Tunnelling in alkanes anchored to gold electrodes via amine end groups

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Abstract
For investigation of electron transport on the nanoscale, a system possessing a simple-to-interpret electronic structure is composed of alkane chains bridging two electrodes via end groups; to date, the majority of experiments and theoretical investigations on such structures have considered thiols bonding to gold electrodes. Recently experiments show that well-defined molecular conductances may be resolved if the thiol end groups are replaced by amines. In this theoretical study, we investigate the bonding of amine groups to gold clusters and calculate electron transport across the resulting tunnel junctions. We find very good agreement with recent experiments for alkane diamines and discuss differences with respect to the alkane dithiol system.

1. Introduction
Alkanes bridging metal electrodes form a simple physical realization of a tunnel junction, thereby presenting a model system for both experimental and theoretical studies regarding the electrical conductivity of molecules. The height of the energy barrier is given by the large separation of the highest occupied/lowest unoccupied molecular orbitals with respect to the Fermi energy, whereas the width of the barrier is controlled by the number of methylene (–CH2–) groups. In addition, the contact resistance of the junction may be changed through the different electron transmission properties of the end groups used to bond the alkanes to the metallic electrodes. Such configurations have been realized experimentally using break junctions and scanning tunneling microscopy (STM) probes as well as in conductance measurements through self-assembled monolayers [1–7].

Experimental and theoretical work to date has focused on the alkane thiol and alkane dithiol systems bonded between gold electrodes, primarily due to favourable bonding properties of thiols to gold. Conductance measurements for these systems have led to a range of values for the decay constant \( \beta \) as determined from the formula

\[
G = G_c \exp(-\beta N),
\]

with \( G \) the conductance, \( N \) the width of the molecular junction (typically given in ångströms or in the number of methylene groups) and \( 1/G_c \) the junction contact resistance. Experimental and theoretical values of \( \beta \) range between 0.5 and 1.0 per methylene group for thiol-anchored alkanes [1–11]. The magnitude of the contact resistance shows a more pronounced spread depending on the experimental technique. These effects can be related to the uncertainty in the binding site and molecular conformation as well as to the effect of localized sulfur states near the Fermi energy [10, 12, 13]. Recently, Venkataraman et al [14] and Chen et al [15] have reported conductance measurements of alkane diamine bonded between gold electrodes and find a well-defined, narrow distribution in the molecular conductances, with decay constants and contact resistances extracted from the two experiments of similar value. Compared to the thiol-anchored alkane bridges, the properties of these molecular junctions are much less studied from the theoretical point of view; in particular for electron transport.

In this study, we first consider bonding of the amine groups to the metal clusters and discuss possible anchoring through the amine group (–NH2) or its dehydrogenated form (–NH). Then, we present our theoretical predictions for the conductance of the alkane diamine junctions. Current–voltage characteristics are calculated by applying a recently developed transport formalism that relies on the maximum entropy principle with application of open system boundary conditions through use of the Wigner function [16]. For treatment of the junction’s electronic structure, a configuration interaction method [17, 18] is employed, thus avoiding many
issues surrounding the use of more approximate electronic structure theory approaches in conjunction with electron transport [11, 19]. Probing for signatures of differing end group terminations, we calculate electron transport for terminations of the form –CH$_2$–NH–Au– and –CH$_2$–NH$_2$–Au– and compare them to recent experimental results [14, 15].

2. Computational methods

The energetics of the bonding of amines and their dehydrogenated form to gold is calculated using density functional theory (DFT) and Hartree–Fock methods; geometries and energies are reported using DFT results. For the DFT calculations, we use the B3-LYP hybrid exchange–correlation functional; for both DFT and Hartree–Fock calculations a split valence polarized SV(P) basis set is used [20]. All density functional and Hartree–Fock calculations have been performed using the TURBOMOLE program package [21]. For the energy and geometry calculations, core electrons in gold were removed using an effective core potential (ECP) leaving 19 electrons per gold atom explicitly treated [22]. Full geometry optimization was performed for all molecular clusters considered; see figures 1 and 2.

To prepare the many-particle basis set used for the transport calculations, the metal electrodes were treated as 20 gold atom clusters as depicted in figure 2. Hartree–Fock calculations were performed on the DFT optimized structures Au$_{20}$–NH–(CH$_2$)$_n$–NH–Au$_{20}$ and Au$_{20}$–NH$_2$–(CH$_2$)$_n$–NH$_2$–Au$_{20}$ with $n$ = 5, 6, 7, 8 or 9 methylene groups. Here, the larger valence double-$\zeta$ correlation-consistent basis set (aug-cc-pvDZ) was used to treat the carbon atoms [23], whereas only the gold 6s electron was explicitly treated [24]. Orbitals with an energy less than 15.5 eV above the junction’s highest occupied molecular orbital were then used in the Monte Carlo configuration selection procedure [17, 18] with a coefficient tolerance of $10^{-3}$. The resulting configuration interaction (CI) vectors range in length from 5000 to 10 000. All transport calculations were performed with the program VICI [25].

Our transport formulation is significantly different to common approaches to electron transport across molecules: for convenience, we outline the main features of the computations. The quantum chemical data used to describe the molecular region are subjected to open system boundary conditions to mimic the action of the electrodes within an experimental set-up. Boundary conditions are imposed using constraints calculated from the equilibrium density matrix to determine the equilibrium inward momentum flow from the electrodes, whereas as a voltage is applied the flow of momentum out of the device region is not constrained. In practice, the inward and outward momentum flows are defined via the Wigner function. Applying these boundary conditions, the reduced density matrix on the device region (the molecule plus part of the electrodes) is then calculated at several values of applied voltage. The procedure results in the best approximation to the density matrix on a region subject to reproducing known system observables in accord with the principle of maximum entropy. One of the features of our approach is that it allows for the expansion of many-body states in terms of a complete set of many-electron configurations

$$|\Psi\rangle = c_0 |\Psi_0\rangle + \sum_{i,a} c_i^a |\Psi_i^a\rangle + \sum_{i<j} \sum_{a<b} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \cdots$$

(2)
[\Psi_0] refers to a reference state composed of \( N \) lowest single-particle states and [\psi_i^a] (|\psi_i^a\rangle \ldots) denotes singly- (doubly- \ldots) excited configurations generated by substituting the \( i \)th (\( j \)th, \ldots) occupied single-particle state with the \( a \)th (\( b \)th, \ldots) single-particle excitation. Notably, our approximation to the device region wavefunction is not excitation-limited and allows for a high degree of electron correlation, if required.

3. Results

3.1. Bond analysis

The bonding of amines to gold is preferentially at adatom sites [14]: hence, we first investigate the bond strength by starting from the simple molecular clusters \( \text{AuNH}_2\text{CH}_3 \) and the dehydrogenated form \( \text{AuNHCH}_3 \). Optimization of the energy with respect to the atomic positions results in bond lengths \( R_{\text{Au-N}} = 2.03 \text{ Å} \) and \( R_{\text{C-N}} = 1.46 \text{ Å} \) in \( \text{AuNHCH}_3 \) and \( R_{\text{Au-N}} = 2.38 \text{ Å} \) and \( R_{\text{C-N}} = 1.46 \text{ Å} \) for \( \text{AuNH}_2\text{CH}_3 \). A strong covalent bonding in the dehydrogenated case is reflected in the shorter gold–nitrogen bond distance \( R_{\text{Au-N}} \) with the dehydrogenated amine \( \text{–NH–} \). The stronger covalent bonding for the dehydrogenated linker is also reflected in the bond energies with

\[
\Delta E = E[\text{AuNHCH}_3] - E[\text{NHCH}_3] - E[\text{Au}] = -1.59 \text{ eV},
\]

whereas the corresponding bond energy for the amine \( \text{–NH}_2 \) bonding to gold via the nitrogen lone pair is

\[
\Delta E = E[\text{AuNH}_2\text{CH}_3] - E[\text{NH}_2\text{CH}_3] - E[\text{Au}] = -0.59 \text{ eV}.
\]

However, the relative energies between the two systems reveal that bonding with the dehydrogenated form is not as stable as for \( \text{NH}_2 \) with the nitrogen lone pair forming the bond to gold:

\[
\Delta E = E[\text{AuNH}_2\text{CH}_3] - E[\text{AuNHCH}_3] - \frac{1}{2}E[H_2] = -1.03 \text{ eV}.
\]

Analysis of the energetics and geometries for the two junctions \( \text{Au}_{20}-\text{NH}-(\text{CH}_2)_n-\text{NH}-\text{Au}_{20} \) and \( \text{Au}_{20}-\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2-\text{Au}_{20} \) yields similar results as to the simple cluster models. Anchoring via the dehydrogenated amine gives \( \approx 2.07 \text{ Å} \) and \( 1.45 \text{ Å} \) for the Au–N and N–C bond length, respectively. For \( \text{Au}_{20}-\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2-\text{Au}_{20} \), the Au–N and N–C bond length are \( \approx 2.34 \text{ Å} \) and \( 1.48 \text{ Å} \), respectively. In this case too, relative energies of the two systems suggest greater stability for the \( \text{Au}_{20}-\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2-\text{Au}_{20} \) junction. For example, the energy difference between the two anchoring structures in hexane- and octane-based molecular junctions is

\[
\Delta E = E(\text{Au}_{20}\text{NH}_2(\text{CH}_2)_n\text{NH}_2\text{Au}_{20}) - E[H_2] \approx -4.9 \text{ eV}, \tag{6}
\]

suggesting that the stronger covalent bond for the dehydrogenated amines causes distortion to the gold electrode when contact is made.

3.2. Transport properties

In table 1, a comparison of the molecular conductances obtained from our transport calculations for both amine and dehydrogenated amine bonding to gold is listed as a function of the number of methylene groups and compared to the recent experimental work of Venkataraman et al [14] and Chen et al [15]. Examples of typical current–voltage characteristics are shown in figure 3. Overall the agreement with experiment is very good both for the magnitude of the currents and for decay constants. The measurements yielded a contact resistance of \( 430 \text{ kΩ} [14] \) and \( 350 \text{ kΩ} [15] \) ‘high’-G configuration, and \( \beta \) values of \( 0.91 \pm 0.03/\text{CH}_2 \) and \( 0.81 \pm 0.01/\text{CH}_2 \) were extracted in [14] and [15], respectively. For the case of bonding with the \( \text{–NH}_2 \) we calculate a decay constant \( \beta = 0.98 \) per methylene and a contact resistance of \( 140 \text{ kΩ} \). Our previous results for alkane diethiols

| Table 1. Comparison of measured values with our predictions for the conductance of alkane molecules between gold electrodes. Theoretical results are calculated for NH– and NH2– anchoring groups. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Molecule       | NH-anchoring    | NH2-anchoring   | L. Venkataraman et al. a | F Chen et al. b |
| Pentane        | 34.52 ± 16.51   | 51.99 ± 24.10   | 27.12 ± 0.77      | —               |
| Hexane         | 12.96 ± 2.98    | 30.64 ± 6.07    | 11.62 ± 1.16      | 20.79/1.27      |
| Heptane        | 4.27 ± 1.03     | 4.91 ± 3.01     | 5.66 ± 1.55       | —               |
| Octane         | 3.65            | 4.33 ± 3.26     | 2.32 ± 2.32       | 3.85/0.22       |
| Nonane         | —               | 1.27 ± 0.39     | —                 | —               |

a Results from the break junction experiments of [14].

b Results from the STM contact experiments of [15].
yielded a similar \( R_c = 1/G_c \) but much slower exponential decay of the conductance with \( \beta = 0.5 \) per methylene [11]. On the other hand, bonding through the dehydrogenated linker gives a theoretical value of \( \beta = 0.79 \) per methylene and a higher contact resistance of 650 kΩ. Note that higher resistance for stronger bonding is not uncommon as it is the resulting orbital hybridization at the contact that largely determines this value. Nevertheless, these results do not explain the difference between ‘high’ and ‘low’ conductance peaks observed in the STM contact experiments [15] (see last column of table 1).

We should also mention that theoretical comparisons between the two anchoring groups should be viewed cautiously. As our CI expansions used for the electronic structure determination are relatively short, it is likely that the prediction of the HOMO–LUMO gap is not exact and this finite size of the cluster may not yield the precise energy level alignment. Additionally, there were numerical sensitivities in the calculated currents for the alkane diamines that we did not encounter for the alkane diithiols. These relate to where we choose within the \( \text{Au}_{20} \) clusters for the application of the open boundary conditions. However, for converged calculations the calculated current values at a given voltage never differed more than ±75% of the mean value; actual uncertainties in each case are given in the table.

Finally, we note that secondary peaks occur in the measurements of Venkataraman et al [14] at slightly higher conductances than for those ascribed to the amine anchoring. Within the context of our results we cannot exclude the possibility that primary and secondary peaks can be explained as different bonding configurations through \( \text{NH}^- \) and \( \text{NH}_2^- \) groups or bonding of \( \text{–NH}_2^- \) to different sites. Energetically the dehydrogenated amine bonding scheme seems unlikely, but the stronger gold–nitrogen bond for the dehydrogenated linker may be able to stabilize within the break junction.

4. Conclusions

Theoretical calculations for the bonding of alkane diamines to gold electrodes have been presented, exploring also the possibility of anchoring via dehydrogenated amines. We find the latter bonding scheme to be energetically unfavoured: nevertheless, electron transport properties across tunnel junctions formed in either case correlate very well with the experiment. Our results support the amine bonding mechanism proposed earlier [14]. Finally, we note that applying the same theoretical methodology as used to study alkane diithiols results in very good agreement with the measured contact resistances and decay constants [14, 15] when applied independently to the new test case of the alkane diamines.

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