective

There is a growing trend of employing theoretical methods to enhance the characteristics of hole transport materials (HTMs) prior to their synthesis and this approach aims to advance the development of next-generation solar technologies (Manzhos, S., *et al.*, 2021; Vella, B. 2024) The most important of these is Density Functional Theory (DFT) which makes it possible to design HTMs logically by accurately forecasting their optoelectronic properties (Rosa, N., & Borges Jr, I. 2024; Jayan, K. D., & Sebastian, V. 2019). This section examines the use of DFT to direct the molecular engineering of HTMs specifically with regard to charge transport characteristics, energy level alignment and general device compatibility. The correct alignment of a hole-transport material's (HTM) highest occupied molecular orbital (HOMO) level with the valence band of the absorber layer such as seen in organic semiconductors or perovskites is essential (Rezaei, F., & Mohajeri, A. 2021). Density Functional Theory (DFT) simplifies the calculation of these orbital energies, allowing researchers to assess potential HTM candidates based on their ability to facilitate effective hole extraction and prevent undesired electron backflow (Shahzad, N. *et al.*, 2024). Density Functional Theory (DFT) is a valuable tool for fine-tuning HOMO levels without the need for time-consuming trial-and-error processes. DFT allows for a more systematic approach by modeling chemical structures with varying degrees of conjugation, different donor-acceptor ratios or changes in functional groups. For instance, increasing π-conjugation can decrease the HOMO-LUMO gap which in turn enhances optical absorption. Additionally, electron-donating substituents typically raise the HOMO level which improves energy alignment between molecules (Schneider, J. A. 2016). Scientists often use specialized functionals such as B3LYP and CAM-B3LYP (Yanai, T. *et al.*, 2024) to achieve accurate predictions of HOMO. These predictions typically align closely with experimental results from techniques like cyclic voltammetry and ultraviolet photoelectron spectroscopy. This approach enhances our understanding of the electronic structure in various chemical systems and produces more reliable results (Bertrandie, J., *et al.*, 2022).

In hole transport materials (HTMs), charge mobility depends on both molecular ordering and reorganization energy (λ), a parameter that can be easily determined using DFT. Reorganization

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energy reflects the energy cost of structural relaxation that occurs during the charge transfer process (Lin, K., & Evans, B. 2020; Olsson, M. H. M., & Ryde, U. 2001). A lower λ indicates a reduced energy barrier for hole hopping between molecules, thereby facilitating greater charge transfer within the HTM layer. Optimizing the structure of both neutral and oxidized species is often necessary for DFT calculations of λ(Olsson, M. H. M., & Ryde, U. 2001). When oxidized, molecules with rigid, planar backbones typically exhibit less structural distortion. This reduction in distortion leads to lower λ values and enhances hole mobility (Low, P. J., *et al.,* 2005). As a result, there is less reliance on external dopants to boost conductivity allowing researchers to focus on alternatives that offer inherent advantages in charge transport.

Time-Dependent DFT (TD-DFT) plays a vital role in predicting the optical properties of HTMs especially when used alongside ground-state calculations. This approach allows us to evaluate key aspects such as the onset of absorption, the strength of oscillators and the nature of electronic transitions. Ensuring that materials have a bandgap wide enough—generally more than 2.5 eV—is critical for minimizing unwanted absorption in the visible spectrum. This consideration is particularly crucial in applications like semi-transparent or tandem solar cells, where efficiency and clarity are essential (Nevonen, D. E. 2022). Additionally, TD-DFT analysis of charge-transfer properties provides a more comprehensive understanding of interfacial dynamics and exciton dissociation particularly when HTM forms a heterojunction with the absorber layer (Teuscher, J., *et al.,* 2017). Molecules often exhibit strong $\pi \rightarrow \pi^*$ transitions which are advantageous due to their lower rates of non-radiative recombination and enhanced photostability.

Molecular geometry is of paramount importance in understanding the packing behavior of materials in solid states, despite DFT generally focusing on individual molecules or small clusters (Pinkard, A. *et al.,* 2018). Structural attributes such as planarity, dipole moments and dihedral angles notably influence the self-assembly of HTMs in thin films (Wu, R. *et al.,* 2022). These characteristics also impact the interfacial interactions with adjacent layers as well as the overall crystallinity of the material (Vasilopoulou, M., *et al.,* 2020). For instance, a molecule that exhibits significant torsional flexibility may encounter difficulties in forming well-ordered domains which can result in diminished hole mobility. In contrast, molecules with symmetrical and planar geometries tend to facilitate effective π-π stacking. It becomes possible to make predictions regarding film morphology and its consequent effects on device efficiency and reproducibility by employing computational screening to analyze these structural features (Zhan, C., & Yao, J. 2016). Recent advancements in computational chemistry have greatly improved high-throughput screening of HTMs. Researchers can now assess thousands of candidate compounds using DFT descriptors such as bandgap, HOMO level and reorganization energy (Omar, Ö. H. *et al.,* 2021). To speed up the discovery of worthy materials, some methods incorporate machine learning algorithms trained on DFT-generated datasets (Wan, X. *et al.,* 2021). These design pipelines allow scientists to pre-select compounds for synthesis by establishing optimal property criteria such as specific thermal stability indices, HOMO levels between -5.1 and -5.4 eV and reorganization energy below 0.2 eV (Wen, J., *et al.,* 2025). This focused approach accelerates the development process while significantly reducing material waste and lowering experimental costs (Faruque, M. O., *et al.,* 2024).

BASIS SETS AND DFT FUNCTIONALS

the cornerstones of precise HTM modeling

A key technique for forecasting the electrical and structural characteristics of hole transport materials (HTMs) is DFT (Janjua, M. R. S. A. 2021). However, the choice of basis sets and exchange-correlation functionals used in simulations significantly affects the accuracy and reliability of DFT calculations (Harvey, J. N. 2006). Since HTMs often exhibit sensitive intermolecular interactions, complex electrical behavior and highly delocalized π-systems so selecting the appropriate combinations is essential for accurately simulating these materials (Cheng, J., & Deming, T. J. 2011). This section discusses commonly used functionals and basis sets in the context of HTM design which highlights their impact on the precision of computational predictions.

Comprehending DFT Functionals for HTM Applications

The approximation of electron exchange and correlation energies in the simulation is determined by a DFT functional (Wu, Q., & Yang, W. 2003). The choice of functionals needs to be carefully considered in the context of HTMs where excited-state behavior and orbital energy

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alignment are both crucial (Kussmann, J. *et al.*, 2024). B3LYP (Becke, 3-parameter, Lee–Yang–Parr hybrid functional) (The, O. F., *et al.*, 1991) is widely used for geometry improvements and frontier orbital calculations because it strikes a balance between computing economy and adequate accuracy (Bursch, M. *et al.*, 2022). However, its tendency to underestimate bandgaps may reduce its capacity to predict optical properties accurately (Sohlberg, K., & Foster, M. E. 2020). The purpose of CAM-B3LYP (Coulomb-attenuating method version of B3LYP) (Hesabi, M., & Ghasemi, G. 2020) is to rectify the bandgap underestimating of B3LYP and enhance long-range charge-transfer predictions. It works especially well with HTMs that have strong donor-acceptor motifs or extended conjugations (Izquierdo, M. A. *et al.*, 2019). WB97XD (ωB97X-D) (Morera-Boado, C. *et al.*, 2020) functional is well-suited for investigating non-covalent interactions including π-π stacking due to its incorporation of empirical dispersion and long-range corrections. These interactions are vital for effective charge transport and the proper formation of HTM films (Antony, J., & Grimme, S. 2006). PBEPBE (Perdew–Burke–Ernzerhof functional) (Hammer, B. 1999) is a generalized gradient approximation (GGA) functional which is often used for initial screening. It allows for faster computations while it may not be as accurate as hybrid functionals for systems requiring precise electronic details (Lehtola, S. 2023). MPW1PW91 (Weisz, K. 2008) is a hybrid functional though not commonly used but consistently delivers reliable predictions for HOMO energy. Research on hole extraction properties and modifying charge transfer has highlighted specific applications for this functional (Adamo, C., & Barone, V. 1998). Each computational functional has its own set of advantages and disadvantages which make the choice and often dependent on the specific attribute being investigated such as charge transport behavior, optical response or energy level alignment.

Role of Basis Sets in Predicting HTM Properties

Atomic orbitals are described by mathematical functions that are defined by basis sets (Dyall, K. G., & Fægri, K. 1996). Since the systems in HTM research typically consist of large and flexible π-conjugated frameworks which is a carefully chosen basis set ensures the accurate computation of crucial features including dipole moments, rearrangement energies and ionization energy (Hickey, A. L., & Rowley, C. N. 2014). 6-31G(d,p) is polarization functions are part of a popular split-valence basis set. It provides a decent balance for property calculations and routine geometry optimizations in organic HTMs (Rassolov, V. A. 1998). 6-311G(d,p) is a bigger, polarized triple-zeta basis set that offers better precision for electrical characteristics. It is commonly used when calculating vertical ionization potentials, reorganization energies or HOMO-LUMO gaps (McLean, A. D., & Chandler, G. S. 1980). def2-SVP/def2-TZVP is contemporary basis sets that yield reliable findings for a variety of atoms. In dispersion interaction computations, these are frequently used in conjunction with functionals such as WB97XD (Weigend, F., & Ahlrichs, R. 2005). The modeling doped systems (such as Cu and Au) or transition metal-based HTMs require the use of LANL2DZ effective core potential (ECP) basis set. In heavier atoms, it streamlines electron treatment without appreciably sacrificing precision (Mukherjee, S. 2020). The choice of basis set affects processing resources and accuracy. Large HTM systems often require a balance between accuracy and processing cost.

The Best Pairing of Functional and Basis Sets for HTMs

The dependability of DFT results is largely dependent on how well the selected functional and basis sets work together (Zhao, Y., & Truhlar, D. G. 2008). The combinations listed below are frequently used in investigations pertaining to HTM:

Table 2. Functional-Basis Set Combinations Often Used in HTM Research

Functional	Basis Set	Best Used For
B3LYP	6-31G(d,p)	Geometry optimization and HOMO-LUMO levels
CAM-B3LYP	6-311G(d,p)	Optical bandgap and absorption predictions via TD-DFT
WB97XD	def2-TZVP	Modeling intermolecular interactions and solid-state packing

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PBEPBE	6-31G(d)	Fast screening of molecular descriptors
MPW1PW91	6-311G(d,p)	Reorganization energy predictions and enhanced HOMO energy

These pairings offer a solid foundation for DFT analysis in HTM research but they are not strict guidelines. Modifications can be made depending on the complexity, size and kind of HTM system being studied.

Basis Set Superposition Error (BSSE) can lead to inaccurate interaction energies when modeling HTMs especially in dimer or cluster configurations. It is beneficial to use counterpoise correction techniques or switch to larger basis sets to reduce this error. Additionally, obtaining accurate and repeatable electrical properties requires establishing strict convergence criteria such as an SCF energy threshold of 10^{-8} and force tolerances below 10^{-5} Hartree/Bohr (Gedeck, P. 1997).

CASE STUDIES

Hole Transport Material Development Guided by DFT

The development of hole transport materials (HTMs) for organic and perovskite solar cells has been significantly facilitated by DFT. DFT enables informed material selection and minimizes the experimental burden by providing predictive insights into optoelectronic properties (Del Cueto, M. *et al.*, 2022; Rosa, N. M. P., & Borges, I. 2025). This section presents key case studies that exemplify the utility of DFT in the design and optimization of HTMs. One of the most extensively studied HTMs is Spiro-OMeTAD (Sallenave, X., *et al.*, 2020). DFT calculations have confirmed that its optimal HOMO level is around -5.2 eV with functional B3LYP/6-31G(d,p) making it effective for hole extraction from perovskite absorbers (G. S. A. A. Jordan. 2021). Simulations indicate a moderate reorganization energy of approximately 0.20 eV which supports a respectable hole mobility (Cao, Y. *et al.*, *et al.*, 2019). However, computational investigations have also revealed its significant synthetic reliance and complexity on dopants, such as Li-TFSI and tBP. This has prompted the development of dopant-free alternatives that exhibit comparable electrical properties (Haji-Khan Mirzaei, L., *et al.*, 2024; Dizaj, M. H. 2024).

P3HT has been comprehensively studied using DFT within the field of organic photovoltaics to gain insights into its orbital alignment and charge transport characteristics. The limited tunability and variability in production of P3HT have led to an increased interest in small HTMs, despite its reliable performance (Conchuir, B. O. *et al.*, 2016). Through the optimization of conjugated backbones and the careful adjustment of HOMO levels, DFT-directed modifications of triphenylamine-based compounds have resulted in notable enhancements in both stability and efficiency (Qiu, M., Pei. *et al.*, 2019; Tong, Z., *et al.*, 2025). The application of density functional theory (DFT) has proven to be invaluable To optimize the HOMO energy, structural planarity and reorganization energy of dopant-free hole transport materials (HTMs) such as X60 and FDT (Wang, J., *et al.*, 2021). These computational insights have contributed significantly to the development of cost-effective materials that facilitate easier manufacturing processes while enhancing the long-term stability of devices (Pham, H. D., *et al.*, 2020; Wang, L., *et al.*, 2018) The study illustrates the application of DFT in the design of custom materials specifically focusing on the derivatives of P3CPenT. A series of functional simulations including CAM-B3LYP and PBEPBE provide valuable insights into thermal stability, charge transport behavior and the electronic properties characterized by the gaps between HOMO and LUMO. For the synthesis of these materials, particular emphasis was placed on selecting molecules that satisfy critical criteria such as reorganization energies below 0.2 eV and HOMO levels between -5.1 eV and -5.4 eV.

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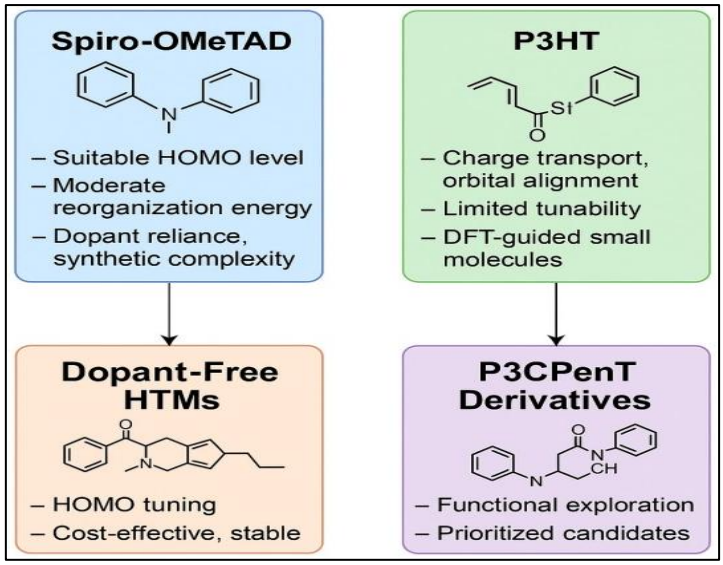

Figure 3. DFT Outcomes in HTM Development

CORRELATING DFT DESCRIPTORS WITH EXPERIMENTAL DEVICE PERFORMANCE

The effective design of high-performance HTMs relies on establishing a strong connection between experimentally measured photovoltaic metrics and theoretically predicted molecular characteristics. DFT calculations can provide valuable insights into molecular-level traits such as dipole moment, HOMO/LUMO energy levels, reorganization energy (λ) and ionization potential (IP). When accurately compared and analyzed research has shown that these characteristics significantly influence key device metrics including fill factor (FF), open-circuit voltage (V_{oc}), operational stability and power conversion efficiency (PCE). Lower reorganization energy (λ) is generally associated with more efficient hole transport, resulting in improved charge carrier mobility and enhanced device PCE and this is because less structural distortion occurs during oxidation. For instance, the reorganization energy of the gold-standard HTM Spiro-OMeTAD has been determined to be approximately 0.31 eV through ωB97X-D/6-31G** DFT calculations. This value is significantly higher than earlier estimates, which ranged from approximately 0.13 to 0.16 eV. This leads to uncertainty margins of ±0.1 eV depending on the computational methods used (Li, Y. 2017). This sensitivity highlights the importance of maintaining methodological consistency when evaluating DFT data.

According to DFT calculations of poly(3-hexylthiophene) (P3HT) and its 19 derivatives, regioregular P3HT exhibits low reorganization energy for hole transport typically ranging from 0.20 to 0.27 eV and this variation depends on the chain length and conformation (Oliveira, E. F. *et al.*, 2016). P3HT-based devices show good alignment with the valence bands of perovskite materials in experiments and achieve lifetimes of up to 600 hours under normal illumination with V_{oc} values between 0.95 and 1.0 V. The X-series (e.g., X55) and triazatruxene-based molecules (e.g., SGT-462) are dopant-free HTMs that achieve advantageous energy-level alignment with perovskite absorbers thereby enhancing stability and efficiency. The X55 demonstrates a deep HOMO level of approximately -5.4 eV after six months of storage in ambient conditions result in high V_{oc} of around 1.15 V and PCEs reaching up to 20.8% while retaining over 90% of its initial efficiency (Vesce, L. *et al.*, 2021). Similarly, SGT-462 derived from triazatruxene, possesses a HOMO of -5.43 eV, exhibits thermal stability and facilitates effective hole extraction and achieving PCEs of about 11.8% without the use of dopants (Kil, D. R. *et al.*, 2020) These findings emphasize how molecular engineering can optimize HOMO levels to improve interfacial charge extraction and extend device lifespan.

CHALLENGES AND LIMITATIONS OF DFT IN HTM DESIGN

DFT has become an indispensable tool in the development of hole transport materials (HTMs) and it is important to acknowledge its limitations. These challenges arise from the complexity of real-world materials and device conditions as well as the inherent approximations associated with DFT. The trade-off between accuracy and computational efficiency represents a significant challenge in the use of DFT. They do so at a

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greater computational cost compared to generalized gradient approximation (GGA) functionals like PBE while hybrid functionals such as WB97XD, B3LYP and CAM-B3LYP deliver enhanced precision in predicting HOMO-LUMO energy levels and reorganization energies. This increased computational demand may restrict the practical application of these methods in the analysis of large HTMs systems or in conducting multi-molecular simulations. The selection of basis sets and functionals plays a crucial role in determining the outcomes of DFT calculations. The choice between B3LYP and MPW1PW91 can lead to variations in energy gaps and dipole moments for the same molecule. Additionally, they also require more computational resources while larger basis sets such as def2-TZVP can enhance the accuracy of results. Conversely, smaller basis sets like 6-31G may fail to adequately capture electron correlation. This variability in functional and basis set selection can hinder consistency and complicate inter-study comparisons (Oh, Y. *et al.*, 2024; Yang, Y. *et al.*, 2017). The underestimation of the band gap is a recognized challenge associated with many DFT functionals particularly local and semi-local variants. This issue can result in misalignment of energy levels with active layers, inaccurate evaluations of the suitability of HTMs and erroneous predictions regarding optical absorption edges. Hybrid and range-separated functionals do not always align with experimental results particularly in solid-state contexts, despite significant advancements in the field (Tahaoğlu, D. *et al.*, 2022).

DFT simulations are typically performed using basic implicit solvent models or in the gas phase. However, HTMs in practical applications operate under a variety of challenging conditions including interfaces with organic or perovskite layers, solid films and exposure to stressors such as heat and light. They are often overlooked by conventional DFT methods while these factors significantly affect material interactions, charge transport and stability. Standard DFT primarily emphasizes ground-state characteristics. TD-DFT is essential to effectively investigate excited-state phenomena such as charge transfer and photoexcitation. However, it is important to note that TD-DFT may not adequately capture long-range electron-hole separation which is vital for HTMs in optoelectronic applications. Furthermore, its application can often lead to inaccuracies when assessing charge-transfer states (Maitra, N. T. *et al.*, 2017). The computational cost associated with DFT increases with larger molecular sizes. Consequently, the time and resources necessary for high-throughput screening of extensive HTM libraries can become significant challenges. The practical integration of these approaches with DFT remains somewhat limited while semi-empirical methods and machine learning techniques have been developed to mitigate this workload.

FUTURE OUTLOOK AND EMERGING TRENDS

DFT will remain a crucial tool in the logical design of improved HTMs as the demand for next-generation solar technologies increases. However, its role is evolving from static molecular simulations to a more dynamic and integrated approach that combines artificial intelligence, multi-scale modeling and green chemistry. One of the most exciting developments is the combination of DFT with machine learning (ML) methods. This hybrid technique enables high-throughput virtual screening of vast chemical libraries and allowing researchers to develop predictive models trained on datasets generated from DFT. By utilizing these methods, researchers can discover unconventional chemical candidates with superior optoelectronic properties while significantly reducing the computational workload (Fiedler, L. *et al.*, 2022).

The ongoing shift towards sustainable, dopant-free HTMs represents a significant trend within the industry. As environmental concerns and the need for long-term stability gain prominence, the demand for materials that are thermally stable, cost-effective and readily synthesized is increasingly critical. In this context, DFT serves an essential role by facilitating the design of simpler organic frameworks that eliminate the need for additives such as lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) or tert-butylpyridine (tBP) while still ensuring suitable HOMO alignment and effective hole mobility (Yin, X. *et al.*, 2020; الاردن, غ. ص. ا. ا. 2021). Moreover, there is a rising interest in the development of multifunctional HTMs. These advanced materials extend beyond mere charge transport capabilities by offering inherent compatibility, light absorption and photostability with flexible substrates. Computational techniques including nonadiabatic dynamics simulations and TD-DFT are broadening the design opportunities for such multifunctional applications. The importance of tailoring HTMs to specific environments will become increasingly significant

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as the development of solar cells progresses toward flexible, tandem and semi-transparent structures.

Advanced computational methods are becoming increasingly important beyond traditional density functional theory (DFT). Scientists are now utilizing time-dependent DFT (TD-DFT) and non-adiabatic molecular dynamics (NAMD) simulations to predict key aspects such as exciton dissociation, photostability and interfacial dynamics which are essential for next-generation HTMs (Zhang, C. *et al.*, 2025). Additionally, many-body perturbation techniques like the GW approximation and the Bethe-Salpeter Equation (BSE) are being employed to accurately describe optical spectra and excited-state properties which offer insights that ground-state DFT alone cannot provide (Himmelsbach, P., and C. Holzer. 2024). The optimization of performance across various device configurations can be achieved through the application of DFT which facilitates the engineering of dielectric tuning, interfacial dipole moments and work function alignment. Furthermore, the democratization of HTM discoveries and the encouragement of collaborative innovation are being advanced by the establishment of open-access databases and cloud-based DFT platforms. These initiatives are expanding the accessibility of computational chemistry to a wider academic community, fostering an environment conducive to shared knowledge and progress.

CONCLUSION

To enhance the stability and performance of both organic and perovskite solar cells, careful design and development of hole transport materials (HTMs) is paramount. An indispensable tool in this endeavor is DFT which facilitates the precise prediction of significant molecular characteristics prior to experimental synthesis. These characteristics encompass thermal stability, reorganization energies, energy levels and charge transport behavior. This review has highlighted how DFT accelerates the process of material discovery, reduces the reliance on trial-and-error methods and informs molecular design decisions, thereby enabling a systematic screening of HTMs. The insights derived from DFT have substantially contributed to improvements in photovoltaic cost-effectiveness, stability and performance across a diverse array of materials, ranging from conventional polymers such as P3HT to innovative small molecules and dopant-free HTMs.

The integration of DFT with machine learning, green chemistry principles and high-throughput screening is poised to significantly transform the discovery and optimization of HTMs. As advancements in theoretical techniques and computational capabilities continue to progress, solar energy materials of the future will increasingly be supported by simulations, data-driven and specifically designed to meet both technological and environmental needs. The continued importance of DFT in connecting theoretical design with experimental implementation will ultimately facilitate the development of effective, scalable and reliable solar energy systems for the next generation.

REFERENCES

1. Kannan, N., & Vakeesan, D. "Solar energy for future world:-A review." *Renewable and sustainable energy reviews* 62 (2016): 1092-1105.
2. Mudakkar, S. R., Zaman, K., Khan, M. M., & Ahmad, M. "Energy for economic growth, industrialization, environment and natural resources: Living with just enough." *Renewable and Sustainable Energy Reviews* 25 (2013): 580-595.
3. jin Kim, C. "Synergizing solar cell technology, radio wave communication, AI integration, and business opportunities: a comprehensive review." *International Journal of Multidisciplinary Sciences and Arts* 3.2 (2024): 252-262.
4. Bouich, A., Pradas, I. G., Khan, M. A., & Khattak, Y. H. "Opportunities, challenges, and future prospects of the solar cell market." *Sustainability* 15.21 (2023): 15445.
5. Syahirah, N., Nor, M., Itam, Z., & Sing, W. L. "Sustainable development perspectives of solar energy technologies with focus on solar photovoltaic—A review." *Energies* (2022): 1–15.
6. Maka, A. O. M., & Alabid, J. M. "Solar energy technology and its roles in sustainable development." *Clean Energy* 6.3 (2022): 476–483.
7. Kumar, N. S., & Naidu, K. C. B. "A review on perovskite solar cells (PSCs), materials and applications." *Journal of Materials* 7.5 (2021): 940–956.
8. Li, C. et al. "Achieving record-efficiency organic solar cells upon tuning the conformation of solid additives." *Journal of the American Chemical Society* 144.32 (2022): 14731–14739.

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9. Huang, J. et al. "Highly efficient organic solar cells consisting of double bulk heterojunction layers." *Advanced Materials* 29.19 (2017): 1–9.
10. Clarke, T. M., & Durrant, J. R. "Charge photogeneration in organic solar cells." *Chemical Reviews* 110.11 (2010): 6736–6767.
11. Lu, L., & Ya, M. E. "Application of organic photovoltaic materials (OPV) as greenhouse roof structures: A review." *Journal of Agricultural and Food Engineering* 1.3 (2020): 1–5.
12. Djurišić, A. B., et al. "Perovskite solar cells—An overview of critical issues." *Progress in Quantum Electronics* 53 (2017): 1–37.
13. Jiang, F. et al. "A two-terminal perovskite/perovskite tandem solar cell." *Journal of Materials Chemistry A* 4.4 (2016): 1208–1213.
14. Sun, Y. et al. "Flexible organic solar cells: Progress and challenges." *Small Science* 1.5 (2021).
15. Yang, D., Yang, R., Priya, S., & Liu, S. (Frank). "Recent advances in flexible perovskite solar cells: Fabrication and applications." *Angewandte Chemie International Edition* 58.14 (2019): 4466–4483.
16. Li, N., Niu, X., Chen, Q., & Zhou, H. "Towards commercialization: The operational stability of perovskite solar cells." *Chemical Society Reviews* 49.22 (2020): 8235–8286.
17. Bui, V. K. H., & Nguyen, T. P. "Advances in hole transport materials for layered casting solar cells." *Polymers (Basel)* 15.22 (2023): 1–29.
18. Jahantigh, F., & Safikhani, M. J. "The effect of HTM on the performance of solid-state dye-sensitized solar cells (SDSSCs): A SCAPS-1D simulation study." *Applied Physics A: Materials Science and Processing* 125.4 (2019): 1–7.
19. Tsuneda, T. *Density Functional Theory in Quantum Chemistry*. Vol. 9784431548. (2013).
20. Burke, K., & Wagner, L. O. "DFT in a nutshell." *International Journal of Quantum Chemistry* 113.2 (2013): 96–101.
21. Schleder, G. R., et al. "From DFT to machine learning: Recent approaches to materials science—A review." *JPhys Materials* 2.3 (2019).
22. de Proft, F., & Geerlings, P. "Conceptual and computational DFT in the study of aromaticity." *Chemical Reviews* 101.5 (2001): 1451–1464.
23. Snaith, H. J. "Perovskites: The emergence of a new era for low-cost, high-efficiency solar cells." *Journal of Physical Chemistry Letters* 4.21 (2013): 3623–3630.
24. Shariatinia, Z. "Recent progress in development of diverse kinds of hole transport materials for the perovskite solar cells: A review." *Renewable and Sustainable Energy Reviews* 119 (2020): 109608.
25. Yin, X., Song, Z., Li, Z., & Tang, W. "Toward ideal hole transport materials: A review on recent progress in dopant-free hole transport materials for fabricating efficient and stable perovskite solar cells." *Energy & Environmental Science* 13.11 (2020): 4057–4086.
26. Alkarsifi, R., Ackermann, J., & Margeat, O. "Hole transport layers in organic solar cells: A review." *Journal of Metals, Materials and Minerals* 32.4 (2022): 1–22.
27. Kim, G. W., et al. "Hole transport materials in conventional structural (n–i–p) perovskite solar cells: From past to the future." *Advanced Energy Materials* 10.8 (2020): 1–30.
28. Ameen, S., et al. "Perovskite solar cells: Influence of hole transporting materials on power conversion efficiency." *ChemSusChem* 9.1 (2016): 10–27.
29. Völker, S. F., Collavini, S., & Delgado, J. L. "Organic charge carriers for perovskite solar cells." *ChemSusChem* 8.18 (2015): 3012–3028.
30. Pham, H. D., et al. "Development of dopant-free organic hole transporting materials for perovskite solar cells." *Advanced Energy Materials* 10.13 (2020).
31. Desoky, M. M. H., Bonomo, M., Barbero, N., Viscardi, G., Barolo, C., & Quagliotto, P. "Polymeric dopant-free hole transporting materials for perovskite solar cells: Structures and concepts towards better performances." *Polymers (Basel)* 13.10 (2021).
32. Desoky, M. M. H., et al. "Dopant-free all-organic small-molecule HTMs for perovskite solar cells: Concepts and structure–property relationships." *Energies* 14.8 (2021).
33. Hannappel, T., et al. "Integration of multijunction absorbers and catalysts for efficient solar-driven artificial leaf structures: A physical and materials science perspective." *Solar RRL* 8.11 (2024).
34. Shahinuzzaman, M., et al. "Roles of inorganic oxide based HTMs towards highly efficient

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and long-term stable PSC—A review." *Nanomaterials* 12.17 (2022): 1–29.
35. Raza, E., Aziz, F., & Ahmad, Z. "Stability of organometal halide perovskite solar cells and role of HTMs: Recent developments and future directions." *RSC Advances* 8.37 (2018): 20952–20967.
36. Ren, G., et al. "Strategies of modifying spiro-OMeTAD materials for perovskite solar cells: A review." *Journal of Materials Chemistry A* 9.8 (2021): 4589–4625.
37. Guo, Y. "A novel organic dopant for Spiro-OMeTAD in high-efficiency and stable perovskite solar cells." *Frontiers in Chemistry* 10 (2022): 1–9.
38. Vivo, P., Salunke, J. K., & Priimagi, A. "Hole-transporting materials for printable perovskite solar cells." *Materials (Basel)* 10.9 (2017): 1–45.
39. Nakka, L., Cheng, Y., Aberle, A. G., & Lin, F. "Analytical review of Spiro-OMeTAD hole transport materials: Paths toward stable and efficient perovskite solar cells." *Advanced Energy and Sustainability Research* 3.8 (2022).
40. "Synthesis of organic materials for optoelectronic applications." (2024).
41. Mbese, J. Z. "Advancements in inorganic hole-transport materials for perovskite solar cells: A comparative review." *Energies* 18.9 (2025): 1–13.
42. Matebese, F., Taziwa, R., & Mutukwa, D. "Progress on the synthesis and application of CuSCN inorganic hole transport material in perovskite solar cells." *Materials (Basel)* 11.12 (2018).
43. Palilis, L. C., et al. "Inorganic and hybrid interfacial materials for organic and perovskite solar cells." *Advanced Energy Materials* 10.27 (2020): 1–34.
44. Rombach, F. M., Haque, S. A., & Macdonald, T. J. "Lessons learned from Spiro-OMeTAD and PTAA in perovskite solar cells." *Energy & Environmental Science* 14.10 (2021): 5161–5190.
45. Burschka, J., et al. "Sequential deposition as a route to high-performance perovskite-sensitized solar cells." *Nature* 499.7458 (2013): 316–319.
46. Li, S., Cao, Y. L., Li, W. H., & Bo, Z. S. "A brief review of hole transporting materials commonly used in perovskite solar cells." *Rare Metals* 40.10 (2021): 2712–2729.
47. Deng, Z., et al. "Dopant-free π-conjugated hole transport materials for highly stable and efficient perovskite solar cells." *Frontiers in Chemistry* 9 (2021).
48. Manzhos, S., et al. "Materials design and optimization for next-generation solar cell and light-emitting technologies." *Journal of Physical Chemistry Letters* 12.19 (2021): 4638–4657.
49. Vella, B. "Novel small-molecule hole transport materials: Towards ideal packing and doping." (2024).
50. Rosa, N., & Borges Jr, I. "Advancing organic solar cells with density functional theory: A comprehensive review of computed properties and applications." (2024): 1–56.
51. Jayan, K. D., & Sebastian, V. "A review on computational modelling of individual device components and interfaces of perovskite solar cells using DFT." *AIP Conference Proceedings* 2162 (2019).
52. Rezaei, F., & Mohajeri, A. "Molecular designing of triphenylamine-based hole-transporting materials for perovskite solar cells." *Solar Energy* 221 (2021): 536–544.
53. Shahzad, N., Chatha, S. A. S., Iqbal, J., Hussain, S., & Hussain, R. "Enhancing perovskite solar cells performance through tailored design: pyridine-functionalized phenothiazine derivatives with modified end-capped acceptor moieties." *Engineering Research Express* 6.4 (2024).
54. Schneider, J. A. "Tailoring the properties of organic semiconductors through heteroatoms." (2016).
55. Yanai, T., Tew, D. P., & Handy, N. C. "A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP)." *Chemical Physics Letters* 393.1–3 (2004): 51–57.
56. Bertrandie, J., et al. "The energy level conundrum of organic semiconductors in solar cells." *Advanced Materials* 34.35 (2022).
57. Lin, K., & Evans, B. "Rational design of hole transport materials: Tools and structure-packing-property relationships." (2020).
58. Olsson, M. H. M., & Ryde, U. "Geometry, reduction potential, and reorganization energy of the binuclear CuA site, studied by density functional theory." *Journal of the American Chemical Society* 123.32 (2001): 7866–7876.
59. Low, P. J., et al. "Towards an understanding of structure-property relationships in hole-transport materials: The influence of molecular conformation on oxidation potential in poly(aryl)amines." *Journal of Materials Chemistry* 15.23 (2005): 2304–2315.

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60. Nevonen, D. E. "Spectroscopic and TDDFT-based electronic structure analysis of porphyrin and phthalocyanine derivatives, and their transition metal complexes." *Thesis* (2022).
61. Teuscher, J., et al. "Charge separation and carrier dynamics in donor-acceptor heterojunction photovoltaic systems." *Structural Dynamics* 4.6 (2017).
62. Pinkard, A., Champsaur, A. M., & Roy, X. "Molecular clusters: Nanoscale building blocks for solid-state materials." *Accounts of Chemical Research* 51.4 (2018): 919–929.
63. Wu, R., Matta, M., Paulsen, B. D., & Rivnay, J. "Operando characterization of organic mixed ionic/electronic conducting materials." *Chemical Reviews* 122.4 (2022): 4493–4551.
64. Vasilopoulou, M., et al. "Molecular materials as interfacial layers and additives in perovskite solar cells." *Chemical Society Reviews* 49.13 (2020): 4496–4526.
65. Zhan, C., & Yao, J. "More than conformational 'twisting' or 'coplanarity': Molecular strategies for designing high-efficiency nonfullerene organic solar cells." *Chemistry of Materials* 28.7 (2016): 1948–1964.
66. Omar, Ö. H., Del Cueto, M., Nematiaram, T., & Troisi, A. "High-throughput virtual screening for organic electronics: A comparative study of alternative strategies." *Journal of Materials Chemistry C* 9.39 (2021): 13557–13583.
67. Wan, X., Zhang, Z., Yu, W., & Guo, Y. "A density-functional-theory-based and machine-learning-accelerated hybrid method for intricate system catalysis." *Materials Reports Energy* 1.3 (2021): 100046.
68. Wen, J., et al. "Accelerated discovery of high-performance small-molecule hole transport materials via molecular splicing, high-throughput screening, and machine learning." *Journal of Materials Informatics* 5.3 (2025).
69. Faruque, M. O., et al. "High-throughput screening, crystal structure prediction, and carrier mobility calculations of organic molecular semiconductors as hole transport layer materials in perovskite solar cells." *Crystal Growth & Design* 24.21 (2024): 8950–8960.
70. Janjua, M. R. S. A. "How does bridging core modification alter the photovoltaic characteristics of triphenylamine-based hole transport materials? Theoretical understanding and prediction." *Chemistry – A European Journal* 27.12 (2021): 4197–4210.
71. Harvey, J. N. "On the accuracy of density functional theory in transition metal chemistry." *Annual Reports Section 'C' (Physical Chemistry)* 102.1 (2006): 203–226.
72. Cheng, J., & Deming, T. J. "Synthesis of polypeptides by ROP of NCAs." *Peptide Materials* 310 (June 2011): 1–26.
73. Wu, Q., & Yang, W. "A direct optimization method for calculating density functionals and exchange-correlation potentials from electron densities." *Journal of Chemical Physics* 118.6 (2003): 2498–2509.
74. Kussmann, J., Lemke, Y., Weinbrenner, A., & Ochsenfeld, C. "A Constraint-Based Orbital-Optimized Excited State Method (COOX)." *Journal of Chemical Theory and Computation* (2024).
75. The, O. F., et al. "Хабарлары." *Proceedings of the National Academy of Sciences* 1726 (1991).
76. Bursch, M., Mewes, J., Hansen, A., & Grimme, S. "Best-Practice DFT Protocols for Basic Molecular Computational Chemistry." *Angewandte Chemie* 134.42 (2022).
77. Sohlberg, K., & Foster, M. E. "What's the gap? A possible strategy for advancing theory, and an appeal for experimental structure data to drive that advance." *RSC Advances* 10.60 (2020): 36887–36896.
78. Hesabi, M., & Ghasemi, G. "A CAM-B3LYP DFT Investigation of Atenolol Adsorption on the Surface of Boron Nitride and Carbon Nanotubes and Effect of Surface Carboxylic Groups." *Russian Journal of Physical Chemistry A* 94.8 (2020): 1678–1693.
79. Izquierdo, M. A., Broer, R., & Havenith, R. W. A. "Theoretical Study of the Charge Transfer Exciton Binding Energy in Semiconductor Materials for Polymer:Fullerene-Based Bulk Heterojunction Solar Cells." *Journal of Physical Chemistry A* 123.6 (2019): 1233–1242.
80. Morera-Boado, C., Gamboa-Suárez, A., Bernal-Uruchurtu, M. I., & Hernandez-Lamoneda, R. "Density Functional Study on the Fundamental and Valence Excited States of Dibromine in T, P, and H Clathrate Cages." *Journal of Physical Chemistry A* 124.38 (2020): 7692–7709.
81. Antony, J., & Grimme, S. "Density functional theory including dispersion corrections for intermolecular interactions in a large benchmark set of biologically relevant

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molecules." *Physical Chemistry Chemical Physics* (2006): 5287–5293.
82. Hammer, B., Hansen, L. B., & Nørskov, J. K. "Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals." *Physical Review B: Condensed Matter and Materials Physics* 59.11 (1999): 7413–7421.
83. Lehtola, S. "Meta-GGA Density Functional Calculations on Atoms with Spherically Symmetric Densities in the Finite Element Formalism." *Journal of Chemical Theory and Computation* 19.9 (2023): 2502–2517.
84. Weisz, K. "Hydrogen Bond." *Nucleic Acids from A to Z: A Concise Encyclopedia* 53.6 (2008): 143.
85. Adamo, C., & Barone, V. "Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models." *Journal of Chemical Physics* 108.2 (1998): 664–675.
86. Dyall, K. G., & Fægri, K. "Optimization of Gaussian basis sets for Dirac-Hartree-Fock calculations." *Theoretical Chemistry Accounts* 94.1 (1996): 39–51.
87. Hickey, A. L., & Rowley, C. N. "Benchmarking quantum chemical methods for the calculation of molecular dipole moments and polarizabilities." *Journal of Physical Chemistry A* 118.20 (2014): 3678–3687.
88. Rassolov, V. A., Pople, J. A., Ratner, M. A., & Windus, T. L. "6-31G* basis set for atoms K through Zn." *Journal of Chemical Physics* 109.4 (1998): 1223–1229.
89. McLean, A. D., & Chandler, G. S. "Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11-18." *Journal of Chemical Physics* 72.10 (1980): 5639–5648.
90. Weigend, F., & Ahlrichs, R. "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy." *Physical Chemistry Chemical Physics* 7 (2005): 3297–3305.
91. Mukherjee, S., Ganguly, S., Samanta, D., & Das, D. "Sustainable green route to synthesize functional nano-MOFs as selective sensing probes for CrVI oxoanions and as specific sequestering agents for $Cr_2O_7^{2-}$." *ACS Sustainable Chemistry & Engineering* 8.2 (2020): 1195–1206.
92. Zhao, Y., & Truhlar, D. G. "Zhao2008." *Accounts of Chemical Research* 41.2 (2008): 157–167.
93. Gedeck, P. "Reviews in computational chemistry." *Reviews in Computational Chemistry* 10.3 (1997): 11.
94. Del Cueto, M., Rawski-Furman, C., Aragó, J., Ortí, E., & Troisi, A. "Data-driven analysis of hole-transporting materials for perovskite solar cells performance." *Journal of Physical Chemistry C* 126.31 (2022): 13053–13061.
95. Rosa, N. M. P., & Borges, I. "Review on the DFT computation of bulk heterojunction and dye-sensitized organic solar cell properties." *Journal of Molecular Modeling* 31.3 (2025): 1–61.
96. Sallenave, X., et al. "Interfacial and bulk properties of hole transporting materials in perovskite solar cells: spiro-MeTAD versus spiro-OMeTAD." *Journal of Materials Chemistry A* 8.17 (2020): 8527–8539.
97. Cao, Y., et al. "Dopant-free molecular hole transport material that mediates a 20% power conversion efficiency in a perovskite solar cell." *Energy & Environmental Science* 12.12 (2019): 3502–3507.
98. الاردن, غ. ص. ا. ا. "eltit oN: قطاع الصناعات ومسد تحضرات الـ تجميل." 1202.الـ كيماوية
99. Widiatmika, K. P. "No title: 主観的健康感を中心とした在宅高齢者における健康関連指標に関する共分散構造分析." *Etika Jurnalisme Pada Koran Kuning Sebuah Studi Mengenai Koran Lampu Hijau* 16.2 (2015): 39–55.
100. Haji-Khan Mirzaei, L., et al. "Dopant-free Spiro-OMe2 imidazole-based hole-transporting material for stable and low-cost organic-inorganic perovskite solar cell." *ACS Omega* 9.50 (2024): 49132–49142.
101. Dizaj, M. H. "Impact of doping Spiro-OMeTAD with Li-TFSI, FK209, and tBP on the performance of perovskite solar cells." *[Journal name missing]* 10 (2024): 165–173.
102. Conchuir, B. O., C. Tarantini, C. R. McNeill, S. Hüttner, and A. Zaccone. "Chain-assisted charge transport in semicrystalline conjugated polymers." *Journal of Physical Chemistry C* 120.27 (2016): 14539–14548.
103. Qiu, M., W. Pei, Q. Lu, Z. Li, Y. Li, and J. Liang. "DFT characteristics of charge transport in DBTP-based hole transport materials." *Applied Sciences* 9.11 (2019): 1–7.
104. Tong, Z., et al. "Theoretical study on charge transfer properties of triphenylamino-

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ethynyl polycyclic aromatic hydrocarbon derivatives." (2025): 1–23.
105. Wang, J., et al. "Dopant-free hole-transporting material with enhanced intermolecular interaction for efficient and stable n-i-p perovskite solar cells." *Advanced Energy Materials* 11.29 (2021): 1–9.
106. Wang, L., et al. "Design and synthesis of dopant-free organic hole-transport materials for perovskite solar cells." *Chemical Communications* 54.69 (2018): 9571–9574.
107. Li, Y., H. Li, C. Zhong, G. Sini, and J. L. Brédas. "Characterization of intrinsic hole transport in single-crystal Spiro-OMeTAD." *npj Flexible Electronics* 1.1 (2017): 1–7.
108. Oliveira, E. F., and F. C. Lavarda. "Reorganization energy for hole and electron transfer of poly(3-hexylthiophene) derivatives." *Polymer* 99 (2016): 105–111.
109. Vesce, L., M. Stefanelli, and A. Di Carlo. "Efficient and stable perovskite large area cells by low-cost fluorene-xantene-based hole transporting layer." *Energies* 14.19 (2021): 1–8.
110. Kil, D. R., C. Lu, J. M. Ji, C. H. Kim, and H. K. Kim. "Dopant-free triazatruxene-based hole transporting materials with three different end-capped acceptor units for perovskite solar cells." *Nanomaterials* 10.5 (2020).
111. Oh, Y., S. Song, and J. Bae. "A review of bandgap engineering and prediction in 2D material heterostructures: A DFT perspective." *International Journal of Molecular Sciences* 25.23 (2024).
112. Yang, Y., et al. "Charge transfer excitations from particle-particle random phase approximation: Opportunities and challenges arising from two-electron deficient systems." *Journal of Chemical Physics* 146.12 (2017): 124104.
113. Tahaoğlu, D., H. Usta, and F. Alkan. "Revisiting the role of charge transfer in the emission properties of carborane-fluorophore systems: A TDDFT investigation." *Journal of Physical Chemistry A* 126.26 (2022): 4199–4210.
114. Maitra, N. T. "Charge transfer in time-dependent density functional theory." *Journal of Physics: Condensed Matter* 29.42 (2017).
115. Fiedler, L., K. Shah, M. Bussmann, and A. Cangi. "Deep dive into machine learning density functional theory for materials science and chemistry." *Physical Review Materials* 6.4 (2022): 1–26.
116. Zhang, C., et al. "Advancing nonadiabatic molecular dynamics simulations in solids with E(3) equivariant deep neural Hamiltonians." *Nature Communications* 16.1 (2025).
117. Himmelsbach, P., and C. Holzer. "Excited state properties from the Bethe-Salpeter equation: State-to-state transitions and spin-orbit coupling." *Journal of Chemical Physics* 161.24 (2024): 1–9.

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