Zero Bias Electron Transport Properties of Molecular Junctions Formed from Smallest Fullerenes C_{20} and C_{24}

Rupan Preet Kaur*, Catherine Stampfl
School of Physics, The University of Sydney, New South Wales, 2006, Australia.

* Corresponding author. Email: rupan.kaur@syndey.edu.au
Manuscript submitted December 10, 2018; accepted March 8, 2019.
doi: 10.17706/ijmse.2019.7.4.89-95

Abstract: Using density functional theory and the non-equilibrium Greens function formalism, we compare the zero bias electronic properties of two molecular junctions formed from the smallest fullerenes: C_{20} and C_{24}. The results show that both junctions exhibit superconducting properties of the order of 2.5G0 and 3.12G0, respectively. The C_{24} junction exhibits a smaller HOMO-LUMO gap and higher zero bias conductance. The electronic wave functions are examined to understand the origin of the transmission peaks and resulting conductance. We find that for the C_{24} junction, the electrodes donate charge to the molecule giving rise to an occupied and unoccupied state very close to the Fermi level, resulting in a high and broad transmission peak that is responsible for the high conductance. For the C_{20} junction, the molecule loses some electron density and transmission is via unoccupied orbitals close to the Fermi level.

Key words: Fullerenes, C_{20}, C_{24}, DFT, molecular junction, DOS, MPSH eigenstates.

1. Introduction

The drive to further miniaturize semiconductor electronic devices has led to significant research into molecular electronics. This is due to their small size of few orders of A^0 and unique electronic, optical, magnetic and thermal properties. Of particular interest is research on single molecules connected to metallic electrodes to form molecular junction (MJ) based electronic devices [1]-[3].

In recent years, extensive efforts have been devoted to investigate the electron transport properties of fullerenes. The most extensively studied being the buckminsterfullerene C_{60} [4]. Various experimental findings have demonstrated its chemically inert nature and stable structure in reference to the isolated pentagon rule (IPR); that is, all its pentagons are isolated by hexagons [5], [6]. Fullerenes having less than 60 carbon atoms cannot fulfill the IPR and therefore are less stable [7], [8]. The electronic properties of molecular devices formed from these smaller fullerenes is the focus of the present paper.

In the present work, we consider two different molecular junctions by connecting the two smallest fullerene molecules, C_{20} and C_{24}, between semi-infinite gold electrodes oriented along the [1,1,1] direction denoted by C_{20}-MJ and C_{24}-MJ respectively using the Atomistic Tool Kit 13.8.0 [9] and its graphical interface Virtual Nano Lab. The atomic geometry of one such MJ is shown in figure 1. Density functional theory (DFT) [10], [11] is used to predict the equilibrium geometry of the gold-fullerene interface. The double-zeta polarized (DZP) basis set is used for all atoms of the molecule and electrodes [12]. The electrostatic potentials are determined on a real-space grid with cut-off energy of 75 hartrees. We optimize the geometry using Gaussian 03 [11] where the forces and stress are converged less than 0.1 eV/A^0. The Hamiltonian is expanded in a minimal *s, p, d* real space linear combination of atomic orbital basis set. The atomic cores are

defined by standard, nonlocal, norm-conserving pseudopotentials and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhoff (PBE) [13], [14], is used for the electron exchange correlation functional. The electrode calculations are performed using periodic boundary conditions with the electrode unit cell being three Au(111) layers along the transport direction. The optimum adsorption height (Au-C bond length) for C_{20}-MJ and C_{24}-MJ are 1.94 A^0 and 2.09A^0 respectively. The Brillouin zone is sampled with a 3×3×100 *k*-point grid using the Monkhorst-Pack sampling scheme. The electronic structure forms the basis for understanding the electronic transport properties of the MJ systems in the absence of applied external electrochemical potential.

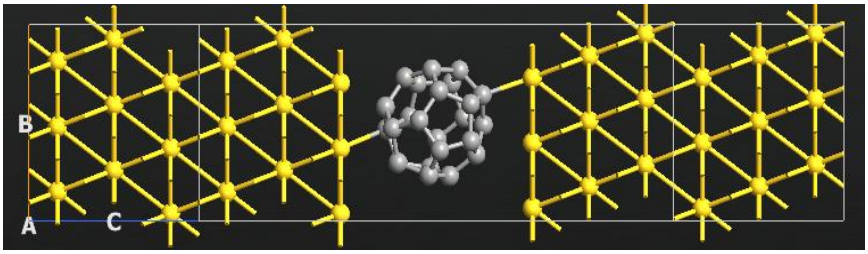


Fig. 1. Schematic diagram of the two probe model of the fullerene junction in which C_{24} is sandwiched between two semi-infinite gold (1, 1, 1) electrodes.

2. Results and Discussions

2.1. Isolated Fullerene Molecules

Lorentzian density of states (DOS) is calculated from an imaginary part of retarded Greens function for molecular device and is denoted by the number of available quantum states per unit energy. It determines the probability that whether a given state at a given energy is occupied or unoccupied. DOS of isolated C_{20} and C_{24} fullerene molecules are shown in Fig. 2.

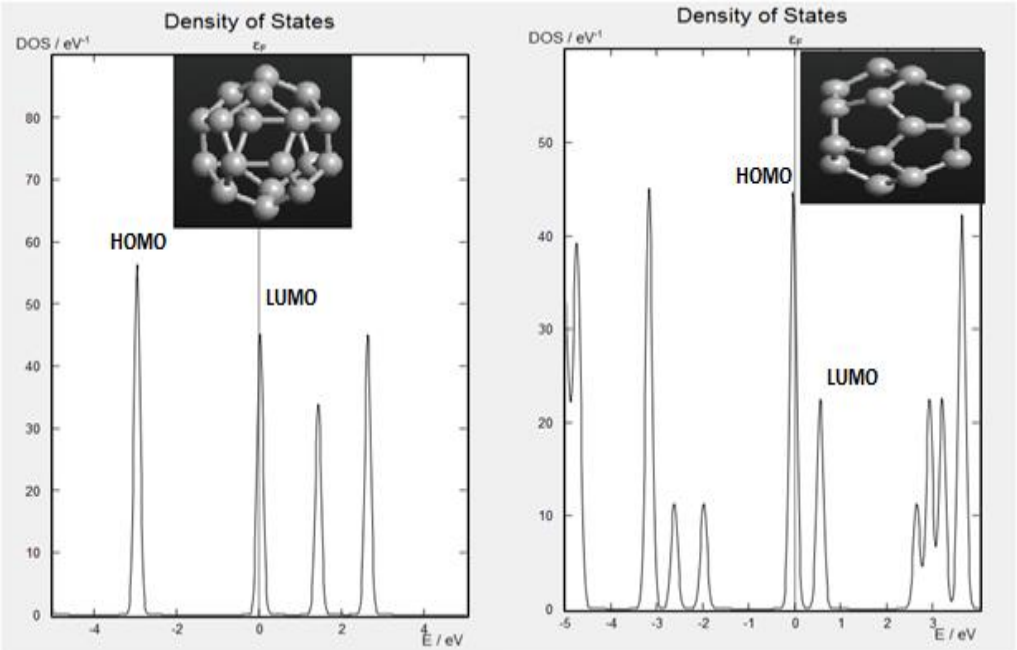
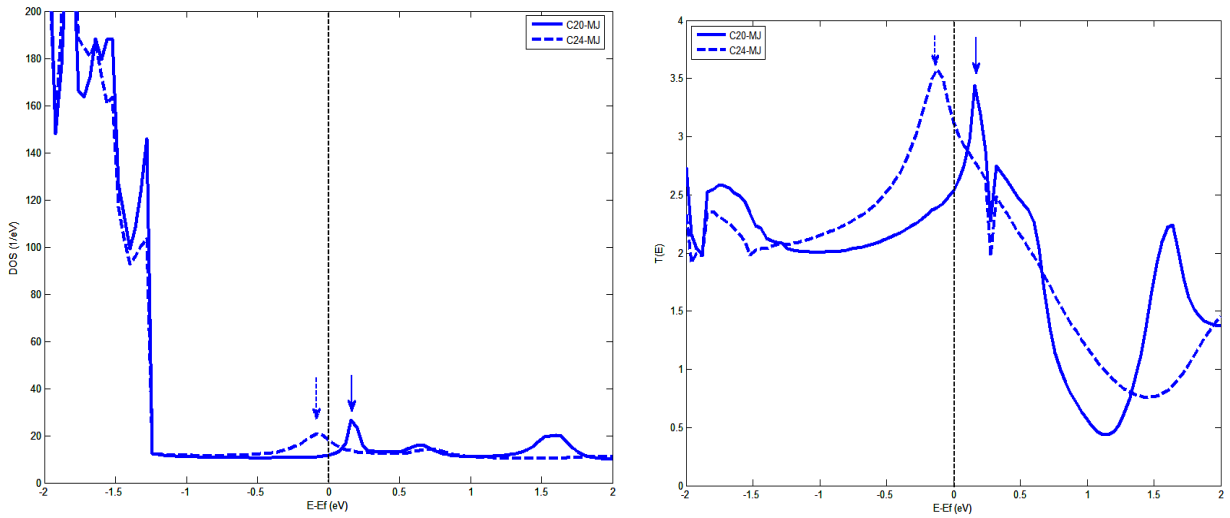


Fig. 2. Lorentzian DOS of isolated C_{20} and C_{24} fullerene molecules as a function of energy (eV), the fermi level (E_F) has been shifted to zero for clarity. Inset depicts the nature of fullerene molecule.

DOS shown in Fig. 2 manifests the number of both available and unavailable quantum states in the vicinity of fermi energy (E_F = 0eV). Isolated C_{24} fullerene molecule exhibits large number of peaks in comparison to that of C_{20} in the DOS-energy spectrum, which implies that former fullerene molecule has large number of available quantum states for electrons to exhibit transmissions. In addition to that, both HOMO and LUMO peaks are in close proximity to E_F in DOS portrayed by C_{24}. However, in DOS assayed by C_{20} molecule, only unoccupied state LUMO is close to E_F whereas occupied counterpart HOMO is found to be away from fermi level. It entails that C_{20} molecule exhibits wide HLG in contrast to that of C_{24}. Third inference that we developed from Fig. 2 is that though both HOMO and LUMO resonant states are close to fermi level in DOS of C_{24}, however, electron transport would be prominently exhibited through HOMO since it is closest to fermi energy and has higher magnitude than that of LUMO. These observations give us the notion that C_{24} should be more conductive than C_{20} fullerene molecule.

2.2. Molecular Junction Formed from Fullerene Molecules

The electron transport properties of the MJs in equilibrium depend on the details of the charge transfer between the electrode–molecule–electrode system. We have calculated the Mulliken charge [15] on the central fullerene molecules C_{20} and C_{24} of the MJs which are tabulated in Table 1. It can be seen that C_{24} in the MJ gains 0.184e compared to isolated C_{24}, whereas C_{20} in the MJ loses 0.056e compared to free C_{20}. For the C_{20}-MJ, the gold electrodes have gained a slight increase in electron density, namely, 0.064e and 0053e for the left and right electrodes, respectively. The gold electrodes of the C_{24}-MJ, on the other hand, have lost a small amount of electron density, i.e. 0071e and 0048e on the left and right electrodes, respectively, consistent with the observed increase on the C_{24} molecule of the junction. This charge transfer alters the orbital energies and occupancies of the free molecules, resulting in a broad transmission peak for the C_{24}-MJ, and a high conductance of 3.12 G_0, and a somewhat smaller conductance of 2.5 G_0 for the C_{20}-MJ.



a) b)

Fig. 3. a) Device (i.e. electrode-molecule-electrode) density of states (DOS) and b) Transmission T(E) at zero bias. The energy zero is at the Fermi energy, E_F. The arrows represent resonant molecular orbitals participating in electron transport.

Fig. 3 illustrates the density of states (DOS) and transmission functions [16], [17] for the C_{20}-MJ and C_{24}-MJ. Superior conducting material is dictated by three factors determined from the DOS and transmission function, T(E), : a) high value of T(E) at E_F , b) transmission peaks lying in the vicinity of E_F (=0 eV), and c) high and broad transmission peaks. C_{24}-MJ is found to be a superior conductive material than C_{20}-MJ

because of its higher value of $T(E_F)$, approximately equal to 3.13, HOMO and LUMO transmission peaks in closer proximity to E_F and broader transmission peak, which gives rise to a conductance of $3.12G_0$, where G_0 is quantized conductance and its value is 77.48 μS [18]. The C_{20}-MJ exhibits transmission prominently through the LUMO, in vicinity of E_F, resulting in $T(E_F) \approx 2.5$, and a conductance of 2.5 G_0. Both MJs formed from the smallest fullerenes are found to be superconductors with conductance more than two times the quantum of conductance. However the MJ formed from the C_{24} fullerene is concluded to be a better superconductor in comparison with that formed from C_{20} when connected between gold electrodes.

Table 1. Total Electron Charge of the C_{20} and C_{24} Fullerenes, and of the Left and Right Gold Electrodes

Molecular Junction (MJ)	Left Gold electrodes (27×11=297e)	Central fullerene (20×4=80e for C_{20}) (24×4=96e for C_{24})	Right Gold electrodes (27×11=297e)
C_{20}-MJ	297.064	79.944	297.053
C_{24}-MJ	296.929	96.184	296.952

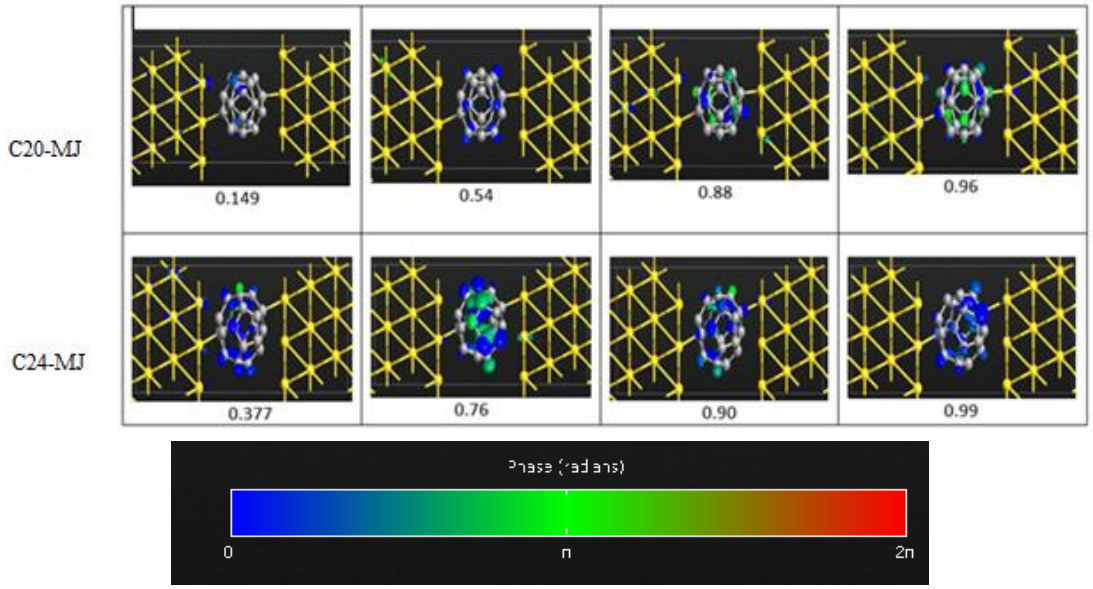


Fig. 4. Transmission eigenstates with transmission modes exhibited by C_{20}-MJ and C_{24}-MJ at zero bias.

From the transmission spectra, we further computed transmission eigenvalues (modes) and their corresponding transmission eigenstates plotted in Fig. 4. The eigenstate corresponds to a scattering state coming from the left gold electrode and traveling towards the right gold electrode via fullerene molecule. In case of testbed C_{24}-MJ, eigenstates with a relatively high transmission eigenvalue portray relatively large amplitude in the right-hand part of the scattering region. This simply reflects the relatively high transmission probability of an incoming state (at a specific energy, spin, and k-point) that travels through the central scattering region and into the right gold electrode. The transmission eigenstates in the left part of the scattering region are composed of an incoming (right -moving) and a reflected (left-moving) state. This leads to interference effects, which can be observed in the first transmission eigenvalues of 0.149 and 0.377 assayed by C_{20}-MJ and C_{24}-MJ respectively. The eigenstate amplitude around the first C atom in C_{24}-MJ is relatively small due to destructive interference between the incoming and reflected state and the eigenstate at the last C atom to the right of scattering region consists only of the transmitted (right-moving) states, and no such interference effects are observed. It signifies that on account of perfect alignment of molecular orbitals of C_{24} with 6s atomic orbitals of gold atoms, testbed C_{24}-MJ manifests large number of

transmission of electrons from left Au leads to right Au leads and thus concludes higher conductance of 3.15 times quantized conductance. However, C_{20} fullerene molecule in testbed C_{20}-MJ displays the contribution of only LUMO state which coupled strongly with Au leads and participated in transport of electrons and depicts 2.5 times quantized conductance. The results portrayed by both DOS and transmission spectra are found to be analogous to each other. Further, the decomposition of transmission channels into molecular orbitals provides an insight into the relevance of molecular levels, which is elaborated in the following section.

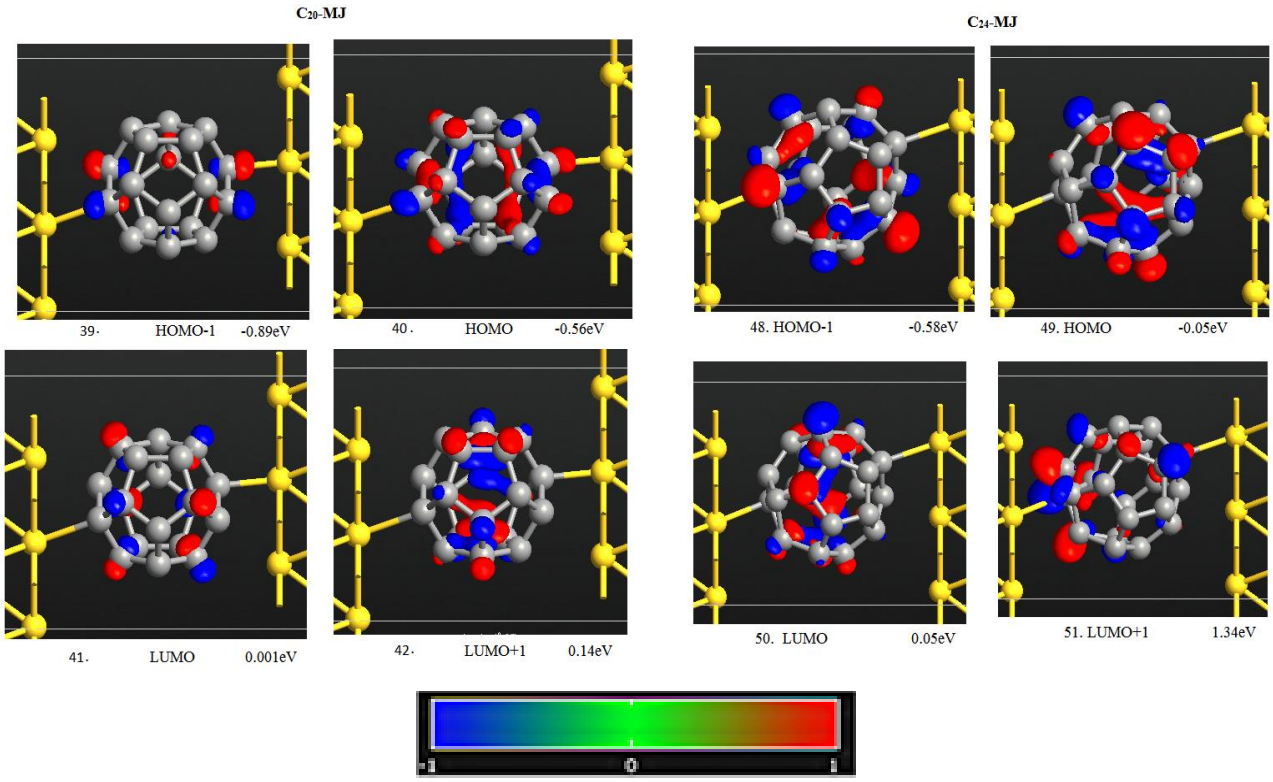


Fig. 5. Spatial distribution of the MPSH eigen states of C_{20}-MJ and C_{24}-MJ where red and blue denote different orbital phases.

The origin of transmission peaks shown in Fig. 3b is explored further from Molecular Projected Self-Consistent Hamiltonian (MPSH) States. From the full Hamiltonian, H, matrix of the molecular junctions, we projected onto the subspace spanned by the basis functions of the C_{20} and C_{24} fullerene molecules [19], as discussed in our previous study [16]. The eigen energies are calculated relative to electrode E_F (0eV) and include the charge transfer between central fullerene molecule and gold electrodes. Fig. 5 shows the frontier orbitals relevant for transmissions around E_F. For the C_{20}-MJ, the significant transmission features in the transmission function are due to the participation of orbital numbers 39, 40, 41 and 42 with energies -0.89eV, -0.56eV, 0.0010eV and 0.14eV respectively, with transmission being due to LUMO and LUMO+1. For the C_{24}-MJ, the peaks in the transmission function are due to the participation of orbital numbers 48, 49, 50 and 51 with energies -0.58eV, -0.05eV, 0.05V and 1.34eV, respectively. These results imply that two molecular states with orbital indices 39, 40 in C_{20}-MJ, and 48,49 in C_{24}-MJ, result in transmission via the HOMO-1 and HOMO states and the other two molecular orbitals with indices 41,42 in C_{20}-MJ and 50,51 in C_{24}-MJ result in transmission due to the LUMO and LUMO+1 states as shown in Fig. 5. Since the orbital states 41 and 42 have vanishing orbital weight close to Au electrodes, the broadening of gold electrodes is fragile, resulting in a narrow LUMO transmission peak [20]. On the other hand, the broad HOMO transmission peak of the C_{24}-MJ at -0.12eV is associated with two eigen states HOMO-1 (orbital number 48)

and HOMO (orbital number 49). Both these states exhibit significant orbital weight near gold electrodes, and efficient coupling with the C_{24} fullerene molecule. Thus, the very strong transmission peak near E_F in the C_{24}-MJ contributes to a high conductance of 3.15 times quantum conductance whereas the comparatively narrow transmission peak in C_{20}-MJ results in a comparatively lower conductance of 2.5 times quantum conductance. Hence, Au-C_{24}-Au is concluded to be more conductive than Au-C_{20}-Au under zero bias conditions.

In a nutshell, We find that the junction formed with C_{24} exhibits superior conductance, namely $3.12G_0$ in comparison to that of the junction formed with C_{20} where the value is $2.5G_0$. This is attributed to the charge transfer from the gold electrodes to C_{24} which results in occupation of a previously unoccupied molecular orbital just below the Fermi level. This gives rise to greater transmission at the Fermi level, and consequent greater conductivity. The junction formed with C_{20}, on the other hand exhibits comparatively low density of states at the Fermi level and consequent lower transmission function and conductivity.

3. Conclusion

We have investigated and compared the molecular junctions formed from the two smallest fullerene molecules C_{20} and C_{24} with gold electrodes employing DFT and the NEGF approach, for zero bias. The results established superior conducting nature of C_{24}-MJ in contrast to C_{20}-MJ. The findings deduced in this work could be very helpful in the development of smaller fullerenes in the field of single moletronic devices.

References

[1] Zotti, L. A., Kirchner, T., Cuevas, J., Pauly, F., Huhn, T., Scheer, E., & Erbe, A. (2010). *Small*, *6*, 1529–1535.

[2] Park, Y. S., Whalley, A. C., Kamenetska, M., Steigerwald, M. L., Hybertsen, M. S., Nuckolls, C., & Venkataraman, L. J. (2007). *Am. Chem. Soc., 129*, 15768–15769.

[3] Seideman, T. (2011). *Current-Driven Phenomena in Nanoelectronics*, Pan Stanford Publishing Pte. Ltd.: Singapore.

[4] Rudnev, A. V., Kaliginedi, V., Droghetti, A., Ozawa, H., Kuzume, A., Haga, M., Broekmann, P., & Rungger, I. (2007). *Sci. Adv., 3*, e1602297.

[5] Kroto, H. W. (1987). *Nature, 329*, 529.

[6] Martin, J. M. L., El-Yazal, J., & Francois, J. P. (1996). *Chem. Phys. Lett., 255(7)*.

[7] Lu, X., & Chen, Z. (2005). *Chem. ReV., 105*, 3643.

[8] Fowler, P. W., Batten, R. C., & Manopoulous, D. E. (1991). *J. Chem. Soc., Faraday Trans*., *87*, 3103.

[9] Atomistic Toolkit Manual, Quantumwise Inc.

[10] Frisch, M. J., Trucks, *et al*. (2004). Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT.

[11] Edyta, M., & Henryk A. W. (2007). *J. Phys. Chem. A, 111*, 6649-6657.

[12] Ke, S. H., Baranger, H. U. & Yang, W. J. *Chem Phys. 127*, 144107.

[13] Basis Set. Retrieved from https://en.wikipedia.org/wiki/Basis_set_(chemistry)

[14] Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Phys. Rev. Lett.*, *77*, 3865.

[15] Kaur, R. P., Sawhney, R. S., & Engles, D. (2016). *Applied Physics A,* Springer, *122(12)*, 1-10.

[16] Kaur, R. P., Sawhney, R. S. & Engles, D. (2016). *Journal of Materials Research*, Cambridge University, USA31, *17*, 2649-2661.

[17] Brandbyge, M., Mozos, J.-L., Ordej´on, P., Taylor, J., & Stokbro, K. (2002). Density-functional method for nonequilibrium electron transport, *Phys. Rev. B, 65*, 165401

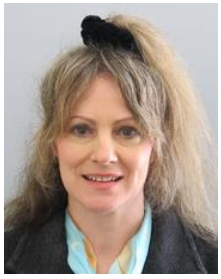
[18] Conductance Quantum. Retrieved from https://en.wikipedia.org/wiki/Conductance_quantum

[19] Beebe, J. M., Kim, B., Frisbie, C. D., & Kushmerick, J. G. (2008). Measuring relative barrier heights in

molecular electronic junctions with transition voltage spectroscopy. *ACS Nano*, *2*, 827.

[20] Tada, T., Nozaki, D., Kondo, M., Hamayama, S., & Yoshizawa, K. (2004). Oscillations of conductance in Molecular junctions of Carbon ladder compounds. *J. Am. Chem. Society, 126*,14182-14189.

Rupan Preet Kaur gets the Ph.D in the field of modeling and simulation of electronic transport properties of molecular junctions for nanoelectronics applications. She is an adjunct research fellow at Swinburne University of Technology, Melbourne. She has around 35 publications to her credit published in various peer-reviewed journals and conference proceedings. Currently she is working on the ab-initio computational electronic properties of two-dimensional materials for futuristic devices.



Catherine Stampfl is a professor at The School of Physics, The University of Sydney. Being an integral part of Condensed materials research group, her research interests are in computational condensed matter and material physics, based on density functional theory, to study new materials and nanostructures with high-performance computers for future technological applications, particularly in the field of heterogeneous catalysis and electronic materials. She has an excellent track record of over 160 publications, h-index of 46, with average citation per paper of 42 (web of science).