

# Contents

<b>1</b>	<b>General Introduction</b>	1
1.1	Limitations of Conventional Electronics	1
1.2	Nanotechnology	2
1.3	Organic Electronics	4
1.4	Experimental Setup	5
1.4.1	Photo-Electron Spectroscopy	5
1.4.2	Scanning Tunneling Microscope	8
1.4.3	Mechanically Controlled Break Junction	10
1.5	This Thesis	11
	References	13
<b>2</b>	<b>Theoretical Foundation</b>	17
2.1	Introduction	17
2.2	Statement of the Problem	17
2.2.1	Hartree Approximation	18
2.2.2	Hartree-Fock Approximation	19
2.2.3	Configuration Interaction	20
2.2.4	Møller-Plesset Perturbation Theory	21
2.2.5	Pseudopotential	21
2.3	Density Functional Theory	22
2.3.1	Kohn-Sham Equations	24
2.3.2	Exchange and Correlation Functional Approximations	27
2.4	The FIREBALL Method	28
2.4.1	Fireball Orbitals	29
2.4.2	The Harris Functional	30
2.4.3	Exchange and Correlation	31
2.4.4	Molecular Dynamics and Structure Relaxation	35
2.5	LCAO-OO Method	37
2.5.1	Local Density LCAO-OO	39
2.6	Calculation of Transport Properties	42

2.6.1	Current Equation . . . . .	42
2.6.2	Stationary Current . . . . .	44
2.6.3	Conductance with Two Electrodes . . . . .	45
2.7	Corrections of DFT Deficiencies . . . . .	47
2.7.1	Weak Chemical and Van der Waals Interaction . . . . .	47
2.7.2	Underestimation of the Gap . . . . .	48
2.7.3	Hybrid HF-LDA Functional . . . . .	49
2.7.4	Koopmans' Shift . . . . .	52
2.7.5	Scissor Operator . . . . .	54
2.8	Other Methods for Correcting the Gap . . . . .	55
2.8.1	GW Method . . . . .	55
2.8.2	LDA+U Method . . . . .	56
	References . . . . .	58
<b>3</b>	<b>Further Developments in IDIS Model . . . . .</b>	<b>63</b>
3.1	Introduction . . . . .	63
3.2	Brief Introduction to Metal/Inorganic Semiconductor Interfaces . . . . .	64
3.2.1	Schottky–Mott Limit . . . . .	65
3.2.2	Bardeen Limit . . . . .	67
3.2.3	Intermediate Case . . . . .	67
3.2.4	Origin of Interface States . . . . .	69
3.3	Brief Introduction to Metal/Organic Interfaces . . . . .	70
3.3.1	Charge Transfer and Chemical Reactions . . . . .	70
3.3.2	Image Effect and Surface Charge Rearrangement: “Pillow” Dipole . . . . .	73
3.3.3	Intrinsic Molecular Dipole . . . . .	74
3.3.4	Effects on Real Devices . . . . .	74
3.3.5	The Integer Charge Transfer Model . . . . .	75
3.4	IDIS Model for Metal/Organic Semiconductor Interfaces . . . . .	76
3.4.1	Interface States and the Charge Neutrality Level . . . . .	76
3.4.2	Level Alignment and Screening Parameter . . . . .	78
3.4.3	Pillow Dipole . . . . .	79
3.4.4	Intrinsic Molecular Dipole . . . . .	81
3.4.5	Surface Dipole . . . . .	81
3.5	Mind the Gap: C <sub>60</sub> /Au(111) and Benzene/Au(111) Interfaces . . . . .	82
3.5.1	Geometry . . . . .	82
3.5.2	Interface Potential with LDA Gap Calculations . . . . .	84
3.5.3	C <sub>60</sub> /Au(111) Interface with a Larger Gap . . . . .	86
3.5.4	Discussion . . . . .	88
3.6	The Gap Problem . . . . .	89
	References . . . . .	90

<b>4</b>	<b>The IDIS Model at the Molecular Limit</b>	95
4.1	Introduction	95
4.2	C <sub>60</sub> Molecule Over a Au(111) Surface	96
4.2.1	IDIS Based Calculation of Charging Energy	98
4.2.2	Practical Implementation	99
4.2.3	Calculation of Pillow and Surface Potential at Low Coverages	101
4.2.4	C <sub>60</sub> /Au(111) Gap Calculation: Summary and Conclusions	101
4.3	Application of the IDIS Model at the Molecular Level: C <sub>60</sub> Between Two Tips	102
4.3.1	Mechanical Study	102
4.3.2	Electronic Analysis: Unified IDIS Model and Self-Interaction Correction	105
4.3.3	Conclusions	106
4.4	Barrier Formation for a Tip/C <sub>60</sub> /Au(111) Configuration	107
4.4.1	Geometry Calculations	107
4.4.2	Barrier Formation and Charging Energy	109
4.4.3	Pillow Potential	111
4.4.4	Conclusions	111
4.5	Conclusions	112
	References	112
<b>5</b>	<b>Results for Various Interfaces: C<sub>60</sub>, Benzene, TTF, TCNQ and Pentacene over Au(111)</b>	115
5.1	Introduction	115
5.2	C <sub>60</sub> /Au(111) Interface at Various Coverages	115
5.2.1	Geometry	116
5.2.2	The $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ Monolayer	117
5.2.3	IDIS Parameters for Various Coverages	118
5.2.4	Charging Energy for High Coverages	121
5.2.5	Extrapolation to the C <sub>60</sub> /Ag(111) and C <sub>60</sub> /Cu(111) Interfaces	123
5.2.6	Conclusions	125
5.3	Benzene/Au(111) Revisited: Realistic Gap and Benzene/Au Distance	126
5.3.1	Interaction Energy and Van der Waals Forces	126
5.3.2	Molecular Limit: $U$ and $\delta U$	127
5.3.3	Benzene Monolayer Interface Dipole	130
5.3.4	Extrapolation to Benzene/Ag, Cu Interfaces	131
5.3.5	Discussion	132
5.3.6	Conclusions	134
5.4	TTF/Au(111) Interface	134
5.4.1	Calculation Details	135

5.4.2	STM Images and TTF Geometry . . . . .	136
5.4.3	Interface Properties . . . . .	137
5.4.4	Discussion and Conclusions . . . . .	140
5.5	TCNQ/Au(111) Interface: Molecular Dipole . . . . .	141
5.5.1	Calculation Details and Geometry . . . . .	142
5.5.2	Theoretical STM Images . . . . .	143
5.5.3	Electronic Structure and Interface Potential . . . . .	144
5.5.4	Conclusions . . . . .	147
5.6	Pentacene/Au(111) Interface: Hybrid Method in Practice . . . . .	147
5.6.1	Geometry . . . . .	148
5.6.2	Density of States, Interface Dipole and Charging Energy . . . . .	149
5.6.3	Discussion and Conclusions . . . . .	152
5.7	Conclusions . . . . .	155
	References . . . . .	156
<b>6</b>	<b>General Conclusions and Future Work . . . . .</b>	<b>159</b>
6.1	Conclusions . . . . .	159
6.2	Future work . . . . .	161
	References . . . . .	161
	<b>Appendix A: Introduction to Second Quantization . . . . .</b>	<b>163</b>
	<b>Appendix B: Different Approximations for a Simple Benzene Model: Hybrid Functionals . . . . .</b>	<b>177</b>
	<b>Appendix C: Spin Dependent Extension of McWEDA and Hybrid Functionals . . . . .</b>	<b>189</b>
	<b>Curriculum Vitae . . . . .</b>	<b>195</b>

Energy Level Alignment and Electron Transport Through  
Metal/Organic Contacts

From Interfaces to Molecular Electronics

Abad, E.

2013, XVIII, 198 p., Hardcover

ISBN: 978-3-642-30906-9