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Applications of Current Density Functional Theory (DFT) Methods in Polymer Solar Cells

Numbury Surendra Babu

Abstract

DFT and time-dependant DFT (TD-DFT) quantum chemical calculations have become helpful for qualitative and quantitative analyses of materials at the molecular level. In this paper, we will attempt to outline successes and opportunities associated with the use of DFT and TD-DFT in OSC research. Density functional theory (DFT) has evolved as a QM method that is both rigorous and efficient enough to be employed in photovoltaic solar cell challenges in the last ten years. DFT is a prominent method for precisely and efficiently calculating molecular systems' electrical and optical characteristics at a low computational cost. The possible uses of DFT to polymer solar cells were comprehensively examined in this article. First, the foundations of DFT are examined. Following that, the precision of DFT for studying photovoltaic properties particular to polymer solar cell design is highlighted. Next, this chapter looks at how DFT is used in polymer solar cell research and its accuracy. Following that, a discussion of how DFT works and how it can investigate polymer solar cell features will be given.

Keywords: DFT, TD-DFT methods, Polymer solar cells, electrical and optical properties

1. Introduction

According to the International Energy Agency, the world utilized 109613 TWh of energy in 2014, with fossil fuels accounting for 80% of that total. The depletion of fossil fuels takes 40 years for oil, 60 years for natural gas, and 200 years for coal. The use of fossil fuels and nuclear energy directly affects the environment by emitting greenhouse gases, causing climatic changes such as global warming, which cause malaria and famine [1]. If adequately developed, these sources can diversify energy supply, while wind, biomass, and geothermal cannot fully replace fossil fuels [2]. Solar energy is unique among renewable energy sources because it delivers 711019 Kcal each year, 10,000 times more than the world consumes. Solar energy is widely used in turning sunshine into useable energy for various applications such as solar water heating, solar transportation, solar ventilation, and solar electricity [3].

Photovoltaic (PV) systems convert sunlight directly into electricity, providing a practical and straightforward option to sustain the growing energy demand. Currently, solar cell research and development focuses on (i) the maturity of silicon solar cells. However, the complex manufacturing process, high energy

consumption, and high cost of classic silicon-based solar cells have slowed their progress. (ii) TFT solar cells GaAs [4]. CIGS [5], and CdTe [6] are examples of thin-film solar cells. Although thin-film solar cells are efficient and stable, gallium and indium are scarce in the crust, and cadmium is poisonous. (iii) New solar cells A new generation of solar cells include organic photovoltaics (OPV) DSSC [7] and perovskite solar cells (PSC) [4, 8, 9]. These solar cells are light and cheap. However, various issues prevent wide-scale application.

Although PSC, photoelectric conversion efficiency (PCE) has increased from 3.8 to 23.3 per cent, device stability has remained an issue limiting applications [10]. Evaporating silicon solar cells require advanced high-temperature manufacturing, high-quality silicon, and intricate energy sources. These cells are also mechanically rigid. Polymer solar cells are a low-cost alternative to silicon solar cells since they may be made by painting or printing [11]. Polymer cells are cheap, light, and flexible [12]. Since 1992, when Sariciftci et al. [13] demonstrated effective photoinduced electron transfer from polymer semiconductors to an electron acceptor, C_{60} polymer solar cells have gained popularity. Utilizing conducting polymers as electron donors could achieve 6–7.9% power conversion efficiency [14]. Conjugated polymers appeal to solar cell efficiency because their bandgap's and energy levels can be tuned chemically. The discovery of new electron-donor and electron-acceptor materials has recently increased OSCs' power conversion efficiencies (PCEs) to above 18% [15]. New materials, improved device processing methods and blend morphology [16, 17], and a better understanding of device physics [18] have contributed to OPV cell progress in the previous 30 years.

High-performance computing and optimization of computational chemistry codes have increased theoretical research in this area. Theoretical approaches are the best way to overcome practical synthesis problems and investigate cost-saving manufacturing and processing options. DFT can help solve these problems because it examines the electronic structure and spectroscopic properties of these materials. The only electronic structural approaches currently relevant to conjugated polymers have relied on density functional theory (DFT) [19, 20]. The highest occupied molecular orbital (HOMO), lowest occupied molecular orbital (LUMO), bandgap (Eg), ionization potential (IP), electron affinity (EA), charge mobility, open-circuit voltage (V_{OC}), and reorganization energies (λ) are key electronic parameters that determine the optoelectronic properties of polymer solar materials. This chapter examines DFT's usage and validity in polymer solar cell research. This will be followed by a description of how the DFT method looks at polymer solar cell characteristics. In addition, to describe the DFT and TD-DFT applications for polymer solar cells characteristics is also highlighted, as is DFT's overall utility in polymer solar cell design.

2. Computational quantum methods for polymer solar cells

Computational quantum chemistry may play an essential role in the development of OPV research and technology. In addition, the results of these computations can be used as a low-cost guide for developing and improving solar materials. Overall, the field's research can be divided into quantum science and charge transfer dynamics, new structures and creative concepts, and materials development for various applications. Understanding the functioning mechanism of polymer solar cells is the primary focus of the study. The main point of contention is how the bonded electron–hole pair breaks. The "hot exciton effect" is the most frequently recognized answer to this subject. When an electron is absorbed by one semiconductor material from another, it brings energy differences, causing the electron to

get heated and acquire velocity, allowing it to escape from the confined exciton state. Even though this idea has recently gained widespread acceptance, numerous investigations have cast doubt on its validity [21].

These methods are now being used to predict component excited-state properties in light-harvesting systems. Nonetheless, this is a difficult task. Furthermore, large systems pose a significant challenge to conventional quantum chemistry techniques for excited states. Thus, calculations and theoretical models are beneficial when used in conjunction with CT experiments. Optical absorption investigations can measure exciton binding energies. Electrochemistry can be used to assess OPV components' oxidation and reduction potentials, as well as their HOMO–LUMO gaps [22]. The charge transfer and recombination kinetics can be studied using femtosecond transient absorption and time-resolved emission measurements [22]. These studies rely on well-established electron and energy transmission [23, 24] and their thermodynamic and kinetic consequences [25].

In polymer solar cells, computational quantum theories such as density functional theory (DFT) are used. TD-DFT is the essential instrument in the quantum mechanical simulation of quantum chemistry for computing excited-state characteristics and charge-transfer (CT) excitations in large systems [26]. TD-DFT can extract excitation energies, frequency-dependent response qualities, and photo-absorption spectra from molecules and materials. There are several hurdles to implementing TD-DFT computations on photovoltaic systems. Assumptions in these applications can cause catastrophic modeling errors. Many hypotheses and refinements to this basic technique have been proposed [27].

Density Functional Theory (DFT) investigates the electronic structure (principally the ground state) of many-body systems, such as atoms, molecules, and condensed phases. A many-electron system's properties can be determined using functionals, i.e. function of another function. Inorganic photovoltaic properties such as bandgap, optical absorption, intra-molecular and inter-molecular charge transfer, exciton binding energy, charge transfer integral, reorganization energy and rate of charge transfer and recombination in donor-acceptor complexes can be calculated or developed using DFT based computational methods. In practice, the effects of organic photovoltaic media on these qualities should be considered. Although the impact of the medium varies depending on the transitions involved, polarization continuum solvation models may commonly be used to account for solvation at a low computational cost [28].

The Schrödinger equation, which explains the behavior of electrons in a system, is reformulated in density functional theory (DFT) so that approximate solutions are tractable for functional materials. Hohenberg and Kohn [29] proposed the idea in 1964, claiming that all ground-state features may be expressed as an operative of the charge density that must be reduced in energy. However, rather than tackling the Schrödinger Equation [30] head-on, these theorems showed that an initial guess of the charge density might be improved iteratively.

Hohenberg, Kohn, and Sham created such a theory in density functional theory (DFT) [31], leading to two of the top ten most preferred articles of all time6 and for which Kohn received the Nobel Prize in Chemistry in 1999. The Schrödinger equation's ground-state solutions are restated in DFT to find energy as a charge density function.

The exchange-correlation functional chosen determines the precision of the DFT calculation. Although theorists may frequently improve computation accuracy by employing more intricate functionals (at a higher processing cost), there are some highly coupled electron systems that most functionals fail. Other disadvantages of traditional DFT include the small system size, the difficulty of modeling weak (van der Waals) interactions, dynamics over long periods, and non-ground state

characteristics (finite temperatures or excited conditions). Larger systems can be tackled with the linear scaling approach [32], finite-temperature effects can be addressed with lattice dynamics [33] and cluster expansion [34], electronic excitations can be modeled with time-dependent DFT [35], the GW method [36], and the Bethe–Saltpeter [37], and several approaches can be used to overcome these limitations. In his assessment, Carter [38] gives a quick outline of some of these options. A DFT calculation requires the coordinates and orientations of the atoms in the material within a repeating lattice, the exchange-correlation functional, parameters and algorithms for numerical and iterative convergence, and, optionally, a method for more efficiently treating the system's core electrons (for example, through the use of pseudopotentials). DFT generates the electronic charge density, total energy, magnetic configuration, and electronic band structure.

3. DFT methods in polymer solar cells

The density-functional theory (DFT) has proven massively popular among the massive panel of current theoretical techniques. This success is mainly because no changeable inputs parameters are required, efficient numerical codes exist, and a high level of adaptability, particularly in representing semiconductor and metal ground state features. The ability of DFT approaches to handle larger systems has grown as computing power has increased. However, the present limit does not yet reach the 10000–10 million atom window involved in the active device region of PV cells. Modern semiconductor optoelectronic devices, such as quantum wells [39] and quantum dots [40], have features with a feature size of a few nanometers. Such systems are composed of various materials and alloys' complex two-dimensional (2D) and three-dimensional (3D) geometries. Nonetheless, DFT approaches can be used to get insight into the physical phenomena of individual device components, such as particular materials or tiny heterostructures. Quantitative PV design, for example, necessitates a valid prediction of electronic bandgap's band-lineups and effective masses.

DFT based on the local density approximation (LDA) [41] or the generalized gradient approximation (GGA) [42] is well recognized for failing to replicate the excited states of molecules adequately. Hybrid approaches that contain a fraction of Hartree-Fock exchange, on the other hand, may be able to avoid the band-gap problem, but their results are highly dependent on the material of interest. Even while Heyd et al. [43]. HSE06 hybrid functional is a good option for computing band gaps, band offsets, or alloy characteristics [44]. It fails to simulate the direct–indirect crossover in GaAsP alloys [45]. Many-body perturbation theory (MBPT) can also provide factual findings, mainly when using the GW technique (GW, where G stands for Green's function and W for the screened potential), which can be utilized in a perturbative scheme [46] or self-consistently [47]. The ionization potential and electron affinity of the donor and acceptor materials, respectively, are essential parameters for charge separation because they determine the relative alignment of electron and hole levels. DFT inside a super-lattice (SL) approximation can be used to estimate the drop of the interface's potential in heterostructures, resulting in a reasonable estimate of the band-lineup. The DFT potential drop at the interface can be quickly compensated by the GW eigenvalues derived for the bulk valence band states [48], but a GW treatment for a complicated stack is out of reach.

In DFT simulation, a reasonable estimation of alloy electrical characteristics is likewise a difficult task. Indeed, even typical semiconductors experience significant band-gap bowing; that is, the band-gap energy follows:

$$E_g(x) = \overline{E}_g(x) - b.x.(1-x) \qquad (1)$$

Where b is a parameter for bowing, super-cell techniques are better than virtual crystal approximations for statistically random alloys. However, DFT with specific quasi-random structures (SQS) (small super-cells) that recreate mixing enthalpies and atomic correlations of extremely large super-cells can provide identical results for specific alloy compositions. Chemical mixing, strain, and atomic relaxation effects are all included in SQS models.

Furthermore, semiempirical approaches for studying mechanical or electronic properties, such as the valence force field (VFF) and the tight-binding approximation [49] or elasticity and the K.P method [50], require precise electronic parameters as input. They can be calculated using DFT or discovered through experiments. For example, the density functional perturbation theory (DFPT) [51] is used to get quantitative estimates of electromechanical tensors of bulk materials. When just by-products of a first-order perturbation computation are required, an efficient application of the "2n + 1" theorem yields second-and third-order derivatives of the total energy, provided that atomic-displacement variables are removed. Various physical responses of insulating crystals, such as elastic constants, linear piezoelectric tensors, and linear dielectric susceptibility, as well as tensor properties related to internal atomic displacements like Born charges and phonons, can be obtained using second-order derivatives [51]. Interference techniques and symmetry analysis must be used in conjunction with the DFPT method for third-order components linked to physical qualities such as nonlinear electrical susceptibilities, nonlinear elasticity, or photoelastic and electrostrictive effects [52].

4. TD-DFT methods in polymer solar cells

TD-DFT has become the workhorse of quantum chemistry for computing excited-state characteristics and charge-transfer excitations in complex networks [53]. Linear and non-linear simulations may be popular due to their scalability and variety of methodologies. However, photovoltaic TD-DFT computations pose significant problems, notably with long-range CT interactions. Furthermore, although standard computer programs make TD-DFT easy to use, it is not a "black box" technique since approximations utilized in TD-DFT tools can occasionally produce major systemic mistakes in estimated results.

Making correct CT excitation energies with TD-DFT is problematic because approximate exchange-correlation (XC) potentials lack the unique features of exact Kohn–Sham (KS) potentials [54]. Thus, a non-local, exact-exchange contribution throughout the exchange-correlation kernel solves the charge-transfer problem in TD-DFT.

Many hybrid functionals (HF) have recently performed well in benchmark tests [55]. For example, Zhao and Truhlar created a functional (M06-2X) that contains the complete non-local exact-exchange contribution [56]. Prior studies investigated comprehensive adjustments for non-hybrid local adiabatic XC potentials targeting the CT problem utilizing constraint variational density functional. According to Ziegler et al. [57], the linear response approach produces qualitative variances between the time-dependent Hartree-Fock (TD-HF) and adiabatic local potential-based TD-DFT excitation energies and also between the TD-DFT and SCF excitation energies. In the variational approach, the mix of occupied and empty orbitals is allowed above linear terms to determine transition densities. However, the recent surge of activity in the field gives reason for optimism.

Constrained DFT (CDFT) [58] is an alternative technique that uses a variational constraint approach to alleviate TD-DFT's drawbacks. To handle charge- and spin-constrained electronic states within the ground state KS DFT technique [59], CDFT was created. Implementation is computational. CDFT has been proven to be useful for long-range electron transmission [60–62]. While TD-DFT's thrilled states (valence states) are inaccessible to CDFT, many of TD-DFT's bothersome excited states are dealt with naturally in CDFT.

CDFT can be used in systems where the ground-state electron density must meet a threshold. The localization of electronic density in space indeed reduces the variation in electron number between donor and acceptor areas by two. To enforce the constraint, Lagrange multipliers are used in CDFT. To counteract self-interaction mistakes caused by approximation XC functionals, CDFT uses semi-local functionals that are denser than the density. It defines diabatic states for electron transfer kinetics and chemical reaction rates. Using a ground state DFT functional, these limitations can also compute long-range charge transfer and low-lying spin states [61, 62].

However, this paradigm has several drawbacks. In CDFT, the electron density is partitioned by nuclear populations, affecting the constraint potential's shape. So the exact electron density partitioning is unknown. As a result, CDFT can only represent a subset of electronic excitations. Therefore, CDFT may not be the best method for simulating some diabatic circumstances. Also, a time-dependent optimal potential treatment of exact exchange can help describe charge-transfer excitations [63]. However, the exchange potential is too local to correctly predict the bandgap (i.e. HOMO–LUMO gap). Semi-quantitative hybrid functionals can forecast band gaps better than orbital dependent functionals. They use correlations to communicate precisely. Somewhat of focusing on density, we can improve approximation solution XC functionals in orbitals. They can also compensate for imperfections in self-interaction, and exchange energy is naturally stated in orbitals.

Dispersion correction to KS-DFT is widely employed to handle long-range electron correlations that cause dispersion forces [64, 65]. Unfortunately, local DFT functionals overestimate dispersion forces, whereas non-local and hybrid DFT functionals underestimate them [64, 65]. Developing DFT functionals optimized for improved management of Vander Waals interactions, on the other hand, appears promising. The Vander Waals density functional (vdW-DF) [65] techniques successfully cope with London dispersion interactions. Modern dispersion-corrected DFT methods include empirical components because they function best for long-range interactions. However, standard density functionals perform well for close interactions. So any dispersion-correction method using DFT has to integrate the short and long-range asymptotic areas, which are both well understood individually.

The most widely used non-empirical method for determining dispersion energy for molecular systems is the vdW-DF approach [66]. Due to the charge transfer reliance of dispersion being incorporated via electron density, this technique naturally accommodates it. Regular adjustments also alter thickness. Despite its mathematical complexity, this approach can achieve a smooth transition between chemical binding at small distances and Vander Waals attraction at long distances.

The KS inherent DFT defect is the KS-dispersion DFT term. Adding damped inter-atomic potentials of the kind C_6R_6 to the KS-DFT energy appears to be another successful empirical way of accounting for dispersion [64]. This approach is substantially faster to calculate, has high numerical stability, and provides physical insight. Despite its semi-classical origin, it can supplement standard density functionals in treating long-range electron correlation. In addition, estimating supramolecular complex binding energies has been proved to be easier with this strategy.

5. Application to DFT and TD-DFT methods in polymer solar cells

Many properties of interest in OPVs can be calculated or developed using DFT based computational methods, including bandgap, optical absorption, intramolecular and intermolecular charge transfer, exciton binding energy, charge transfer integral (to quantify electronic coupling), reorganization energy, and the rate of charge transfer and recombination in D–A compositors. In addition, in natural systems, the effects of the surrounding OPV media on these properties should be addressed. Although the impact of the medium varies depending on its nature and the nature of the transitions involved, low-cost polarization continuum solvation models can be utilized to account for solvation. In such situations, the solvent is treated as a continuous with a static dielectric constant, polarizing and polarized by the solute.

The following is a discussion of the theoretical methodologies and computational techniques mentioned above to foster a greater understanding of the connection between chemical structures and the optical and electrical properties of D–A systems about the rational design of OPV devices.

5.1 Bandgap engineering

A range of experimentally observed methods utilized may or may not indicate appreciable quantities in diverse contexts. Band gaps (see infra) are essential features to consider when evaluating conducting polymers. Controlling band gaps can improve the electroluminescence of OLEDs or the light absorption efficiency of photovoltaic cells [67]. To make organic polymers with good nonlinear optical response [67] or semiconductors having high electrical conductivity [68], materials with tiny band gaps are sought.

The phrase "bandgap" has multiple meanings. An infinite periodic system's electrical structure is called a "band." Also examined are monomers of conjugated polymers and oligomers of various sizes. The term bandgap also refers to a finite method feature that converges to the infinite periodic (band-structure) limit with oligomer size. The "gap" is the difference in electronic energy levels. Such as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied one, or computed energy gaps MO or CO (LUMO) [69]. Lowest optically permissible electronic excitation energy A visible energy gap (also known as an adiabatic or vertical optical gap) is an EO. Also, adiabatic or vertical electron attachment/detachment has associated energies like electron affinity (EA), ionization potential (IP) and electronegativity (EF) = IP-EA. Orbital energies and eigenvalues in KS DFT and HF may or may not be visible. However, approximations in actual computations might lead to big mistakes (see below). Furthermore, an orbital energy gap cannot reflect both EO and EF. Although the interpretation of the orbital energy gap as the fundamental gap is accurate in principle, the multiple approximations in the functionals make this interpretation useless in practice.

Band gaps often exhibit a roughly linear dependence on 1/m, allowing extrapolation to m → ∞, 1/m → 0. Generally, the quality of calculated results for different properties strongly relies on the physical models employed [70]. Extrapolating the infinite-periodic limit from a sequence of oligomer simulations requires prudence. Band gaps can diverge from linearity in 1/m [71]. These can also compute band gaps for polymers with unlimited chain lengths. PBCs have the advantage of not requiring further computations or extrapolation. However, PBC quantum chemistry algorithms are less functional than their molecular counterparts, which is a disadvantage.

The cheap computational cost of DFT and TD-DFT allows for the study of large systems. In contrast, the most commonly used functionals for molecules, such as generalized gradient approximations (GGA) and global hybrid GGA functionals,

result in the incorrect asymptotic behavior of a potential, significant delocalization errors, and lack of derivative discontinuity, all of which negatively impact o They showed that the band gaps computed with different hybrid functionals differ significantly, indicating that present hybrid functionals do not yield proper band gaps [72–74]. The link between projected orbital energy gaps and measured band gaps absorption energies is also poor for nonhybrid density functionals. Therefore, typical hybrid and meta-hybrid functionals are not acceptable for assessing the performance of organic photovoltaics, according to Savoie et al. Other hybrid functional analyses found striking agreement with measured optical gaps [75]. Many studies suggest that DFT and TD-DFT have limited predictive potential in this critical field [74]. Using hybrid functionals to integrate eX solves some of the DFT difficulties in extended systems [76]. However, estimated transfer integrals in organic semiconductors are sensitive to eX fraction [77].

5.2 Intramolecular and intermolecular charge transfer

To explain the transport properties, the charge transfer rate between donor and acceptor moieties could be calculated. Using DFT calculations of the electronic coupling, reorganization energy, and free energy difference associated with one electron transfer from donor to acceptor at the high-temperature limit, we can determine a rate using Marcus's formula [78, 79]. These predictions are then discussed in light of DFT's intrinsic flaws, such as overestimation of actual ground state energy, failure of the basis set to represent the system, and the inability of the functional to approximate critical interactions, to name a few. When it comes to charge transfer, however, there is another problem that is often overlooked.

A system where an extra account is localized on a single molecular unit is impossible to simulate using conventional DFT. As a result, calculations are frequently performed first on the charge donor, then on the charge acceptor, with or without the charge transferred. The overall energy of the system is calculated by adding the energies of the individual components. This is true when a considerable distance separates the donor and acceptor, and the electron density distribution of one entity has no effect on the electron density distribution of the other [79]. The size of the organizations participating in the charge transfer and the quantity and location of the surplus charge should naturally establish this limit. More sophisticated (and consequently more expensive) techniques, such as charge-constrained DFT [80], have been proposed for situations where this limit can never be achieved, such as intramolecular charge transfer [79]. However, standard ground state DFT remains the approach of choice for intermolecular charge transfer in solar cells, which usually involves larger molecular assemblies.

5.3 Extion binding energy

Exciton binding energy (E_b) is an essential element in polymer electronics and fundamental polymer physics, and it has been a source of debate for a long time. For example, a big Eb is required for a light-emitting polymer so that charge recombination takes precedence. Both the semiempirical model study [81] and the DFT/LDA Bethe–Salpeter equation (BSE) or GW approaches [82] have relied heavily on theoretical research of E_b of conjugated polymers. The semiempirical model can be addressed nearly precisely for the electron correlation, but the results depend highly on the parameters, even though a qualitative comprehension has been reached [81].

Although the BSE or GW approach is first-principles, it is unclear if the Hohenberg–Kohn–Sham framework might accommodate these many-body adjustments at the Green's function level.

Furthermore, the final results differ from one another [82]. We highlight two recent advances in quantum chemistry: (i) Time-Dependent Density Functional Theory (TD-DFT) and its successful application to the lowest-lying excited states [83], and (ii) the hybrid GGA Becke three-parameter Lee–Yang–Parr (B3LYP) functional for the quantitative prediction of chemical and electronic structures [82]. In examining the excitation processes in conjugated systems, the combination of the two has proven quite effective [84]. Tretiak et al. [85] demonstrated that hybrid density functionals might simulate excitonic phenomena and provide satisfactory E_b findings. Pure local spin density approximation (LSDA), generalized gradient approximation (GGA, such as BLYP, BP86, BPBE, PBEPBE, BPW91), meta-GGA (such as PBEKCIS), and hybrid density functionals (H-GGA, such as O3LYP, B3LYP, B972, PBE1PBE) are used to optimize the ground-state geometries of the molecules at the DFT level.

5.4 Electron transfer parameters

The ET parameters are now frequently calculated using ab initio quantum chemistry methods. In classical Marcus theory [86], two critical parameters determine the temperature-dependent kinetics of electron transfer: the driving force and the reorganization energy. The activation energy, G#, is calculated as follows:

$$\Delta G^{\#} = \frac{\left(\lambda + \Delta G^0\right)}{4\lambda} \qquad (2)$$

which then can be used in the Arrhenius relationship for the rate constant

$$k_{ET} = A \exp\left(\frac{\Delta G^{\#}}{k_B T}\right) \qquad (3)$$

The Boltzmann constant is denoted by k_B. Note that Eq. (3) is essentially classical, and when quantum effects are relevant, the temperature dependence of Eq. (3) breaks down [87].

Although free energies will be used in natural systems, ab initio calculations usually overlook entropy changes and instead use potential energy. When the reactant and product structures are known, G° may readily determine the difference between respective equilibrium energies. However, calculating is more complicated since it involves nonequilibrium energy.

Abs Initio algorithms have difficulties determining since it is not a ground-state attribute. In the adiabatic representation, the ground state potential energy curve is lower than the excited state potential energy curve. To compute, one must first know the energy of the product state at the reactant state's equilibrium structure. Excited-state energies are more difficult to calculate than ground-state energies. TD-DFT methods provide good excited-state energies (e.g., up to 100 atoms). The energy of long-range CT states in TD-DFT is underestimated [88, 89], limiting its use in ET reactions.

In ET research, constrained DFT has various advantages. For starters, restricted DFT makes accessing diabatic states and calculating Marcus parameters a breeze. Second, from ground-state computations, constrained DFT generates diabatic conditions. Excited-state calculations are avoided. Third, the equilibrium structures of the reactant and product states are obtained by optimizing constrained geometry. Third, the quality of diabatic potential energy curves from limited DFT is superior to adiabatic curves from DFT to optimize in adiabatic conditions because fractional charge systems are more susceptible to self-interaction errors [90]. Fourth, the

localization of an unpaired electron is forced via constrained DFT. As a result, restricted DFT energy values are more precise. Limited DFT cannot be used for ET reactions involving a locally excited state as a ground-state approach. To investigate such responses, TD-DFT and limited DFT could be utilized. Our method, in particular, is before the electron source and acceptor. In systems in which the donor and acceptor are not separated, this can be a problem. As a result, our method is now the most effective for long-range ET responses, which is why it was created.

The coupling constant should be computed to obtain correct adiabatic energies from diabatic ones, making limited DFT more useful. In the adiabatic representation, the two curves create an upper and lower curve, with the energy gap at qc being twice the electronic coupling constant H_{ab}, which is a significant coupling constant in nonadiabatic dynamics. DFT overestimates H_{ab}, which could lead to erroneous RobinDay class III compound assignment. The limited DFT methodology for calculating high-quality diabatic energies could also be used to forecast exact H_{ab} values. One of the difficulties is that constrained DFT techniques do not provide the proper wave function. H_{ab} is the union of two independent wave functions with no equivalent in static density-dependent observables. As a result, some estimates are required to extract H_{ab} from constrained DFT. We are now doing an active study on this topic, and the results will be released soon. H_{ab} can also be employed with restricted DFT to study the issue of degenerate charge transfer states. It can also tackle problems similar to those that the restricted open-shell Kohn-Sham approach can solve [45].

5.5 Scharber's model-electronic properties

They are using density functional theory and Scharber's model to forecast the power conversion efficiency of organic solar cells. The scientific community has long sought improved polymers with excellent power conversion efficiency. Because polymer synthesis and device production take time, a guide would help find the best polymers. They published a simple model in 2006 that outlines how to estimate the power conversion efficiency of bulk heterojunction solar cells, and they claimed that these devices could attain 10% power conversion efficiencies. To evaluate a polymer's photovoltaic potential, Scharber's model requires knowledge about energy levels. Commonly, cyclic voltammetry is used to obtain these energy levels after polymer production. Modern theoretical tools like density functional theory come into use. These technologies can theoretically predict polymer properties before they are made.

The DFT has been extensively used to develop, explain, and predict the features of present and future organic solar cells [91]. Even though the model predicts certain qualities like open-circuit voltage (V_{OC}) and short-circuit current density (J_{SC}), one may wonder if the model estimates some attributes more precisely than others when combined with density functional theory. The dependability of theoretical computations is critical for understanding and predicting device attributes. There have been extensive research on oligomers [92] and crystals [93], but few comparisons of computations on polymers with experimental evidence. These highest values for power conversion efficiency can be derived by integrating density functional theory determined attributes with Sharber's model.

5.5.1 Scharber's model

This is equivalent to the maximum power density output of the device divided by the total power density receiving from the Air Mass 1.5 solar spectrum [94], which is 1000 W/m^2. The device's power density comprises the open-circuit

voltage, short-circuit current density, and fill factor (FF). According to Scharber's model, the V_{OC} is connected to the difference between the acceptor's LUMO and the donor's HOMO. The V_{OC} is obtained by subtracting 0.3 eV from the energy level difference. This shift was discovered empirically and is linked to residual carrier binding energy and interface effects [95]. An integral of external quantum efficiency (EQE) multiplied by the number of photons from the Air Mass 1.5 sun spectrum at all frequencies. For energies below and above the donor's optical band gap (E_{opt}), the EQE is just a step function with a value of 0%. The fill factor is FF = 0.65 for all devices. Other EQE and FF assumptions can be made if desired. For example, the EQE could be determined by investigating the Kohn-Sham joint density of states, revealing the frequency-dependent absorption cross-section behavior. In this situation, the polymer layer is thick enough to absorb any photon over the optical band gap, and the film shape essentially limits the EQE. The following equations describe Scharber's mode.

$$PCE = \frac{V_{OC}J_{SC}FF}{1000W/m^2} \qquad (4)$$

$$LUMO_{donor} > LUMO_{acceptor} + 0.3eV \qquad (5)$$

$$eV_{OC} = LUMO_{acceptor} - LUMO_{donor} \qquad (6)$$

$$E_{opt} = LUMO_{donor} - HOMO_{donor} \qquad (7)$$

$$EQE(\omega) = 0.65 \times \Theta(\hbar\omega - E_{opt}) \qquad (8)$$

$$J_{SC} = \int EQE(\omega) \times \#photons_{AirMass1.5}(\omega)d\omega \qquad (9)$$

As seen in Eq. (5), this model implies a 0.3 eV energy difference between the donor and acceptor Lumos to enable effective charge transfer. This LUMO offset should not be confused with the 0.3 eV empirical shifts for Eq. (6). So E_{opt} = 0.6 eV is the maximum value for eV_{OC}.

5.6 Photoabsorption spectrum

Time-dependent DFT has surpassed all other methods for calculating organic compounds' excitation energies and optical characteristics in the last decade. Visual features like absorption spectra and optical band gap can be used to validate structures further. To better understand the electronic transitions of polymer monomers, used TD-DFT/CAMB3LYP/with varied basis set levels to perform quantum calculations on electronic absorption spectra in the gaseous phase and solvent. Aside from the bandgap, the computational prediction of whole spectrum excitation energies and cross-sections above the bandgap is equally crucial to solar cell efficiency. The excited electron tends to decay toward the conduction level (or the LUMO level) before being injected into the anode due to vibronic (molecular dyes) or photonic (solid dyes) contact with the environment, resulting in thermalization loss of the cell efficiency. The choice of time-dependent TD-DFT can be critical in accurately reproducing absorption, especially when using donor-acceptor dyes with charge-transfer excitations, as in the current study, where range corrected functionals become a viable option. The band maximum (λ_{max}) is an apparent essential feature of the absorption spectra.

These are significant for optical properties of polymers in polymer solar cell applications, ranging from TD-DFT methodologies to predicted absorption wavelengths (λ_{max}), oscillator strengths (f), and vertical excitation energies (E).

6. Concluding remarks

New materials have emerged as an appealing and profitable replacement to inorganic semiconductors due to the desire to manufacture more cost-effective electronic devices using simple manufacturing processes. Organic materials, such as conjugated polymers, tiny organic molecules, and self-assembling organic semiconductors, have recently piqued interest due to their ability to fabricate flexible, lightweight, semi-transparent, and large-area devices. As a result, DFT based computational computations have become a valuable method for investigating materials in OSC research. The relevance of DFT calculations in the knowledge of the structure-properties relationship in the design of new polymer solar cells has been highlighted in this paper. Furthermore, we discovered that DFT's improved power in understanding and forecasting features of polymer solar cells is caused by increased computational capacity and the emergence of robust and diverse computational methodologies. We have explored how theoretical calculations based on the KohnSham energy levels of density functional theory combined with Scharber's model can be utilized to locate viable photovoltaic polymers in this paper.

Within the generalized Kohn–Sham formalism that offered proper excitation energies, density functional theory and its time-dependent extensions made substantial progress along the range separated hybrid functionals. DFT has been effectively used to explain and predict molecular geometries, electronic structure, frontier molecular orbital (FMO) energy levels, absorption spectra, and intramolecular charge transfer for known conjugated organic compounds (ICT). These characteristics significantly impact the open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), charge separation at the donor/acceptor interface, and solar photon absorption.

Author details

Numbury Surendra Babu
Computational Quantum Chemistry Lab, Department of Chemistry, College of Natural and Mathematical Sciences, The University of Dodoma, Dodoma, Tanzania

*Address all correspondence to: nsbabusk@gmail.com

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