Single-channel conductance of H_2 molecules attached to platinum or palladium electrodes

V. M. García-Suárez,[1,*] A. R. Rocha,[2] S. W. Bailey,[3] C. J. Lambert,[3] S. Sanvito,[2] and J. Ferrer[1]

[1]*Departamento de Física, Universidad de Oviedo, 33007 Oviedo, Spain*
[2]*Physics Department, Trinity College, Dublin 2, Ireland*
[3]*Department of Physics, Lancaster University, Lancaster, LA1 4YB, United Kingdom*

We report a detailed theoretical study of the bonding and conduction properties of an hydrogen molecule joining either platinum or palladium electrodes. We show that an atomic arrangement where the molecule is placed perpendicular to the electrodes is unstable for all distances between electrodes. In contrast, the configuration where the molecule bridges the electrodes is stable in a wide range of distances. In this last case the bonding state of the molecule does not hybridize with the leads and remains localized within the junction. As a result, this state does not transmit charge so that electronic transport is carried only through the antibonding state. This fact leads to conductances of $1G_0$ at most, where $G_0=2e^2/h$. We indeed find that G is equal to 0.9 and $0.6G_0$ for Pt and Pd contacts, respectively.

The main obstacle to using single molecules as conducting elements[1] is the difficulty in establishing stable and reproducible contacts to metallic electrodes. Conductance quantization in atomic constrictions was predicted several years ago,[2] but the practical realization in single-molecule contacts only became possible in the mid-1990's, with the advent of the scanning tunneling microscope[3–5] and mechanically controllable break junctions.[6]

An important testing ground for both theory and experiment is the simplest of all molecular bridges, namely, the H_2 molecule. This molecule has just one bonding and one antibonding state in the available energy range. Therefore it should be possible to predict the effect of tuning a range of adjustable parameters, including the position and orientation of the molecule, the distance and voltage between the electrodes and the materials that make up the electrodes. Despite the apparent simplicity of this junction, there is currently no agreement about what are the position and orientation of the molecule for given separation between the electrodes, even for zero applied bias.

Smit and co-workers[7] found that the conductance histograms of the molecule, sandwiched between Pt leads, had a sharp peak at about $0.9G_0$ ($G_0=2e^2/h$ is the conductance quantum) and therefore argued that electronic transport was dominated by a single channel with an almost perfect transmission. In addition, from the experimental phonon spectra they concluded that the molecule bonds to the electrodes in a bridge configuration (BC), i.e., with the H_2 bond axis parallel to the transport direction [see Fig. 1(a)]. This was also confirmed by Cuevas *et al.*[8]

A different interpretation was given by García and co-workers[9] who showed theoretically that an arrangement where the molecule bonds perpendicularly to the transport direction [perpendicular configuration (PC)] has a lower energy, and therefore should also be the preferred atomic configuration [see Fig. 1(b)]. Their simulations gave conductances of order $1G_0$ and $0.2G_0$ for PC and BC, respectively. Very recently, Thygesen and collaborators[10] challenged García's results. They performed a careful study of the vibrational spectra providing further theoretical evidence in favor

of the initial interpretation of Smit *et al.*[7] They found that the current is carried by the antibonding state of the molecule with a conductance of the order of $1G_0$, but in agreement with García, they predicted that the PC has a lower energy than the BC, when the separation between leads is small.

As a summary, the analysis of the experimental data performed in terms of vibration modes and conduction channels indicates that the H_2 molecule places itself in a BC configuration and therefore, current is carried by a single channel,[7,8] identified to be the antibonding state of the molecule.[10] But the energetic analyses carried out so far indicate that the PC arrangement is more stable and should therefore be realized in a wide range of separation distances between the electrodes. Since the transport in this arrangement is carried by
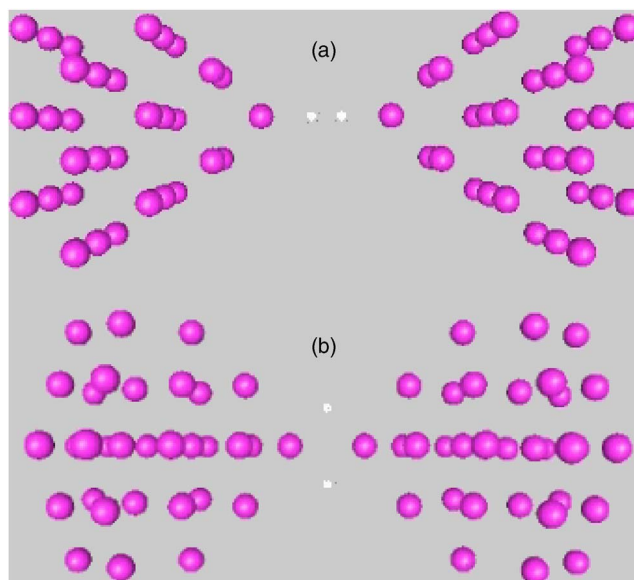

FIG. 1. (Color online) Atomic configuration of the scattering region for the BC (a) and PC (b) arrangements. Shaded and white balls indicate Pt (or Pd) and H atoms, respectively. (b) has been rotated 45° around the z axis with respect to (a), to achieve a better view of the orientation of the hydrogen molecule.
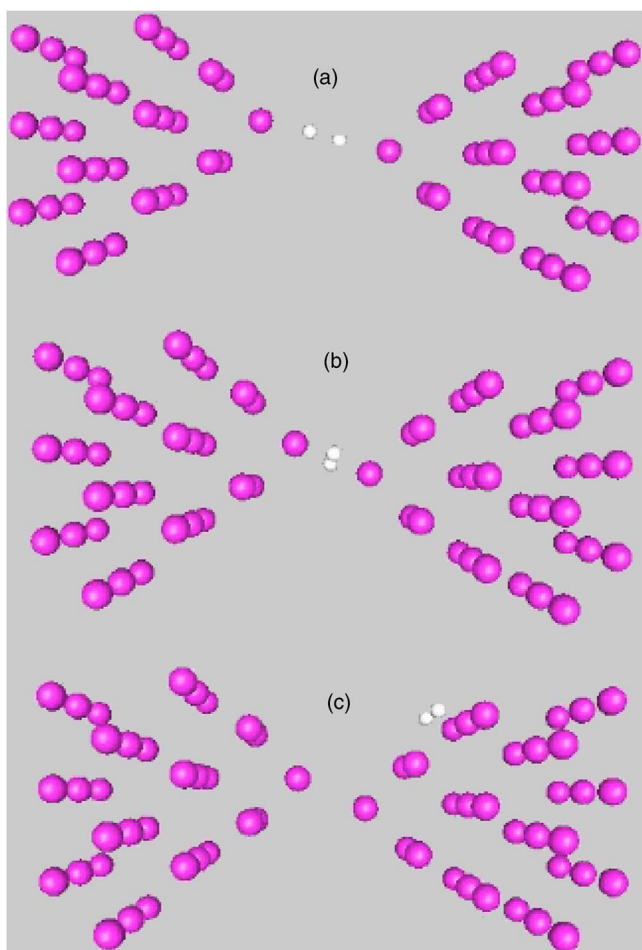
FIG. 2. (Color online) New atomic configurations studied in this work: BC zigzag (a), PC zigzag (b) (top view of the molecule), and zigzag with the molecule chemisorbed on the surface (CZ) (c).

two channels, the whole interpretation of data in terms on a single channel seems jeopardized. Even if the PC configuration turns out not to be energetically favourable, there remains the question of why the bonding state does not carry any current and how does this fact manifest in the electronic spectra of the molecular setup. To resolve these contradictions and open questions, we present a detailed investigation of the stability, electronic structure and conductance of the H_2 molecule attached to either Pt or Pd electrodes.

First, we have simulated, in adition to the atomic configurations analysed previously by other authors,[8–10] a number of new arrangements that could very likely occur, and that we depict in Figs. 1 and 2, respectively. We show that, for short distances, H_2 molecules prefer to bind rather to the surface of one of the electrodes than in between them. Therefore, at those distances, the atomic constriction involves only the Pt electrodes and current is carried directly through Pt atoms, which involves several channels. PC begins to compete in energy with these atomic configurations in a narrow range of intermediate distances. Since all such configurations are likely to occur, and each of them has a different number of transport channels, we do not expect a peak in conductances histograms. As the distance increases further, the energy of BC starts to be competitive and eventually becomes the most

stable configuration since for long enough distances all the other configurations break.

Second, we have studied the density of states (DOS) projected on the different atoms of the junction for both PC and BC arrangements. For the BC configuration, we find that the bonding state of the molecule does not hybridize with the Pt electrodes and remains a localized state of the junction. This state is therefore a closed conduction channel that can not swap charge from one electrode to the other. On the contrary, the antibonding state completely spreads out due to hybridization, and therefore becomes the single conduction channel of the junction. For the PC configuration, on the contrary, both bonding and anti-bonding states hybridize strongly to the Pt electrodes. Therefore, in this atomic arrangement, both states become conduction channels that exchange electrons between the electrodes.

Third, a detailed study of the transmission coefficients shows that $T(E)$ is essentially constant and equal to 0.9–1.0 for a wide range of energies around E_F and distances about the equilibrium distance of the BC configuration, as expected for a junction with a single conduction channel. This shows that the antibonding channel has almost perfect transmission. The transmision coefficient $T(E)$ shows strong variations for the PC arrangement. It indeed varies from about 1 to 2.5 in a relatively narrow range of energies. This fact reveals that at least three channels are open in this configuration.

Finally, we have also studied another closely related experiment, performed by Csonka *et al.*,[11] where H_2 was placed between Pd leads. In this case, the conductance histogram showed a single peak centered at $0.6G_0$, provided the gas pressure inside the chamber was high enough. Our simulations show that transport in BC is also carried only through the antibonding state. We find that the total conductance is smaller for Pd than for Pt in both arrangements. The value we obtain for the BC configuration agrees with the experimental result, and indicates that the BC configuration is also realized for these junctions.

We use our recently developed *ab initio* quantum transport code SMEAGOL (Refs. 12 and 13) for determining both the stable and metastable H_2/electrode atomic configurations and for computing their low-bias conductances. SMEAGOL combines the nonequilibrium Green's function (NEGF) formalism[2,14–18] with density functional theory (DFT),[19] using the numerical implementation contained in the SIESTA code.[20,21] The system (molecule plus leads) is ideally divided in three regions: namely, a left and a right lead, and a scattering region comprising the H_2 molecule and part of the leads themselves.[22] The two leads act as current/voltage probes and are assumed to be in equilibrium, with well-defined chemical potentials. In contrast, the potential of the scattering region is calculated self-consistently for each applied bias.[14–16] For this purpose we define the Green's function of the scattering region in the presence of the leads as

$$\hat{G} = \lim_{\delta \to 0}[(E + i\delta)\hat{S} - \hat{H}_S[\rho] - \hat{\Sigma}_L - \hat{\Sigma}_R]^{-1}, \qquad (1)$$

where $\hat{H}_S[\rho]$ is DFT Hamiltonian and $\hat{\Sigma}_L$ and $\hat{\Sigma}_R$ are the self-energies, respectively, for the left and right lead. This allows us to evaluate the density matrix

$$\rho = \int \frac{dE}{2\pi} \hat{G}[\hat{\Gamma}_L f(E - \mu_L) + \hat{\Gamma}_R f(E - \mu_R)]\hat{G}^\dagger, \quad (2)$$

with $\hat{\Gamma}_\alpha = i[\hat{\Sigma}_\alpha - \hat{\Sigma}_\alpha^\dagger]$. Since the DFT Hamiltonian H_S depends solely on the density matrix, Eqs. (1) and (2) can be iterated until reaching self-consistency. Then the current is extracted using a Landauer-type formula[18] $G(E) = G_0 T(E)$, where $T(E)$ is the transmission coefficient for electrons of energy E relative to the Fermi energy E_F.

In what follows, the leads have an fcc crystalline structure and are oriented along the (001) direction. Their unit cell is a slab containing two 3×3 atomic layers. The scattering region, presented in Figs. 1 and 2 consists of an H$_2$ molecule attached to the tips of two pyramids of Pt or Pd atoms. These pyramids can be viewed as a sequence of two atomic fcc (001) layers comprising 4 and 1 atoms, respectively. The scattering region also includes three bulk Pt (or Pd) buffer layers with the same atomic configuration of the leads, that are seamlessly attached to the pyramids. The Hydrogen molecule is placed both in the BC and in the PC setup, as shown in Figs. 1(a) and 1(b), respectively, or elsewhere. For the simulations, periodic boundary conditions are applied in the basal plane, and four irreducible k points in the two-dimensional Brillouin zone are used.[23] We label every simulation according to the distance d between the innermost buffer layers of the scattering region. For a given distance d, we always relax the pyramids and the Hydrogen atoms, and compute the total energy at zero applied bias.

Consider first the case of Pt electrodes. We find that the molecule in isolation has an equilibrium distance of 0.81 Å, and a bonding-antibonding energy gap of about 11.5 eV. This bond is weakened when the molecule is attached to the electrodes. The relaxed distances are 0.99 Å for BC and 2.46 Å for PC, which indicate that this last configuration is close to a dissociated state. The densities of states projected onto either hydrogen or the Pt atom at the apex are shown in Fig. 3 for both BC and PC configurations. Figure 3(a) demonstrates that the bonding state in BC arrangement remains a localized state of the junction. The DOS projected onto the hydrogen atom shows that this state is essentially unaffected by the proximity of the electrodes. It indeed remains as a sharp peak located at almost the same energy as for the isolated molecule, somewhat below the lower Pt valence band edge. These results are confirmed by also plotting the DOS projected onto the neighboring Pt atoms, where the weight of such bonding state has decreased by a factor of 4. In contrast, the antibonding state is completely spread, coupling strongly to the leads. We are therefore led to conclude that the bonding channel of conduction is completely closed down, having zero transmission, while the antibonding state must be open. Moreover, a closer examination of the density of states projected onto single orbitals and also of the Hamiltonian shows that such antibonding state hybridizes only with the s and $d_{z^2-r^2}$ orbitals of the leads, as expected by symmetry. Indeed, we find that each hydrogen atom gains 0.27 electrons, that populate the antibonding state DOS below the Fermi energy.

The situation of the PC arrangement is somehow different. In this case the H$_2$ molecule again hybridizes both with
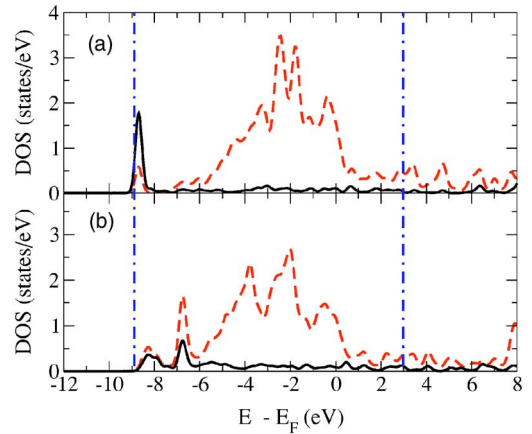

FIG. 3. (Color online) Pt electrodes: DOS projected on one of the hydrogen atoms and the Pt atom at one of the two apexes (solid and dashed lines, respectively) in (a) BC and (b) PC configurations. Dashed-dotted vertical lines: position of the bonding and antibonding energy levels of an isolated H$_2$ molecule. Energies have been referred to the Fermi energy of the Pt leads.

the s and $d_{z^2-r^2}$ orbitals of the tip of the electrodes. However, Fig. 3(b) shows that the bonding state of the molecule now participates in the chemical bond to the leads. First, notice that the corresponding peak in the DOS has slightly moved up in energies and splitted, to place itself at the band edge of the d band of the Pt electrodes. Second, the amplitude of the peak does not decrease when moving from the hydrogen to the Pt atom at the apex. This fact demonstrates that the bonding state becomes delocalized and therefore opens up as a conduction channel. These features will become more apparent for Pd electrodes, as we shall discuss below.

Let us now turn our attention to the electron transmission through these states in the BC configuration. We have shown above that the bonding channel is completely closed down. That means that only the antibonding channel can swap electrons between both electrodes and, therefore, the conductance can be as large as $1.0G_0$ at most. We find numerically that the conductance is almost flat, and approximately equal to $0.9G_0$, for a wide range of energies around E_F within the Pt bandwidth, see Fig. 4. Moreover, we have found that $T(E)$ remains essentially the same for the whole range of distances where BC is stable until the contact breaks. This almost perfect and constant transmission of the antibonding channel leads to the prediction of a narrow peak in conductance histograms, with low fluctuations.

In contrast, for the PC arrangement we obtain a conductance of about $2G_0$. In this case $T(E)$ shows strong variations around E_F, and achieves values even higher than 2 for distances around $d_{eq} \approx 9.5$ Å which implies the existence of more than two channels available for conduction. This arises from direct transport through Pt atoms at the apices of the pyramids, which at such a short distance have a small but finite overlap. Therefore if the PC is realized experimentally, we expect the conductance histograms to display a peak centered at $2G_0$, with rather strong fluctuations around that value. This result is in contradiction with that of García.[9]

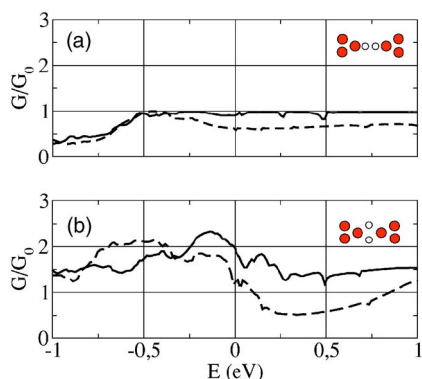We now discuss the stability of the equilibrium configu-

FIG. 4. (Color online) Transmission coefficients in (a) BC and (b) PC settings at their equilibrium distances. Solid and dashed lines indicate platinum and palladium, respectively. Energies are all referred to E_F.

ration of the junction. Our simulations confirm that the PC has a lower energy than the BC as shown in Fig. 5, in agreement with other authors.[9,10] At first sight, this seems to be in contradiction with the experimental data, since the PC configuration has a conductance of about $2G_0$ instead on $1G_0$. However, a closer look into the energetics of the problem reveals two important features.

First, the last Pt atoms of the tips may prefer to bond in a zigzag configuration, thereby continuing the fcc alignment. We have performed further simulations using such zigzag arrangements and found that their energy is substantially lower than that of their aligned counterparts whenever the two Pt atoms at the tip bond directly. In contrast, the energy-cohesion curves are insensitive to the alignment of the pyramids if a hydrogen molecule sits between the two Pt atoms, independently of whether we choose BC or PC configurations.

Secondly, if the distance between electrodes is too short, the hydrogen molecule may prefer to gain energy by bonding elsewhere on the Pt surface. We have therefore simulated zigzag configurations (CZ) where the hydrogen molecule is on the surface of one of the leads, as shown in Fig. 2(c). We
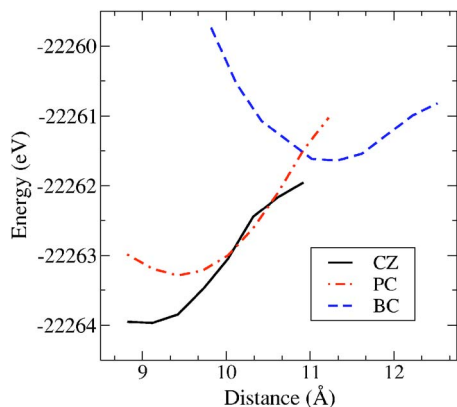

FIG. 5. (Color online). Energy-cohesion curves $E(d)$: energy E of different atomic configurations of the junction as a function of distance d. Solid, dashed, and dash-dotted lines indicate CZ, BC, and PC arrangements.

have then relaxed coordinates to let both atoms achieve their equilibrium position on top of the triangular sites between the pyramid and the lead. Figure 5 shows that the CZ arrangement is indeed lowest in energy for short distances, as expected, while there is a window of about 1 Å, where the PC is stable and competes in energy with all the different possible realizations of CZ. We find that CZ snaps for distances larger than 11 Å (and gives zero conductance). For these distances the BC becomes then the most stable configuration.

We are therefore able to explain why the conductance histograms of the break junctions do not show a peak at $2G_0$, since the PC is unstable at short distances against configurations where the H_2 molecule is absorbed on the surface of the electrodes, and against the BC configuration at large distances, where all other arrangements break. Therefore we conclude that the typical experimental situation is that of a H_2 molecule bridging the Pt leads in a BC configuration, with a conductance of approximately G_0.

Based on the above results, we propose the following evolution of a Pt break junction in presence of hydrogen as a function of the Pt-Pt lead separation. For short distances (up to about 10 Å) the junction arranges itself as a zigzag Pt point contact. H_2 molecules attach to the Pt surface at the triangular sites, away from the atomic constriction. In this case, electrons travel between leads through several Pt channels and the conductance is much larger than G_0. As the separation between the contacts increases from 10.0 to 11.0 Å, the PC configuration may take over in a few of the pulling cycles of the break junction. For distances larger than about 11 Å, all configurations other than BC snap. The junction therefore arranges in a BC configuration before eventually also snapping at a distance 12.5 Å. This latter arrangement provides a single channel conductance of about $0.9G_0$, that results in the sharp peak found in the experimental conductance histograms.[7]

Finally we consider the case of palladium leads, whose bonding properties are similar to those of Pt. For the BC, we find again that the bonding state of the H_2 molecule does not participate in the chemical bond. Figure 6(a) shows that the bonding state remains a sharp peak that is now clearly detached from the lower edge of the d band of Pd. The amplitude of the peak in the density of states again decays very fast as one moves away from the hydrogen atom. We find as before that the antibonding state strongly hybridizes with the s and $d_{z^2-r^2}$ orbitals of neighboring Pd atoms, so that electronic conduction is carried again by the antibonding channel. For the PC configuration, the bonding state hybridizes, leading to the opening of a second conduction channel. Figure 6(b) shows that the peak of the bonding state moves up in energies by 2 eV when the molecule hybridizes with the Pd electrodes in the PC configuration, placing itself at the band edge of the d band. Moreover, the amplitude of the peak is almost the same for Hydrogen and for the Pd atom at the apex of the electrode.

The transmission coefficients for the BC and PC are presented as dashed lines in Fig. 4. In complete agreement with the experimental data,[11] we find a conductance of $0.6G_0$ for the BC arrangement at distances around $d_{eq} \approx 11$ Å. This means that the transmission through the antibonding channel
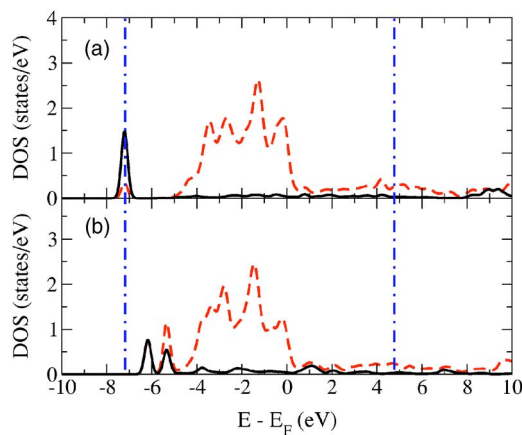
FIG. 6. (Color online) Pd electrodes: DOS projected on one of the hydrogen atoms and the Pd atom at one of the two apexes (solid and dashed lines, respectively) in (a) BC and (b) PC configurations. Dashed-dotted vertical lines: position of the bonding and antibonding energy levels of an isolated H_2 molecule. Energies have been referred to the Fermi energy of the Pd leads.

is not so perfect as in the case of Pt electrodes. We also find that the conductance of the PC is somewhat larger than $1G_0$ for distances around $d_{eq} \approx 9.2$. Interestingly we obtain that in the BC configuration, Pd atoms in the tip acquire a net magnetic moment for distances larger than about 12 Å. This results in the spin polarization of the current, since the transmission coefficients are different for up and down spins.

Experimental evidence for spin-polarized transport in Pd point contacts has been recently provided.[24]

The different transmissions found for the isostructural Pt and Pd leads may be understood in terms of the alignment of the centers of the s-d band of the leads and the hybridized antibonding state. Indeed, a simple one-dimensional tight-binding model consisting of two leads connected to a single level[14] shows that the transmission coefficient $T(E)$ has a long plateau with value close to 1, if the on-site energies of the level and the atoms at the leads differ only slightly. The plateau is rounded and the transmission decreases as the difference between both energies is made larger. This behavior is evident in Fig. 4.

In conclusion, we find that H_2 molecules typically bind to Pt or Pd leads in the BC configuration. The bonding state of the H_2 molecule does not participate in the chemical bond, and does not contribute to the low bias conductance. The transmission coefficient is close to $1G_0$ for Pt leads, since the energy of the hybridized antibonding orbital is close to the center of the s-d band of Pt. Such alignment is not realized for Pd electrodes, leading to a smaller conductance.

*Present address: Department of Physics, Lancaster University, Lancaster, LA1 4YB, U. K.

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