

# QUANTUM STATES OF PROTEIN – NANODIAMOND HYBRIDS

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Nanodiamond show unusually high affinity and specificity to proteins. This effect was first observed on rapid isolation of recombinant apoobelin from *Escherichia coli* [1]. Wetting phenomenon plays major role in determining whether high affinity between distinct phases may occur, and when it is the case wetting in general sense is necessarily present. However, quantum-mechanical explanation of the underlying wetting mechanism is poorly understood. We propose the rationale behind high nanodiamond – protein affinity based on the consideration of collective electron states in dielectric nanoparticles.

The concept of collective states has been widely used in theoretical investigation of metallic compounds, where overlap between “delocalized” non-bonding conduction band and “localized” bonding valence band occurs. When band gap is present, there is clear separation between the two, leading to the introduction of tight-binding approximation. Being extremely successful at large scale near-perfect crystals, tight-binding model should be extrapolated with great care to nanoscale dielectric particles.

We provide evidence for existence of collective electron bonding states in nanodiamond particles using both numerical integration of the Schrödinger equation on 1D one-particle Kronig-Penney potential model and *ab initio* investigations of ground-state wavefunctions morphology of diamondoids C<sub>123</sub>H<sub>100</sub>, C<sub>211</sub>H<sub>140</sub> and C<sub>302</sub>H<sub>172</sub> at DFT R-B3LYP level of theory with 6-31G(d,p) basis set in the GAMESS-US package. We also conclude from qualitatively identical behavior of 1D and *ab initio* models that foundation of the observed effect lay in the symmetry of the system and is unrelated to particular theory level. Several computations at HF level of theory with at least 6-31G(d,p) basis set were performed, showing qualitative invariance of the result. In order to take surface tension into account, we have deformed the particle non-uniformly from the surface, decreasing deformation gradually. This resulted in simultaneous presence of “deformed” and “perfect” regions in diamond molecule. We then have studied localization of the collective states. Deformation results in bonding states wavefunction localization shift from particle core to the subsurface layer.

Our results show that bonding states in nanodiamond particles are collective, i.e. they show highly delocalized nature and have considerable spatial extent. However, while conductivity cannot be achieved on non-collective states, there is no need for collective states to be conducting. Taking these facts into account, we suggest the concept of spin-density fluctuations of bonding collective states as the fundamental mechanism allowing unpaired electron spin existence in dielectric nanoparticles without introducing dangling bond concept either in surface-localized form or as complex lattice defect. Situation is somewhat similar to well-known singlet instabilities in long conjugated polyenes. LUMO morphology also shows collective nature and dominant surface localization, accounting for hydrogen-terminated nanodiamond surface conductivity.

Proposed model allows correct qualitative interpretation of experimental data, notably paramagnetic invariant of nanodiamond revealing existence of “deep” unpaired spins and PEELS scans of single nanodiamond particles, clearly showing gradual change in “deformed” to “perfect” layer fractions ratio. We argue that nanodiamond – protein wetting interaction cannot be interpreted without consideration of collective electron states and spin-density fluctuations.

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