A computational chemistry approach to modelling conducting polymers in ionic liquids for next generation batteries

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Abstract

An overview of modern quantum chemical methods is presented followed by a discussion of their application in the field of conducting organic polymers (COPs), with a view towards modelling the cathodic half-cell of a poly(3,4-ethylenedioxythiophene) (PEDOT) cathode in an $AlCl_3$-1-ethyl-3-methylimidazolium chloride (EMImCl) ionic liquid electrolyte. The most popular combination of hybrid DFT functional and polarized moderate basis set has been broadly and successfully applied to COPs in the literature. However, in the presence of anions and intermolecular interactions, diffuse functions and dispersion corrections must also be included. A comprehensive specification of these elements appears well suited to the determination of many relevant parameters including molecular geometry, bandgap of oligomers and energies for systems including multiple chains and chloroaluminate anions. However, range-separated hybrid functionals may be more suitable for determining electron transport properties of very long chains. The clearest benefit of DFT to this system is the ability to visualize charge distribution and the interaction between charged PEDOT and the active species, which will help to explain the specific capacity, voltage and charge/discharge characteristics — insights that may help identify further improvements.
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1. Introduction

Computational chemistry has only really become practical in recent decades due to the proliferation of affordable, high-power computational resources, and the simultaneous development of theoretical methods that offer a favourable balance between accuracy and computational demand [1]. The ability to accurately simulate molecular behaviour provides powerful insight into material properties and reactions, allowing faster, cheaper, and lower risk development of materials for applications including semiconductors, alloys, coatings, catalysts and energy materials

such as photovoltaics [2]. These techniques are also ideally applied to the field of energy storage, where much of current progress focuses on developing better materials for batteries, supercapacitors, and fuel cells [3–6].

In the quest for next generation batteries that are sustainable, affordable, and power and energy dense, aluminium batteries are of great interest due to the abundance and high charge density of Al. However, finding electrolytes and cathodes which work with Al is challenging; Al cannot be directly stored in a cathode, and so $AlCl_4^-$ is stored in the cathode (e.g. graphite) during charge, to combine with Al from the anode on discharge to form $Al_2Cl_7^-$. One such system showing promise experimentally combines an Al anode with a PEDOT cathode in an $AlCl_3$-EMImCl ionic liquid electrolyte. PEDOT can be synthesized to have high discharge potential in the battery ($\sim$2 V) and long cycle life ($>$1000 cycles); it is characterized by a mix of faradaic and non-faradaic charge storage [7–11]. However, while Al deposition from $AlCl_3$-EMImCl [12] and conducting polymers including PEDOT [13] are both popular research topics, the behaviour of PEDOT as a cathode in an $AlCl_3$-EMImCl electrolyte has not been explored theoretically at all. This article delivers a brief background of quantum chemistry methods, then reviews the literature on modelling conducting polymers with the aim of highlighting the opportunity for exciting progress to be made in this area.

1.1. Schrödinger equation and wavefunction theory

The general (time-dependent) Schrödinger equation describes the quantum phenomena that determine the behaviour of the microscopic world [14], and indeed holds true for the macroscopic world as well (though macroscopic phenomena are more easily described, and their behaviour predicted, via classical mechanics) [15]. Clearly, an exact solution of the Schrödinger would predict the behaviour of a molecular system with complete accuracy. However, for all but the simplest systems, the Schrödinger cannot be solved exactly and approximations must be made.

The Schrödinger equation underlies all computational chemistry approaches. However, computational chemistry generally deals with a simplified version, which is based largely on classical mechanics and ignores relativistic effects — the time-independent non-relativistic Schrödinger equation, where Ψ is the wave function, H is the Hamiltonian operator and E is the system energy [16]:

$$\hat{H}|\psi\rangle = E|\psi\rangle \tag{1}$$

One precept of quantum mechanics is that a microscopic system can be characterized by a wave function which determines its physical characteristics. Each physically observable characteristic has an associated quantum mechanical operator, which when applied to the wave function, allows prediction of the value(s) of that characteristic. The Hamiltonian operator yields the total energy of the system and typically includes five terms — electron kinetic energy, nucleic kinetic energy, electronic attraction to the nuclei, interelectronic repulsion, and internuclear repulsion, with additional terms if the influence of external electric or magnetic fields, relativistic effects or spin–orbit coupling are included [15].

All computational chemistry approaches discussed here use the Born–Oppenheimer approximation. One of the difficulties in providing an exact solution to the Schrödinger equation is that the movement of every particle in a system is, in reality, dependent on every other particle. However, compared to the movement of nuclei, electronic relaxation occurs in an essentially negligible time. This allows separation of the two motions, so the computation of electronic energies is based on fixed nucleic positions, which significantly simplifies the wave function [17]. This key assumption also allows the conceptual existence and calculation of the potential energy surface, which can only exist for electrons in reference to stationary nuclei [15].

Relativistic quantum mechanical systems obey an important rule, which is that fermions such as electrons must change sign when their positions are exchanged. This means that no two electrons can have the same set of four quantum numbers — if they have the same principle, orbital angular momentum, and magnetic quantum numbers, they must have opposite spin. This is termed antisymmetry. Electrons can be either spin $^1/_2$ (α) or $-^1/_2$ (β). This rule is termed the Pauli Exclusion Principle [18]. The multiplicity of the system is a way of referring to its spin state. Multiplicity is given by $|2S| + 1$, where S is the number of α electrons * $^1/_2$ + the number of β electrons * $-^1/_2$, where S is the total spin of the unpaired electrons in the system, where each unpaired alpha electron is $^1/_2$ and each unpaired beta electron is $-^1/_2$. This gives a positive integer value with which to describe a system. A closed-shell system with only spin-paired electrons has a multiplicity of 1 and is referred to as a singlet; a single unpaired electron gives a multiplicity of 2 and is referred to as a doublet, a system with 3 unpaired electrons is a triplet, and so on [15]. A triplet is termed a 'high spin' state relative to a singlet, which is a 'low spin' state [19].

Although the wave function of a system can be used to accurately determine the system properties (up to the limit of the form of Schrödinger equation used), its form is not known. Therefore wavefunction theory (e.g. Hartree–Fock) and related semi-empirical methods begin by guessing the wavefunction. To construct the trial wavefunction, a combination of relatively convenient functions are used to approximate the actual wavefunction. The term 'basis set' describes this set of convenient functions [15], which are combined linearly, which simplifies the approach to finding the minima [16]. The initial guess is then optimized using the self-consistent field method (generate a set of spin orbitals, use them to generate an average field, form a new set of spin orbitals, and repeat until convergence), and then arranged into a single Slater determinant that is easily solved [15]. The variational principle, which states that an approximate wave function will always have too high an energy, is used to guide the optimization towards the minimal energy (and best) wavefunction [16].

1.2. Hartree–Fock and post-Hartree–Fock methods

Hartree–Fock (HF) begins by forming an approximate wavefunction, an approach common to all wavefunction methods [15]. If the basis set used to form the wavefunction was of infinite size, the HF approach could produce an exact solution to the wavefunction, termed the HF limit [16]. However, a critical assumption is made in expressing the HF wavefunction as a single Slater determinant, which is to account for same-spin electron correlation according to the Pauli exclusion principle, but exclude correlation between electrons of opposite spin [20,21]. This means HF always overestimates system energy, and the difference between the HF limit and the exact solution of the non-relativistic Schrödinger equation is called the electron correlation energy. Because electron correlation is a well-defined inaccuracy, one approach is to calculate it and therefore correct it directly — an area termed post-HF [15].

Lack of electron correlation causes a range of significant issues. Spin parallel electrons (e.g. the two valence electrons in a triplet state) particularly repel each other, so they are less screened by other electrons from the nucleus, causing the electron cloud to shrink. Although this increases the electron–electron interaction energy, this is not enough to offset the energy benefits from reducing the size of the electron cloud, and so the high spin state is favoured [19]. Accounting for spin correlation between electrons of opposite spin would find additional system relaxation from the pairing of electrons to fill a given subshell before filling the next highest one, leading to a greater probability of low spin states having lower energy.

HF also suffers from spin contamination, where some character of higher spin states is mixed into lower spin states. It arises from treating the α and β (up spin and down spin) electrons differently [15]. Using the restricted approach solves this problem by forcing α and β electrons to be treated the same way, but is unsuitable for open-shell molecules. Restricted open-shell Hartree–Fock (ROHF) models valence orbitals using the unrestricted, and core orbitals using the restricted approach, which effectively removes spin contamination for open shell systems [22]. The restricted approach also reduces computing power by about half, which is also useful for closed-shell DFT, which does not suffer from spin contamination [23]. Further issues include no dispersion (van de Waals) effects as these are caused by charge distributions induced by intermolecular electron correlation, an inability to calculate heats of formation whenever the number of electron pairs changes, and incorrect calculation of permanent charge distributions. Using a moderate (incomplete) basis set can introduce opposing errors that improve results [15].

In the form described here, Hartree–Fock is an *ab initio* (from first principles) method — no prior information is required about the molecular system being generated. While HF is undemanding for simple systems, it has poor scaling behaviour, with computing time scaling with N^4 where N is the number of basis functions [15].

1.2.1. Semi-empirical methods

Semi-empirical methods build on HF by including calibrated parameters designed to achieve two goals: account for electron correlation via parameterization and reduce computational time for large systems (computational time can scale with N^2 rather than N^4 as for HF) [15]. Earlier functionals included PM3, AM1, MNDO and CNDO, with newer types including OM1, OM2 and OM3 [24]. Semi-empirical methods can produce excellent results with the lowest possible computational resource, but only for systems similar to that for which they have been parameterized [25].

1.2.2. Post Hartree–Fock

Ab initio post HF methods introduce electron correlation calculations to HF. They include Moller–Plesset (MP), Coupled Cluster (CC), and configuration interaction (CI) methods. These methods significantly improve on HF, and can be accurate for predicting COP properties for small chains, but become very computationally expensive for longer chains [25], rendering them unattractive for complex systems consisting of multiple PEDOT chains, electrolyte molecules, and active species found in the Al-PEDOT battery system.

1.3. Density Functional Theory (DFT)

Kohn–Sham DFT differs from Hartree–Fock by providing an approach that accounts for every element in the non-relativistic Schrödinger, including electron correlation. It does this by generating an electron probability density rather than constructing a Hamiltonian, and the Kohn–Sham density matrix is subsequently assembled in a single Slater determinant as the Hamiltonian is for HF. To avoid the impossible-to-solve problem of accounting for every electron's interaction with every other electron, a fictitious non-interacting system is created in which every electron interacts with an effective potential. This can be expressed as a (relatively) easy to solve single Slater determinant, and the solution uses the SCF process just like Hartree–Fock, but in this case taking advantage of the fact that the non-interacting, fictitious system must have the same density as the real, interacting system for the system of interest. However, to achieve this, it combines the hardest elements of system, including electron correlation, the correction for the classical self-interaction energy, and the kinetic energy difference between the real and fictitious systems, into the exchange–correlation energy (ϵ_{xc}) term, for which it cannot provide an exact description. Therefore every DFT functional has some approximation to calculate this term, with varying degrees of success [26].

In contrast to HF, DFT provides an exact approach to the solving the non-relativistic time-independent Schrödinger, but an approximate solution [15]. Self-interaction error (SIE) is one of the main issues with DFT, resulting from the approximation for the exchange-energy correlation term. It occurs because each electron is modelled with an average potential — which the electron also contributes to. Therefore each electron is modelled as interacting with a fraction of itself, which is clearly unrealistic. One role of the approximate exchange–correlation functional is to remove this effect, which it does imperfectly [27].

The simplest (and original) DFT functional used the local density approximation (LDA) which stated that the kinetic energy of the electrons depended only on the electron density at a particular point (rather than its gradient). LDA functionals are now rarely used. Generalized gradient approximation functionals (GGA) improved on this by introducing a dependence on the density gradient, and meta-GGA functionals (m-GGA) also depend on the kinetic energy density at that point [28]. Examples include BLYP (a GGA functional) [29] and TPSS (a m-GGA functional) [30]. Becke developed the first widely used GGA exchange functional, which combines appropriate mathematical form for long range energy density with an empirical parameter optimized by fitting to known data for noble gas atoms He to Rn [31]. BLYP combines this with the GGA correlation functional of Lee, Yang and Parr [15].

DFT functionals can be improved (for many applications, but not all) by introducing some element of Hartree–Fock exact exchange energy [32]. This solves many problems with plain DFT and improves accuracy, and the B3LYP hybrid GGA functional (also known as an adiabatic connection method), which was invented in the early 2000s, is still the most popular functional today. B3LYP makes use of three empirical coefficients – a_0, a_X and a_C, which are fitted to experimental data. E_X^{exact} is the exact exchange energy, ΔE_X^{B88} is Becke's 1988 gradient correction (to the LSDA) for exchange, and ΔE_C^{PW91} is the 1991 gradient correction for correlation of Perdew and Wang [33].

$$E_{xc} = E_{xc}^{LSDA} + a_0 \left(E_X^{exact} - E_X^{LSDA} \right) + a_X \Delta E_X^{B88} + a_c \Delta E_C^{PW91} \tag{2}$$

The balance between accuracy and computational resource is very good and B3LYP is well accepted for an extremely wide range of problems. However, rigour demands that its use requires justification against alternate methods for particular problems, and the extreme sensitivity of COP electronic structures to changes in energy level demand a careful comparison with other forms of theory. A number of other methods based on one-parameter models have been suggested, which change the percentage of HF exchange in the functional (B1PW91, B1LYP, etc.), based on the tendency for HF errors to cancel favourably against GGA functional errors [15].

Generally speaking, DFT is slower than HF for a small molecule, but scales with N^3 rather than N^4 – so for large systems it becomes faster. DFT currently represents the best balance partly because of a degree of parameterization that allows good fits across a range of systems [15]. Plain, unrestricted DFT does not suffer from spin contamination [34], although hybrid DFT, due to the inclusion of some HF exact exchange, does to some extent [15].

1.4. Dispersion effects

Intermolecular electron correlation induces charges that cause mutual attraction between molecules, termed 'dispersion', 'London force' or 'attractive van de Waals' – a key force in determining intermolecular interactions. Dispersion is attractive, but is offset by the interaction of electron densities (exchange repulsion) when atoms are very close [15]. None of HF (only models exact exchange), KS-DFT (approximate DFT only models local electron correlation), hybrid DFT (combined issues of HF and KS-DFT [15]) or semiempirical methods account for dispersion effects. This has necessitated a significant research effort to produce additional corrections that can be included with these methods with the goal of reaching 1 kcal/mol accuracy. These are particularly required for non-covalent intermolecular interactions and are most frequently applied to DFT calculations [35].

Grimme et al. developed the D1, D2 [36] and D3 [37] approaches; D1 (2004) covered limited numbers of elements, while D2 (2006) is fully empirical based on the behaviour of each element. While computationally efficient, D2 neglects the influence of the molecular environment, but nevertheless its wide-ranging applicability made its use extremely widespread. D3 (2010) also accounts for the molecular environment, requires only the molecular geometry as input and is very computationally efficient, providing higher accuracy than D2. D3 has split into two variants, D3(0) and D3(BJ), the latter of which has Becke-Johnson damping and has superseded D3(0) for almost every application. Unlike other methods (Tkatchenko-Scheffler, vdW-WF) [35], D3(BJ) is available in popular modern software and appears to be the most appropriate dispersion correction to use in COP calculations. Its inclusion on DFT calculations on crystals and molecular complexes can reach energies with relative errors of around 5% [35].

1.5. Basis sets

Appropriate mathematical functions are required to model the atomic orbitals. Slater-type orbitals (STOs) have a radial decay of $e^{-\alpha r}$. They are very similar to hydrogenic atomic orbitals, but require iterative solution, which in practise makes them unusable for molecules with more than a few atoms. Boys therefore proposed Gaussian-type orbitals (GTOs) with radial decay $e^{-\alpha r^2}$, which allow analytical solution [38]. However they lack the cusp at the nucleus of STOs, and their amplitude reduces too fast with increasing distance from the nucleus — therefore they are used in linear combinations to approximate STO behaviour. Each GTO in these combinations has a coefficient and exponent. A series of contracted GTOs makes up a basis function; based on a trade study of computational resource and accuracy, a degree of contraction of three was chosen to form the STO-3G basis set — still used sometimes to provide preliminary results before moving on to more sophisticated basis sets [15].

To achieve better accuracy it is necessary to have more than one basis function (single-ζ) for each orbital type. A double-ζ basis set has two basis functions per orbital, the first having two GTOs and the second having one. This level is still in common use today. A further sophistication is to have three basis functions with a GTO each, termed triple-ζ [15]. To improve computational efficiency, one can treat the non-reactive core orbitals differently; they can have fewer basis functions than valence orbitals without sacrificing accuracy. Split-valence basis sets are built this way, and include Pople's 3-21G, 6-31G (split valence double-ζ) and 6-311G (split valence triple-ζ) [39]. The first number indicates the number of GTOs in the core orbital functions, and the valence orbitals are described after the hyphen, so for 6-311G, there are 3 GTOs in the contracted valence orbital function and 2 further complete basis functions (each 1 means a complete basis function). 6-31G is the next largest basis set after 3-21G that actually produces better results, negating the intermediate basis sets [15]. Alternatively to split-valence sets, there are also general contractions where all basis functions contain a single GTO, but with different coefficients for each function – these are optimized for electron correlation. Hence, these are called correlative-consistent polarized valence double-zeta (cc-pVDZ), triple-zeta (cc-pVTZ) or quadruple-zeta (cc-pVQZ) [40].

1.6. Diffuse functions

Highly excited electronic states, particularly those involved in intermolecular interactions and of anions, are often weakly bound. Most basis sets are not flexible enough to allow electrons to be far from the main electron density, causing serious inaccuracy. Diffuse functions are required in these instances, which are additional basis functions with small exponents (slow decay from nucleus). In Pople, adding a '+' onto the basis set name indicates an extra set

of s and p functions on heavy atoms, and '++' indicates additional s functions on H as well [41]. The cc-pVDZ and cc-pVTZ basis sets also do not contain diffuse functions by default; they are prefixed with 'aug' in order to include s and p diffuse functions [40,42]. Anything to do with an anion (including its formation), acidity calculations, and intermolecular interactions, all require diffuse functions to be included [41]. Therefore any simulation examining the interaction between PEDOT and its intercalant/dopant will require diffuse functions. Fig. 1 shows the Mulliken charge distribution on $AlCl_4^-$ with and without diffuse functions; the relative error is 14% for Cl and 31% for Al.
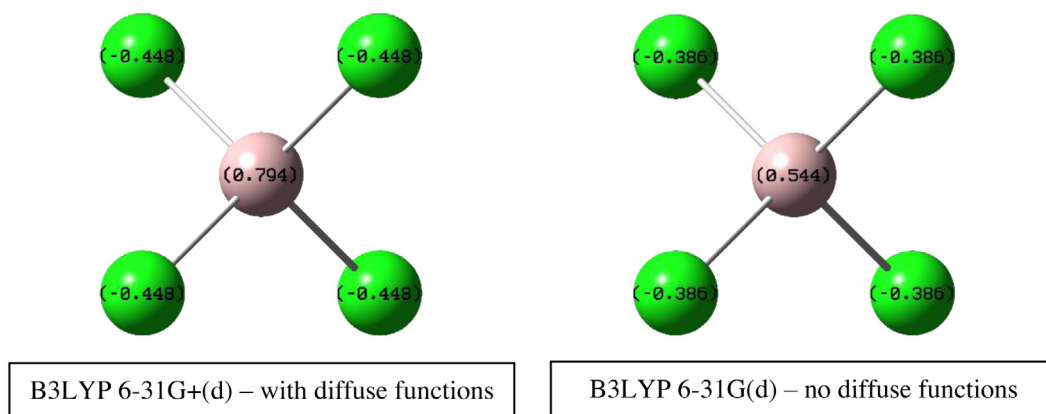

Fig. 1. $AlCl_4^-$ Mulliken Charge Distribution with and without diffuse functions, calculations done using Gaussian 09 [43].

1.7. Polarization functions

Because standard s and p functions are centred on atoms, they do not have the mathematical flexibility to handle more complex molecular orbitals. This can be addressed by adding a basis function for one orbital higher than the valence electrons. This is indicated for Pople basis set by * (d functions to polarize p functions) or ** (p functions on H and He as well). It is more modern to specify (d) or (d, p) respectively; 6-31G(d) and 6-31G* are equivalent, but the former is more specific which is helpful when using additional polarization functions [15]. The correlative-consistent basis sets (cc-PVDZ, cc-PVTZ etc.) already include polarization functions, with increasing numbers of functions with increasing size [44]. The use of polarization functions is practically default and 6-31G(d) is the most popular basis set [45]; the improvement of 6-31G(d,p) may be evaluated vs. computational time for a given system.

2. Applying computational chemistry to conducting polymers

Conducting polymers are π-conjugated chains with a carbon backbone, that when oxidized can conduct electricity as well as some metals [13]. Oxidation creates positive charges on the carbon backbone, which can be counterbalanced with anionic species stored near the positive charges [46]. Conducting polymers are of great interest in solar cells and fuel cells [47], as well as batteries [48]. In a next-generation PEDOT cathode, the properties of interest are the polymer's ability to store charge in the battery environment. This concerns oxidation level and doping level — how much can the polymer be oxidized relative to the number of polymer units present, and how many of these charges can be balanced by doping anions from the electrolyte? In the Al-PEDOT battery, the doping anions are $AlCl_4^-$ [11].

COPs are very geometrically sensitive to oxidation state and doping level, so very accurate predictions of geometries are required. Intermolecular forces, both between PEDOT chains and the doping anions, are also required to be modelled with great accuracy to calculate voltage behaviour, requiring accurate representation of electrons in highly excited states that may be a long way from and weakly bound to their nuclei. The energy change of PEDOT chains gaining and losing electrons during discharge/charge must be accurately predicted (electron affinity (EA) and ionization potential (IP) respectively) [20]. Finally, PEDOT undergoes morphological changes during charging (grains swell, merge and change stiffness with increased charge) [11]. Explaining this phenomenon directly may

prove impossible as a representative PEDOT grain is almost certainly too large to model using today's techniques and resources; however periodic boundary conditions may help extrapolate towards larger systems [25].

2.1. Bandgap

For metals, the fundamental energy gap, G, is zero — allowing conduction with no bandgap. However, for semiconductors, G is positive. For a neutral solid, G, although it is an excitation energy, is defined as the difference between the ionization energy and electron affinity [25]. KS theory for solids predicts a band structure with theoretical bandgap g as the energy required for one electron to travel from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Although G cannot be obtained from a single KS band-structure calculation, high-level approximations result in band gaps g equal to the fundamental gap G [20,26], though not all researchers agree that this is a scientifically rigorous approach [49]. In the case of COPs, predictions of band gap and polymer structure have been shown to converge towards experimental values (specifically in the case of B3LYP 6-31G(d)) as chain lengths approach 10 units [50] and reach a good accuracy when chain lengths reach or exceed 20 units, in the case that the modelling is in the gas phase and the experimental results in solid state [41,47].

Plain DFT performs badly at estimating bandgaps in semiconductors, due to the approximations of the exchange–correlation energy term, and especially with basic LDA functionals under predicts bandgaps by around 40% [51]. Hybrid DFT improves upon DFT for most systems, but still causes significant problems for larger systems due to the reintroduction of HF issues [26,50,52]. For molecules, hybrid DFT performs very well. However for longer chains or solids involving many molecules, a fixed amount of HF exchange causes inflexibility [53]; here, range-separation is a promising solution. These have tunable distances at which the percentage of HF exact exchange begins to increase, up to 100% at long distances; wB97XD is an example, and also includes dispersion and polarization effects — 22% HF exchange at close range, and 0.2 as a range-separation parameter, works well for all chain lengths of conjugated polymers [49].

It has been observed that different hybrid functionals predict a significant range of band gaps, possibly suggesting the unsuitability of these type of functionals [53]. Screened, range-separated hybrids such as HSE further improve on range-separation by screening the long-range exchange interactions, removing the issue of HF exact exchange at long-range [52]. Essentially, HF exchange is kept only for the short-range interactions [54]. Particularly, performance is improved for modelling solids (many molecules). HISS was developed as a middle-range exchange–correlation hybrid that outperforms screened hybrids for prediction of bandgaps in semiconductors, both at the molecular and solid scale [52]. However, it cannot be ignored that several studies have found that the computationally efficient B3LYP 6-31G(d) level of theory gives good results for bandgap in conducting polymers, better than various other methods including HF, MP2 and even wB97XD [20,41,50,55–57], due in part to favourable error cancellation between functional and basis set. The benefits persist in the presence of doping anions [50].

The properties for single molecules (gas phase) and solid state require different setups, with solid state requiring a cluster of oligomers to assess the properties [20]. For clusters, dispersion effects must be included due to intermolecular forces — wB97XD functional includes these effects but B3LYP does not. The solid state electronic polarization energy, in the closely related field of materials used in the organic solar cells, influences the charge transfer excitations; for this, screened, optimally tuned (OT) range-separated hybrid functionals have been shown to give correct predictions of transport gap renormalization, over and above non-screened functionals [58]. Gas phase results on single molecules or very small systems will over predict the charge transfer energies because electronic polarization is not accounted for, by which attractions between the molecules are created by the polarized charges on those molecules. A polarizable continuum model (PCM) can be used to recreate this effect [59].

2.2. Geometry

Computational chemistry is commonly used for finding the 'optimized' geometry of molecules — the one having the lowest energy state. The ability to calculate and visualize an optimized molecule provides insight into characteristics such as reaction behaviour. However, an equilibrium mixture of a substance will include molecules over a range of energies at a finite temperature, and as such, a range of different geometries will exist. A potential energy surface (PES) is a hypersurface that describes all possible geometries of a molecule, with the various low energy points on the PES reflecting the most likely geometries to be found, and the lowest energy routes

between them describing the shapes encountered during transition from one local minimum energy state to another. Some kind of statistical averaging must be applied to the PES to establish a good comparison with experimental measurements [15].

Despite their now widespread use, the electronic structure of COPs is not well understood [20,50,60]. While the neutral equilibrium geometry is straightforward, charged chains of COPs have a complex charge distribution pattern, characterized by complex partial charge structures and localized changes in bond lengths. A localized charge on a polymer chain is termed a polaron; when two polarons overlap, a bipolaron is formed. The bipolaron model has retained popularity for years as a means of explaining experimental results, and states that it is energetically preferable for two like charges to co-locate due to structural relaxations in the chain [60]; however, modern DFT methods are repeatedly demonstrating that two polarons will only overlap if there is not room in the chain for them to separate, as demonstrated by plain DFT, hybrid DFT, and range-separated functionals. Of course, electron interaction, which dominates COP charge behaviour, remains part of the non-exact exchange–correlation energy approximation in modern DFT [20]. What is more, the problem of computing accurate geometries is particularly significant for COPs because large structural changes occur as a result of relatively small energy differences.

Hybrid DFT is a justifiably popular choice for optimizing geometries in both molecules and solids and calculating ground-state energies and energy differences between different stable geometries [26]. Several papers use B3LYP 6-31G(d) without further justification to optimize molecular geometries of conducting polymers and other organic molecules, demonstrating its widespread acceptance and good performance [41,47,58].

2.3. Partial charge

SIE is a particular concern for conjugated polymers, as they fall into the category of systems having fractional charge. The SIE causes over predictions of charge delocalization and under predictions of system energy [61]. The presence of HF exchange has an opposing effect due to the lack of electron correlation so hybrid functionals experience favourable cancellation [15]; however they do not error-cancel perfectly [61]. SIE also causes too-high binding energy due to overpolarized charge transfer interactions, and logically, also causes chemical reaction barriers to be too low, and over predicts molecular conductance. The functionals B05 and MCY were developed to eliminate the SIE by using 100% exact exchange, and are free of SIE for one-electron systems. However they do not solve the problem for many-electron SIE — no functionals have yet been developed that satisfy this demand [62].

Partial charges cannot be determined experimentally [15]; computational chemistry software allows the visualization of the charge distributed over each atom in the molecule, and hence provides insight into the electronic structure and the probable reaction behaviour of the molecules. While DFT is affected by SIE, other methods are worse for calculating partial charges; HF theory predicts significantly over-delocalized charge carriers and should be avoided for π-conjugated systems (spin contamination and electron correlation issues) and RO semi-empirical methods do perform significantly better, but are not as flexible as DFT [20]. Plain DFT also has issues due to a lack of long-range electron correlation [61]. Hybrid DFT combines these approaches and gives reasonably good charge distribution, but again, longer chains benefit from range-separated or screened RS functionals [20].

3. Conclusion

A review of modern quantum chemistry methods, and a discussion of their application to COPs, has been presented, demonstrating the applicability of computational chemistry to the task of accelerating the development of batteries with next generation conducting polymer cathodes. In conclusion, hybrid DFT is an appropriate tool with which to study COPs, with B3LYP 6-31G(d) used in the majority of studies reviewed [20,41,47,50,55–58]. However, the bandgap of long oligomers (>20 units) has been shown by some studies to be better predicted by range-separated functionals, i.e. wB97XD. Overall, both work well across a range of COPs. Plain DFT is unsuitable as it does not adequately represent behaviour at longer chain lengths [20,47]. Chain lengths must be long enough (at least 20 units) to represent the polymer effects. The lack of electron correlation rules out HF. More expensive correlated wave-function methods and coupled–cluster theory have too high computational cost in the context of chains of more than a few polymer units, let alone any attempt to model solids [20]. Polarization functions should always be included. It is necessary to use diffuse functions and dispersion corrections when modelling intermolecular interactions, including between $AlCl_4{}^-$ and PEDOT. Anionic species particularly require diffuse functions [15], while dispersion corrections such as Grimme's D3 [35] can be easily included in popular software codes without significant additional computational expense.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Ben Craig: Writing - original draft. **Chris-Kriton Skylaris:** Writing - review & editing, Supervision. **Theresa Schoetz:** Writing - review & editing. **Carlos Ponce de León:** Writing - review & editing, Supervision.

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