

Contents

1	General Introduction	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
2	Theoretical Foundation	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
3	Further Developments in IDIS Model	63
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 ₆₀ /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 ₆₀ /Au(111) Interface with a Larger Gap	86
3.5.4	Discussion	88
3.6	The Gap Problem	89
	References	90

4 The IDIS Model at the Molecular Limit	95
4.1 Introduction	95
4.2 C ₆₀ 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 ₆₀ /Au(111) Gap Calculation: Summary and Conclusions	101
4.3 Application of the IDIS Model at the Molecular Level: C ₆₀ 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 ₆₀ /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
5 Results for Various Interfaces: C₆₀, Benzene, TTF, TCNQ and Pentacene over Au(111)	115
5.1 Introduction	115
5.2 C ₆₀ /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 ₆₀ /Ag(111) and C ₆₀ /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 δU	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
6	General Conclusions and Future Work	159
6.1	Conclusions	159
6.2	Future work	161
	References	161
	Appendix A: Introduction to Second Quantization	163
	Appendix B: Different Approximations for a Simple Benzene Model: Hybrid Functionals	177
	Appendix C: Spin Dependent Extension of McWEDA and Hybrid Functionals	189
	Curriculum Vitae	195