

Literature Review

Bonded interactions in silica polymorphs, silicates, and siloxane molecules

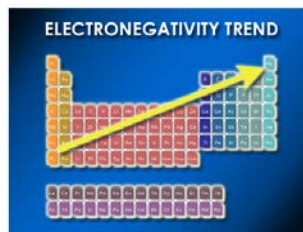
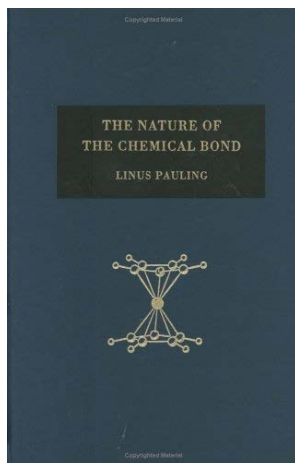
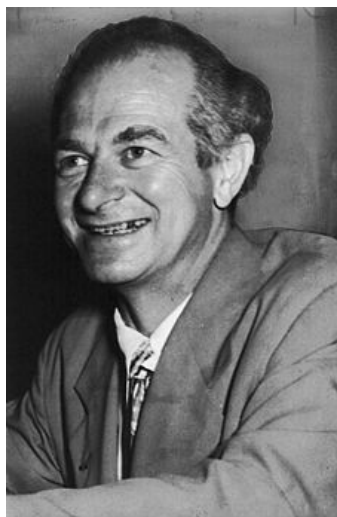
G. V. Gibbs, A. F. Wallace, D. F. Cox, R. T. Downs, N. L. Ross,
and K. M. Rosso

American Mineralogist, Volume 94, **2009**

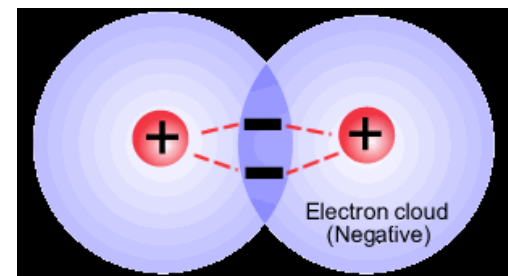
The Peters Group
Bryan Goldsmith



Chemical Bonds

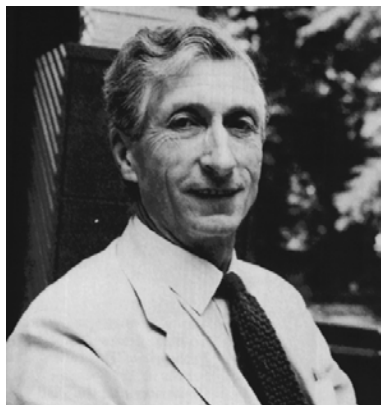


Chemical bond is the result of the net electrostatic attraction exerted on the nuclei of a pair of atoms by the electron density accumulated between the nuclei (Feynman 1939)



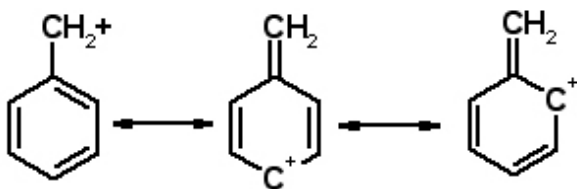
The chemical bond is *not* a quantum mechanical observable!

Charles Coulson

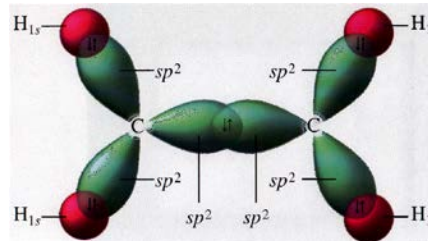


THE ROYAL
SOCIETY

“A chemical bond is not a real thing: it does not exist, no one has ever seen it, no one ever can. It is a figment of our imagination.” (1955)



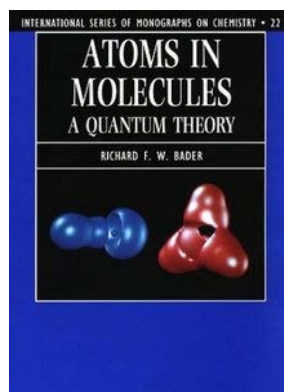
Benzyl cation resonance



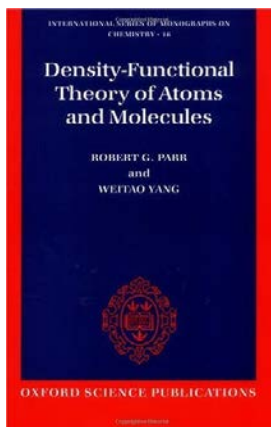
Hybridization of ethylene

Bader's Model for Electron Density

- No chemical bonds, only bonded interactions (Bader 1985)
- Electron density (ED) is an observable $\rho(r) = \langle \psi | \hat{\rho}(r) | \psi \rangle$



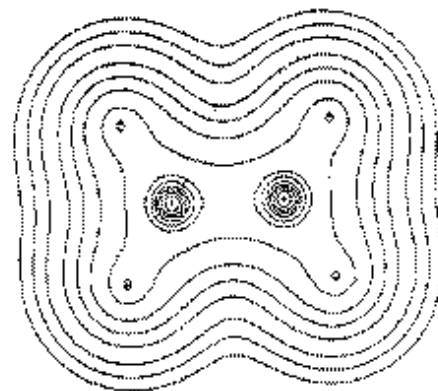
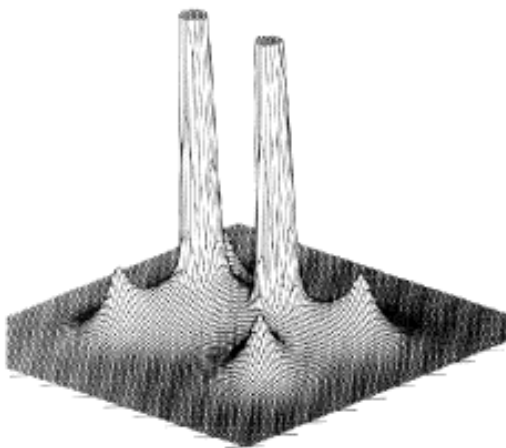
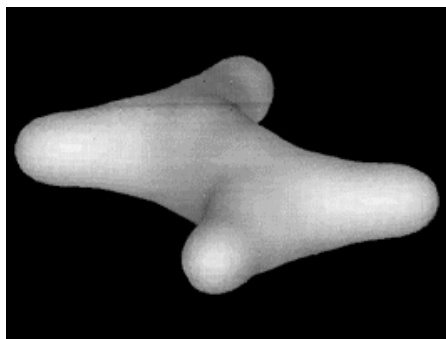
‘The electron density provides a description of the distribution of charge throughout real space and is the bridge between the concept of state functions in Hilbert space and the physical model of matter in real space.’



Electron density embodies all the information that can be known about a ground state material, including its kinetic, potential and total energies. (Parr and Yang 1989)

Electron Density Distribution

Bonded atoms are connected by well defined continuous pathways of maximum ED.

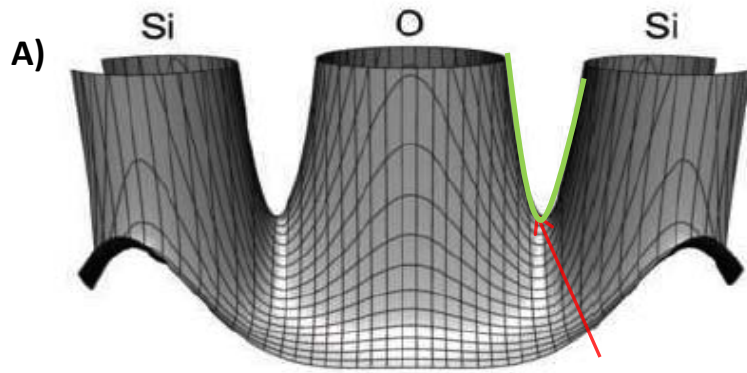
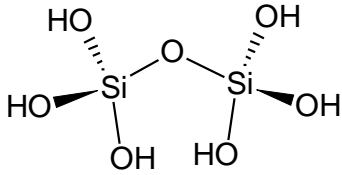


Theory of Atoms in Molecules

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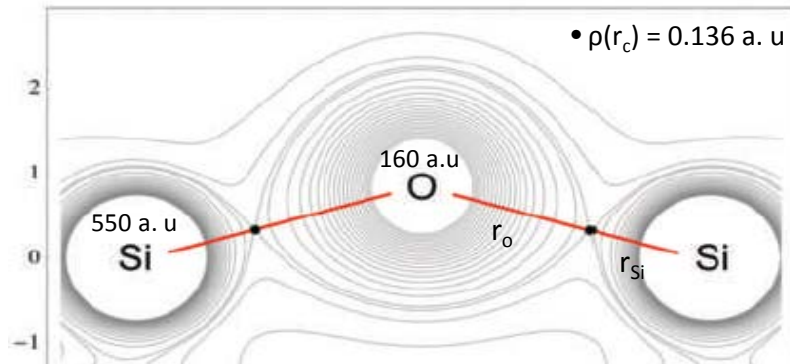
http://www.chemistry.mcmaster.ca/aim/aim_0.html

Bond Paths and bridging Si-O bonded interactions for $\text{H}_6\text{Si}_2\text{O}_7$



$\nabla\rho(\vec{r}) = 0$ Bond Critical Point (bcp). Denote this point as \vec{r}_c

B)



B3LYP/6-311(2d,p) functional and basis set

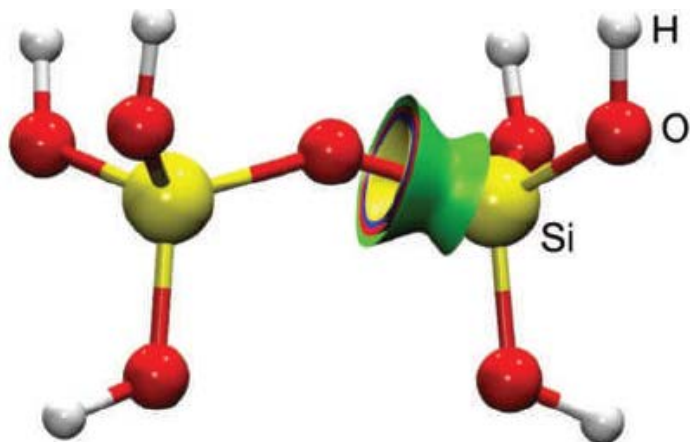
Bond path: Path of maximum electron density between bonded pair

Real-space carrier of quantum mechanical exchange. (Pendas 2007)

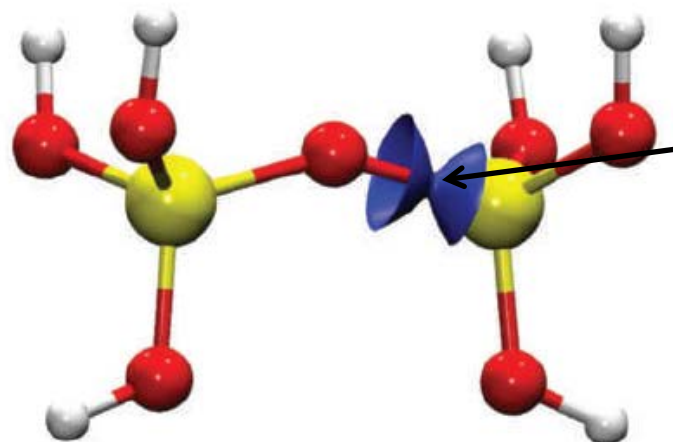
- $\rho(r_c) \uparrow$, bond length \downarrow , strength of interaction \uparrow
- Can count bond paths to find coordination number of atom

A) level line relief ED map calculated between $\rho(r) = 0.0$ and 0.3 a.u. ($1 \text{ a.u.} = 6.748 \text{ e}/\text{\AA}^3$).

B) level line contour map calculated between $\rho(r) = 0.0$ and 1.0 a.u. in intervals of 0.05 a.u.



(a) Set of level isosurfaces of the ED distribution calculated at intervals of 0.0275 a.u. at the B3LYP/6-11(2d,p) level around one of the Si-O bridging bond paths



'Zoom' on to bond critical point

- $\rho(r) = 0.13$ level ($\rho(r_c) = 0.136 \text{ e}/\text{\AA}^3$)
- Single-sheeted hyperboloid around the Si-O bond path
- Cylindrical distribution represents sigma-bond character

$$\rho(r) = \rho(r_c) + (r - r_c) \nabla \rho(r) + \frac{1}{2} (r - r_c) H_{ij} (r - r_c)$$

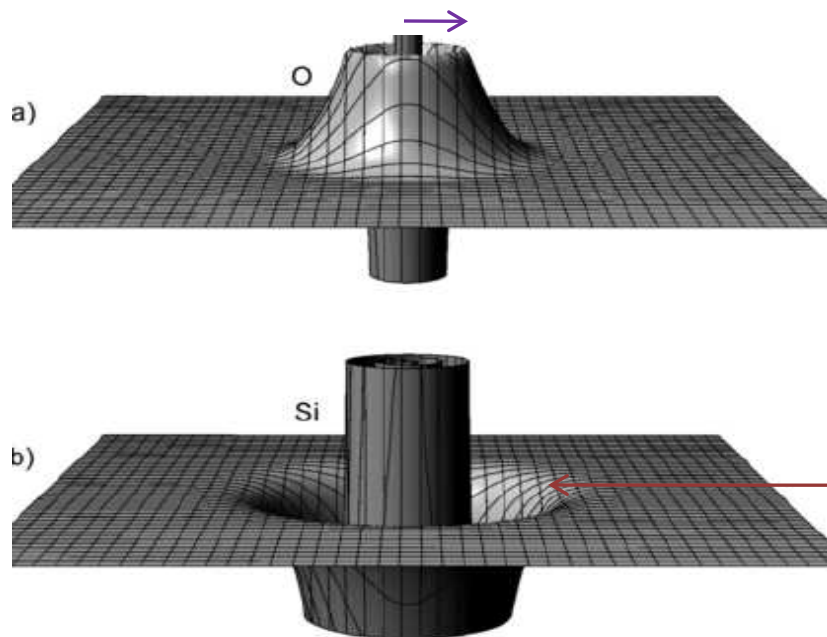
$$H_{ij} = \frac{\partial^2 \rho(r_c)}{\partial x_i \partial x_j} \quad \underline{\text{diagonalize}} \quad \text{tr}(\lambda) = \sum_{i=1}^3 \frac{\partial^2 \rho(r_c)}{\partial x_i^2}$$

Principal components of curvature

The Laplacian as a tool for locating Lewis acid and base sites

$$\begin{aligned}\nabla^2\rho(r) < 0 &= \text{Sink (Concentrated)} \rightarrow \text{Lewis Base} \\ \nabla^2\rho(r) > 0 &= \text{Source (Depleted)} \rightarrow \text{Lewis Acid} \quad (\text{Bader 1984})\end{aligned}$$

Example using $L(r) = -\nabla^2\rho(r)$ level line relief maps for isolated oxygen and silicon



Valence shell charge concentration (VSCC)

Distance to outmost shell of local ED from nucleus

For oxygen:

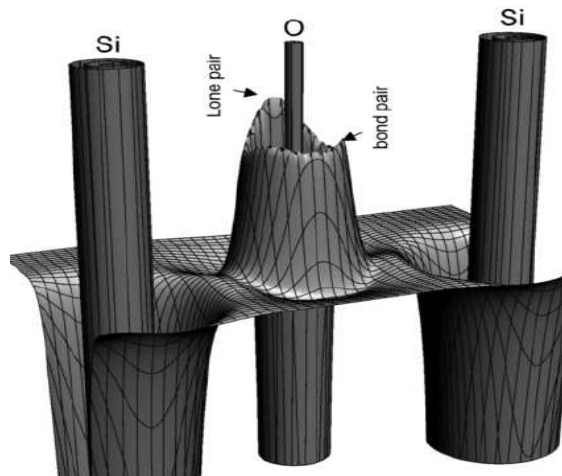
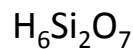
- Outmost shell of local ED (0.66 Å)
- Comparable to atomic radius (0.65 Å) (Bragg 1920)
- Max radial charge density of shell (0.60 Å) (Slater 1964)

- Diffuse, low lying valence shell
- Farther away from nucleus than oxygen

a) O atom with the contribution of one core orbital neglected

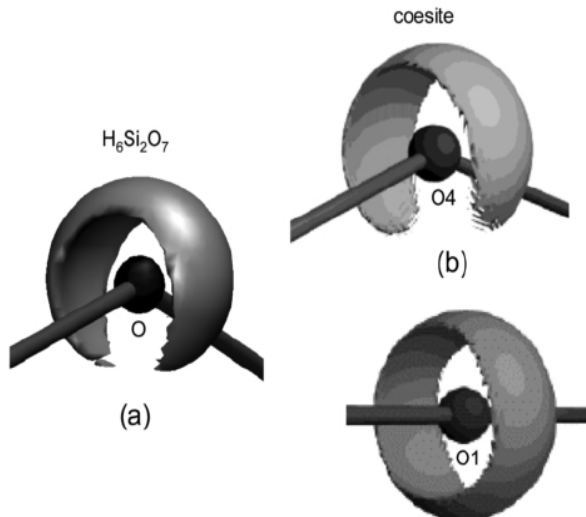
b) Isolated Si atom

Cutoff at ± 15 a. u. (1 a.u. = 24.099 e/Å⁵)



level line relief map for the $\text{H}_6\text{Si}_2\text{O}_7$ molecule calculated at the B3LYP/6-311(2d,p) level in the plane containing the Si-O-Si angle. The map was cut off at ± 5 a.u. level.

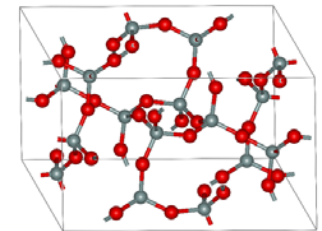
Zoom in local maximum ED for oxygen and compare to coesite oxygens



Si-O-Si angle $\sim 144^\circ$ for O4 and $\text{H}_6\text{Si}_2\text{O}_7$
- Similar ED maximum

Si-O-Si angle is 180° for O1
- If $\text{H}_6\text{Si}_2\text{O}_7$ has Si-O-Si 180° looks like O1

Supports hypothesis that the forces that govern the structures and properties of the silica polymorphs are largely short-ranged

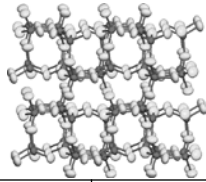


coesite

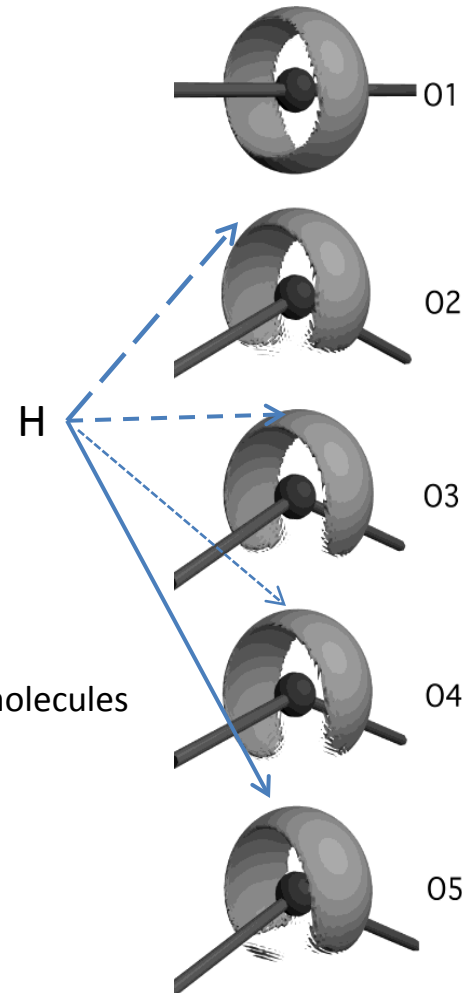
Lewis base sites

Hydrogen incorporation in coestite at high temperature and pressure

Coestite



Oxygen atom	Max ED (a.u.)	<Si-O-Si
O1	7.59	180
O4	7.84	149.7
O3	7.93	144.2
O2	7.93	142
O5	7.97	136.7



Similar trend exists in siloxane molecules

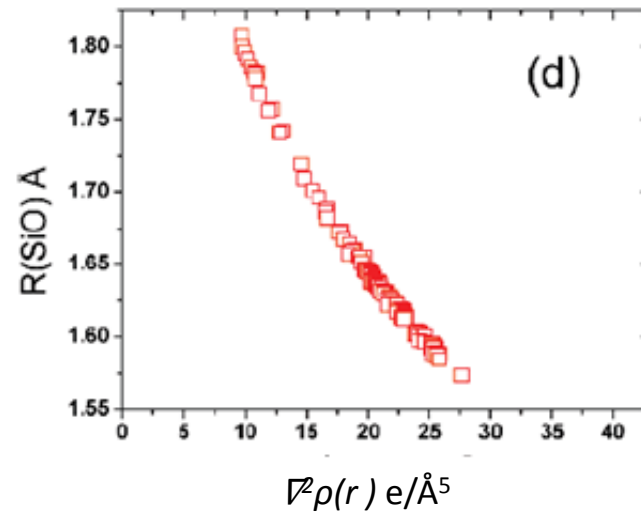
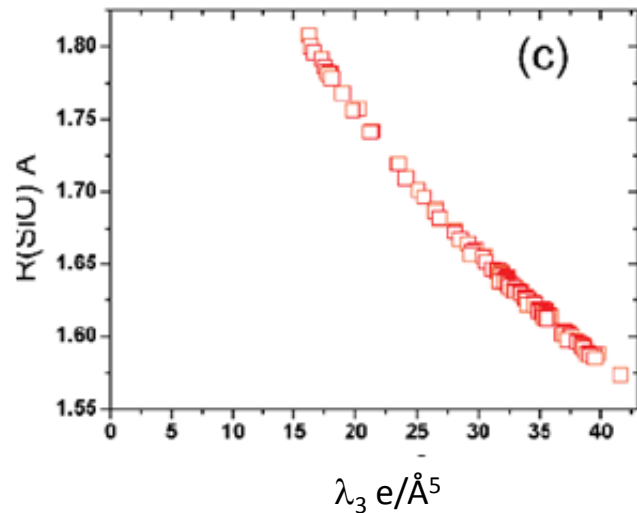
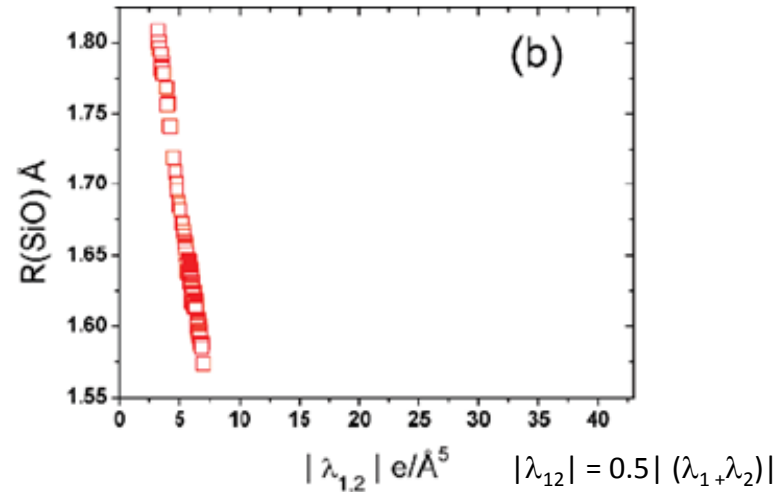
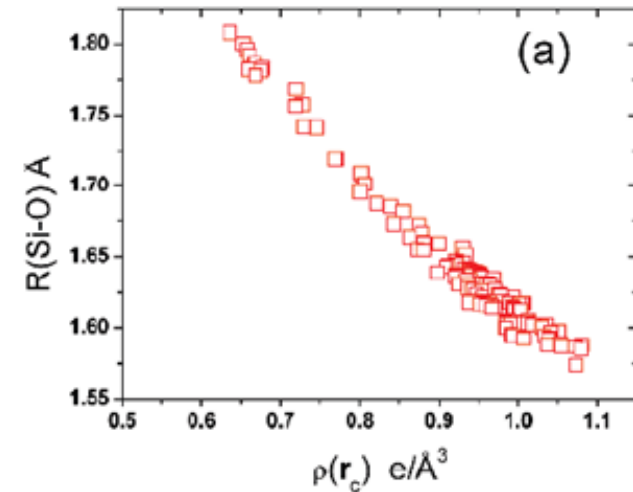
Supports hypothesis that bonded interactions in siloxane molecules are similar for that of silica polymorphs

Smyth (2006): Ad hoc electrostatic site model.

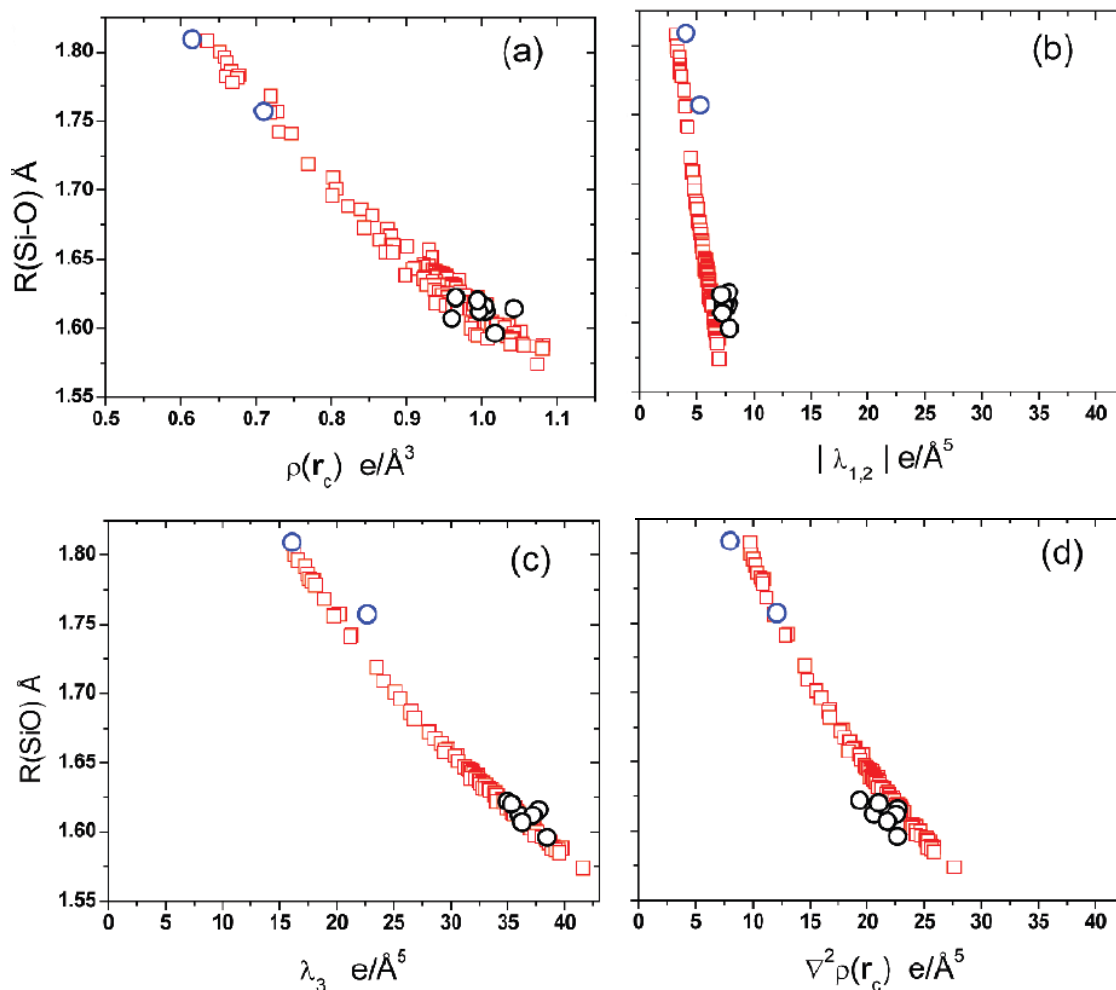
Concluded O1 is most likely to be protonated, contrary to findings of Koch-Muller et al. (2001) infrared study.



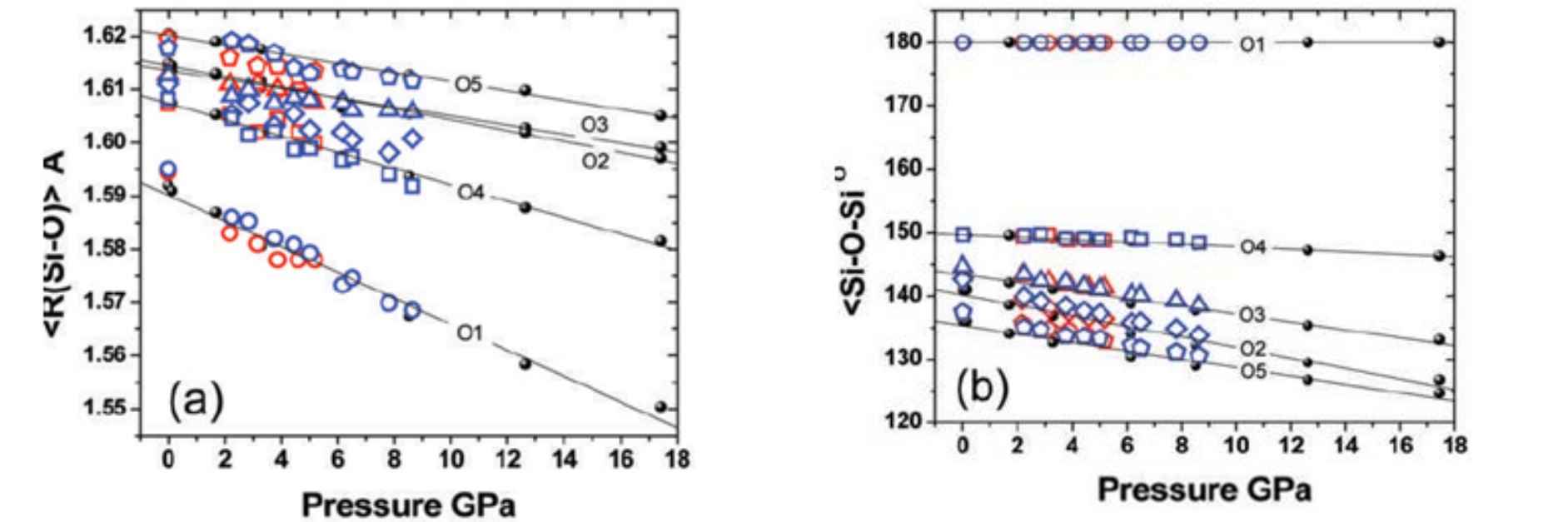
Si-O bond critical point properties



- λ_1 and λ_2 (curvature) measure extent to which the ED is locally concentrated perpendicular to the bond path
- λ_3 measure extent to which the ED is concentrated along bond path at r_c
 - $\lambda_3 \uparrow$, great ED in atomic basis and shielding increases



Geometry optimized bond lengths and angles for coesite compared to experiment bond values as a function of pressure

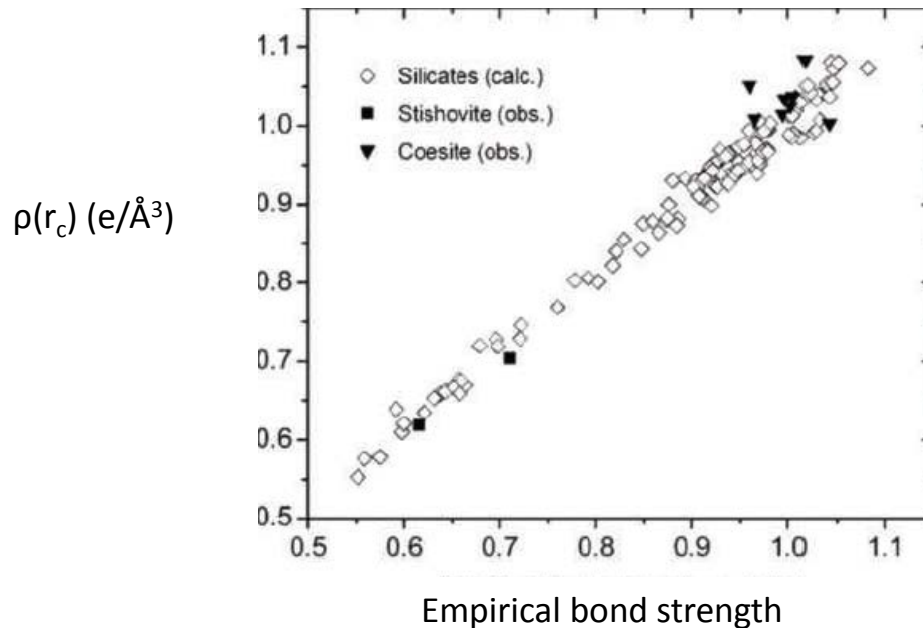


a) Comparison of $\langle R(\text{Si-O}) \rangle$, the average of the two Si-O bond lengths comprising each of the nonequivalent Si-O-Si angles

b) the five nonequivalent Si-O-Si angles for coesite plotted with respect to pressure.

- data obtained by optimizing the coesite structure as a function of pressure
- red symbols, represent experimental data determined by Levien and Prewitt (1981)
- blue ones, represent experimental data determined by Angel et al. (2003)
- ,○: Si-O1 bonded interactions
- ◇,◇: Si-O2 bonded interactions
- △,△: Si-O3 bonded interactions
- ,□: Si-O4 bonded interactions
- ⬠,⬠: Si-O5 bonded interactions.

Siloxane molecules and silicates



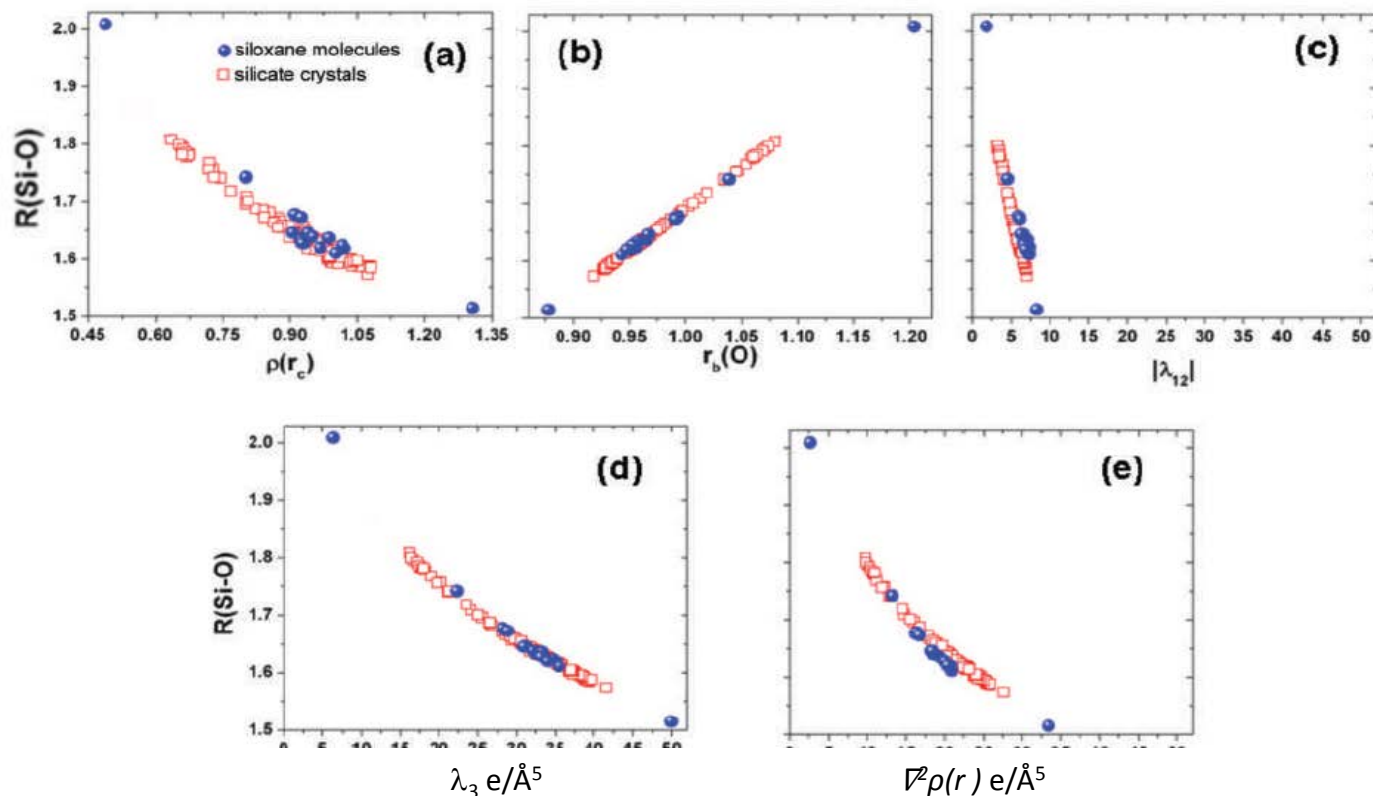
Correlation for empirical bond strength of Si-O in silicates

$$s = [(R(\text{Si}-\text{O}) / 1.625)]^{4.5}$$

Brown and Shannon (1973)

The $\rho(r_c)$ values calculated for silicate crystals (diamonds) and the model experimental $\rho(r_c)$ values determined for coesite (solid triangles) and stishovite (solid squares), plotted with respect to the Brown and Shannon (1973) empirical bond strength, s , *calculated with* the experimental Si-O bond lengths (Gibbs et al. 2004).

Comparison of the bond critical point properties calculated for silicate crystals



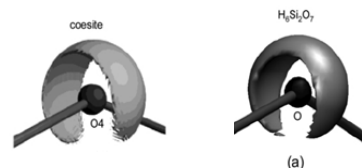
Comparison of the bond critical point properties calculated for silicate crystals (open red squares) with the bond critical point properties calculated for a variety of geometry optimized siloxane molecules (blue spheres).

Molecules, (cluster models) are well suited to study larger silica system

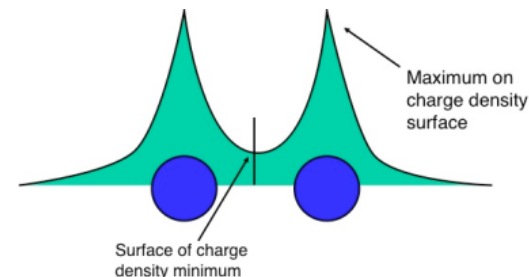
H_{quartz} Si-O = 467 kJ/mol

$H_{\text{H}_2\text{Si}_2\text{O}_7}$ Si-O = 462 kJ/mol

Similar ED distribution between coesite and $\text{H}_2\text{Si}_2\text{O}_7$



Conclusion



Quantum theory of atoms-in molecules (QTAIM)

Predicts bond lengths, atomic radii, the dipole moment, diamagnetic contribution to the nuclear screening constant, the electric field, and the electric field gradient.

Provide deeper understanding of crystal chemistry, structure-properties relationships, and chemical reactions beyond the unobservable.

Representative siloxane molecules work well as models for studying Si-O bonded interactions, reactions, and dissolution.

