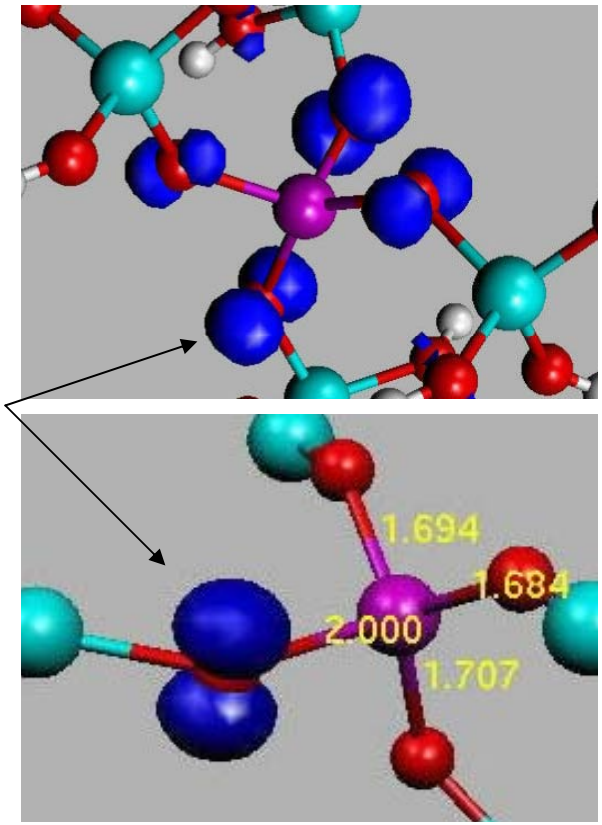
Immobilization of Radionuclides in oxides

Univ. of Washington
and EMSL/PNNL

Spin density



Upper figure: Regular DFT/PBE calculation
Lower figure: Calculation including self-interaction correction - localized spin density

Improved Methodology: Self-consistent DFT calculations with self-interaction correction, including atomic forces and relaxation in extended systems implemented in NWChem.

Regular DFT using LDA and GGA functionals tends to delocalize electronic defects such as holes and excitons. A well documented example is quartz where one Si atom(cyan) has been replaced with Al atom (purple). The calculations predict equal distribution of the hole on the 4 oxygen atoms (red) surrounding the Al (see upper figure), in contradiction with experimental measurements showing that only one Al-O bond lengthens. Our calculation using DFT/PBE with self-interaction correction (see lower figure) is in good agreement with experiment.
We have similar results on excitons and electron holes in quartz and amorphous silica.

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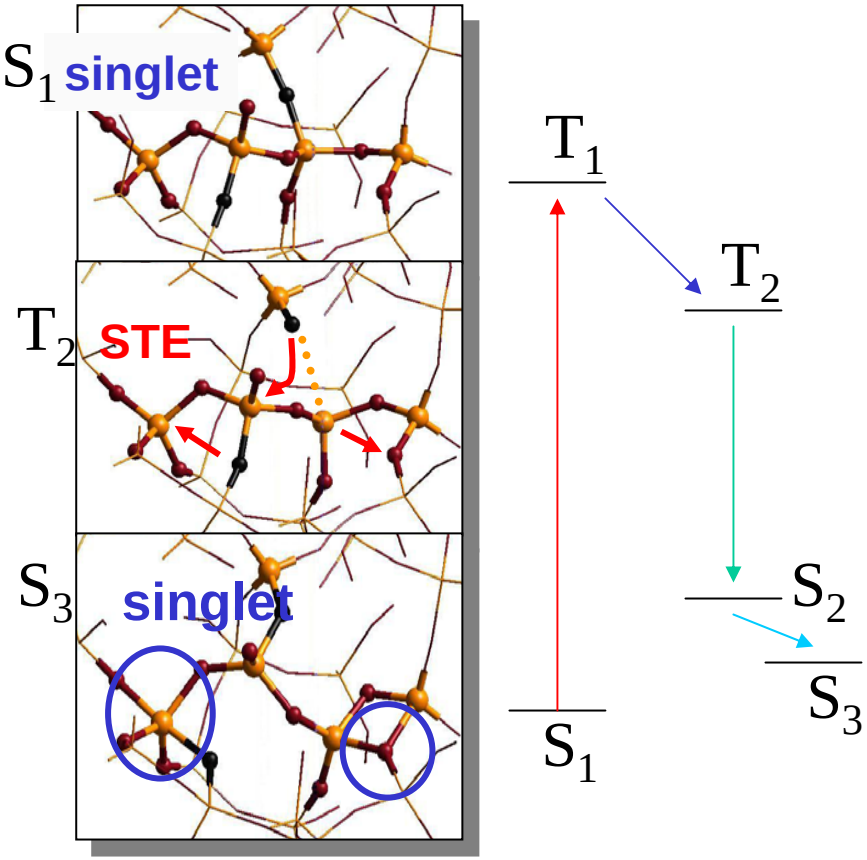

Top figure: Initial stable singlet state config.
Middle figure: Self-trapped exciton, relaxed.
Bottom figure: Defected singlet state formed.

Exciton induced defects in silica: Excitons formed, for example as a result of radioactive decay, can lead to formation of defects in silica.

DFT/PW91 calculations of exciton induced defect formation. Initially, the glass sample has no configurational defects (top figure). Then, a triplet state exciton is formed (red arrow) and atomic coordinates relaxed in the triplet state (blue arrow). This leads to bond breaking (see dashed line in middle figure). After decay of the exciton (green arrow) to return of the system to singlet ground state and further relaxation (cyan arrow), the glass sample contains two configurational defects, a five-fold coordinated Si-atom and a two-membered ring. The energy barrier to healing is found to be 0.76 eV, but paths representing migration of the defects have similar activation energy - damage could persist.