Conductance of a hydrogen molecule

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A recent experiment reported that a single hydrogen molecule can form a bridge between Pt electrodes, which has a conductance close to one quantum unit, carried by a single channel. We present density functional calculations explaining these experimental findings. We show that the symmetry of the molecular orbitals selects a single conduction channel. The transmission of this channel is close to unity due to a combination of charge transfer between H2 and the Pt contacts and the strong hybridization between the bonding state of the molecule and the d band of the Pt leads.

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The recent advances in nanofabrication have triggered the hope that electronic devices can be shrunk down to the single molecule scale.1–3 Single molecules have been shown to perform functions analogous to those of the key microelectronics components such as switches,4–5 rectifiers6 and electronic mixers.7 However, the future of molecular electronics depends crucially on our understanding of the transport mechanisms in single-molecule junctions. From the experimental side an unambiguous contact to a single molecule is difficult to achieve8, and in many cases the measurements are not reproducible. On the other hand, the discrepancies between theory and experiment and even between different theories are notorious.9

From this perspective the measurement of the conductance of an individual hydrogen molecule reported by Smit et al.10 provides a valuable opportunity to analyze the emerging concepts on the electrical conduction in single-molecule devices in the perhaps simplest possible system. In Ref.10 it was shown that a single hydrogen molecule can form a stable molecular bridge between platinum contacts. In contrast to results for organic molecules11–13, this bridge has a conductance close to one quantum unit, carried by a single channel. This result belies the conventional wisdom because the closed-shell configuration of H2 results in a huge gap between its bonding and antibonding states, making it a perfect candidate for an insulating molecule. Thus, the observations of Ref.10 pose an interesting theoretical challenge and their understanding can help to elucidate some of the basic transport mechanisms at the single-molecule scale.

In this paper, we develop (i) a simple theoretical model to understand the conduction mechanism through the hydrogen bridge which (ii) we match to quantitative density functional theory (DFT) calculations of the conductance. The interplay of these two approaches permits us to identify the two relevant mechanisms that give rise to the large conductance of the hydrogen molecule. First, the catalytic activity of platinum is responsible for a significant charge transfer between H2 and the Pt contacts, which moves the bonding state of the molecule towards the Fermi energy. Then, the strong hybridization with the d band of the Pt leads provides a large broadening of the bonding state, finally allowing for a high transmission. These two key findings are at variance with the central conclusion of the theoretical analysis presented in the experimental paper. Additionally, we show that, due to the symmetry of its molecular orbitals, H2 filters out only one of the Pt conduction channels. We discuss the fundamental implications of these findings for the proper description of the transport properties of single-molecule devices.

In order to investigate the transport through the hydrogen bridge reported in Ref.10 we have performed DFT calculations of the linear conductance using the method described in Ref.14, similar in spirit to Refs.13,15. In this approach, we first decompose the Hamiltonian of a molecular junction as \( \hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_C + \hat{V} \), where \( \hat{H}_C \) describes the “central cluster” of the system, which contains the molecule plus part of the leads, \( \hat{H}_{L,R} \) describe the left and right electrode respectively, and \( \hat{V} \) gives the coupling between the electrodes and the central cluster. The electronic structure of the central cluster is calculated within the DFT approximation.17 The left and right reservoirs are modeled as two perfect bulk crystals of the corresponding metal using the tight-binding parameterization of Ref.18. The inclusion of part of the leads in the ab initio calculation assures the correct description of (i) the molecule-electrodes coupling, (ii) the charge transfer between the molecule and the leads and (iii) the lineup of the molecular levels relative to the metal Fermi level.12 The Fermi level is set naturally by the highest occupied molecular orbital (HOMO) for a sufficiently large number of metallic atoms in the central cluster.

As in the experiment,10,12 we concentrate on the analysis of the linear conductance, which is given by the Landauer formula

\[ G = G_0 \text{Tr}(\hat{t}^2) \]

where \( G_0 = 2e^2/h \) is the quantum of conductance, \( \hat{t} \) is the transmission matrix and the \( T_i \)'s are the transmission eigenvalues at the Fermi energy \( E_F \). The transmission matrix is given by

\[ \hat{t}(\epsilon) = 2 \hat{T}_L \hat{C}_L^{-1} \hat{G}_C^{-1}(\epsilon) \hat{C}_R \hat{T}_R \hat{C}_R^{-1}(\epsilon) \]

with the scattering...
rate matrices $\hat{\Gamma}_{L,R} = \text{Im}(\hat{\Sigma}_{L,R})$. Here $\hat{\Sigma}_{L,R}$ are the self-energies which contain the information of the electronic structure of the leads and their coupling to the central cluster. Finally, the Green functions of the central cluster are given by $G_C(\epsilon) = \left[\epsilon \hat{1} - \hat{H}_C - \hat{\Sigma}_L(\epsilon) - \hat{\Sigma}_R(\epsilon)\right]^{-1}$.

For the case of non-orthogonal basis sets it is straightforward to implement the overlap matrix into these formulas via a Löwdin transformation (see e.g. Ref. [2]).

In Ref. [10] a break junction was used to produce pure Pt contacts of atomic size. Then, it was shown that the transport through these contacts was markedly altered in the presence of hydrogen. Following the experiment we first analyze the transport through a pure Pt single-atom contact. In the DFT calculations we use the BP86 functional [21] and the basis set of Christiansen et al. [22]. For the description of the Pt reservoirs we use a basis with the $5d$, $6s$, $6p$ orbitals.

FIG. 1: Transmission and LDOS at the central atom as a function of energy for the pure Pt structure shown in the inset. The LDOS is projected into the Pt valence orbitals. The Fermi energy is set to zero. Inset: Pt one-atom contact consisting of a fcc structure with bulk interatomic distances grown along the (111) direction. The blue atoms represent the bulk atoms used to model the reservoirs.

Let us now study how the presence of H$_2$ modifies the conduction. Usually the lack of knowledge of the precise geometry of the molecular junction complicates the comparison between theory and experiment. However, in Ref. [10] the presence of H$_2$ was identified by means of the signature of its vibrational modes in the conductance. This information establishes clear constraints on the geometries realized in the experiment. In this sense, we only consider configurations which are compatible with the observed vibrational modes. The most probable configuration is shown in the inset of Fig. 2, where the H$_2$ is coupled to a single Pt atom on either side (top position). In this geometry the vibrational mode of the center of mass motion of H$_2$, which is the one seen in the experiment, has an energy of 55.6 meV, lying in the range of the experimental values. In Fig. 2(a) we also show the transmission and the LDOS projected into the orbitals of one of the H atoms. The total transmission at the Fermi energy is $T_{\text{tot}} = 0.86$ and it is largely dominated by a single channel, in agreement with experimental results. We would like to draw the attention to the following two features in the LDOS: (i) the bonding state of the molecule appears as a peak at $\sim 6$ eV below $E_F$ and the antibonding state, not shown in Fig. 2, is located at $\sim 18$ eV above $E_F$. This indicates that the molecular character of H$_2$ is largely conserved. (ii) Around the Fermi energy the gap between the molecular states is filled due to the strong hybridization with the Pt leads.

We now proceed to explain the underlying physics with the help of a simple model. To illustrate the ingredients necessary to reproduce the full DFT results we shall progressively sophisticate the model. We describe H$_2$ with a two-sites tight-binding model, see Fig. 3(a). In this scheme $\epsilon_0$ represents the 1s energy level of H and $t_H$ is the hopping connecting the H atoms. This hopping is simply related to the splitting between the bonding ($\epsilon_+$) and the antibonding state ($\epsilon_-$) of the molecule, namely $\epsilon_{\pm} = \epsilon_0 \pm t_H$, and its value is $\sim -12$ eV. The molecule is coupled symmetrically to the leads with a single hopping $t$. Obviously, within this model the conductance is made up of a single channel, but let us postpone the discussion of this point for the moment. The transmission is given by

$$T(\epsilon) = \frac{4\Gamma^2 t_H^2}{[(\epsilon-\tilde{\epsilon}_+)^2 + \Gamma^2][(\epsilon-\tilde{\epsilon}_-)^2 + \Gamma^2]}.$$  

Here, $\tilde{\epsilon}_{\pm} = \epsilon_0 \pm t_H - t^2 \text{Re}(g^0)$ are the renormalized molecular levels, $g^0(\epsilon)$ being the advanced Green function.
FIG. 2: Transmission and LDOS projected into one of the H atoms as a function of energy for the Pt-H$_2$-Pt structure, the central cluster of which is shown in the inset. At $E_F$ $T_1 = 0.83$ and $T_2 = 0.03$. The H-H and Pt-H distances are 0.8 Å and 2.1 Å respectively. We use the cc-pVDZ basis set for H.

which describes the local electronic structure of the leads. The scattering rate $\Gamma$, which determines the broadening of the molecular levels, is given by $\Gamma(\epsilon) = t^2 \text{Im} \{g^a\} = \pi t^2 \rho$, where $\rho(\epsilon)$ is the LDOS of the Pt contacts. Let us first assume that $\Gamma$ is energy independent and that the levels are not renormalized ($\epsilon_+ = \epsilon_-$. In Fig. 3(b) we show the transmission as a function of energy for different values of $\Gamma$ in units of $t_H$. We also show in Fig. 3(c) the corresponding DOS projected into the bonding and antibonding states of H$_2$, which are given by $\rho_\pm = \Gamma/\pi \{(\epsilon - \epsilon_\pm)^2 + \Gamma^2\}$ respectively. Taking into account the huge value of $t_H$, one might naively expect the curve for $\Gamma = 0.05t_H$ to represent the relevant situation. Assuming that H$_2$ remains neutral, the bonding state is occupied by two electrons and 2 bond with Pt by sharing electrons. The DFT calculations show that while the Pt-Pt coupling is negligible, this is not the case for the Pt and the second H atom. In principle there are two paths for the current, i.e. two channels may occur. Due to the spherical symmetry of the H orbitals there is only coupling to the $s$ and $d_{z^2}$ orbitals of Pt. In addition, the Hamiltonian matrix elements between these orbitals fulfill approximately the condition $H_{1,s}H_{2,d_{z^2}} = H_{1,d_{z^2}}H_{2,s}$, where 1 and 2 stand for the first and second atom of H$_2$. Therefore, the

the large DOS around the Fermi energy coming from the $d$ band of Pt. We test this idea assuming that $g^a$ is the bulk Green function of Pt. The Pt bulk DOS is shown in Fig. 3(d). We also show in Fig. 3(e-f) the transmission and the LDOS projected into one of the H atoms for two values of the coupling to the leads $t$. One can see that for realistic values of $t \approx 1-2$ eV, the transmission at $E_F$ can now indeed reach values close to one. Therefore, we conclude that the high conductance of H$_2$ is due to the charge transfer between H$_2$ and the Pt leads and the strong hybridization between the bonding state and the $d$ band of Pt. This mechanism is not exclusive of Pt and it must also operate in other transition metals, as it was shown experimentally for Pd (see Ref. 10).

Let us now address why only a single channel is observed. In view of the model described above a simple explanation could be that all the current flows through the $1s$ orbital of the closest H atom to the Pt atom. However, the DFT calculations show that while the Pt-Pt coupling is negligible, this is not the case for the Pt and the second H atom. In principle there are two paths for the current, i.e. two channels may occur. Due to the spherical symmetry of the H orbitals there is only coupling to the $s$ and $d_{z^2}$ orbitals of Pt. In addition, the Hamiltonian matrix elements between these orbitals fulfill approximately the condition $H_{1,s}H_{2,d_{z^2}} = H_{1,d_{z^2}}H_{2,s}$, where 1 and 2 stand for the first and second atom of H$_2$. Therefore, the
but generic feature of the top position and thus a direct symmetry induced destructive interference is a unique, and sound propagation in periodic structures [28]. This reduces the actual number of channels to one not couple to the metallic states due to symmetry reasons, in other words, one of the molecular states does not couple to the metallic states due to symmetry reasons, reducing the actual number of channels to one. This phenomenon of symmetry-inhibited modes is well-known in the contexts of light propagation in photonic crystals [27] and sound propagation in periodic structures [48]. This symmetry induced destructive interference is a unique, but generic feature of the top position and thus a direct indicator of the relative orientation of the H$_2$ axis to the electrodes.

In principle there are other geometries compatible with the vibrational modes analysis. However, based on the channel analysis performed in the experiment many geometries can be ruled out. As an example we consider the situation sketched in the inset of Fig. 4 where each H is bound to three Pt atoms (hollow position). Indeed this configuration is suggested in studies of the chemisorption of H on Pt surfaces [29]. The conductance is carried by up to 7 individual channels (see Fig. 4). Due to the short distance between the Pt leads most of the current is bypassing the H$_2$ going directly from Pt to Pt. This analysis allows us to conclude that this type of geometries is not realized in the experiment and illustrates the importance of the channel analysis.

In conclusion, we have presented a theory for the conductance of a hydrogen bridge between Pt contacts explaining the experimental observations of Ref. [10]. We have shown how H$_2$ filters out one of the conduction channels of Pt with nearly perfect transmission. Our analysis of this ideal test system illustrates that ingredients such as charge transfer and the electronic structure of the metallic contacts are essential for the proper description of the electrical conduction in single-molecule devices.

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