Description: Research into Chemical Bond Relaxation

Sun Changqing (ecqsun@ntu.edu.sg; +65 94356426)\(^1\)


Consolidated in the *Relaxation of the Chemical Bond* \[^7\], *Coordination-Resolved Electron Spectrometrics* \[^8\], and *The Attribute of Water* \[^9\], efforts made in past two decades have derived a set of framework for undercoordination physics and heterocoordination chemistry. The framework has enabled comprehension, quantification, and operation of the atomic bond-electron-phonon relaxation and the associated properties of substance, for the irregularly-coordinated atoms/molecules in the aqueous and solid states under stimulation, particularly.

PACS numbers:

I MOTIVATION AND OUTCOME

Since *The Nature of the Chemical Bond* (Pauling, 1931) bridges the structures and properties of crystals and molecules, controllable Formation and Relaxation of the Bond would be the unique means for mediating the performance of substance \[^1\]–\[^3\]. This practitioner has been working on this theme since late 1980s towards controlling bond and nonbond formation, dissociation, relaxation, and vibration and the associated energetics and dynamics of electron densification, localization, entrapment, polarization, and transition. Contributions including the formulation, verification, and application of a set of original theories and the theory-enabled analytical techniques and numerical methods with numerous breakthroughs, have been documented in two monographs \[^1\]–\[^3\] (Fig.1) and a number of treatises \[^2\], \[^4\]–\[^20\] .

![FIG. 1: Covers of monographs \[^1\]–\[^3\].](image)

II ATOMICISTIC ELECTRON-PHONON SPECTROMETRICS

2.1 Coordination-Resolved Electron Spectrometrics (ZPS)

Complementing the STM/S and XPS, the patented ZPS \[^2\] has enabled distillation of atomistic, dynamic, local and quantitative information on the electronic binding energy of undercoordinated adatoms, terrace edges, monolayer skins, point defects, nanostructures, and heterocoordinated atoms in heterojunction interfaces. The ZPS purification proceeds by subtracting the reference spectrum (collected from clean surface at direction close to the surface normal) from those collected from the same surface upon being conditioned or at larger emission angles. The residual spectrum discriminates the point defects, conditioned monolayer skin, and heterocoordinated atoms from its bulk mixture \[^2\] .

This invention has enabled \[^2\]: 1) determination of the edge-discriminative generation of graphitic Dirac-Fermi polarons from graphite surface with and without defects (Fig.2b); 2) classification of the Pt adatoms and the Cu/Pd alloy serving as acceptor-type while the Rh adatoms, graphene z-edge, Ag/Pd and BeW alloys share the same features of the defect, resolving their p-type and n-type catalytic nature, and the skin hydrophilic/hydrophobic behaviour \[^2\] .

![FIG. 2: (a) Coordination-Resolved Electron Spectrometrics introductory and (b) ZPS purified energy states of monolayer skin (entrapment: \(T_{\text{skin}}\)) and point defects (\(T_{\text{defect}}, \text{polarization: } P_{\text{defect}}\)) of graphite (0001) surface. The length/energy of bonds are quantified as 0.112/1.383, 0.127/1.014, 0.142/0.757, 0.154/0.615 nm/eV for the point defects, graphite monolayer skin, graphite bulk, and diamond bulk, respectively. Having the same identity for point defects, bonds surrounding graphene z-edge contract even further (0.107/1.548 nm/eV) associated with polarization that splits and screens the interatomic potential (the energy shift is proportional to the bond strength gain). (Pt adatoms and Cu/Pd alloy share the same ZPS feature of the skin; Rh adatoms, graphene z-edge, Ag/Pd and BeW alloys share the same features of the defect, resolving their p-type and n-type catalytic nature, and the skin hydrophilic/hydrophobic behaviour) \[^2\].](image)
III UNDERCOORDINATION PHYSICS AND MECHANICS

3.1 Bond-Order-Length-Strength (BOLS) Notion
An extension of the Atomic Coordination-Radius Correlation of Goldschmidt (1927) and Pauling (1945) to including the electronic and energetic response of bonds between undercoordinated atoms has resulted in the BOLS notion indicating that atomic undercoordination shortens and stiffens the bond between undercoordinated atoms associated with local quantum entrapment and densification of bonding electrons, energy, and mass. See Fig. 3a.

The BOLS premise has enabled: 1) reconciliation of the anomalous properties of atomic chains, atomic ribbons, hollow tubes, vacancies, defects, grain boundaries, kink edges, surfaces, and nanostructures of various shapes and sizes in terms of bond-order deficiency as the common origin; 2) clarification of the nature difference between the bulk solid and these undercoordinated systems as a result of the tunable fraction of undercoordinated atoms and the BOLS effect; 3) generalization of the tunability of nanostructures in mechanical strength, thermal and chemical stability, vibronic, photonic, electronic, magnetic, dielectric, and transport properties to the shortened and strengthened bonds between the undercoordinated atoms and its consequences on atomic coherency, electroaffinity, Hamiltonian, and the additional traps in the surface skins; 4) quantification of bond length, energy, elasticity, thermal stability and extensibility in the gold monatomic chain (Fig. 3b), single-walled carbon nanotube, and graphene interior and graphene ribbon edges.

FIG. 3: (a) Atomic undercoordination-induced local bond contraction, quantum entrapment and densification of the binding energy and core electrons, which perturbs the Hamiltonian and atomic cohesive energy and the associated properties.

3.2 Nonbonding-Electron Polarization (NEP)
The densely entrapped core electrons polarizes the nonbonding electrons (lone pairs, dipoles, C sp^2 unpaired electrons, and the otherwise conducting electrons of metals) at edges, which gives rise to unusual properties associated with adatoms, kink edges, defects, ribbon edges, and nanostructures. Because of the extremely weak interaction of these kinds of electrons with binding energy about 1/20 eV or lower and the localized nature, these electrons neither contribute to the Hamiltonian nor follow the regular dispersion relations; they rather add the mid-gap impurity states, such as carriers for topological insulators.

This NEP notion has clarified the common origin of: 1) superhydrophobicity, superlubricity, superfluidity, and supersolidity at the nanoscaled contact interfaces of liquid-solid and solid-solid as arising from the Coulomb repulsion between the anchored dipoles at highly elastic boundaries (elasticity is proportional to the local binding energy density); 2) edge discriminative generation and hydrogen annihilation of the graphitic Dirac-Fermi polarons that are massless with extremely high group velocity and non-zero spin, which serve as vehicles for the topologic insulators and the spin quantum Hall effect; 3) enhanced catalytic ability of undercoordinated noble metal atoms; and 4) the dilute magnetism of compound semiconductors.

3.3 Atomic Multifield Solid Mechanics
The local bond average (LBA) approach (LBA) the arithmetic idea of Fourier transformation, correlates the detectable properties of a substance directly to the identities (nature, order, length, strength) of a representative bond for the entire specimen and the response of these identities to the applied stimuli. This approach has enabled discoveries of factors: 1) responsible for the nano-hydro-thermo behavior of atomic chains, nan-
otubes, nanowires, nanograins, nanocavities, liquid and solid skins, interfaces and nanocomposites, as a union; 2) enhancing the superelasticity, superplasticity, superrigidity of nanomaterials by the highly curved skins; 3) dictating intrinsically and extrinsically the strongest size of nanocrystals (inverse Hall-Petch effect) and the joint effect of size, composition, temperature, and pressure on the mechanical properties of materials of any sizes; 4) maximal extensibility of the monoatomic chain at various temperatures, (Fig.5a), and 5) unification of the performance of graphene [9], ZnO [12], and nanostructured silicon [13] under the coupled fields.

IV HETEROCOORDINATION CHEMISTRY: CHEMISORTION AND INTERFACE

4.1 Bond-Band-Barrier (3B) Correlation
An integration of the initially independent theories of chemical bond, energy band, and potential barrier/trap has resulted in the 3B correlation premise [13][13], indicating that the sp-orbit hybridization occurs essentially to the most basic C, N, and O elemental atoms upon reacting with other electropositive elements in any phase, which alters the energy band, the nature of the bond, and the properties of the substance. See Fig.4a.

4.2 O, N, C Chemisorption Dynamics
This 3B premise has led to: 1) formulation of the reaction dynamics of O on Cu, Ni, Co, Ag, V, Pd, Pt, Rh, Ru, and diamond surfaces of different registries and various reconstruction phases, and N and C on Ni surfaces, as well Cu$_2$H$_2$ skin bonding dynamics in terms of evolution of the valence values of individual atoms and bond geometries; 2) quantification of the O-Cu bond angles and lengths and the C-Ni, N-Ni, and O-Rh lengths and stresses; and, 3) enhancement of the capacity of existing experimental techniques for crystallography (LEED and XRD), microscopy (STM), vibronic (EELS and Raman), electronic (XPS/UPS/STS), and thermal desorption spectroscopy (TDS), with a unification of spectral signatures gained from ~50 phases on O, N, C, and C$_2$H$_2$ adsorbed surfaces in terms of tetrahedron bond and 3B making kinetics.

The 3B theory has also led to discoveries of: 1) generalized nature of the O-, N-, and C-derived tetrahedral bonding identities and the evolution of valence density-of-states (DOS) in terms of bonding electron pairs, nonbonding lone pairs, electronic holes, and antibonding dipoles (see Fig.4a); 2) factors (lattice scale, electronegativity difference, temperature and adsorbate concentration) dominating chemisorption 3B formation with involvement of the outermost two atomic layers of a solid skin; and, 3) essentiality of surface-bond contraction that laid the foundation for the undercoordination physics.

Application of the 3B theory has led to designer materials and processes for intensive blue light emission (PZT), optical switches (infilled photonic crystals), electron emission (nitrogenation and oxidation), diamond-metal adhesion (TiCN graded buffer), self-lubrication (nitrogenation), and biosensor applications (surface modification) applications [11][14].

4.3 Four-Stage Cu$_2$O$_2$ Bonding Kinetics
A combination of the 3B theory with STM/S and LEED has enabled discovery of a Cu$_2$O$_2$ pairing tetrahedron that forms on O-Cu(001) surface in four-discrete stages, see movie and Fig.4[b].

V WATER, ICE, AND AQUEOUS SOLUTIONS
5.1 O:H-O Bond Cooperativity
Extending a water molecule to its four tetrahedron neighbours results in the segmented O:H-O bond whose cooperative relaxation in length and energy determines all detectable properties of water and ice [3][7][13][20]. The O:H-O bond integrates both the O:H intermolecular and the H-O intramolecular asymmetrical, ultra-short-range interactions and the O-O Coulomb repulsion. The O-O Coulomb repulsion and the O:H-O bond segmental disparity dictate the extraordinary adaptivity, cooperativity, recoverability, and sensitivity of water and ice when respond to perturbation at any level. External stimulus always dislocates O anions in the same direction but by different amounts; the O:H always relaxes more than the H-O bond. See Fig.5a.

5.2 Aqueous Solution Point Switchers
Incorporating the acid-base-salt definitions of Lewis (1923) and Arrhenius (1903) into the current water structure and O:H-O bond relaxation scheme results in the
H$_2$H point breaker, O-:e=O pinto compressor, and Y$^+$ and X$^-$ ionic polarizers in the acid-base-salt hydration networks, which resolve the phonon spectral features and the chemical properties of the solutions.

5.3 Resolution of Multiple Myths

This premise has enabled consistent resolution of numerous issues for water and ice, as epitomized below [3]:


Numerical reproduction of the Mpemba effect, see Fig. 5b confirmed the O:H-O bond memory and water skin supersolidity dictating heat emission-conduction-dissipation in the source-path-drain cycling system.

VI PROSPECTS

The dedication has been advancing the direction of Coordination Bond and Electronic Engineering with creation of the Bond Relaxation Theory that has enabled:

1) Invention of the Coordination-Resolved Electron and Phonon Spectrometrics; 2) Reconciliation of the performance of bonds and electrons associated with the irregularly-coordinated atoms and the heterocoordinated atoms in chemisorption and interfaces; 3) Formulation of atomistic multifield solid mechanics; and, 4) Resolution of numerous best-known mysteries of water and ice. The work could have been extremely important in changing the ways of thinking and advancing the atomistic, multifield, irregularly-coordination chemistry and physics of the aqueous and solid states.