

1. Record Nr.	UNINA9910830133103321
Titolo	Chemical reactivity in confined systems : theory, modelling and applications // edited by Pratim K. Chattaraj, Debducta Chakraborty
Pubbl/distr/stampa	2021 Hoboken, New Jersey : , : John Wiley & Sons, Inc., , [2021]
ISBN	1-119-68338-6 1-119-68335-1 1-119-68323-8
Descrizione fisica	1 online resource (451 pages)
Disciplina	541.39
Soggetti	Reactivity (Chemistry)
Lingua di pubblicazione	Inglese
Formato	Materiale a stampa
Livello bibliografico	Monografia
Nota di contenuto	Cover -- Title Page -- Copyright -- Contents -- Preface -- List of Contributors -- Chapter 1 Effect of Confinement on the Translation Rotation Motion of Molecules: The Inelastic Neutron Scattering Selection Rule -- 1.1 Introduction -- 1.2 Diatomics in C60: Entanglement, TR Coupling, Symmetry, Basis Representation, and Energy Level Structure -- 1.2.1 Entanglement Induced Selection Rules -- 1.2.2 H@C60 -- 1.2.3 H2@C60 -- 1.2.3.1 Symmetry -- 1.2.3.2 Spherical Basis and Eigenstates -- 1.2.3.3 Energy Level Ordering with Respect to -- 1.2.4 HX@C60 -- 1.3 INS Selection Rule for Spherical (Kh) Symmetry -- 1.3.1 Inelastic Neutron Scattering -- 1.3.2 Group Theory Derivation of the INS Selection Rule -- 1.3.2.1 GroupTheory Based INS Selection Rule for Cylindrical (Cv) Environments -- 1.3.2.2 GroupTheoryBased INS Selection Rule for Spherical (Kh) Environments -- 1.3.3 Specific Systems, Quantum Numbers, and Basis Sets -- 1.3.3.1 H@sphere -- 1.3.3.2 H2@sphere -- 1.3.3.3 HX@sphere -- 1.3.4 Beyond Diatomic Molecules -- 1.3.4.1 H2O@sphere -- 1.3.4.2 CH4@sphere -- 1.3.4.3 Any Guest Molecule in any Spherical (Kh) Environment -- 1.4 INS Selection Rules for NonSpherical Structures -- 1.5 Summary and Conclusions -- Acknowledgments -- References -- Chapter 2 PressureInduced Phase Transitions -- 2.1 Pressure, A Property of All Flavours, and Its Importance for the Universe and Life --

2.2 Pressure: Isotropic and Anisotropic, Positive and Negative -- 2.3 Changes of the State of Matter -- 2.4 Compression of Solids -- 2.4.1 Isotropic or Anisotropic Compressibility -- 2.4.2 Negative Linear Compressibility -- 2.4.3 Negative Area Compressibility -- 2.4.4 Anomalous Compressibility Changes at High Pressure -- 2.5 Structural SolidSolid Transitions -- 2.5.1 Structural Phase Transitions Accompanied by Volume Collapse -- 2.5.2 Effects of Volume Collapse on Free Energy. 2.5.3 StructureInfluencing Factors at Compression -- 2.5.4 Changes in the Nature of Chemical Bonding upon Compression and upon Phase Transitions -- 2.6 Selected Classes of Magnetic and Electronic Transitions -- 2.6.1 High Spin-Low Spin Transitions -- 2.6.2 Electronic Com vs Disproportionation -- 2.6.3 MetaltoMetal Charge Transfer -- 2.6.4 NeutraltoIonic Transitions -- 2.6.5 Metallization of Insulators (and Resisting It) -- 2.6.6 Turning Metals into Insulators -- 2.6.7 Superconductivity of Elements and Compounds -- 2.6.8 Topological Phase Transitions -- 2.7 Modelling and Predicting HP Phase Transitions -- Acknowledgements -- References -- Chapter 3 Conceptual DFT and Confinement -- 3.1 Introduction and Reading Guide -- 3.2 Conceptual DFT -- 3.3 Confinement and Conceptual DFT -- 3.3.1 Atoms: Global Descriptors -- 3.3.2 Molecules: Global and Local Descriptors -- 3.3.2.1 Electron Affinities -- 3.3.2.2 Hardness and Electronic Fukui Function -- 3.3.3 Inclusion of Pressure in the E & equals -- $E[N,v]$ Functional -- 3.4 Conclusions -- Acknowledgements -- References -- Chapter 4 Electronic Structure of Systems Confined by Several Spatial Restrictions -- 4.1 Introduction -- 4.2 Confinement Imposed by Impenetrable Walls -- 4.3 Confinement Imposed by Soft Walls -- 4.4 Beyond Confinement Models -- 4.5 Conclusions -- References -- Chapter 5 Unveiling the Mysterious Mechanisms of Chemical Reactions -- 5.1 Introduction -- 5.1.1 Context -- 5.1.2 Ideas and Methods -- 5.1.3 Application -- 5.2 Energy and Reaction Force -- 5.2.1 The Reaction Force Analysis (RFA) -- 5.2.2 RFABased Energy Decomposition -- 5.2.3 Marcus Potential Energy Function -- 5.2.4 Marcus RFA -- 5.3 Electronic Activity Along a Reaction Coordinate -- 5.3.1 Chemical Potential, Hardness, and Electrophilicity Index -- 5.3.2 The Reaction Electronic Flux (REF). 5.3.2.1 Physical Decomposition of REF -- 5.3.2.2 Chemical Decomposition of REF -- 5.4 An Application: the Formation of Aminoacetonitrile -- 5.4.1 Energetic Analysis -- 5.4.2 Reaction Mechanisms -- 5.5 Conclusions -- Acknowledgments -- References -- Chapter 6 A Perspective on the SoCalled Dual Descriptor -- 6.1 Introduction: Conceptual DFT -- 6.2 The Dual Descriptor: Fundamental Aspects -- 6.2.1 Initial Formulation -- 6.2.2 Alternative Formulations -- 6.2.2.1 Derivative Formulations -- 6.2.2.2 Link with Frontier Molecular Orbital Theory -- 6.2.2.3 StateSpecific Development -- 6.2.2.4 MO Degeneracy -- 6.2.2.5 Quasi Degeneracy -- 6.2.2.6 Spin Polarization -- 6.2.2.7 Grand Canonical Ensemble Derivation -- 6.2.3 RealSpace Partitioning -- 6.2.4 Dual Descriptor and Chemical Principles -- 6.2.4.1 Principle of Maximum Hardness -- 6.2.4.2 Local Hardness Descriptors -- 6.2.4.3 Local Electrophilicity and Nucleophilicity -- 6.2.4.4 Local Chemical Potential and Excited States Reactivity -- 6.3 Illustrations -- 6.3.1 Woodward Hoffmann Rules in DielsAlder Reactions -- 6.3.2 Perturbational MO Theory and Dual Descriptor -- 6.3.3 Markovnikov Rule -- 6.4 Conclusions -- References -- Chapter 7 Molecular Electrostatic Potentials: Significance and Applications -- 7.1 A Quick Review of Some Classical Physics -- 7.2 Molecular Electrostatic Potentials -- 7.3 The Electronic Density and the Electrostatic Potential -- 7.4 Characterization of Molecular Electrostatic

Potentials -- 7.5 Molecular Reactivity -- 7.6 Some Applications of Electrostatic Potentials to Molecular Reactivity -- 7.6.1 Hole and Hole Interactions -- 7.6.2 Hydrogen Bonding: A Hole Interaction -- 7.6.3 Interaction Energies -- 7.6.4 Close Contacts and Interaction Sites -- 7.6.5 Biological Recognition Interactions -- 7.6.6 Statistical Properties of Molecular Surface Electrostatic Potentials. 7.7 Electrostatic Potentials at Nuclei -- 7.8 Discussion and Summary -- References -- Chapter 8 Chemical Reactivity Within the SpinPolarized Framework of Density Functional Theory -- 8.1 Introduction -- 8.2 The SpinPolarized Density Functional Theory as a Suitable Framework to Describe Both Charge and Spin Transfer Processes -- 8.3 Practical Applications of SPDFD Indicators -- 8.4 Concluding Remarks and Perspectives -- Acknowledgements -- References -- Chapter 9 Chemical Binding and Reactivity Parameters: A Unified Coarse Grained Density Functional View -- 9.1 Introduction -- 9.2 Theory -- 9.2.1 Concept of Electronegativity, Chemical Hardness, and Chemical Binding -- 9.2.1.1 Electronegativity and Hardness -- 9.2.1.2 Interatomic Charge Transfer in Molecular Systems -- 9.2.1.3 Concept of Chemical Potential and Hardness for the Bond Region -- 9.2.1.4 SpinPolarized Generalization of Chemical Potential and Hardness -- 9.2.1.5 Charge Equilibration Methods: Split Charge Models and Models with Correct Dissociation Limits -- 9.2.1.6 Density Functional Perturbation Approach: A Coarse Graining Procedure -- 9.2.1.7 Atomic Charge Dipole Model for Interatomic Perturbation and Response Properties -- 9.2.1.8 Force Field Generation in Molecular Dynamics Simulation -- 9.3 Perspective on Model Building for Chemical Binding and Reactivity -- 9.4 Concluding Remarks -- Acknowledgements -- References -- Chapter 10 Softness Kernel and Nonlinear Electronic Responses -- 10.1 Introduction -- 10.2 Linear and Nonlinear Electronic Responses -- 10.2.1 Linear Response Theory -- 10.2.1.1 GroundState -- 10.2.1.2 Linear Responses -- 10.2.2 Nonlinear Responses and the Softness Kernel -- 10.2.3 Eigenmodes of Reactivity -- 10.3 OneDimensional Confined Quantum Gas: Analytical Results from a Model Functional -- 10.4 Conclusion -- References. Chapter 11 Conceptual Density Functional Theory in the Grand Canonical Ensemble -- 11.1 Introduction -- 11.2 Fundamental Equations for Chemical Reactivity -- 11.3 TemperatureDependent Response Functions -- 11.4 Local Counterpart of a Global Descriptor and NonLocal Counterpart of a Local Descriptor -- 11.5 Concluding Remarks -- Acknowledgements -- References -- Chapter 12 Effect of Confinement on the Optical Response Properties of Molecules -- 12.1 Introduction -- 12.2 Electronic Contributions to Longitudinal Electric Dipole Properties of Atomic and Molecular Systems Embedded in Harmonic Oscillator Potential -- 12.3 Vibrational Contributions to Longitudinal ElectricDipole Properties of Spatially Confined Molecular Systems -- 12.4 TwoPhoton Absorption in Spatial Confinement -- 12.5 Conclusions -- References -- Chapter 13 A Density Functional Theory Study of Confined Noble Gas Dimers in Fullerene Molecules -- 13.1 Introduction -- 13.2 Computational Details -- 13.3 Results and Discussion -- 13.3.1 Changes in Structure -- 13.3.2 Changes in Interaction Energy -- 13.3.3 Changes in Bonding Energy -- 13.3.4 Changes in Energy Components -- 13.3.5 Changes in Noncovalent Interactions -- 13.3.6 Changes in InformationTheoretic Quantities -- 13.3.7 Changes in Spectroscopy -- 13.3.8 Changes in Reactivity -- 13.4 Conclusions -- Acknowledgments -- References -- Chapter 14 Confinement Induced Chemical Bonding: Case of Noble Gases -- 14.1 Introduction -- 14.2 Computational Details and Theoretical Background -- 14.3 The Bonding in He@C10H16: A Debate -- 14.4 Confinement

Inducing Chemical Bond Between Two Ngs -- 14.5 XNgY Insertion Molecule: Confinement in One Direction -- 14.6 Conclusions -- Acknowledgements -- References -- Chapter 15 Effect of Both Structural and Electronic Confinements on Interaction, Chemical Reactivity and Properties -- 15.1 Introduction. 15.2 Geometrical Changes in Small Molecules Under Spherical and Cylindrical Confinement.

Sommario/riassunto

"This book provides a theoretical basis for the molecular phenomena observed in confined spaces. State-of-the-art theoretical and computational approaches are described, with a focus on obtaining physically relevant understanding, enabling the reader to build a good appreciation of the underlying chemical principles. Real life' examples of confined systems are presented, highlighting how the reactivity of atoms and molecules changes upon encapsulation. Recent developments related to the following host-guest systems are discussed. *Al² Cucurbit[n]uril *Al² ExBox 4 *Al² Clathrate hydrates *Al² Octa acid cavitand *Al² Metal organic frameworks (MOFs) *Al² Covalent organic frameworks (COFs) *Al² Zeolites *Al² Fullerenes *Al² Carbon nanotubes."--
