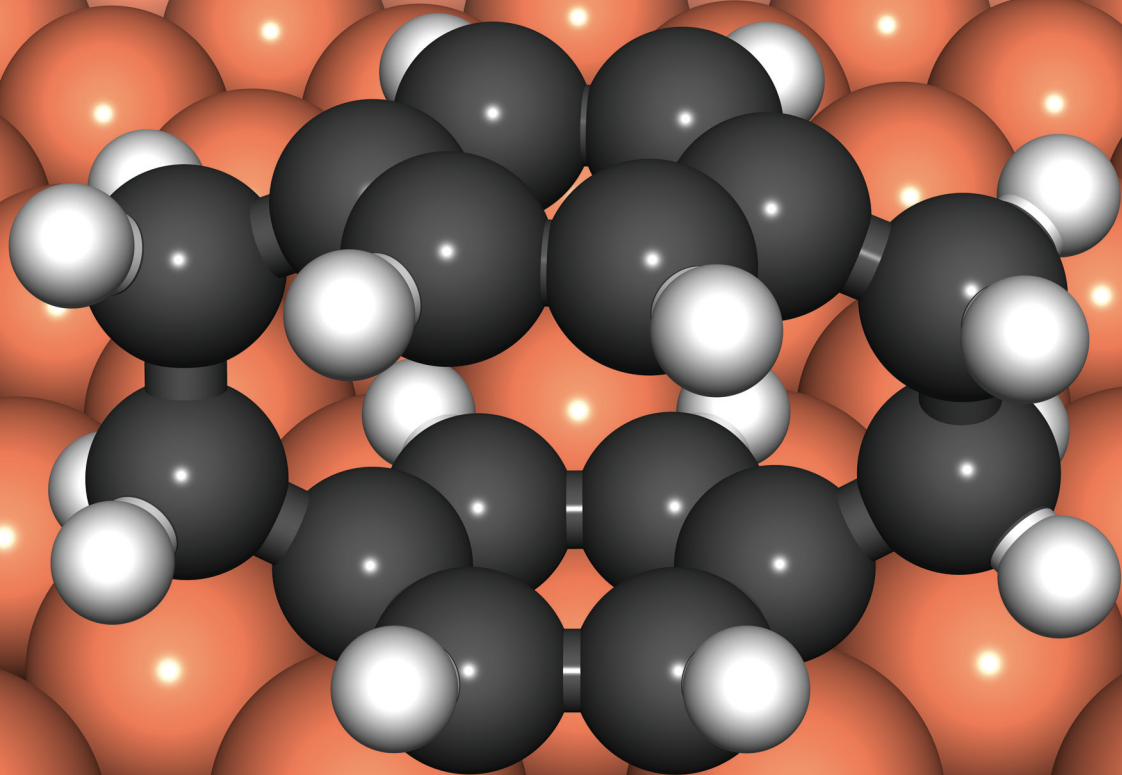




## Ab initio investigations of $\pi$ -conjugated-molecule-metal interfaces for molecular electronics and spintronics

Martin Callsen

Forschungszentrum Jülich GmbH  
Peter Grünberg Institute (PGI)  
Quantum Theory of Materials (PGI-1 / IAS-1)

# **Ab initio investigations of $\pi$ -conjugated- molecule-metal interfaces for molecular electronics and spintronics**

Martin Callsen

Schriften des Forschungszentrums Jülich  
Reihe Schlüsseltechnologien / Key Technologies

Band / Volume 92

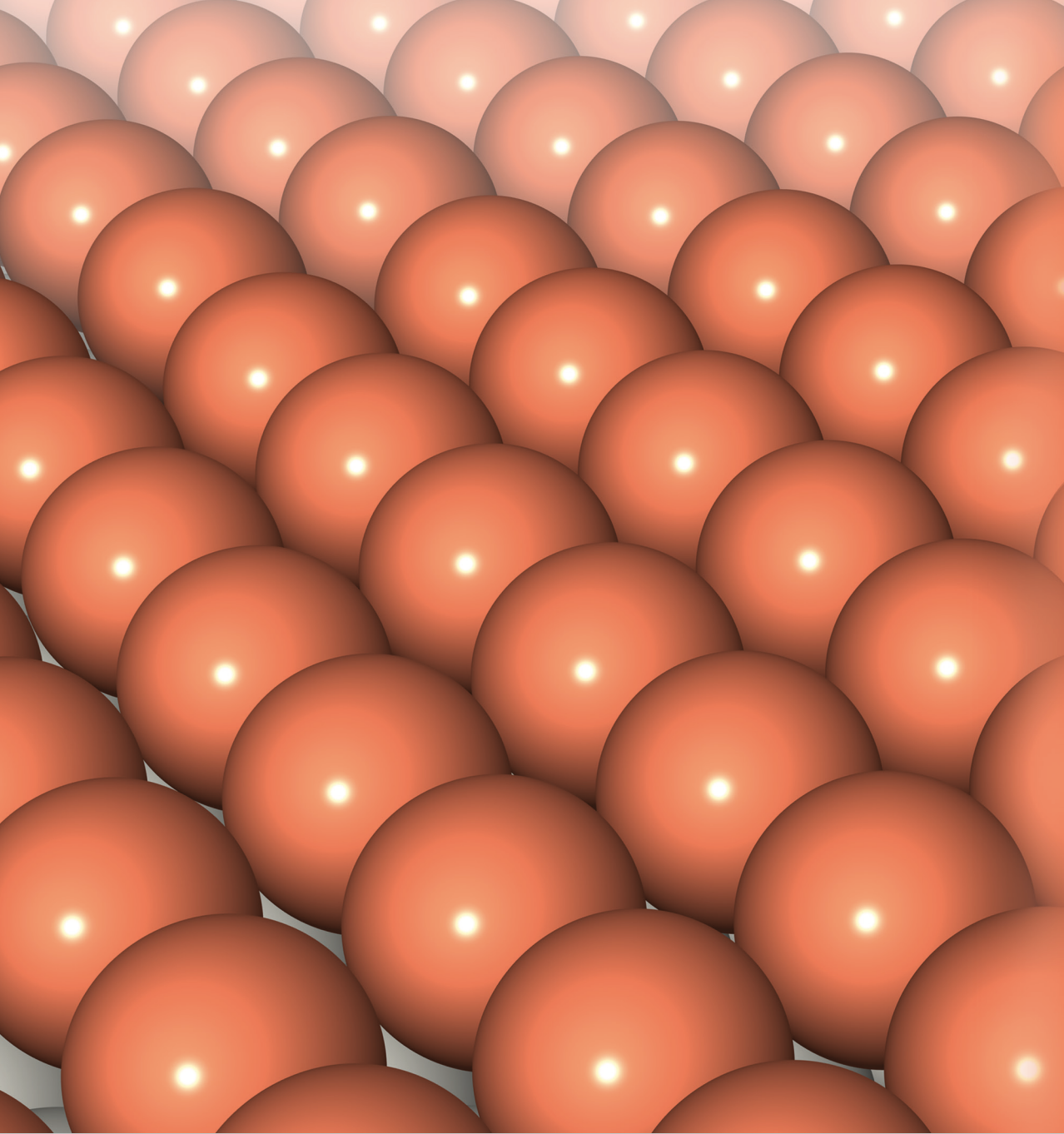
ISSN 1866-1777

ISBN 978-3-89336-992-8

# Contents

|                                                                                            |           |
|--------------------------------------------------------------------------------------------|-----------|
| <b>1. Molecular electronics and spintronics: an introduction</b>                           | <b>1</b>  |
| 1.1. Molecular electronics . . . . .                                                       | 2         |
| 1.2. Physisorption and chemisorption . . . . .                                             | 5         |
| 1.3. Molecular spintronics . . . . .                                                       | 7         |
| 1.4. Magnetic exchange and anisotropy . . . . .                                            | 9         |
| <b>2. Density functional theory</b>                                                        | <b>13</b> |
| 2.1. Basics of DFT . . . . .                                                               | 15        |
| 2.2. Extension to the spin-polarized case . . . . .                                        | 18        |
| 2.3. Spin-Orbit-Coupling . . . . .                                                         | 20        |
| 2.4. Exchange and correlation functionals . . . . .                                        | 20        |
| 2.5. DFT in practice . . . . .                                                             | 24        |
| <b>3. Van der Waals interactions</b>                                                       | <b>27</b> |
| 3.1. London dispersion . . . . .                                                           | 28        |
| 3.2. Van der Waals interactions in DFT . . . . .                                           | 31        |
| 3.3. vdW-DF in JuNoLo . . . . .                                                            | 39        |
| <b>4. Semi-empirical dispersion versus <i>ab initio</i> correlation effects</b>            | <b>41</b> |
| 4.1. Thiophene on Cu(111) . . . . .                                                        | 41        |
| 4.2. From weak to strong coupling - COT on Au(111), Au(100), Ag(100) and Cu(100) . . . . . | 60        |
| <b>5. Molecular spintronics</b>                                                            | <b>79</b> |
| 5.1. Cyclooctatetraene on magnetic and nonmagnetic adatoms on Au(111) . .                  | 80        |
| 5.2. Paracyclophane on Fe/W(110) . . . . .                                                 | 87        |

|                                                                                                            |            |
|------------------------------------------------------------------------------------------------------------|------------|
| 5.3. Paracyclophane on Fe/W(100) . . . . .                                                                 | 99         |
| <b>6. Summary</b>                                                                                          | <b>105</b> |
| <b>A. Ansatz for a spin dependent version of vdW-DF</b>                                                    | <b>107</b> |
| A.1. XC-Functional from the ACFD-theorem . . . . .                                                         | 107        |
| A.2. The response function $\chi_{\lambda}^{\sigma\sigma'}$ and the Full-Potential-Approximation . . . . . | 109        |
| A.3. The mostly local part of $E_{\text{xc}}$ . . . . .                                                    | 114        |
| A.4. Derivation of vdW-DF continued . . . . .                                                              | 115        |
| A.5. A model for $S(\mathbf{k}, \mathbf{k}', \omega)$ . . . . .                                            | 119        |
| A.6. The kernel function $\phi$ . . . . .                                                                  | 120        |
| A.7. The VV10 kernel . . . . .                                                                             | 121        |
| A.8. Additional thoughts based on modern theory of polarization . . . . .                                  | 123        |
| <b>B. An efficient implementation of vdW-DF: The Soler scheme</b>                                          | <b>125</b> |
| B.1. Decomposition of the kernel . . . . .                                                                 | 125        |
| B.2. Adjustments of the VV10 functional . . . . .                                                          | 127        |
| B.3. The potential $v_{\text{c}}^{\text{nl}}$ . . . . .                                                    | 128        |
| B.4. Test calculations . . . . .                                                                           | 129        |
| <b>Bibliography</b>                                                                                        | <b>131</b> |
| <b>Publications</b>                                                                                        | <b>155</b> |



**Schlüsseltechnologien / Key Technologies**  
**Band / Volume 92**  
**ISBN 978-3-89336-992-8**

