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SUBSURFACE COLLECTIVE ELECTRON STATES IN NANODIAMOND

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Despite relative simplicity of covalent crystals electronic structure, significant discrepancies between theory and experiment are still present for nanodiamond particles, e.g. nature of paramagnetic invariant and disordered shell cannot be described even qualitatively. It is possible to resolve the problem and provide qualitative agreement with experiment if one takes collective electron states into account. Collective electron states are widely used and accepted when it comes to metallic compounds, while applicability of the concept to semiconductor and dielectric materials remains at least questionable. In our research we have studied existence and localization of the collective electron states in nanodiamond particles both by solving one-particle one-dimensional Schrödinger equation in Kronig-Penney potential and by ab initio computations of ground state wave functions and eigenenergies of diamondoids $C_{123}H_{100}$, $C_{211}H_{140}$ and $C_{302}H_{172}$ at the DFT R-B3LYP level of theory with 6-31G(d,p) basis set done in the GAMESS-US software package.

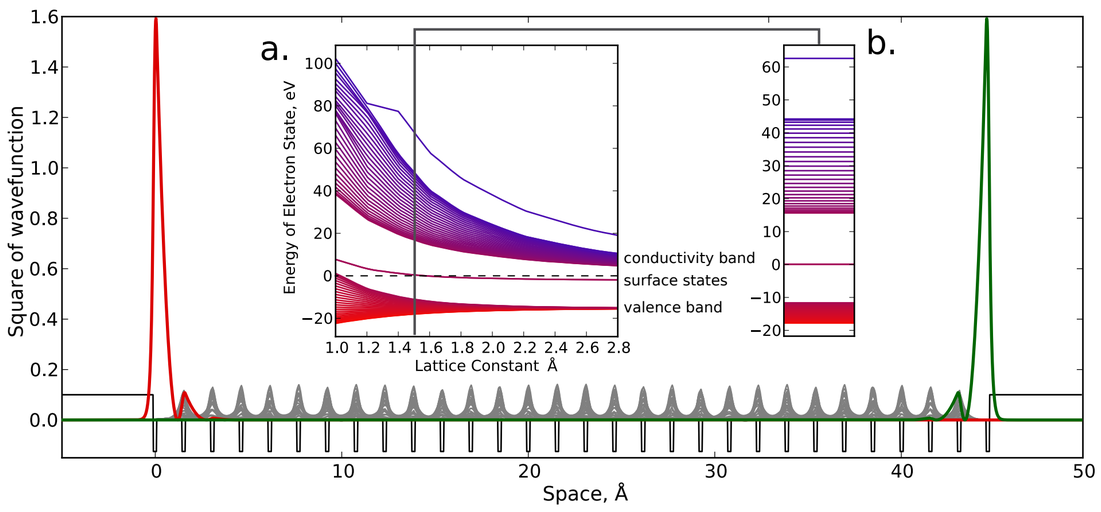

Fig. 2. Square of electron wavefunctions in limited periodic potential (holes deepness 25eV, width 0.2Å lattice constant 1.54Å boundary 5Å×20eV. (a) Energy spectrum versus latticeconstant of one-dimensional crystal. (b) Energy spectrum for 1.54Å lattice constant.

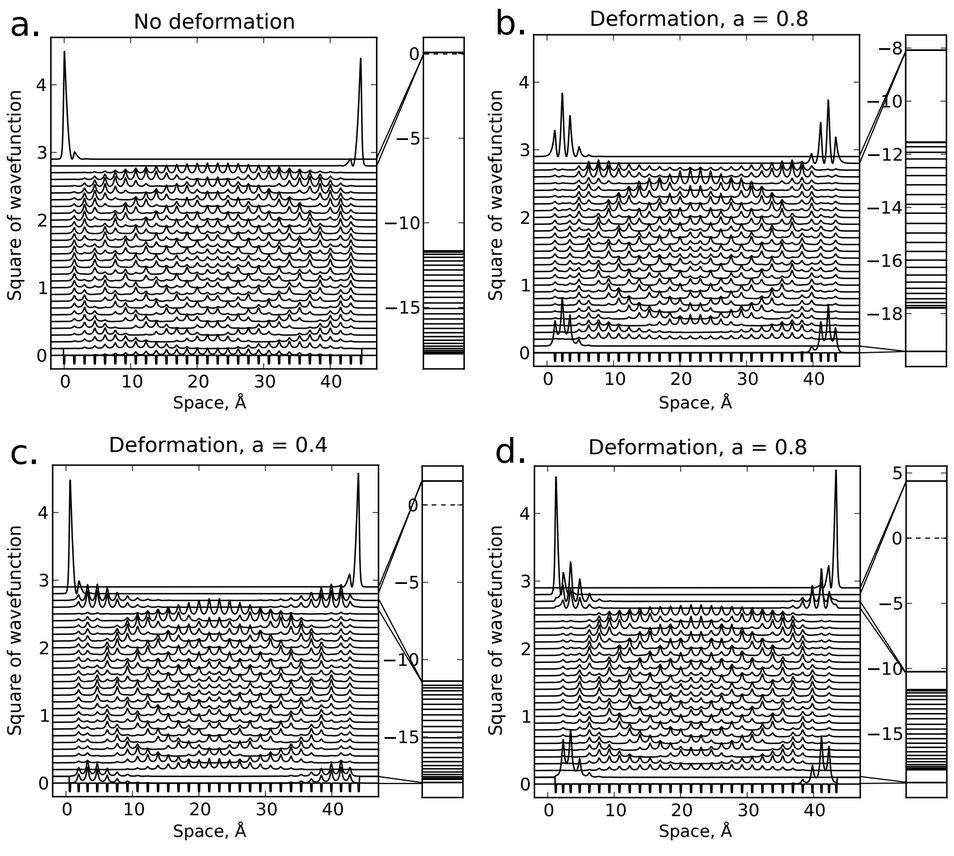

Fig. 3. Collective 1D electron states for: (a) Tamm surface states with barrier, (d) subsurface states in presence of barrier and compression

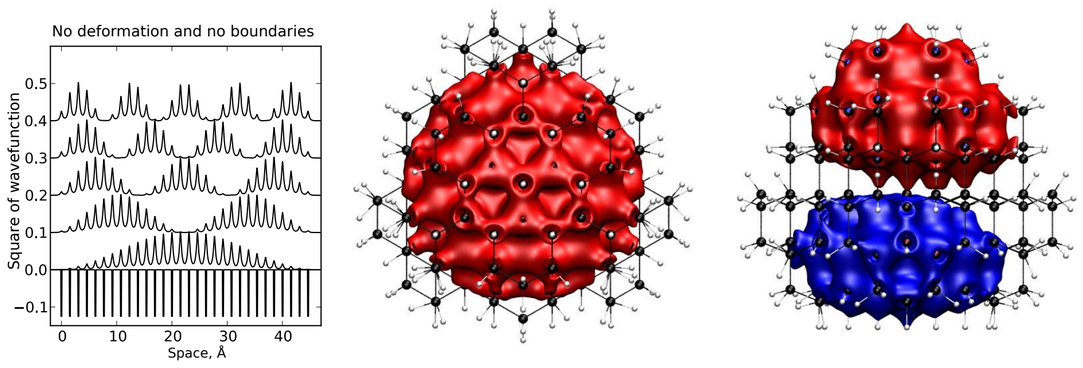

Fig. 6. (a) First five bonding molecular orbitals for 1D case are resembling modulated particle-in-a-box solutions. (b, c) Isosurface of the first two bonding molecular orbitals #212 and #213 of C_{211} H_{140} molecule resemble typical shapes and nodal structure of atomic s- and p-orbitals. Visualization is made in the VMD software package using PovRay

$$dr(r) = \frac{-a}{\left(s - \frac{rs}{R}\right)^2 + 1}, \quad (1)$$

where dr — atom position shift to the origin; r — distance from atom to the origin; R — radius of molecule; a — parameter regulating shift amplitude; s — parameter regulating shift decay rate inside diamond ball.

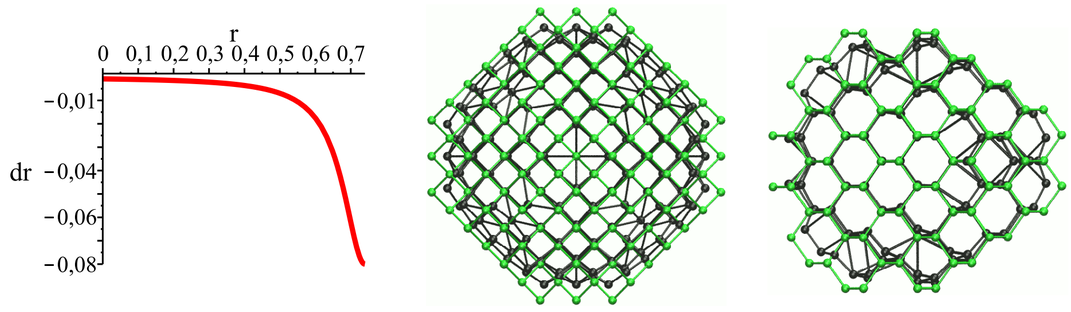

Fig. 1. The demonstration of the deformation method (a) Atom position shift to the origin vs. coordinate (fitted to function (1) with parameters s = 10, a = 0.08). (b, c) Deformation of diamond ball carbon lattice C_{302} accordingto function (1) in two projection: initial molecule shown by green, deformed by black.

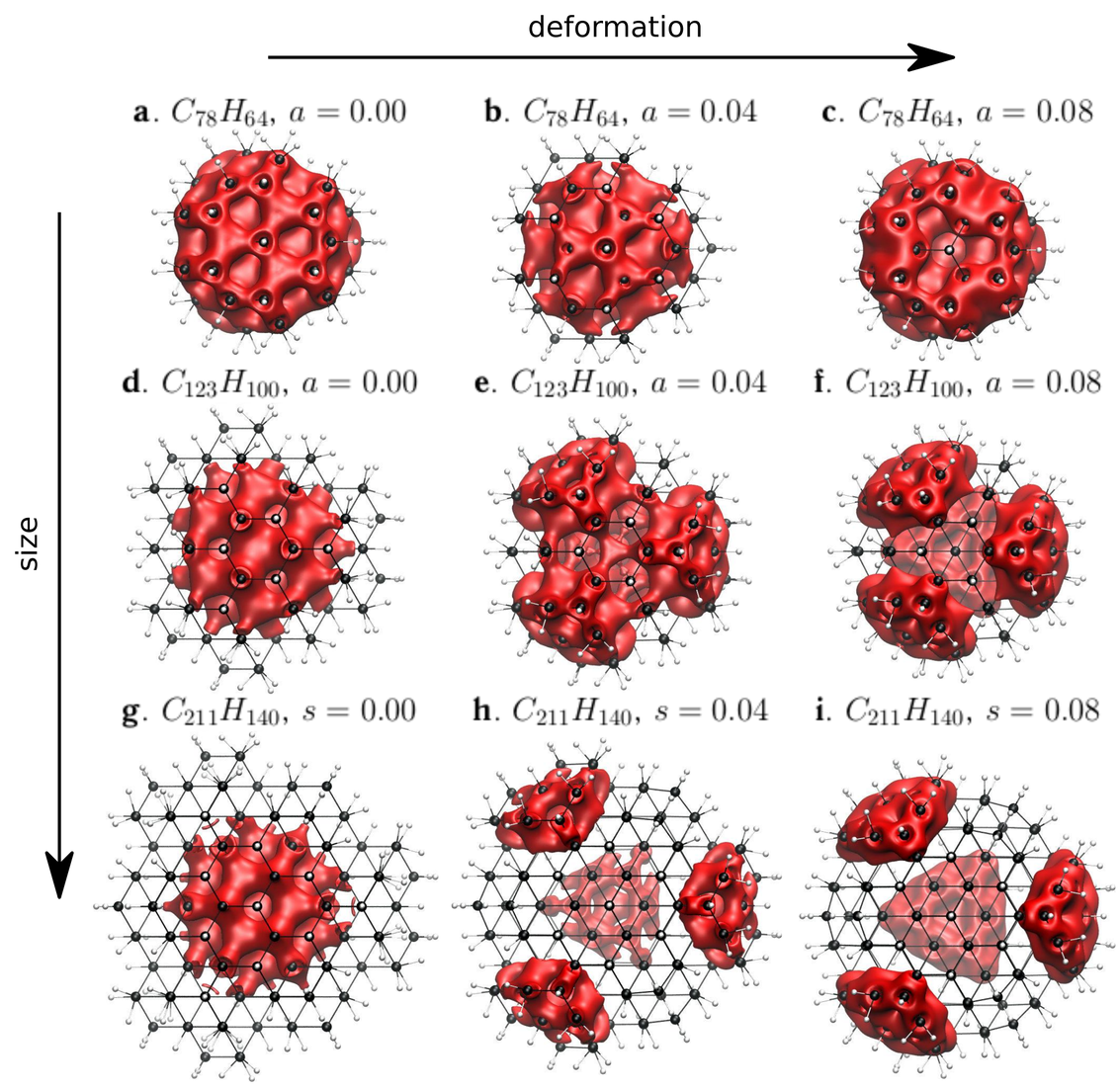

Fig. 4. Wavefunctions isosurfaces (0.02) for lowest binding orbital of diamond balls three sizes with number of carbon atoms: (a–c) 78, (d–f) 123, (g–i) 211 and three fixed deformations.

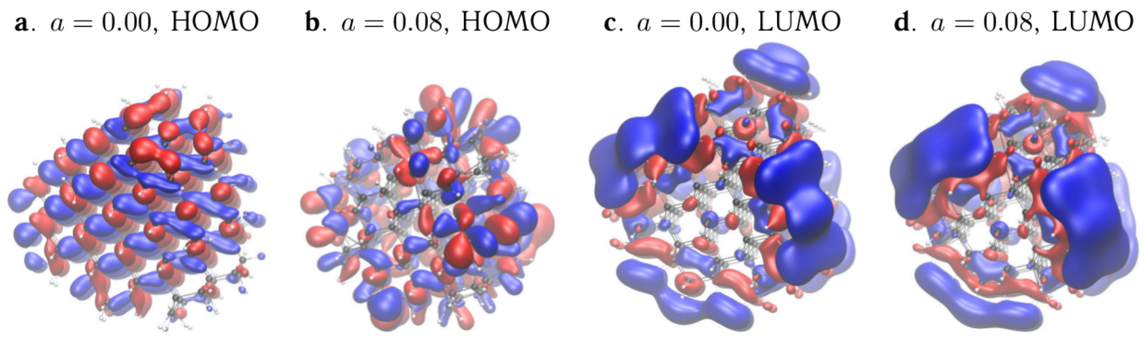

Fig. 5. Isosurfaces of wavefunction of 1.34 nm diamondoid $C_{211}H_{140}$

CONCLUSIONS

Three distinct classes of collective electron states have been found: collective bonding orbitals resembling 3D-modulated particle-in-a-box solutions; subsurface-localized binding states for deformed nanodiamond and surface-localized nonbonding conductive Tamm's states. Deformation results in localization shift of lower binding orbitals from core to thin subsurface layer.

Spread nature of collective bonding states may increase significance of spin-density fluctuations and lead to singlet instability of the ground state solution like in the well-known case of π-conjugated polyene chains. We would like to emphasize that paramagnetic invariant behavior of nanodiamond with respect to field strength and temperature is explained if spin density fluctuations of deep bonding states are considered, while subsurface localization of these states is consistent with g-factor independence of chemical modification of nanodiamond surface. Subsurface collective electron states localization and particle deformation are closely interrelated, i.e. self-consistency between wavefunctions and nuclear positions is satisfied in nanodiamond molecule.

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Computations have been performed in **BlackBox Component Builder**
Oberon microsystems, Inc. (Zürich, Switzerland)

VMD Visual Molecular Dynamics

GAMESS

Poster prepared with the free vector graphics editor Inkscape