Electronic transport in molecular devices is currently an area of much research interest. Possible applications of such devices include high-performance computer components [1], chemical sensors [2], disposable electronics, as well as possible medical applications [3].

Recently, it has become possible to construct single molecule junctions and measure their transport properties. Methods used to construct such devices include mechanically controllable break junctions [4-6], STM tips [6-7], lithographically fabricated nanoelectrodes [8], and colloid solutions [9]. However, there is much disagreement between the results for different experimental methods, with differences in the conductance of up to three orders of magnitude being reported for the same molecule [4-6, 9]. For this reason, ab initio quantum transport algorithms are becoming increasingly important.

Most computational methods for calculating electronic transport involve the combination of scattering theory in the form of the non-equilibrium Green’s function (NEGF) formalism [10], with an electronic structure method such as density-functional theory (DFT) [11-13]. Other schemes include time-dependent DFT [14] or many-body methods [15]. However, there is also much disagreement between the different theoretical methods, as well as between experiments and theory. In the prototypical case of benzenedithiol (BDT) attached to gold surfaces, the conductance for the most probable conformation of the molecule junctions and measure their transport properties. The method is implemented in the Green’s function non-equilibrium transport code Smagol and applied to the prototypical cases of benzene molecules sandwiched between gold electrodes. The self-interaction corrected Kohn-Sham highest occupied molecular orbital now reproduces closely the negative of the molecular ionization potential and is moved away from the gold Fermi energy. This leads to a drastic reduction of the low bias current in much better agreement with experiments.

FIG. 1: Schematic diagram of a metal-molecule-metal junction. (a) A scattering region is sandwiched between two current/voltage probes kept at the chemical potentials $\mu_1$ and $\mu_2$. (b) Energy level line up and (c) transmission coefficient as a function of energy. $H_s$, which is used to construct the non-equilibrium Green’s function $G(E)$

$$G(E) = \lim_{\eta \to 0} [(E + i\eta) - H_s - \Sigma_1 - \Sigma_2]^{-1},$$

where $\Sigma_{1/2}$ are the self-energy for the electrodes. $G(E)$ enters in a self-consistent procedure [10, 12, 13] for evaluating the energy level line up (see Fig 1b) and hence the two probe current. This is simply the integral between $\mu_1$ and $\mu_2$ (the bias window) of the transmission coefficient $T(E)$, which is a superposition of resonances located in correspondence to the molecular energy levels (the highest occupied molecular orbital - HOMO - and the lowest unoccupied molecular orbital - LUMO - in Fig. 1b).

The crucial point is that $H_s$ and thus $G(E)$ are constructed from the single-particle states calculated by an associated electronic structure theory, which needs to meet several re-
DFT in its Kohn-Sham (KS) formulation \[21\] is the most widely used electronic structure theory for transport, although in principle it does not meet any of the previous requirements. In fact DFT observables are integral quantities of the KS eigenvalues (the total energy) or of the KS wave-functions (the charge density), with the individual KS orbitals having little meaning. There is however an important exception since the energy of the KS HOMO (\(\epsilon_{\text{HOMO}}\)) is the negative of the ionization potential \(I\) of the system \[22, 23\]. This suggests that, at least for moderate bias and HOMO transport, KS theory can be used for transport calculations \[24\]. Unfortunately for standard local functionals, such as the local density approximation (LDA), \(\epsilon_{\text{HOMO}}\) is nowhere near \(-I\).

Most of the failures of LDA can be traced back to the self-interaction (SI), i.e. the spurious interaction of an electron with the Hartree and exchange-correlation (XC) potentials generated by itself \[25\]. In the case of an exact exchange theory (for instance Hartree-Fock) the self-Hartree cancels with the self-XC potential, however for LDA the cancellation is incomplete. This results in the eigenstates of a molecule being too high in energy, which translates in erroneously positioned peaks in the transmission coefficient. Self-interaction corrections (SIC) are possible \[25\], however their implementation in typical solid state codes is cumbersome, since the theory becomes orbital dependent and the energy minimization cannot follow the standard KS scheme.

These problems become even more serious when SIC is combined with the NEGF method since the KS orbitals are never individually available. Recently we have implemented \[26\] an alternative and approximated method for dealing with SIC. This is based on an atomic approximation (ASIC) \[27\], where the SIC orbitals that minimize the energy are assumed to be atomic-like. The correction thus becomes atomic and no information are needed other than the charge density and the ASIC projectors \[26\]. Importantly ASIC produces single-particle energy levels rather close to the experimental molecular removal energies, and in particular \(\epsilon_{\text{HOMO}} \approx -I\) and the \(\epsilon_{\text{LUMO}}\) for negatively charged molecules is close to the molecular affinity. As an example ASIC places \(\epsilon_{\text{HOMO}}\) for 1,2-BDT at 8.47 eV to compare with the LDA value of 4.89 eV and the experimental ionization potential \(\sim 8.5\) eV \[28\].

We have numerically implemented the ASIC method \[26\] in the localized atomic orbital code SIESTA \[29\], which is the DFT platform for our transport code Smaegol \[12\], and carried out calculations for the prototypical Au/Benzene/Au molecular devices. We use a double zeta polarized basis set \[29\] for carbon and sulfur \(s\) and \(p\) orbitals, double zeta for the \(1s\) orbitals of hydrogen and \(6s\)-only double zeta for gold.
and away from $E_F$. At variance from LDA (Fig. 3a), where $T(E_F)$ is dominated by a resonance at $\epsilon_{\text{HOMO}}$, the ASIC transmission (Fig. 3b) is through the BDT gap and therefore it is tunneling-like. This results in a drastic reduction of the low-bias current when going from LDA to ASIC (Fig. 3c).

The ASIC-calculated conductance at zero bias is now about $0.06G_0$ ($G_0 = 2e^2/h$), compared to $0.23G_0$ of LDA. A conductance of $0.06G_0$ is much closer to the value of $0.011G_0$ obtained by Xiao et. al. [7] and is actually lower than values $0.09-0.14G_0$ obtained by Tsutsui et. al. [6].

Other anchoring configurations to the (111) surface were investigated and their zero-bias conductance are shown in Table I. Note that ASIC returns values in the region of about $0.01G_0$ for several different anchoring geometries. Such stability with variation of the anchoring structure is important as the peaks in the experimental conductance histograms are relatively sharp [7]. This indicates that the different metal-molecule junctions have similar conductances, despite the fact that the anchoring of the molecule to the surface/tip may vary.

As a second case we investigate benzenedimethanethiol (BDMT) molecules on the same gold surface (Fig. 4). Also for this molecule we consider a number of anchoring structures, although here we report only for the hollow site since different structures do not present qualitatively different results.

In contrast to BDT, the DOS of BDMT already presents a large HOMO-LUMO gap in LDA (see Fig. 5a), which is further increased by the ASIC (5b). This time ASIC has the only effect of changing the alignment of $\epsilon_{\text{HOMO}}$ with respect to $E_F$, which cuts through the HOMO-LUMO gap for both LDA and ASIC. Therefore both LDA and ASIC offer a picture of tunneling-like transport through the molecular gap, and little difference can be found (see Fig. 5d, e and f). Hence, the $I$-$V$ curves are quite similar, with currents approximately one order of magnitude smaller than those of BDT.

With these results in hand we can conclude that in general ASIC drastically improves the agreement between theory and experiments. However some disagreement still remains. In particular it appears that even in the case of ASIC the current at low bias is larger than that typically measured. Although an exhaustive comparison is complicated by the fact that the experimental spread of the data is large, here we speculate on the possible source of such disagreement. First one may argue that the contact geometry is not correct. Indeed recent X-ray standing wave experiments [31] demonstrate that S atoms in thiol groups on gold join more favorably to adatoms. This means that the Au-S-molecule moiety may be the one relevant for the transport experiments. However calculations with two Au adatoms as anchoring sites lead to strong pinning of $\epsilon_{\text{HOMO}}$ to the gold $E_F$ [17, 19]. ASIC does not change this feature and the conductance remains large. An asymmetric anchoring configuration with one hollow site and one adatom

![FIG. 4: BDMT molecule attached to the hollow sites of the gold (111) surface. The contact geometry is identical to that for BDT. Color code: Au=yellow, C=black, S=dark yellow, H=blue.](image)

![FIG. 5: Transport properties of a BDMT molecule attached to the gold (111) hollow site. The left panels correspond to LDA and the right ones to ASIC. The upper panels are the DOS of the S and C $\pi$ orbitals ((a) and (b)), the middle are the transmission coefficients as a function of energy for various bias ((c) and (d)) and the lower are the $I$-$V$ curves. Figure (i) is a zoom of (e) and compares our results with experiments from reference [7]. The vertical lines in (c) and (d) mark the bias window.](image)

| Anchoring | $d$ (Å) | $G_{\text{LDA}}$ ($G_0$) | $G_{\text{ASIC}}$ ($G_0$) |
|-----------|---------|------------------------|------------------------|
| Ho        | 1.9     | 0.23                   | 0.06                   |
| Ho        | 1.8     | 0.16                   | 0.05                   |
| Ho        | 2.1     | 0.32                   | 0.07                   |
| Ho        | 2.5     | 0.77                   | 0.14                   |
| Ho (30°)  | 1.9     | 0.18                   | 0.04                   |
| Br        | 2.09    | 0.11                   | 0.06                   |
| Ad        | 2.39    | 0.11                   | 0.10                   |
| Asy Ho    | 1.9/2.3 | 0.33                   | 0.06                   |
| Ho/Ad     | 1.9/2.39| 0.35                   | 0.03                   |

TABLE I: Zero-bias conductance for different configurations of BDT on gold (111). Experimental values include $0.011G_0$ [6] and $0.09G_0$ [7]. The anchoring configurations investigated are: hollow site (Ho), bridge site (Br), Au adatom (Ad). Ho (30°) describes a hollow site with BDT at a 30° angle with respect to the transport direction, and the two last rows correspond to asymmetric anchoring to the two electrodes. $d$ is distance between the S atom of the thiol group and the plane of the gold surface (or to the adatom for Ad).
(see last column of table [32]) gives us a ASIC conductance of 0.03 $G_0$, still higher than experiments. Note that the presence of the mobile Au-S-molecule moieties seems also difficult to reconcile with the relative robustness of the peaks in the conductance histograms of breaking-junctions [7].

Hence we perhaps have to accept the fact that the disagreement between theory and experiments persists. Notably the problem is now that of calculating accurately tunneling matrix elements between the S and the surface. The problem is thus critically dependent on the quality of the wave-function and in turn of the actual scattering potential, for which ASIC does not offer substantial improvement over the LDA. In particular ASIC still overestimates the polarizability of molecules [32], with a quantitatively incorrect prediction of the response exchange and correlation field. In addition it is important to remark that we have applied the ASIC only to the molecular degrees of freedom, without correcting the Au atoms. It is thus likely that the Au 6s orbitals at the surface are too extended, leading to a larger current.

In conclusion, we have demonstrated that a simple SIC scheme is able of lowering the energy levels of the occupied molecular orbitals, which now resemble closely the actual vertical removal energies. This has profound consequences over the transport properties of metal/molecule/metal junctions since spurious resonances at the Fermi level can be removed, leading to tunneling transport for molecules for which LDA erroneously predicts metallic conductance. The agreement with experiments is thus greatly improved.

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