

Contents

1	An Introduction to Linear-Scaling Ab Initio Calculations	1
1.1	The Challenges of Spatial and Electronic Complexity	1
1.2	Outline of Dissertation	2
1.3	The Born–Oppenheimer Approximation	5
1.4	Density Functional Theory	7
1.5	The Kohn–Sham Equations	10
1.6	Exchange, Correlation and the Local Density Approximation	13
1.7	Spin-Density Functional Theory	15
1.8	The Pseudopotential Approximation	16
1.9	Periodicity and Brillouin Zone Sampling	20
1.10	The Plane-Wave and Psinc Basis Sets	22
1.11	Density-Matrix Formulation of DFT	25
1.12	Wannier Function and Density-Matrix Localisation	27
1.13	The ONETEP Method	29
	References	32
2	Linear-Scaling DFT + U for Large Strongly-Correlated Systems	37
2.1	Strongly-Correlated Systems	37
2.2	The DFT + U Method	40
2.3	Framework for Linear-Scaling DFT + U	45
2.4	Variations with Respect to the Density Kernel	48
2.5	Variations with Respect to the NGWFs	52
2.6	Variations with Respect to Ionic Positions	54
2.7	Scaling Tests on Nickel Oxide Nano-Clusters	56
	2.7.1 Computational Methodology	56
	2.7.2 Scaling of Computational Effort for DFT + U	57
2.8	Concluding Remarks	60
	References	61

3	Projector Self-Consistent DFT + U Using Nonorthogonal Generalised Wannier Functions	65
3.1	Localised Strongly-Correlated Subspaces	65
3.2	Methodological Framework	67
3.3	The Spatial Form of Hydrogenic Subspaces	68
3.4	Wannier Functions for Localised Subspaces	70
3.5	The Self-Consistent Projector Method	72
3.6	Application to Ligated Iron Porphyrins	74
3.6.1	Iron Porphyrin Derivatives	75
3.6.2	Computational Methodology	76
3.6.3	U and Z -Dependence of Magnetic Dipole Moments and Interaction Energies	76
3.6.4	Z -Dependence of Subspace Occupancy in FeP and FeP(CO)	78
3.6.5	Z -Dependent Kohn–Sham Bandgap of FeP and FeP(CO)	78
3.6.6	Z -Dependent Electric Dipole Moments of FeP and FeP(CO)	79
3.6.7	Dependence on the Interaction Parameter U	80
3.7	Convergence of the Projector Self-Consistency Algorithm	83
3.8	Computational Cost of Projector Self-Consistency	84
3.9	Forces in Projector Self-Consistent DFT + U	85
3.10	Concluding Remarks	86
	References	86
4	Subspace Representations in Ab Initio Methods for Strongly Correlated Systems	89
4.1	Motivation	89
4.2	Nonorthogonal Representations of the Occupancy Matrix	90
4.2.1	The “Full” and “On-Site” Representations	91
4.2.2	The “Dual” Representation	93
4.2.3	Requirement for a Subspace-Localised Hermitian Projection Operator	94
4.2.4	The “Tensorial” Representation	96
4.3	Application to the DFT + U Method	97
4.3.1	The Tensorially Invariant DFT + U Functional	98
4.3.2	DFT + U Potential and Ionic Forces	99
4.3.3	The Case of Orthonormal Hubbard Projectors	100
4.3.4	Invariance Under Generalised Löwdin Transforms	102
4.4	Strongly-Correlated Insulator: Bulk Nickel Oxide	103
4.4.1	Computational Methodology	103
4.4.2	Occupancies and Magnetic Dipole Moments	106
4.4.3	Kohn–Sham Eigenspectra	110

4.5	Magnetic Molecule: The Copper Phthalocyanine Dimer	113
4.5.1	Computational Methodology	115
4.5.2	Magnetic Dipole Moments	116
4.5.3	Kohn–Sham Eigenstates	118
4.6	Concluding Remarks	120
	References	121
5	Geometric Aspects of Representation Optimisation	125
5.1	Motivation	125
5.2	Tensor Calculus Applied to Electronic Structure Theory.	128
5.2.1	Tensorial Invariance.	129
5.3	Partial Differentiation of Tensors	131
5.4	A Metric Connection on the Support Manifold	133
5.5	Variation of the Density Kernel and Hamiltonian.	135
5.5.1	Uncorrected Matrix Updates	135
5.5.2	Geometrically Corrected Matrix Updates	137
5.6	Tensorial Consistency in Energy Gradients	140
5.7	First-Order Density-Matrix Preservation	144
5.8	Concluding Remarks	148
	References	149
6	A Numerical Study of Geometric Corrections for Representation Optimisation	151
6.1	Computational Methodology for Naphthalene	151
6.2	Geometric Density Kernel Corrections in Naphthalene	153
6.3	Commutator and Gradient Conjugacy in Naphthalene.	155
6.4	Total-Energy Convergence in Naphthalene	159
6.5	Computational Methodology for Oligoacene Polymers	160
6.6	Geometric Density Kernel Corrections in Oligoacenes	164
6.7	Commutator and Conjugacy Condition in Oligoacenes	164
6.8	Computational Performance in Oligoacenes.	166
6.9	Concluding Remarks	168
	References	168
7	Tensorial Aspects of Calculating Hubbard U Interaction Parameters.	171
7.1	The Linear Density-Response Method	172
7.1.1	Towards a Projector-Decomposed Method	173
7.1.2	The Non-Locally Resolved Four-Index U Tensor.	175
7.1.3	The Scalar Interaction U	176
7.1.4	The Locally Resolved Two-Index U Tensor	176
7.1.5	Generalisation of the DFT + U Potential and Ionic Forces to the Tensorial Formalism.	177
7.1.6	Prospects for a Linear-Scaling Implementation	178

7.2	The Constrained Random Phase Approximation	179
7.2.1	The Independent-Particle Green's Function and Irreducible Polarisability Operator	180
7.2.2	Spectral Functions	181
7.2.3	The Low-Energy Hubbard Model of cRPA	182
7.2.4	Dielectric Function, Screened Coulomb Interaction and Hubbard U Tensor	183
7.2.5	Making Use of a Frequency-Dependent U	185
7.3	Interaction Tensor Update with Hubbard Projectors	186
7.3.1	Geometry of the Hubbard Support Manifolds	187
7.3.2	First Order Changes to the Hubbard U Tensor	188
7.3.3	Invariance of the Interaction Anisotropy	190
7.3.4	Applicability of the Method	192
7.3.5	Changes in Non-Invariant Scalars	193
7.4	Concluding Remarks	195
	References	196
8	Discussion and Conclusion	199
8.1	Synopsis	199
8.2	Future Work	201
	Appendix: Geometric Observations	203
	Curriculum Vitae	211

<http://www.springer.com/978-3-642-23237-4>

Optimised Projections for the Ab Initio Simulation of
Large and Strongly Correlated Systems

O'Regan, D.D.

2012, XVI, 216 p., Hardcover

ISBN: 978-3-642-23237-4