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Predictive DFT-Based Approaches to Charge and Spin Transport in Single-Molecule Junctions and Two-Dimensional Materials: Successes and Challenges

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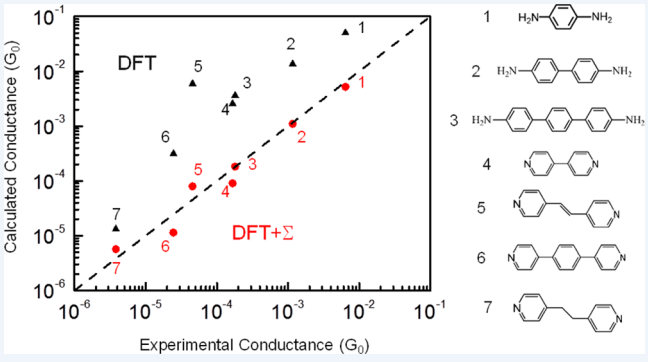
CONSPECTUS: The emerging field of flexible electronics based on organics and two-dimensional (2D) materials relies on a fundamental understanding of charge and spin transport at the molecular and nanoscale. It is desirable to make predictions and shine light on unexplained experimental phenomena independently of experimentally derived parameters. Indeed, density functional theory (DFT), the workhorse of first-principles approaches, has been used extensively to model charge/spin transport at the nanoscale. However, DFT is essentially a ground state theory that simply guarantees correct total energies given the correct charge density, while charge/spin transport is a nonequilibrium phenomenon involving the scattering of quasiparticles.



In this Account, we critically assess the validity and applicability of DFT to predict charge/spin transport at the nanoscale. We also describe a DFT-based approach, DFT+Σ, which incorporates corrections to Kohn–Sham energy levels based on many-electron calculations. We focus on single-molecule junctions and then discuss how the important considerations for DFT descriptions of transport can differ in 2D materials. We conclude that when used appropriately, DFT and DFT-based approaches can play an important role in making predictions and gaining insight into transport in these materials. Specifically, we shall focus on the low-bias quasi-equilibrium regime, which is also experimentally most relevant for single-molecule junctions.

The next question is how well can the scattering of DFT Kohn–Sham particles approximate the scattering of true quasiparticles in the junction? Quasiparticles are electrons (holes) that are surrounded by a constantly changing cloud of holes (electrons), but Kohn–Sham particles have no physical significance. However, Kohn–Sham particles can often be used as a *qualitative* approximation to quasiparticles. The errors in standard DFT descriptions of transport arise primarily from errors in the Kohn–Sham energy levels (self-energy errors). These errors are small in the strong-coupling regime where the molecular levels are significantly broadened at the Fermi level but are large in the coherent off-resonant tunneling regime where DFT overestimates conductance by orders of magnitude. The DFT+Σ approach uses a physically motivated, parameter free estimate of the self-energy corrections to correct the energy levels in DFT, giving conductance in *quantitative* agreement with experiment for a large *but nonexhaustive* class of single-molecule junctions. In 2D materials, the self-energy error is relatively small, and critical issues stem instead from the large length scales in experiments, which make it necessary to consider band-bending within the 2D material, as well as scattering due to electron–phonon interactions, spin-flip interactions, defects, etc.

1. INTRODUCTION

The past decade has witnessed revolutionary increases in the packing density of integrated circuits. As we approach the limits of Moore's law, technical challenges faced in further miniaturization must be overcome by a paradigm shift in materials innovation and by a fundamental understanding of charge and spin transport at the nanoscale. Rapid experimental advancements have led to the emergence of novel functionalities in materials such as single molecules or 2D materials, for example, graphene and MoS_2.

This emerging field opens up many opportunities for theory. Theoretical studies of charge and spin transport make use of phenomenological modeling and first-principles calculations such as density functional theory (DFT), and the impact of DFT on charge and spin transport can be seen from the exponentially increasing number of such publications and citations (Figure 1).

This Account aims to discuss specific roles and challenges for DFT and DFT-based approaches in the field of nanoscale

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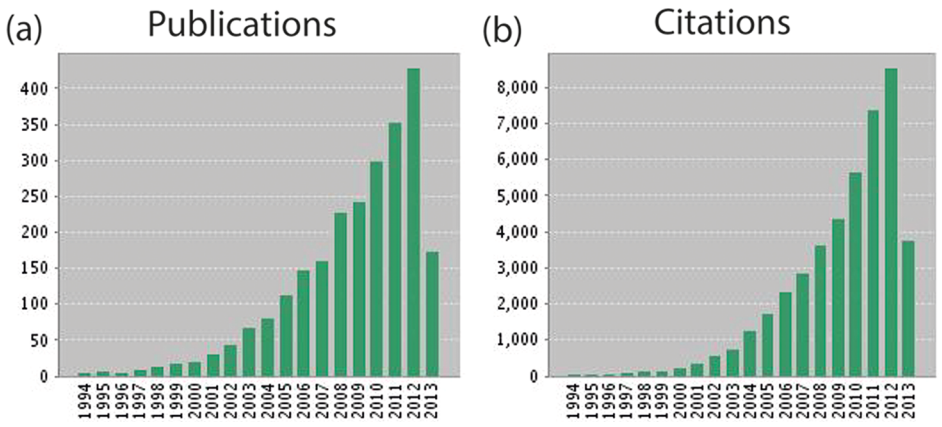

Figure 1. Number of (a) publications and (b) citations related to DFT studies of charge and spin transport (ISI Web of Science, July 2013).

charge and spin transport. We will focus on single-molecule junctions and discuss concepts, limitations and applications of the DFT+Σ approach,[1−6] which is motivated by many-electron GW calculations.[7−9] We conclude with a discussion of how critical issues for transport differ between 2D materials and single-molecule junctions.

2. BASIC CONCEPTS: CHARGE AND SPIN TRANSPORT IN THE SINGLE-PARTICLE PICTURE

2.1. DFT Kohn−Sham Particles versus Quasiparticles

One key concept in the DFT Kohn−Sham approach is the *single-particle picture*. The single-particle picture dates back to Landau who introduced the concept of weakly interacting *quasiparticles* as an alternative to many-electron wave functions. The quasiparticles in charge transport are "dressed" electrons, or electrons surrounded by a dynamical cloud of holes and electrons. Importantly, the weak interactions between quasiparticles make them amenable to perturbation theory, such as the GW approximation.[7,8]

While total ground state energies in DFT are governed by the Hohenberg−Kohn theorems, Kohn−Sham eigenenergies are only Lagrange multipliers with no physical significance. Fortunately, these eigenvalues often give a *qualitative* picture of the quasiparticle energy levels or band structure in the system. However, HOMO−LUMO gaps in molecules are typically underestimated by several electronvolts.[9]

2.2. Charge and Spin Transport

Most undergraduate texts introduce scattering using the concept of free electrons encountering one-dimensional potential barriers. In real systems, one thinks of quasiparticles from electrodes tunneling through potential barriers creating a current. These quasiparticles carry spin, which is conserved in the absence of spin−orbit coupling.

Within this single-particle picture of transport, one can include other scattering mechanisms present in experiments. Electron−electron scattering is typically suppressed at the Fermi level due to the Pauli exclusion principle and thus may be ignored. However, electron−phonon coupling can sometimes be significant, especially for long molecules or large scale devices and as part of reorganization energies in Marcus' theory of electron transfer between molecules.[10] Another important scattering mechanism for spin transport is spin-flip scattering due to impurities, which can reduce spin diffusion lengths.

The concept of quasiparticles enters explicitly into the well-established Landauer formalism for charge transport. Nonequilibrium electron transport involves open boundary conditions at the electrodes, and this is treated within the Landauer formalism using either scattering state approaches or nonequilibrium Green's functions.[11] Based on these calculations, the transmission matrix $\mathbf{t}$ can be obtained, and the current $I_{\uparrow,\downarrow}$ for spin up and spin down electrons, under an applied potential bias V, is given by

$$I_{\uparrow,\downarrow} = \frac{e}{h}\int_{E_F-eV/2}^{E_F+eV/2} \tau_{\uparrow,\downarrow}(E)\,\mathrm{d}E$$

where the transmission spectrum τ is given by $\mathrm{Tr}(\mathbf{t}^{\dagger}\mathbf{t})$.

The conductance G is defined as

$$G_{\uparrow,\downarrow} = \left.\frac{\mathrm{d}I_{\uparrow,\downarrow}}{\mathrm{d}V}\right|_{E_F} = \frac{e^2}{h}\tau_{\uparrow,\downarrow}(E_F)$$

3. DFT DESCRIPTION OF CHARGE TRANSPORT IN SINGLE-MOLECULE JUNCTIONS: SUCCESSES AND CHALLENGES

3.1. Overview

Single-molecule junctions are junctions in which a single molecule is attached to two metallic leads. Previously, molecular transistors having large on−off ratios have been realized experimentally for nanoscale electronics applications.[12,13] The field of single-molecule electronics/spintronics is complementary to that of organic electronics/spintronics, where the organic/metal interface is crucially important to reproducibility.[14] A better understanding of charge and spin transport at the organic/metal interface is required, and single-molecule junctions provide the simplest platform for such systematic studies. Furthermore, single-molecule junctions are a miniature laboratory to explore electron transport at the nanoscale, providing insights into quantum transport phenomena.[15]

When a molecule is bonded to the electrodes, its discrete energy levels shift and broaden (Figure 2). Electron transport through a single-molecule junction depends critically on (1) the energy barrier, E_{mol}, given by the energy difference between the frontier levels of the molecule (HOMO/LUMO) and the Fermi level E_F in the electrodes and (2) the coupling strength, Γ, between the molecular state and the electrodes. It is instructive to classify charge transport across single-molecule junctions into different regimes according to Γ (Figure 3). For

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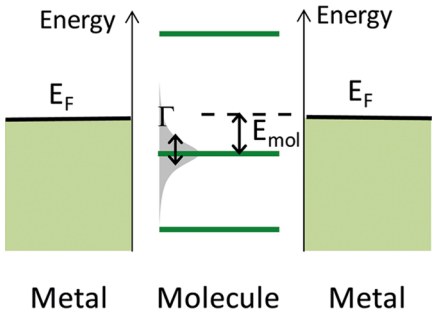

Figure 2. Energy level diagram for a single-molecule junction. Here, the frontier level is the HOMO. The energy barrier is E_{mol}, and the metal-induced broadening of the HOMO is illustrated, with a broadening width of Γ.

very large Γ, for example, H_2–Pt junctions,[16,17] the discrete levels are significantly broadened and coherent resonant transport occurs. For very small Γ, the lifetime of electrons on the molecule becomes longer, leading to incoherent transport and effects like Coulomb blockade, electron hopping, and the Kondo effect.[12,18] Between these two extremes, coherent, off-resonant tunneling occurs. Inelastic effects are typically negligible at zero bias; however when the bias increases to the energy scale of vibrations in the junction, inelastic tunneling can occur due to electron–phonon coupling.[19−22]

The electrode–molecule coupling strength determines whether standard DFT implementations of the Landauer formalism can properly describe charge transport. Resonant transport can be quite accurately described by DFT (Figure 3).[16,17] However, standard DFT implementations typically severely overestimate conductance in the off-resonant coherent tunneling regime.[1,23−27] A self-energy-corrected DFT-based approach, DFT+Σ, can predict conductance values in good agreement with experiment for some classes of junctions in the off-resonant tunneling regime.[6] However, the approach is currently restricted to single-molecule junctions in which the molecule remains intact from the gas phase, and in which the coupling is weak enough so that there is negligible mixing of molecular states compared with the gas phase. A predictive DFT-based treatment for off-resonant tunneling is still elusive for molecules whose bonds break upon binding to the electrodes, such as in the thiol–Au junctions.

In section 3.2, we discuss in more detail the DFT and DFT +Σ approaches for describing *coherent off-resonant* charge transport through single-molecule junctions. Inelastic effects relevant to the hopping regime can be included on top of standard DFT–Landauer implementations, and we refer the reader to the many great works in this field.[19−22] In section 3.3, we describe how the inclusion of spin poses additional challenges.

3.2. Coherent Off-Resonant Charge Transport through Single-Molecule Junctions: DFT and DFT+Σ

An accurate description of transport requires a good, representative description of the atomic and electronic structure of the junction. This is especially challenging for single-molecule junctions where conductance can be very sensitive to contact geometry.[23,27] Strain and finite temperature allow the system to access many different possible configurations, so that calculations on single-molecule junctions should include a representative number of reasonable model geometries.

The transmission probability for free electrons with mass m and energy E tunneling through a one-dimensional rectangular potential barrier V ($V > E$) is given approximately by $T \approx \exp(-2\kappa L)$, where L is the length of the barrier and $\kappa = (2m(V - E))^{1/2}/\hbar$. Off-resonant tunneling in single-molecule junctions can be understood in terms of quasiparticles scattering off the potential barrier in the junction. A predictive theory for transport in single-molecule junctions thus relies on an accurate prediction of the energy barrier E_{mol}.

The two requirements of an accurate description of E_{mol} and a representative sampling of junction geometries pose orthogonal difficulties, because E_{mol} is determined by quasiparticle level alignments that can only be predicted reliably using computationally demanding many-electron

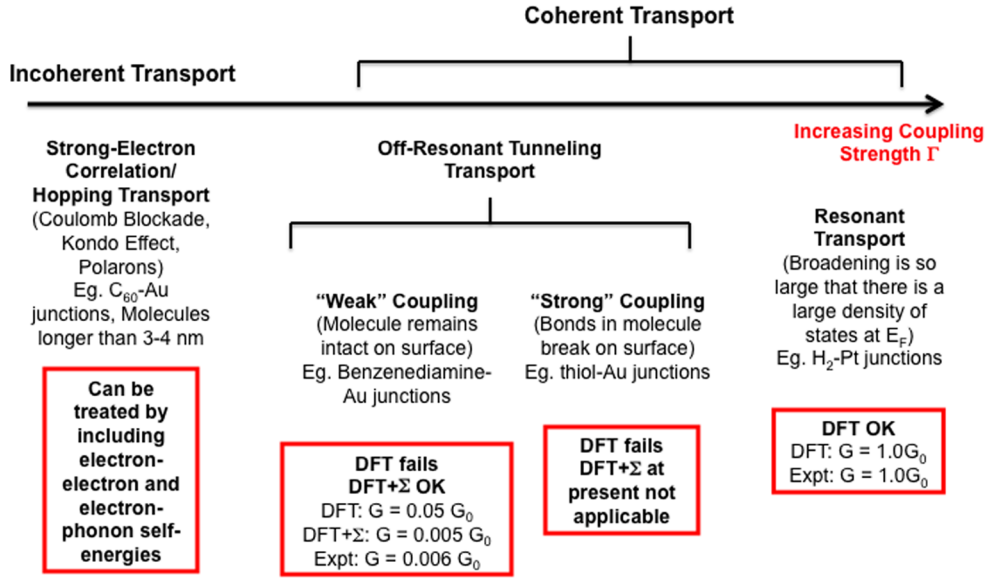

Figure 3. Different regimes of transport in single-molecule junctions. DFT+Σ refers to the approach described in section 3.2. Values for G come from refs 2 and 17.

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approaches such as the GW approximation.[7,8] These calculations are especially challenging for inhomogeneous interfaces, where absolute convergence for the energy levels of each constituent part is required.[28] Time-dependent current-density functional theory (TDCDFT) is another DFT-based framework for studying nonequilibrium electron transport. Conductances of prototypical systems have been studied and a dynamical exchange−correlation correction to the conductance has been identified.[29−31] However, issues such as the lack of nonlocal character in available exchange−correlation functionals still limit its applicability. Since Kohn−Sham DFT is the most tractable first-principles approach, most first-principles approaches to charge transport rely on a Landauer formalism with quasiparticles replaced by the fictitious Kohn−Sham particles in DFT.[24,32−38] In practice, since single-molecule junctions are usually mechanically unstable under large biases, we are mostly concerned with the quasi-equilibrium problem (current under small biases). Yet, even under quasi-equilibrium conditions, other fundamental issues remain. As discussed in section 2.1, the Kohn−Sham single particle energies have no quantitative significance. There is only one exception: if the exact exchange−correlation functional is known, Koopmans' theorem states that the energy of the highest occupied Kohn−Sham state gives the ionization potential for a gas-phase molecule. However, nonlocal correlation changes the level alignment in the junction,[9,39,40] and the exact exchange−correlation functional is unknown.

The most commonly used local and semilocal approximations to the exchange−correlation functional in DFT significantly underestimate the HOMO−LUMO gap in gas phase molecules. The energy barrier, E_{mol}, is thus significantly underestimated, usually by several electronvolts.[1] Since conductance depends approximately exponentially on $(E_{mol})^{1/2}$ in the one-dimensional rectangular barrier model, it is not surprising that this standard first-principles approach typically overestimates the conductance in single-molecule junctions, by orders of magnitude.[1,23−27] Even qualitative conductance trends can be wrongly predicted in the standard DFT−Landauer approach, for example, if the frontier levels in two distinct systems have similar energy levels but very different broadening Γ.[6]

To better estimate E_{mol}, several groups have used the DFT−Landauer framework with self-interaction corrections,[41] hybrid exchange−correlation functionals,[42] and optimized effective potentials.[38] These approaches have proven to be useful in practice; however, the quantitative prediction of E_{mol} would ultimately rely on a many-electron approach instead of DFT. In particular, many of the DFT methods have been optimized to reproduce gas phase ionization potentials or HOMO−LUMO gaps, while missing the long-range correlation effects from the electrodes (such as image charge effects).[9,39,40] For prototypical small molecules such as benzene-diamine, image charge effects can correct E_{mol} by about 1 eV.[1]

An alternative approach, called DFT+Σ, was developed by Quek and Neaton et al. for incorporating many-electron effects in a DFT-based calculation without the computational cost of many-electron methods.[1−4,6,43,44] The essential idea is to use mean-field DFT to obtain the charge density of the system, while solving for scattering states using a modified Hamiltonian, with an additional self-energy correction operator Σ that corrects the energy barrier in the junction. (The self-energy is defined as the difference between the true quasiparticle energy and the corresponding DFT Kohn−Sham eigenvalue.) Thus, we have

$$H(n_{DFT}) \rightarrow H(n_{DFT}) + \hat{\Sigma}$$

where

$$\hat{\Sigma} = \sum_n \Sigma_n |\psi_n^{mol}\rangle\langle\psi_n^{mol}|$$

$|\psi_n^{mol}\rangle$ denotes a gas-phase molecular orbital and $\{\Sigma_n\}$ are the self-energy corrections to the DFT values for each level. The DFT charge density, n_{DFT}, is used in this Hamiltonian, because DFT in general should give a reasonable charge density (no theoretical basis exists for updating the density based on the imposed self-energy corrections for DFT+Σ).

The success of DFT+Σ relies on a physically motivated, parameter-free estimate for the self-energy correction in the junction, developed based on many-electron GW calculations.[9] This estimate splits the self-energy correction Σ into two parts: (1) the self-energy correction already present in the gas-phase molecule, Σ_{local}, and (2) the additional self-energy correction that comes from the molecule bonding to the electrodes, $\Sigma_{nonlocal}$.[1−4,6,43,44] Σ_{local} arises from the fact that even in the gas-phase, the Kohn−Sham eigenvalues are not the true quasiparticle energies. To estimate $\Sigma_{nonlocal}$, it is helpful to understand what happens when a molecule binds to a metal surface. We shall consider the case where bonding is weak enough so that there is no mixing of molecular states when the molecule binds to the surface. As shown in Figure 4, charge

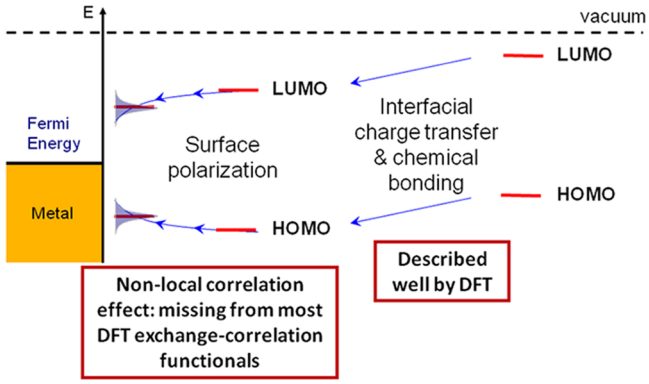

Figure 4. Changes in the frontier molecular levels for a molecule approaching a metal surface. We assume here that the molecular levels are not mixed by binding to the metal surface.

transfer and chemical bonding tend to shift the molecular levels down compared with the gas phase. Effects of charge transfer and chemical bonding are quite well captured within DFT. However, in addition to these changes, there are also nonlocal, possibly dynamical, effects arising from the metal surface, which renormalize the molecular levels.[9,45,46] In general, if the frontier molecular levels have negligible overlap with the Fermi level, dynamical effects can be neglected.[9,45,46]

Using GW calculations for benzene physisorbed on graphite, Neaton et al. showed that, assuming the polarizability of the molecule is negligible, $\Sigma_{nonlocal}$ equals exactly the static image charge energy term.[9] Physically, the image charge term can be understood from noting that the HOMO (LUMO) level relative to vacuum corresponds to how much energy it takes to remove (add) an electron from (to) the molecule. When an electron (hole) is added to the physisorbed molecule, the free

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electrons in the metal screen this effect by effectively creating an image hole (electron) in the metal. This screening effect stabilizes the added charge, making it easier to add an electron (hole), which in turn lowers the LUMO and raises the HOMO (Figure 4). Since the effective potential within ground-state DFT does not contain information about the added electron or hole, the image charge effect is completely missing from DFT.[9,39] Therefore, for molecules physisorbed on metal surfaces, the total self-energy correction would consist of (1) the self-energy correction in the gas phase and (2) the image-charge energy term.[9] Applying this correction to benzene-diamine molecules on flat Au(111) surfaces also gives excellent agreement with high-resolution photoemission spectroscopy.[43]

Single-molecule junctions are not physisorbed systems. However, if one can expand the wave function of the molecule–electrode system in terms of an orthonormal basis of gas-phase molecular wave functions and metal wave functions, we can show that under the same assumptions of negligible charge transfer (molecule levels far from E_F) and negligible polarizability of the molecule, $\Sigma_{nonlocal}$ is also approximately equal to the image charge term.[6] Thus, for such chemisorbed systems, which include prototypical benzene-diamine–Au and bipyridine–Au junctions, we can apply the DFT+Σ approach, with the same self-energy correction given by the sum of (1) the gas-phase self-energy and (2) the image-charge energy term. In practice, Σ_{local} may be computed by comparing the gas-phase Kohn–Sham HOMO (LUMO) levels to the ionization potential (electron affinity), which can be computed from DFT by using total energy differences between neutral and charged gas-phase molecules.[47] Generally, we find that the magnitudes of the gas-phase Σ_{local} and the image charge $\Sigma_{nonlocal}$ are ∼2–3 and ∼0.7–1.5 eV, respectively.[1−4,6,43,44]

The DFT+Σ conductance values for different amine–Au and pyridine–Au single-molecule junctions show significant improvement over DFT results, and excellent agreement with experiment (Figure 5).[1−4,6] Using this approach, we have also

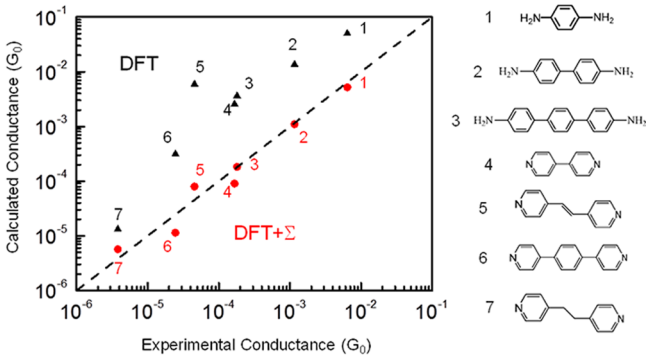

Figure 5. Comparison of conductances computed by DFT (black triangles) and DFT+Σ (red circles) to experimental measurements on a log–log scale. The conductances are computed for a geometry in which the molecule (1–7) is oriented vertically in a Au junction, with each N bonded to the atop sites of Au trimers (groups of three Au atoms) on Au(111) surfaces. Data obtained from refs 2, 3, 50, and 51.

predicted quantitative conductance trends,[2] the thermopower of single-molecule junctions,[4] as well as deciphered complex structure–conductance relationships[3] by sampling a large number of different geometries. The DFT+Σ approach has also been implemented by other groups[48,49] and has recently been extended to predict current–voltage characteristics in single-molecule junctions,[44] with good agreement with experiment.[44,48,49]

To conclude, we note that many groups have successfully used DFT transport methods to achieve a qualitative understanding of conductance in single-molecule junctions, especially with the help of nonlocal functionals or self-interaction correction methods.[38,41,42] However, sometimes DFT fails to make correct qualitative predictions.[6] The DFT+Σ approach described here is an alternative approach that relies on many-electron formalisms giving accurate, physically meaningful, quasiparticle energy barriers.[8,9,52] This approach predicts conductance and low bias $I-V$ characteristics in good *quantitative* agreement with experiment, in the off-resonant, coherent tunneling regime, where molecular levels are far from the metal E_F. The method is currently restricted to single-molecule junctions in which the molecule remains intact upon adsorption in the junction, a restriction which excludes the most commonly accepted model for the widely studied thiol–Au junctions, in which the molecular S–H bond is broken upon reaction with Au.[53] Because thiols remain the link group of choice in organic electronic studies of self-assembled monolayers,[54] a quantitative theoretical understanding of charge transport through single-molecule thiol–Au junctions is still an important goal our group is currently working to attain.

3.3. Coherent Spin Transport through Single-Molecule Junctions: DFT and DFT+Σ

Spin transport in single-molecule junctions is intrinsically interesting because it is one manifestation of quantum mechanical properties in charge transport. Magnetic molecules interacting with metallic electrodes can give rise to the Kondo effect, while nonmagnetic molecules with magnetic electrodes are of interest in understanding magnetoresistance in organic spin-valve structures, the latter having potential applications in cheap, flexible next generation data storage. DFT cannot describe the many-electron Kondo effect. However, DFT calculations[55−58] have provided some of the first insights into spin injection into single molecules, a phenomenon that is of immense importance in organic spintronics applications. Indeed, the molecule–metal interface is thought to be key to governing the sign (and magnitude) of magnetoresistance in organic spintronics systems.[14,59] While the negative magnetoresistance in LSMO/Alq_3/Co devices was once thought to be widely reproducible,[60] recent experiments measured positive magnetoresistance in these systems.[14] Indeed, DFT predicts that the sign of the magnetoresistance can change by introducing asymmetry or strain in the widely studied thiol–Ni model junction.[61,62]

If a molecule with a small HOMO/LUMO gap is directly bound to the metal electrode (e.g., phthalocyanines between cobalt electrodes[63]), transport is close to the resonant regime and the error in DFT approaches to transport is relatively small. However, for off-resonant tunneling, DFT poses the same problems in spin transport as in charge transport. We have recently used the DFT+Σ approach to investigate spin transport through single-molecule spin-valve junctions. The objective of our study was to search for electrodes and link groups that could give reproducible magnetoresistance; the discovery that amine–Au link groups could give reproducible conductance was a key step toward recent advancements in single-molecule charge transport; likewise, a systematic understanding of spin transport through single-molecule junctions

must start with the discovery of similar link groups for spin transport.

Motivated by the success of amine−Au link groups in molecular electronics, and the excellent lattice match between Au and Fe, we computed the magnetoresistance in Fe−Au−benzenediamine−Au−Fe single-molecule junctions.[5] We found that the Au layers allow only states with sp character to tunnel into the molecule; the flexible amine−Au links then result in a magnetoresistance that is fairly independent of the details of the amine−Au binding geometry for a given Au thickness. The magnetoresistance does demonstrate a Au thickness dependence, but its sign remains robust (positive) provided the number of Au layers is the same on both sides of the junction. This is a key step to data storage applications, because data is read according to the sign of the magnetoresistance. Since the number of Au layers on Fe surfaces and nanoparticles can now be controlled,[64] amine−Au links can provide a route toward robust magnetoresistance in molecular spintronics.[5]

Compared with non-spin-polarized transport, adding spin brings the following complications. First, for typical magnetic electrodes, the d electrons accumulate at the magnetic/nonmagnetic interface, forming interface states with d character. Such interface states result in hot spots in the two-dimensional Brillouin zone (2DBZ), exhibiting resonant transmission. These hot spots have been widely discussed in the literature,[57,58,65] and our DFT+Σ calculations show that the hot spots correspond specifically to k points with states that not only have d character, but also sp character, which allows the states to transmit into the nonmagnetic region.[5] Furthermore, sp states in the Au layers also form quantum well states, which have a major impact on spin-dependent tunneling probabilities.[5] Finally, we also note that the hot spots make it necessary to sample the 2DBZ extensively, significantly increasing the computational expense.

Moving forward, molecular spintronics is an emerging field in which DFT and DFT+Σ can play a major role in guiding experimentalists, such as in the design of junctions with new functionalities[66,67] or in obtaining better reproducibility to pave the way for more systematic studies.[5] Our DFT+Σ calculations suggest that better reproducibility can be obtained by using some of the successful link groups in molecular electronics. Furthermore, it is likely that using magnetism from sp states (e.g., in carbon-based materials) instead of d states could circumvent some of the problems highlighted above. Specifically, besides large magnetoresistance in zigzag graphene nanoribbons,[68] we have also recently predicted using DFT that armchair graphene nanoribbons can give rise to large magnetoresistance if engineered to form a junction structure, consisting of a middle resistive part connected to wider nanoribbon electrodes via zigzag edge interfaces.[69]

4. TWO-DIMENSIONAL MATERIALS VERSUS SINGLE-MOLECULE JUNCTIONS

Following the isolation of graphene and other 2D materials, intense experimental efforts have been channeled toward the use of 2D materials in electronic and spintronic applications. We comment briefly, based on our recent experience, on how the challenges and roles for DFT may be different in transport through 2D materials compared with single-molecule junctions.

The self-energy corrections to DFT eigenvalues for the frontier levels of 2D materials is usually much smaller than that in single molecules. For example, DFT can reproduce the key band structure features of graphene and only underestimates the quasiparticle band gap for single-layer MoS_2 by ∼0.7 eV.[70] Image charge effects would also be smaller in the extended 2D material. Thus, DFT gives a much better estimate of the interface level alignment for 2D material junctions compared with single-molecule junctions. On the other hand, in experiments, the 2D material is often at least micrometers in dimension. Band-bending in semiconducting 2D materials becomes important,[71] and converging the size of the resistive region in the transport calculation becomes challenging. Furthermore, resistance within the 2D material becomes important at these length scales. In that case, it would be important to predict intrinsic mobilities limited by electron−phonon coupling or scattering rates off impurities and defects. Fortunately, all these can be performed reasonably accurately within DFT, although the effects of disorder are not treated within standard DFT implementations and require additional vertex corrections.[72]

Finally, we note a few computational challenges specific to graphene and 2D transition metal dichalcogenides. The Dirac cone in graphene corresponds to a very small region of the 2D Brillouin zone (2DBZ). Special care must be taken to sample the 2DBZ such that this small region of $k_{\|}$-space is included. For 2D chalcogenides, different exchange−correlation potentials in DFT give different valence band minima and conduction band maxima, and calculations must be carefully benchmarked against experiments or many-electron calculations.[73] Spin−orbit coupling can also alter the band structure, with significant implications for transport.[73]

5. CONCLUDING REMARKS

In this Account, we have discussed the limitations and applications of DFT transport approaches to single-molecule junctions and 2D materials. For single-molecule junctions, level alignment is a major challenge with DFT, but this can be solved for certain cases using a computationally inexpensive DFT+Σ approach motivated by many-electron calculations. For 2D materials, the challenge is instead to model systems that are large enough compared with micrometer-sized experimental samples and capture the relevant physical processes in transport. We believe that when used with care, DFT and DFT-based approaches such as DFT+Σ will continue to play a major role in complementing experiments and phenomenological theory to make important predictions and gain insight into transport through emerging materials such as single-molecule junctions and 2D materials.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

Biographies

Su Ying Quek graduated with B.A. Honors (1st class) in Mathematics from the University of Cambridge in 2000 and obtained her Ph.D. in Applied Physics from Harvard University in 2006, working with Efthimios Kaxiras and Cynthia Friend. After a year of exchange studies at University of California, Berkeley, in 2005 with Steven G. Louie, she joined Jeff Neaton in Lawrence Berkeley National Laboratory as his first postdoctoral associate, from 2006 to 2010. From 2011 to 2013, she was an Independent Investigator in the Institute of High Performance Computing, Singapore. In August 2013, she joined the National University of Singapore as an Assistant Professor, supported by the Singapore National Research Foundation Fellowship. Her

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Khoong Hong Khoo received her Bachelor's Degree in Physics from the National University of Singapore and Ph.D. from the University of California at Berkeley, where she worked on electronic transport through nanostructures with Steven G. Louie. She then spent 3 years as a postdoctoral researcher with James R. Chelikowsky at the University of Texas at Austin before joining the Institute of High Performance Computing in Singapore as a scientist. She is interested in the study of materials using first-principles electronic structure methods.

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