Designing multifunctional chemical sensors using Ni and Cu doped carbon nanotubes

D. J. Mowbray[*,1,2], **J. M. García-Lastra**[1,2], **K. S. Thygesen**[2], **A. Rubio**[1,3], **K. W. Jacobsen**[2]

[1] Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre, Dpto. Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain
[2] Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
[3] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

[*] Corresponding author: e-mail duncan_mowbray@ehu.es, Phone: +34-943-01-5366, Fax: +34-943-01-8390
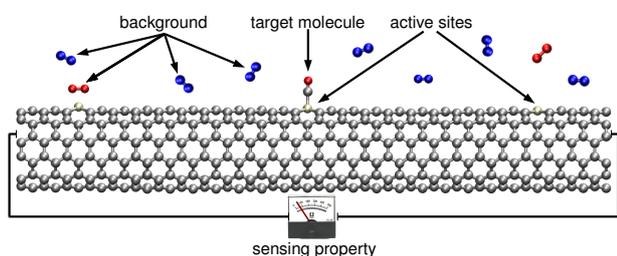
We demonstrate a "bottom up" approach to the computational design of a multifunctional chemical sensor. General techniques are employed for describing the adsorption coverage and resistance properties of the sensor based on density functional theory (DFT) and non-equilibrium Green's function methodologies (NEGF), respectively. Specifically, we show how Ni and Cu doped metallic (6,6) single-walled carbon nanotubes (SWNTs) may work as effective multifunctional sensors for both CO and NH$_3$.
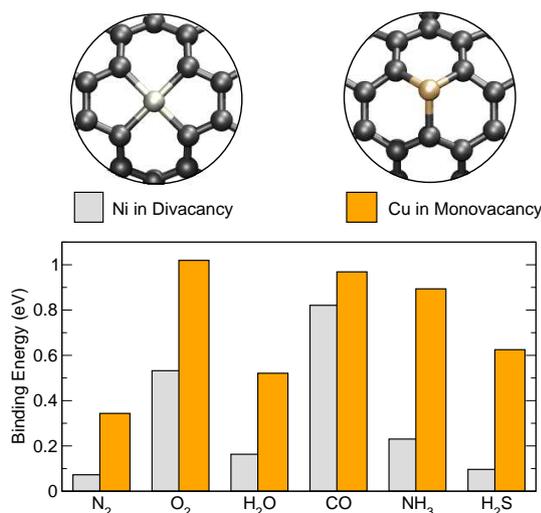
1 Introduction Detecting specific chemical species at small concentrations is of fundamental importance for many industrial/scientific processes, medical applications, and environmental monitoring [1]. Nanostructured materials are ideally suited for sensor applications because of their large surface to volume ratio, making them sensitive to the adsorption of individual molecules. Specifically, single-walled carbon nanotubes (SWNTs) [2] work remarkably well as detectors for small gas molecules, as demonstrated for both individual SWNTs [3–8] and

Figure 1 Schematic of a chemical sensor consisting of active sites (metal dopants in a (6,6) carbon nanotube), a target molecule (CO), a background (atmospheric air), and a sensing property (resistance).

SWNT networks [9, 10]. Previous studies have shown that SWNTs are highly sensitive to most molecules upon functionalization [11–19]. However, the difficulty is determining which specific molecules are present. In this study we show how changing the functionalization provides "another handle" for differentiating the SWNTs response of different gases/molecules.

Recent experimental advances now make the controlled doping of chirality selected SWNTs with metal atoms a possibility. Specifically, these include (1) photo-moluminesence, Raman and XAS techniques for measuring the fraction of various SWNT chiralities in an enriched sample [20–22]; (2) the separation of SWNT samples by chirality using DNA wrapping [23–26], chromatographic separation [26, 27] and Density Gradient Ultracentrifugation (DGU)[28]; (3) SWNT resonators for measuring individual atoms of a metal vapour which adsorb on a SWNT [29, 30]; and (4) aberration corrected low energy (<50 keV) transmission electron microscopy (TEM) [31]. The latter provides control over the formation of defects *in situ* by adjusting the energy of the electron beam above and below the threshold energy for defect formation at a specific location in the SWNT. These methods provide such a high level of control that it is now possible for experimentalists to take a specific SWNT chirality and dope

Figure 2 Binding energies in eV for N_2, O_2, H_2O, CO, NH_3, and H_2S on a Ni atom occupying a divacancy site (grey) and on a Cu atom occupying a monovacancy site (orange) in a (6,6) carbon nanotube. Schematics of the two active sites are shown above.

the structure with individual metal atoms at a specified location.

At the same time, theorists are now able to embrace a "bottom up" approach to the design of nanosensors, harnessing the thermodynamics of self-assembly to find useful sensing systems *in silico*. With recent advances in both computational power and methodologies, theorists can now efficiently and accurately screen hundreds of candidate sensor designs using a combination of density functional theory (DFT) for energetics of adsorption and stability, and non-equilibrium Green's function (NEGF) methodologies for the electrical response [32].

In general, any nanosensing system consists of the following four main components: (1) a "target molecule" to be detected, (2) an "active site" where the target molecule may adsorb on the sensor, (3) a property of the sensor which changes upon adsorption of the target molecule, and (4) a "background" of adsorbing molecules which make up the background signal, as depicted in Fig. 1. For the sensor to be effective, the active site must be designed so that adsorption of the target molecule in the presence of the background is sufficient to change the sensing property.

In this study we shall consider Ni and Cu doped metallic (6,6) SWNTs as our active sites, specifically when Ni replaces two C atoms in a divacancy structure, and Cu replaces a single C atoms in the monovacancy structure, as shown schematically in Fig. 2. Of the two possible orientations for a divacancy in an armchair SWNT, we here consider the one in which Ni adsorption has been shown to be more favourable. These two active sites have previously been shown to be both stable, and somewhat resistant to oxidation under standard atmospheric pressure
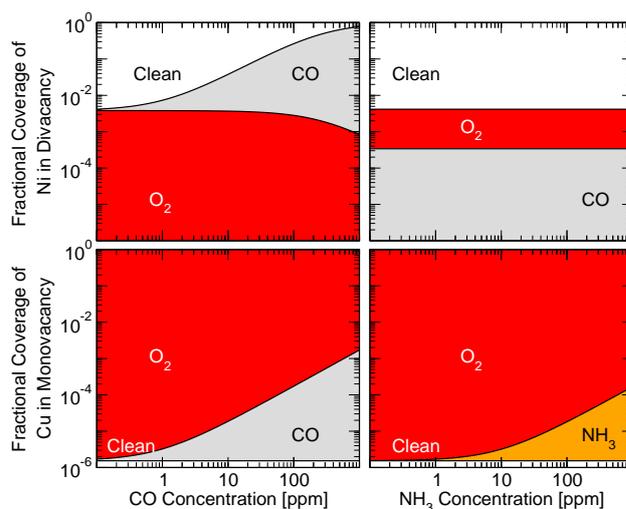
Figure 3 Fractional coverage in thermal equilibrium of Ni in a divacancy (top) and Cu in a monovacancy (bottom) versus CO concentration (left) and NH_3 concentration (right) in a background of air at room temperature and 1 bar of pressure.

Table 1 Equilibrium atmospheric concentrations at 4% absolute humidity.

Background	Concentration	Target	Concentration
N_2	74.96%	CO	96.00 ppb
O_2	20.11%	NH_3	16.32 ppb
H_2O	4.00%	H_2S	0.96 ppb

and room temperature [32]. As such, we shall consider the background to have a standard atmospheric composition with an absolute humidity of 4%, shown in Table 1.

2 Methodology All DFT calculations have employed the PBE exchange correlation (xc)-functional [33]. Adsorption energies and structural minimization calculations have been performed using the real-space projector-augmented-wave method DFT code GPAW [34], with a grid spacing of 0.2 Å, taking spin polarization into account. NEGF transport calculations [35] have employed the electronic Hamiltonian obtained from the DFT code SIESTA [36], with a double zeta polarized (DZP) localized basis set.

Vacancies in the (6,6) metallic carbon nanotube have been modelled using six repeated minimal unit cells, with a supercell of 15 Å × 15 Å × 14.622 Å. Such a large supercell was necessary to both minimize interactions between defects and adsorbates and to ensure the Hamiltonian of the nanotube layers adjacent to the cell boundaries was converged to within 0.1 eV of that for the pristine nanotube. For such a large supercell, a Γ point calculation was found to be sufficient to describe the nanotube's periodicity.
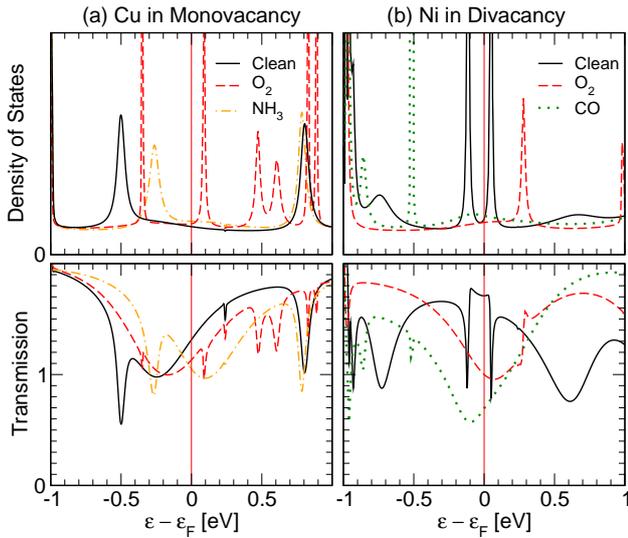
Figure 4 Density of states (top) and transmission function (bottom) versus energy ε relative to the Fermi level ε_{F} in eV for clean (solid line; black), O_2 occupied (dashed line; red), NH_3 occupied (dash-dotted line; orange), and CO occupied (dotted line; green) (a) Cu in monovacancy and (b) Ni in divacancy II of a (6,6) carbon nanotube.

Binding energies E_{bind} are defined as the difference in total energies between a gas phase target/background molecule with a clean active site and a target/background molecule adsorbed on an active site. As seen in Fig. 2, CO has a strong binding energy to both active sites, while NH_3 binds only to Cu in a monovacancy site. We shall use this in our design of a multifunctional sensor for both CO and NH_3.

3 Results & Discussion For a sensor containing hundreds, if not thousands of sites, the fractional coverage of sites is reasonably described by the fractional coverage in thermodynamic equilibrium Θ at standard temperature and pressure in terms of the target molecule concentration. Specifically for a sufficiently large ensemble of active sites, the fractional coverage of sites by a given adsorbate X in a background set of molecules $\mathcal{B}$ at equilibrium is given by
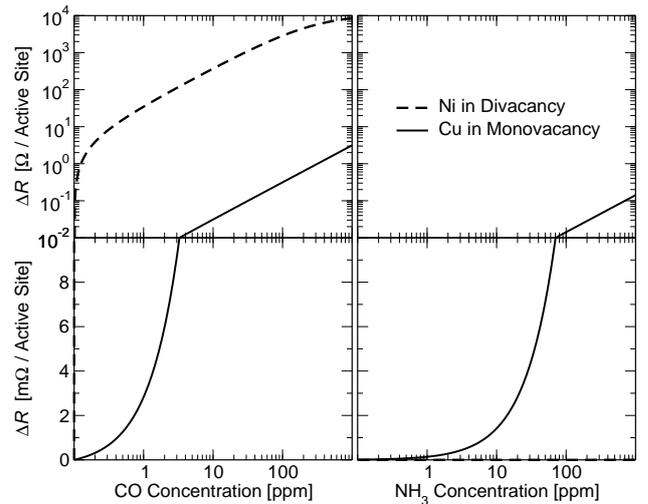
$$\Theta[X] = \frac{K[X]C[X]}{1 + \sum_{Y \in \mathcal{B}} K[Y]C[Y]}, \tag{1}$$

where $K = k_+/k_-$ is the ratio of forward and backward rate constants for the adsorption reaction. This may be expressed as

$$K[X] = \exp\left[\frac{E_{\mathrm{bind}}[X] - TS_{\mathrm{gas}}[X]}{k_B T}\right], \tag{2}$$

where $S_{\mathrm{gas}}[X]$ is the gas phase entropy of species X [37], k_B is Boltzmann's constant and T is the temperature.

In Fig. 3 we see the coverages of both Ni and Cu active sites as a function of CO and NH_3 concentration. Clearly,

Figure 5 Change in resistance ΔR in Ω (top) and mΩ (bottom) per active site versus CO (left) and NH_3 (right) concentration in ppm for Ni in a divacancy II (dashed line) and Cu in a monovacancy (solid line) of a (6,6) carbon nanotube. The reference concentrations of CO and NH_3 are 0.1 and 0.01 ppm, respectively, in a background of air at room temperature and 1 bar of pressure.

both Cu and Ni active sites will be sensitive to the adsorption of CO. On the other hand, the coverage of the Cu active sites is sensitive to NH_3 concentration, while Ni active sites are not. This suggests that by combining the response of Cu and Ni active sites, we may obtain a multifunctional sensor for both CO and NH_3.

However, although molecules may adsorb on the active sites, the sensing property of the SWNT resistance must change significantly for the sensor to be useful. In Fig. 4 we show both the density of states (DOS) and transmission probability $T(\varepsilon)$ for an electron of a given energy ε to travel past an active site as calculated within the NEGF method. Since the energy levels of a given molecule may be thought of as its electronic "finger print", so long as there is sufficient binding between the molecule and active site, this "finger print" is evidenced in the DOS of the system. Furthermore, the peaks of the DOS due to the molecule tend to form Fano anti-resonances in the transmission, as electrons are scattered off these states (*c.f.* Fig. 4). In this way, any adsorbed molecule tends to leave its "finger print" in the transmission probability through an active site. For this reason, conductance/resistance is generally an effective sensing property.

Finally, we may estimate the average change in resistance ΔR of an active site as a function of target molecule concentration. As discussed in Ref. [32], this change in resistance is reasonably well described by

$$\Delta R \approx \sum_X R_s(X)(\Theta[X, C] - \Theta[X, C_0]), \tag{3}$$

where C is the concentration, C_0 is the concentration at standard temperature and pressure, $R_s(X) = G_0(1/\text{T}(\varepsilon_F, X) - 1/(2)$, $G_0 \equiv 2e^2/h$ is the quantum of conductance, and $\text{T}(\varepsilon_F, X)$ is the transmission probability at the Fermi level through an active site with species X adsorbed.

In Fig. 5 we show ΔR for a single active site (Ni or Cu) as a function of target molecule concentration (CO or NH$_3$). Keeping in mind that a change in concentration from 1 ppm to 50 ppm amounts to a change from allowable to toxic concentrations for both CO and NH$_3$, we see that this sensor design should work effectively for both target molecules.

4 Conclusions In conclusion, we have demonstrated *in silico* how a combined Cu and Ni doped metallic SWNT device may work effectively as a multifunctional sensor for both CO and NH$_3$. The methodology employed is applicable to other sensor designs and different environments. Also, by varying the metal dopant, we obtain "another handle" for tuning the sensitivity of our sensor.

References

[1] *Gas Sensing Materials, MRS Bull.*, vol. 24 (1999).

[2] J. C. Chalier, X. Blase, and S. Roche, "Electronic and transport properties of nanotubes", Rev. Mod. Phys. **79**(2), 677 (May 2007), doi:10.1103/RevModPhys.79.677.

[3] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, "Nanotube molecular wires as chemical sensors", Science **287**(5453), 622 (Jan. 2000), doi:10.1126/science.287.5453.622.

[4] P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, "Extreme oxygen sensitivity of electronic properties of carbon nanotubes", Science **287**(5459), 1801 (Mar. 2000), doi:10.1126/science.287.5459.1801.

[5] C. Hierold, *Carbon Nanotube Devices: Properties, Modeling, Integration and Applications* (Wiley-VCH, Weinheim, 2008).

[6] F. Villalpando-Páez, A. H. Romero, E. Muñoz-Sandoval, L. M. Martínez, H. Terrones, and M. Terrones, "Fabrication of vapor and gas sensors using films of aligned CN$_x$ nanotubes", Chem. Phys. Lett. **386**(1-3), 137 (Mar. 2004), doi:10.1016/j.cplett.2004.01.052.

[7] A. R. Rocha, M. Rossi, A. Fazzio, and A. J. R. da Silva, "Designing real nanotube-based gas sensors", Phys. Rev. Lett. **100**(17), 176803 (May 2008), doi:10.1103/PhysRevLett.100.176803.

[8] S. Brahim, S. Colbern, R. Gump, and L. Grigorian, "Tailoring gas sensing properties of carbon nanotubes", J. Appl. Phys. **104**(2), 024502 (Jul. 2008), doi:10.1063/1.2956395.

[9] C. Morgan, Z. Alemipour, and M. Baxendale, "Variable range hopping in oxygen-exposed single-wall carbon nanotube networks", Phys. Stat. Solidi A **205**(6), 1394 (May 2008), doi:10.1002/pssa.200778113.

[10] D. J. Mowbray, C. Morgan, and K. S. Thygesen, "Influence of O$_2$ and N$_2$ on the conductivity of carbon nanotube networks", Phys. Rev. B **79**(19), 195431 (May 2009), doi:10.1103/PhysRevB.79.195431.

[11] S. B. Fagan, R. Mota, A. J. R. da Silva, and A. Fazzio, "*Ab initio* study of an iron atom interacting with single-wall carbon nanotubes", Phys. Rev. B **67**(20), 205414 (May 2003), doi:10.1103/PhysRevB.67.205414.

[12] Y. Yagi, T. M. Briere, M. H. F. Sluiter, V. Kumar, A. A. Farajian, and Y. Kawazoe, "Stable geometries and magnetic properties of single-walled carbon nanotubes doped with $3d$ transition metals: A first-principles study", Phys. Rev. B **69**(7), 075414 (Feb. 2004), doi:10.1103/PhysRevB.69.075414.

[13] S. H. Yang, W. H. Shin, J. W. Lee, S. Y. Kim, S. I. Woo, and J. K. Kang, "Interaction of a transition metal atom with intrinsic defects in single-walled carbon nanotubes", J. Phys. Chem. B **110**(28), 13941 (Jun. 2006), doi:10.1021/jp061895q.

[14] K. T. Chan, J. B. Neaton, and M. L. Cohen, "First-principles study of metal adatom adsorption on graphene", Phys. Rev. B **77**(23), 235430 (Jun. 2008), doi:10.1103/PhysRevB.77.235430.

[15] C. S. Yeung, L. V. Liu, and Y. A. Wang, "Adsorption of small gas molecules onto Pt-doped single-walled carbon nanotubes", J. Phys. Chem. C **112**(19), 7401 (Apr. 2008), doi:10.1021/jp0753981.

[16] T. Vo, Y.-D. Wu, R. Car, and M. Robert, "Structures, interactions, and ferromagnetism of Fe-carbon nanotube systems", J. Phys. Chem. C **112**(22), 400 (May 2008), doi:10.1021/jp0761968.

[17] J. A. Fürst, M. Brandbyge, A.-P. Jauho, and K. Stokbro, "*Ab initio* study of spin-dependent transport in carbon nanotubes with iron and vanadium adatoms", Phys. Rev. B **78**(19), 195405 (Nov. 2008), doi:10.1103/PhysRevB.78.195405.

[18] J. M. García-Lastra, K. S. Thygesen, M. Strange, and Ángel Rubio, "Conductance of sidewall-functionalized carbon nanotubes: Universal dependence on adsorption sites", Phys. Rev. Lett. **101**(23), 236806 (Dec. 2008), doi:10.1103/PhysRevLett.101.236806.

[19] A. V. Krasheninnikov, P. O. Lehtinen, A. S. Foster, P. Pyykkö, and R. M. Nieminen, "Embedding transition-metal atoms in graphene: Structure, bonding, and magnetism", Phys. Rev. Lett. **102**(12), 126807 (Mar. 2009), doi:10.1103/PhysRevLett.102.126807.

[20] C. Kramberger, H. Rauf, H. Shiozawa, M. Knupfer, B. Buchner, T. Pichler, D. Batchelor, and H. Kataura, "Unraveling van hove singularities in x-ray absorption response of single-wall carbon nanotubes", Phys. Rev. B **75**(23), 235437 (Jun. 2007), doi:10.1103/PhysRevB.75.235437.

[21] P. Ayala, Y. Miyata, K. De Blauwe, H. Shiozawa, Y. Feng, K. Yanagi, C. Kramberger, S. R. P. Silva, R. Follath, H. Kataura, and T. Pichler, "Disentanglement of the electronic properties of metallicity-selected single-walled carbon nanotubes", Phys. Rev. B **80**(20), 205427 (Nov. 2009), doi:10.1103/PhysRevB.80.205427.

[22] K. De Blauwe, D. J. Mowbray, Y. Miyata, P. Ayala, A. Rubio, P. Hoffman, H. Kataura, and T. Pichler (2010), (submitted).

[23] M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. Mclean, S. R. Lustig, R. E. Richardson, and N. G. Tassi, "Dna-assisted dispersion and separation of carbon nanotubes", Nature Materials **2**(5), 338 (May 2003), doi:10.1038/nmat877.

[24] M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, S. G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. McLean, G. B. Onoa, G. G. Samsonidze, E. D. Semke, M. Usrey, and D. J. Walls, "Structure-based carbon nanotube sorting by sequence-dependent dna assembly", Science **302**(5650), 1545 (Nov. 2003), doi:10.1126/science.1091911.

[25] X. M. Tu, S. Manohar, A. Jagota, and M. Zheng, "Dna sequence motifs for structure-specific recognition and separation of carbon nanotubes", Nature **460**(7252), 250 (Jul. 2009), doi:10.1038/nature08116.

[26] X. L. Li, X. M. Tu, S. Zaric, K. Welsher, W. S. Seo, W. Zhao, and H. J. Dai, "Selective synthesis combined with chemical separation of single-walled carbon nanotubes for chirality selection", J. Amer. Chem. Soc. **129**(51), 15770 (Dec. 2007), doi:10.1021/ja077886s.

[27] J. A. Fagan, J. R. Simpson, B. J. Bauer, S. H. D. Lacerda, M. L. Becker, J. Chun, K. B. Migler, A. R. H. Walker, and E. K. Hobbie, "Length-dependent optical effects in single-wall carbon nanotubes", J. Amer. Chem. Soc. **129**(34), 10607 (Aug. 2007), doi:10.1021/ja073115c.

[28] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, and M. C. Hersam, "Sorting carbon nanotubes by electronic structure using density differentiation", Nature Nanotechnology **1**(1), 60 (Oct. 2006), doi:10.1038/nnano.2006.52.

[29] B. Lassagne, D. Garcia-Sanchez, A. Aguasca, and A. Bachtold, "Ultrasensitive mass sensing with a nanotube electromechanical resonator", Nano Lett. **8**(11), 3735 (Oct. 2008), doi:10.1021/nl801982v.

[30] K. Jensen, K. Kim, and A. Zettl, "An atomic-resolution nanomechanical mass sensor", Nature Nanotech. **3**, 533 (Sep. 2008), doi:10.1038/nnano.2008.200.

[31] C. Jin, H. Lan, K. Suenaga, L. Peng, and S. Iijima, "Metal atom catalyzed enlargement of fullerenes", Phys. Rev. Lett. **101**(17), 176102 (Oct. 2008), doi:10.1103/PhysRevLett.101.176102.

[32] J. M. García-Lastra, D. J. Mowbray, K. S. Thygesen, Á. Rubio, and K. W. Jacobsen (2010), arXiv:1001.2538v1, [cond-mat:mes-hall] (submitted).

[33] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple", Phys. Rev. Lett. **77**(18), 3865 (Oct. 1996), doi:10.1103/PhysRevLett.77.3865.

[34] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, "Real-space grid implementation of the projector augmented wave method", Phys. Rev. B **71**(3), 035109 (Jan. 2005), doi:10.1103/PhysRevB.71.035109.

[35] M. Strange, I. S. Kristensen, K. S. Thygesen, and K. W. Jacobsen, "Benchmark density functional theory calculations for nanoscale conductance", J. Chem. Phys. **128**(11), 114714 (Mar. 2008), doi:10.1063/1.2839275.

[36] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejón, and D. Sánchez-Portal, "The SIESTA method for *ab initio* order-n materials simulation", J. Phys.: Condens. Matter **14**(11), 2745 (Mar. 2002), doi:10.1088/0953-8984/14/11/302.

[37] D. Lide, *Handbook of Chemistry and Physics*, 87th ed. (CRC-Press, 2006–2007).