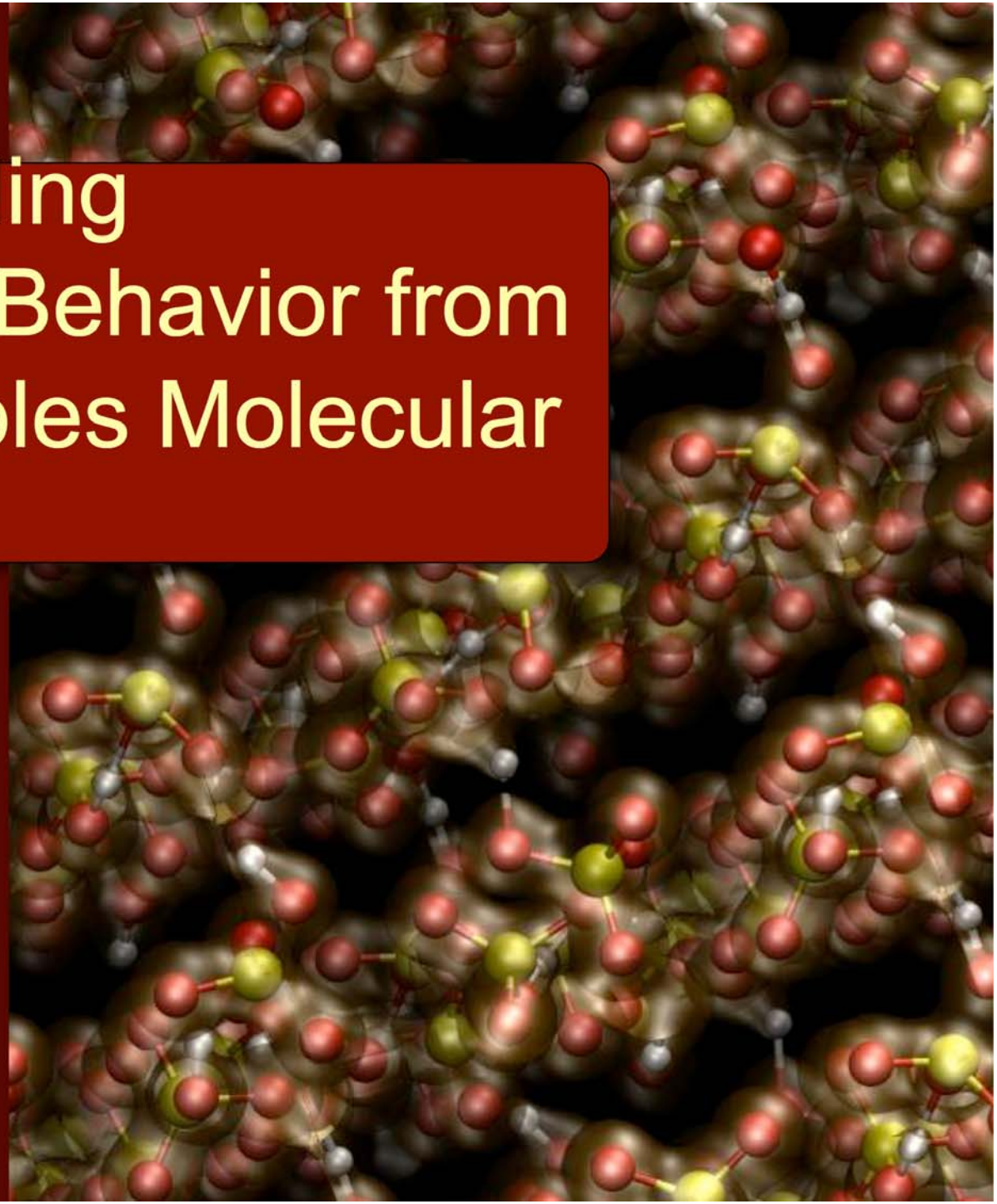
Understanding Superionic Behavior from First-principles Molecular Dynamics



Brandon Wood &
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MIT

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Superionic conductors

- One or more ionic species demonstrates liquid-like diffusive behavior
- Typical ionic conductivities: $\sigma \sim 10^{-5}$ to 1 $(\Omega \cdot cm)^{-1}$
- Electronic conductivity usually at least two orders of magnitude lower
- Microscopic diffusive events in many conductors are sufficiently frequent to allow modeling on atomistic timescales
- Future research would benefit from a microscopic understanding of conductivity mechanisms

Fuel cells

proton electrolyte and hydrogen storage materials

Biological membranes

proton and ion channels

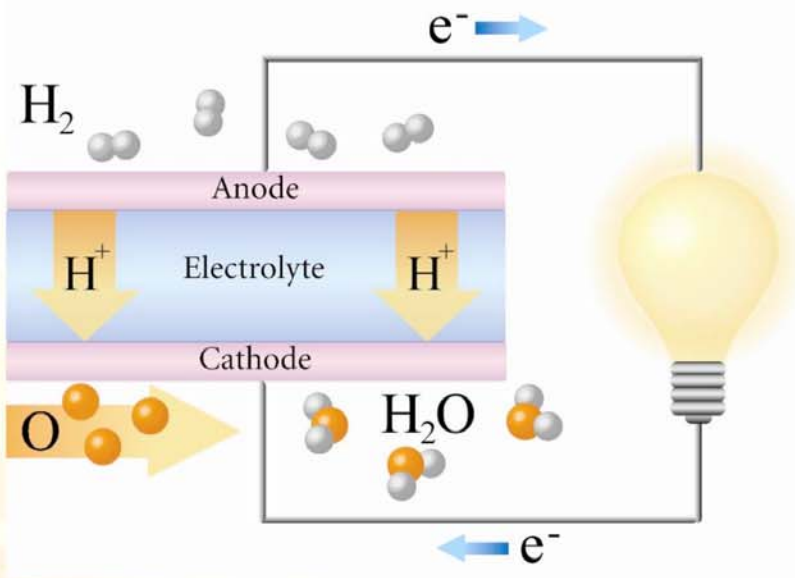
Superionics

Nanoelectronics

sensors and switches

Ion batteries

electrolytes



First-principles molecular dynamics

First principles (DFT)

- ✓ Highly accurate (quantum mechanics)
- ✓ Predictive (no experimental input)
- ✓ Does not depend on chemical environment
- ✘ Limited to very small system sizes (few hundred atoms)
- ✘ Limited to very small timescales (tens of picoseconds)
- ✘ Nonideal scaling behavior

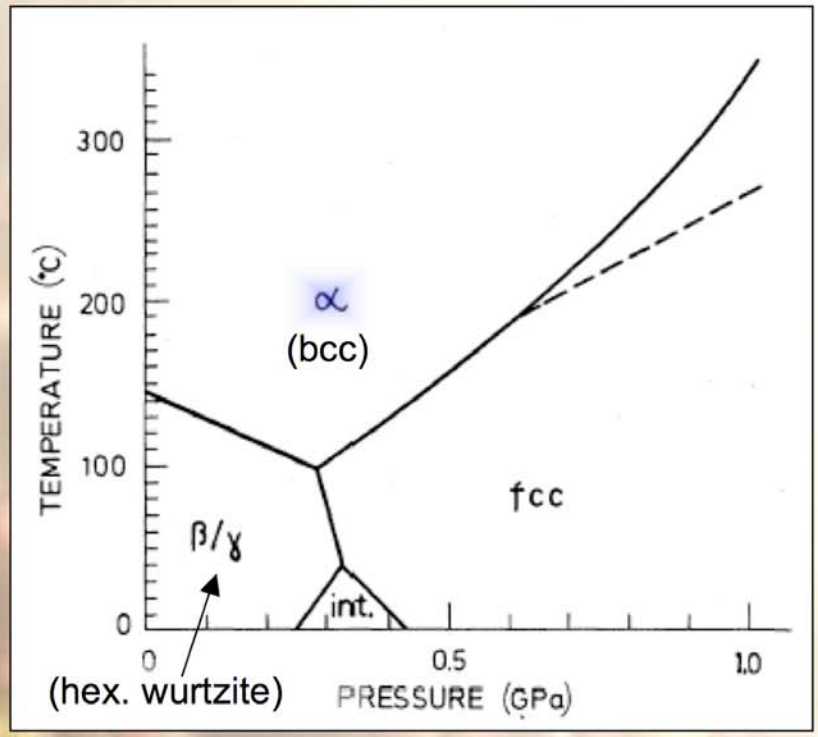
$$\mathcal{H}\Psi = E\Psi$$

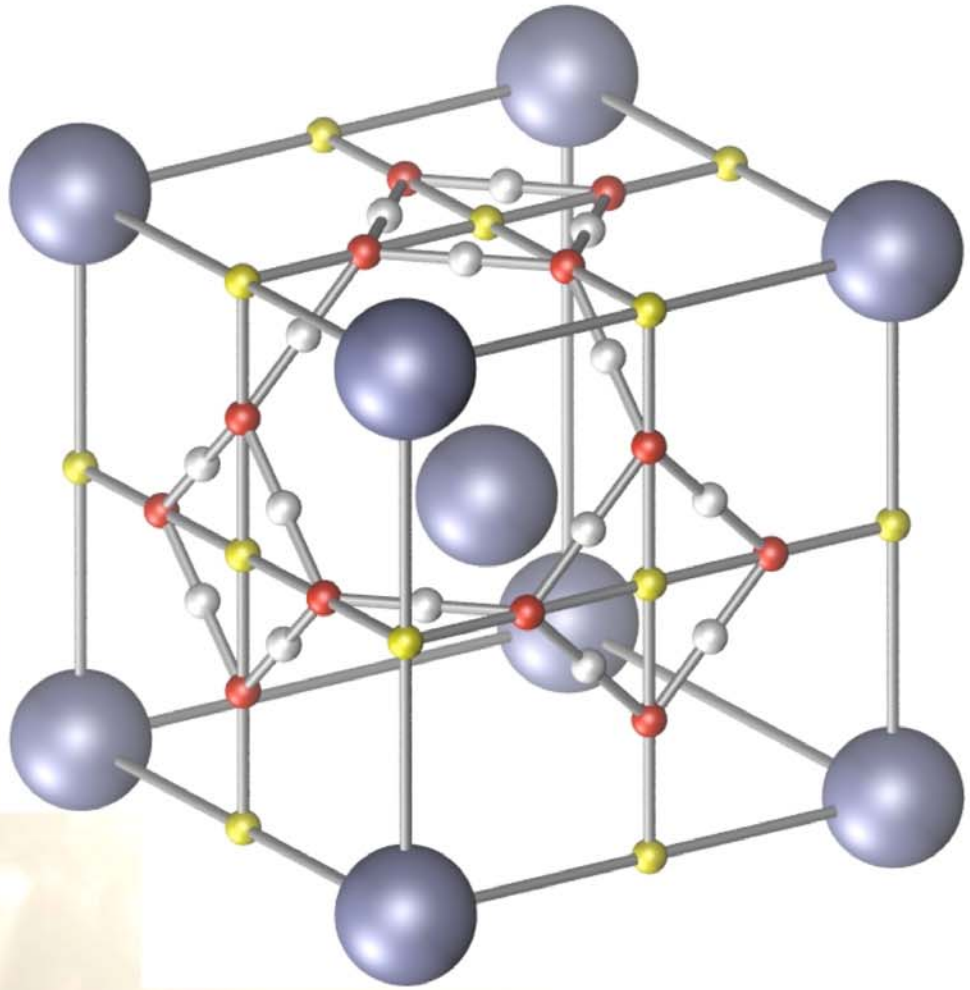
Molecular dynamics

- ✓ Can probe dynamic events (mechanisms, pathways, etc.)
- ✓ Can get kinetic information
- ✓ Can get thermodynamic information
- ✘ Too slow for rare-event sampling
- ✘ Can get stuck in local potential minimum
- ✘ Need lots of statistics for good convergence of dynamic and thermodynamic quantities

$$M_i \ddot{\mathbf{R}}_i = -\nabla U(\mathbf{R}_i)$$

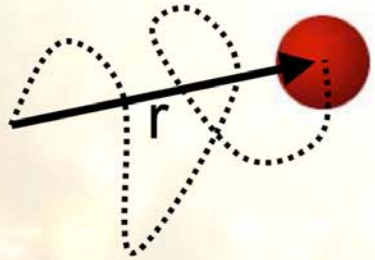
AgI: The archetypal superionic solid

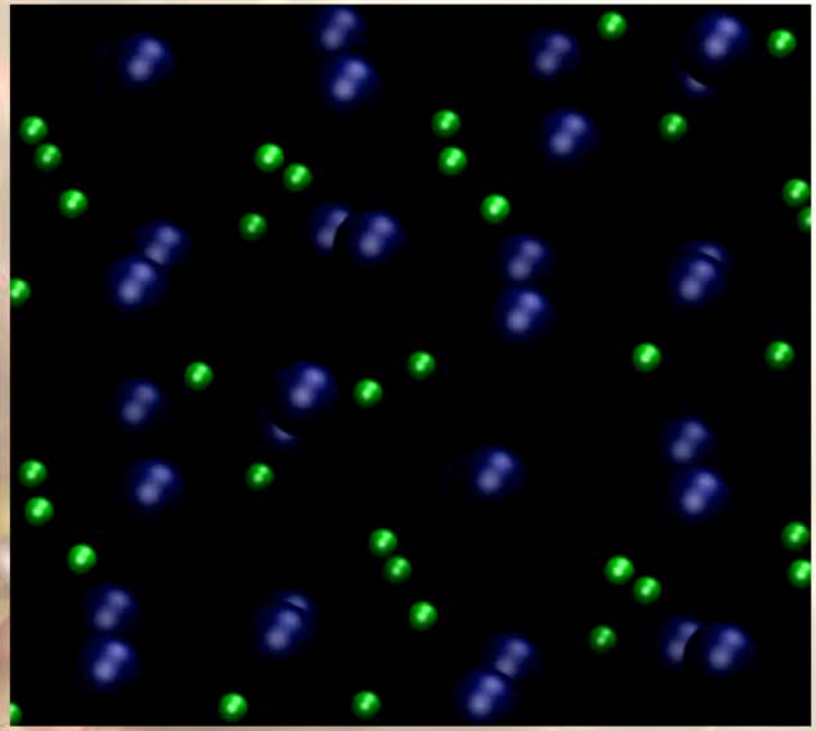


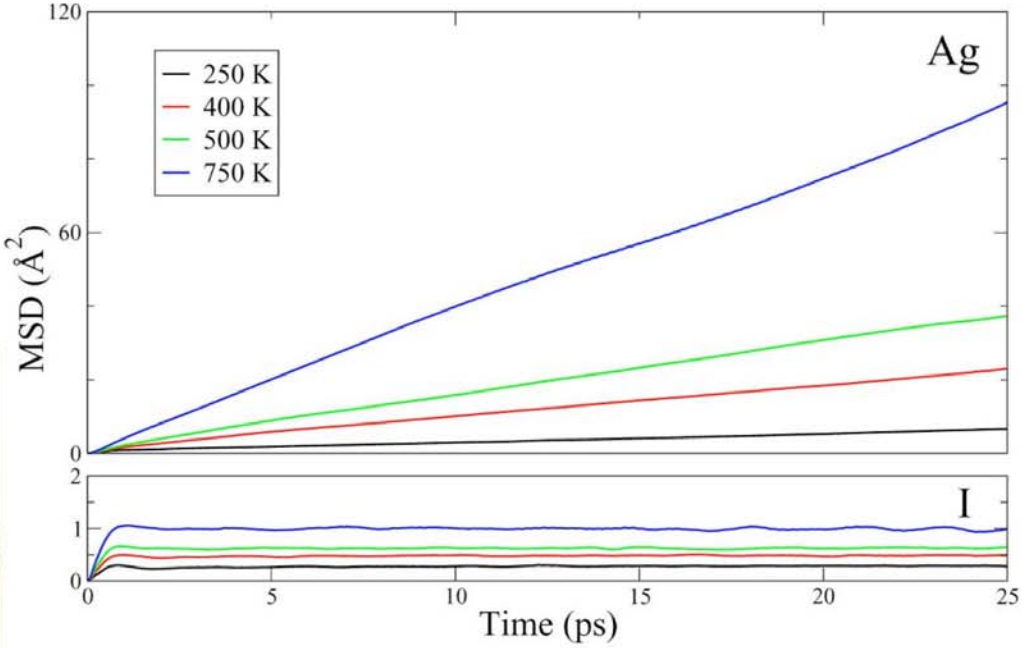


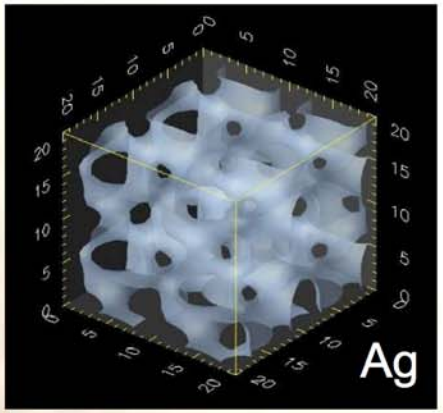
Mellenader et al., *Phys. Scripta* **22**, 541 (1980); Akella et al., *J. Appl. Phys.* **40**, 2800 (1969).

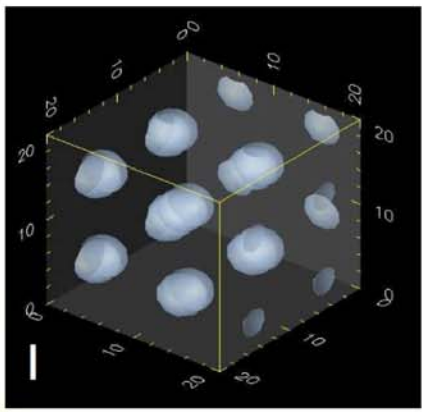
Identifying superionicity



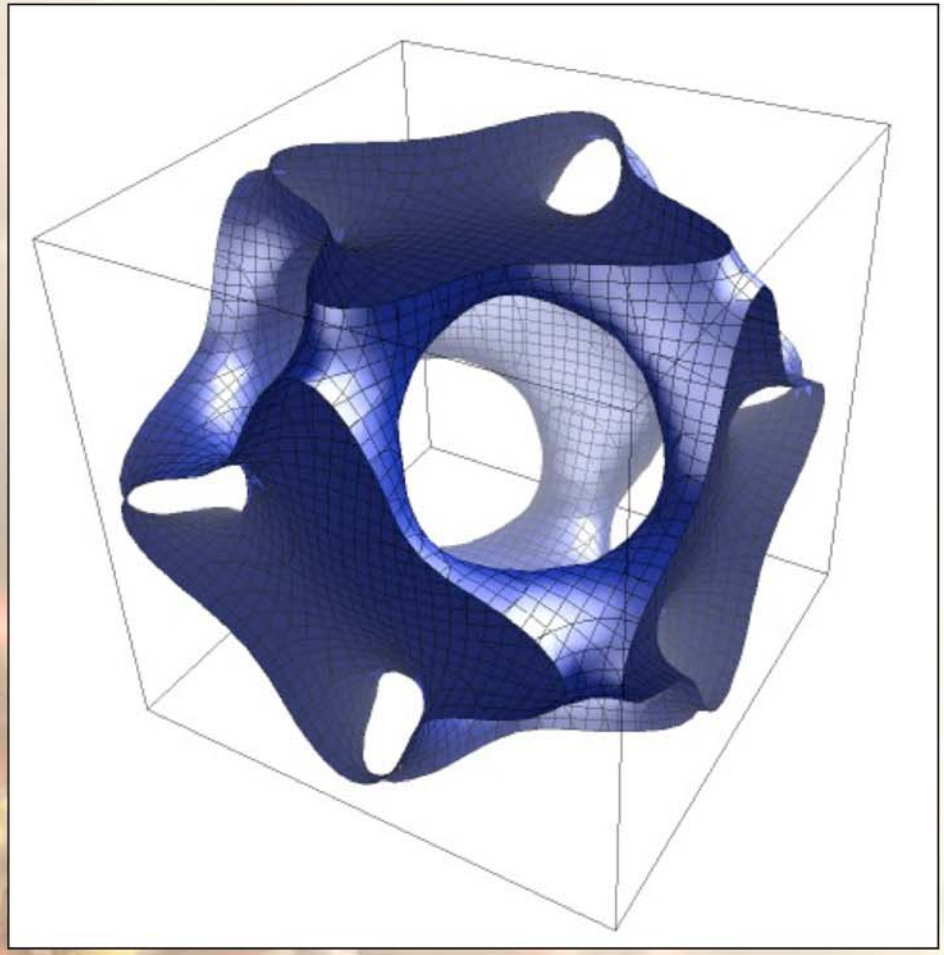


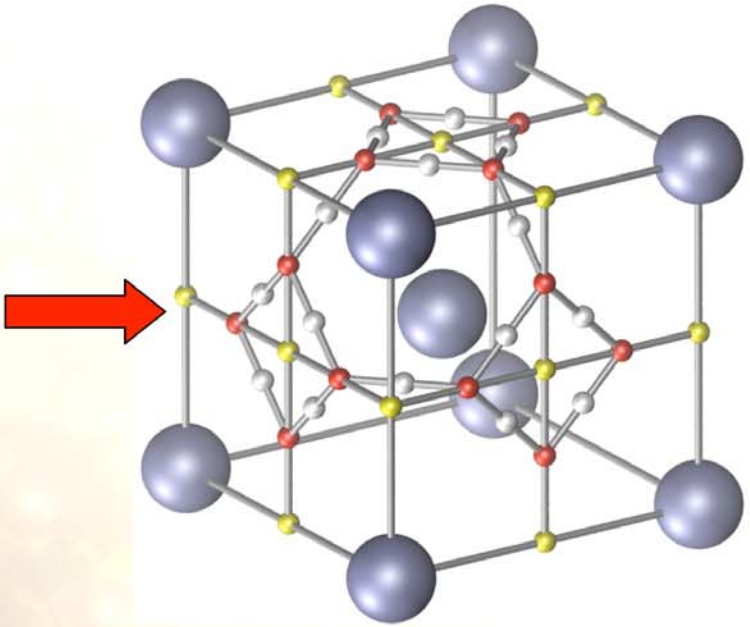






Time-averaged dynamical structure





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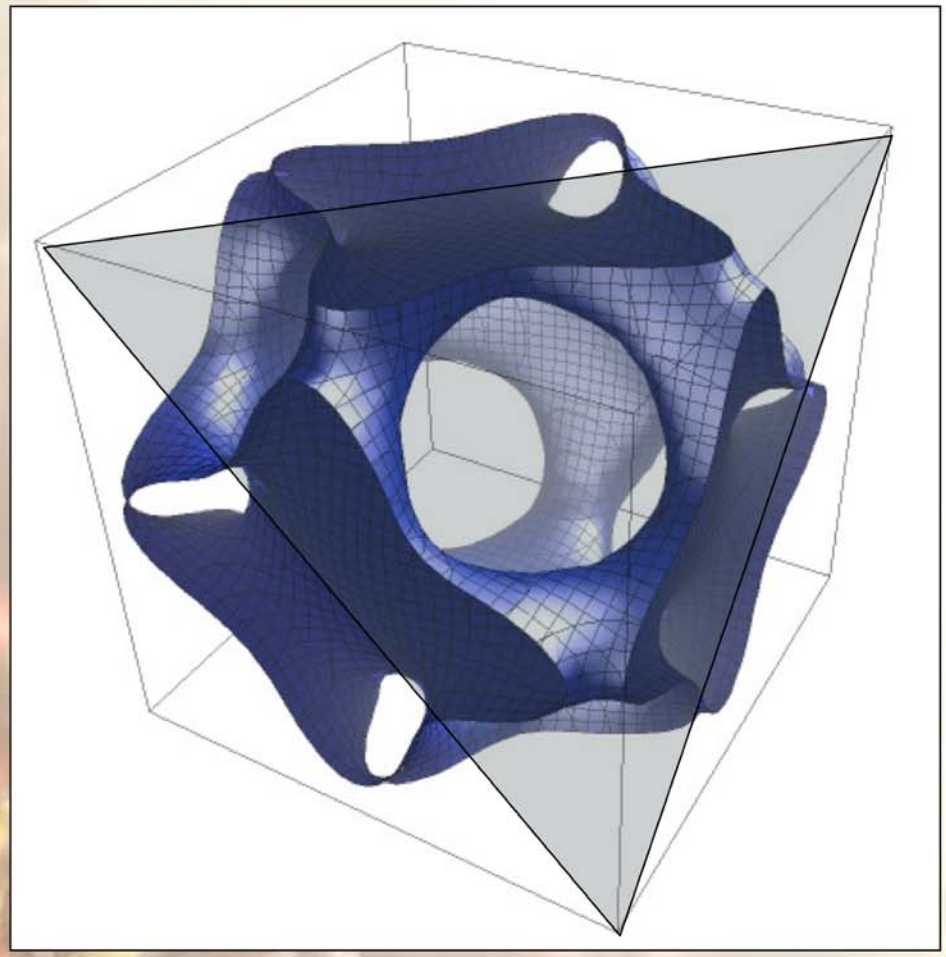

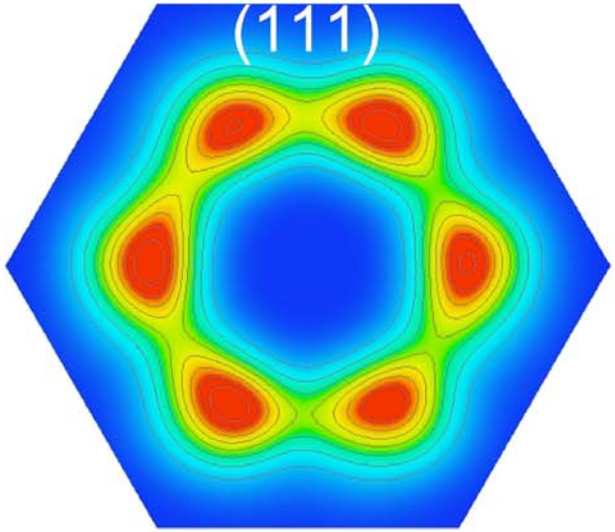

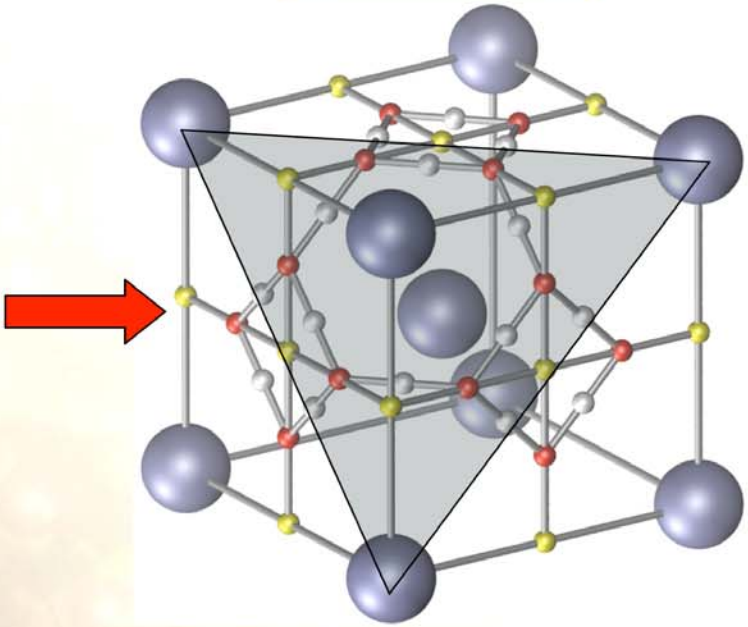

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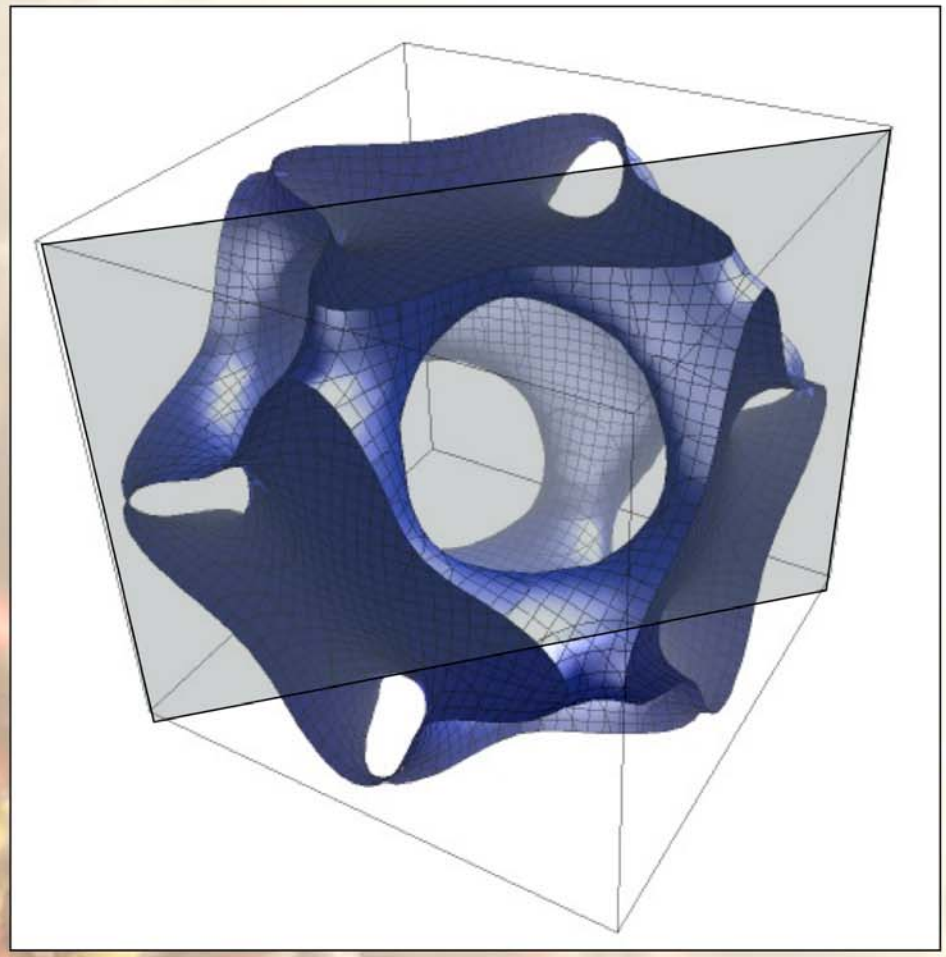

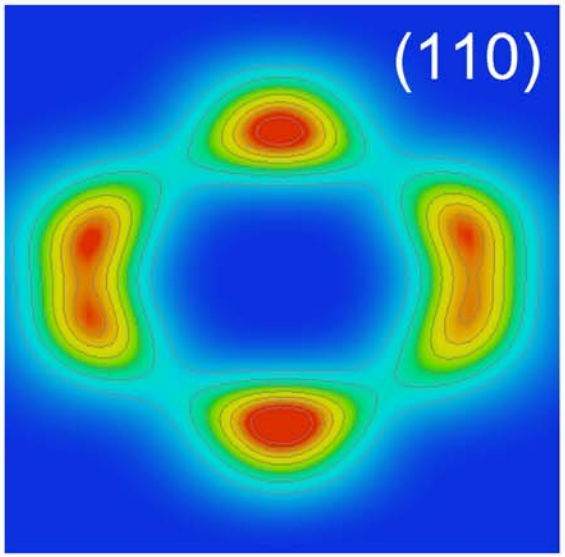

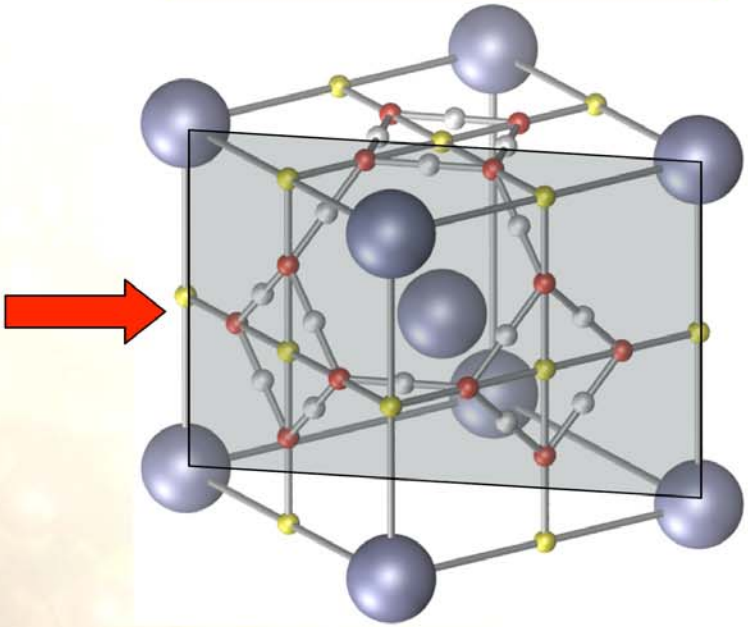

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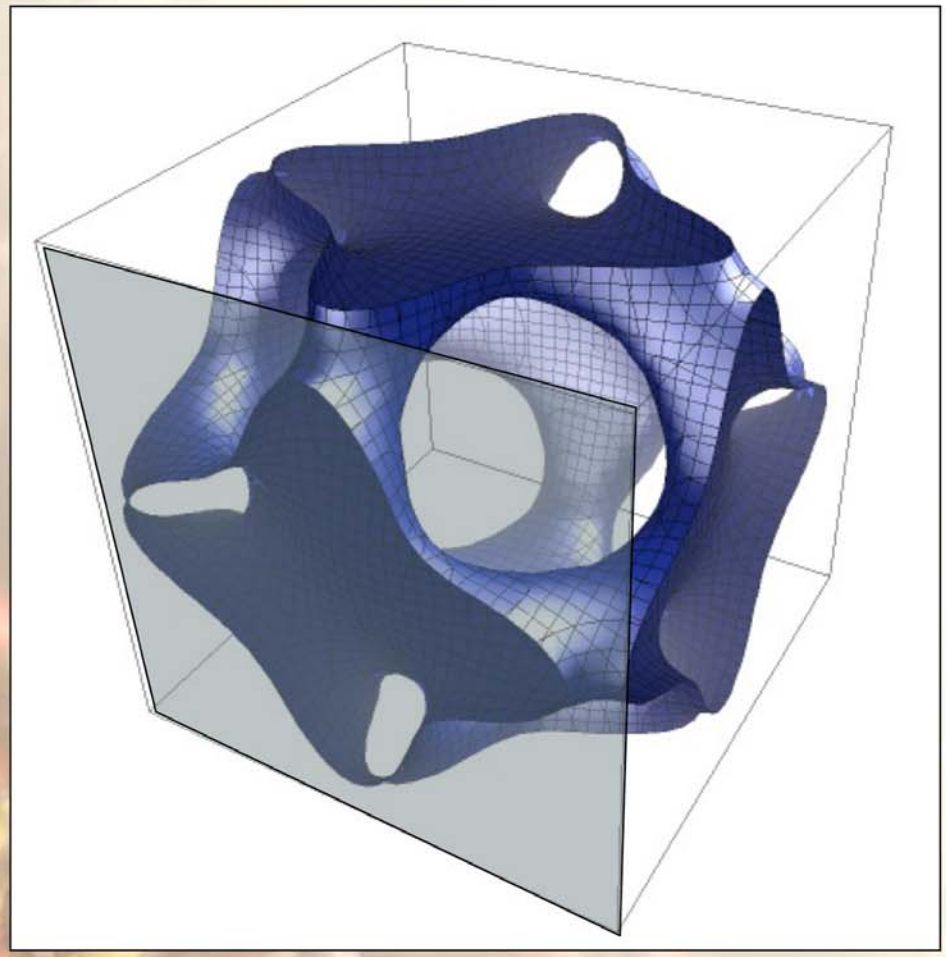

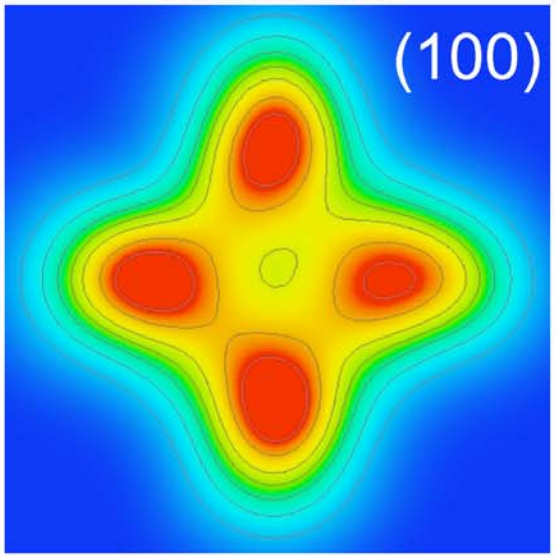

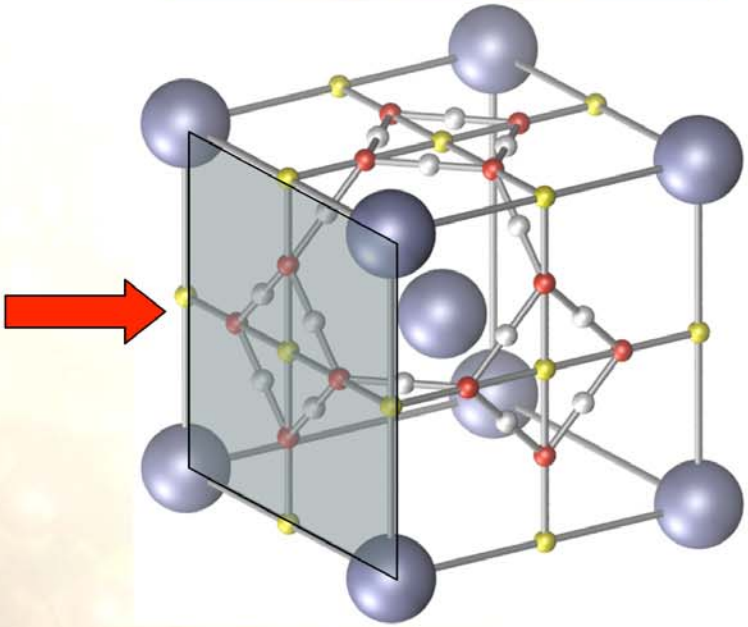

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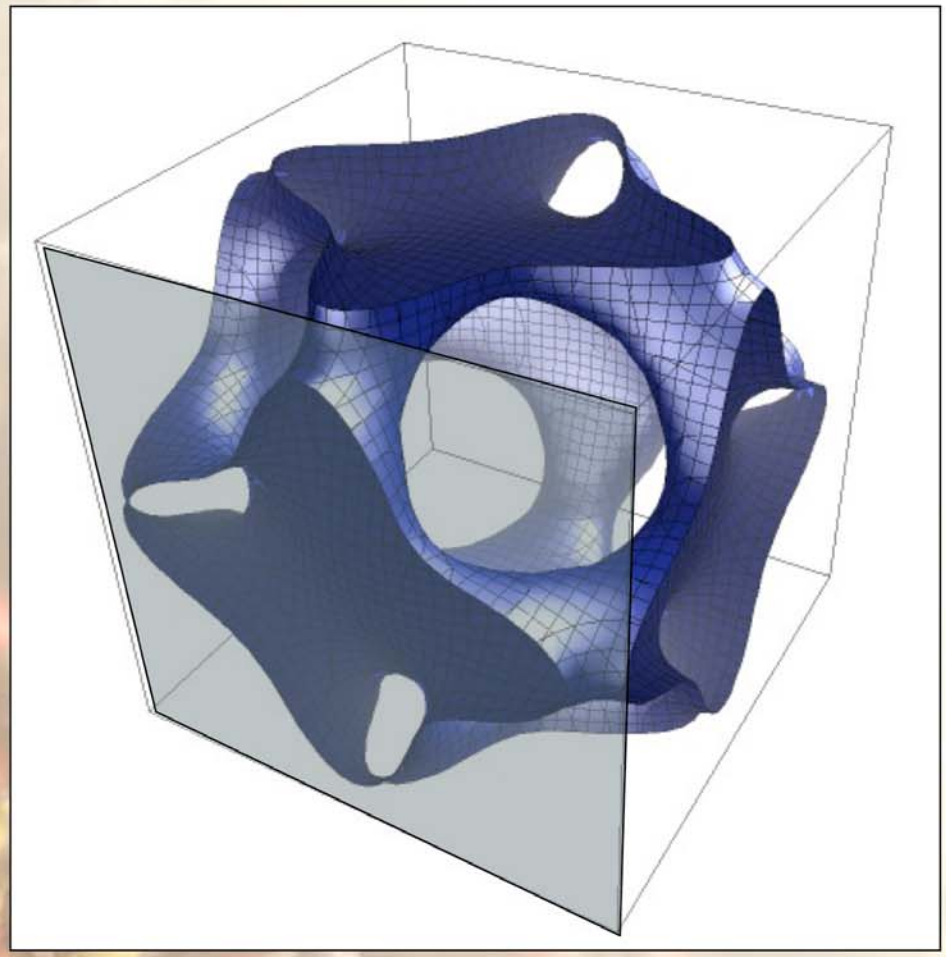
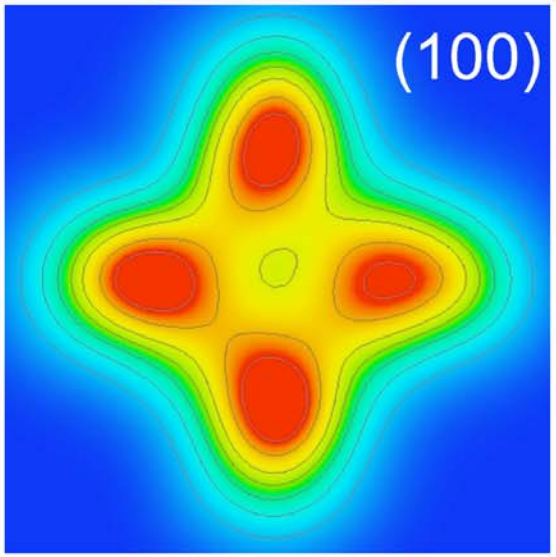
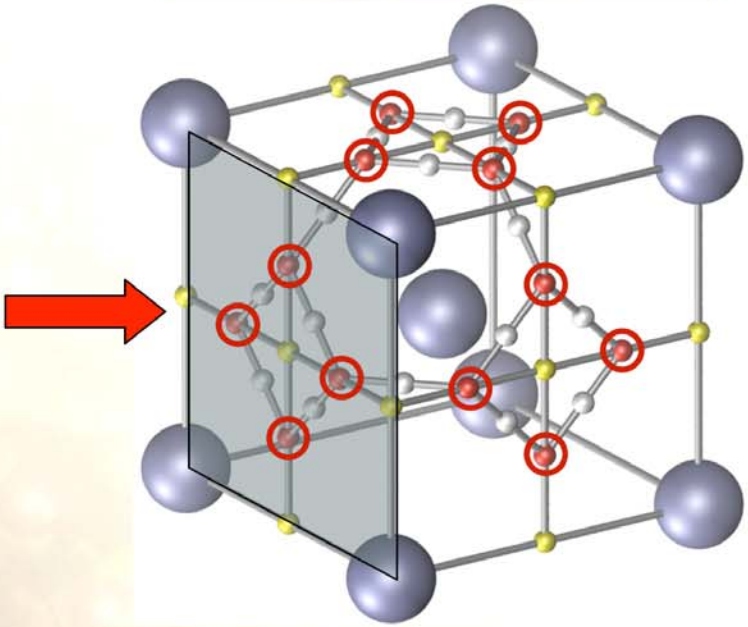
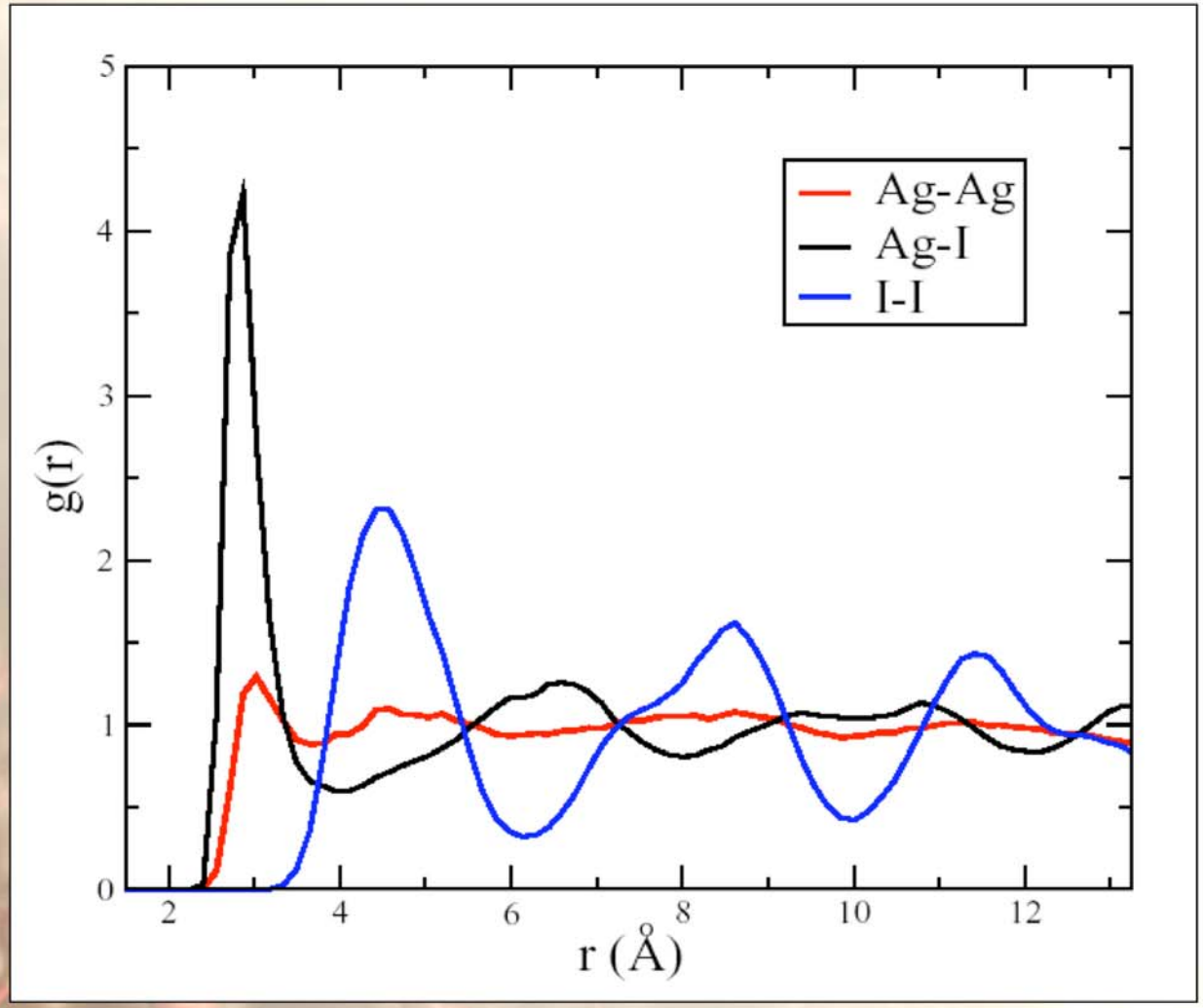
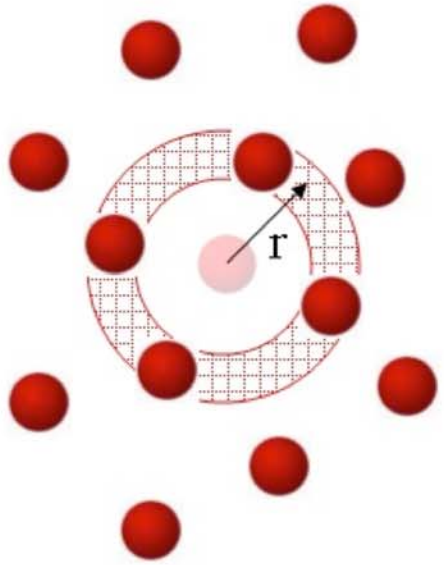






Instantaneous dynamical structure (I)





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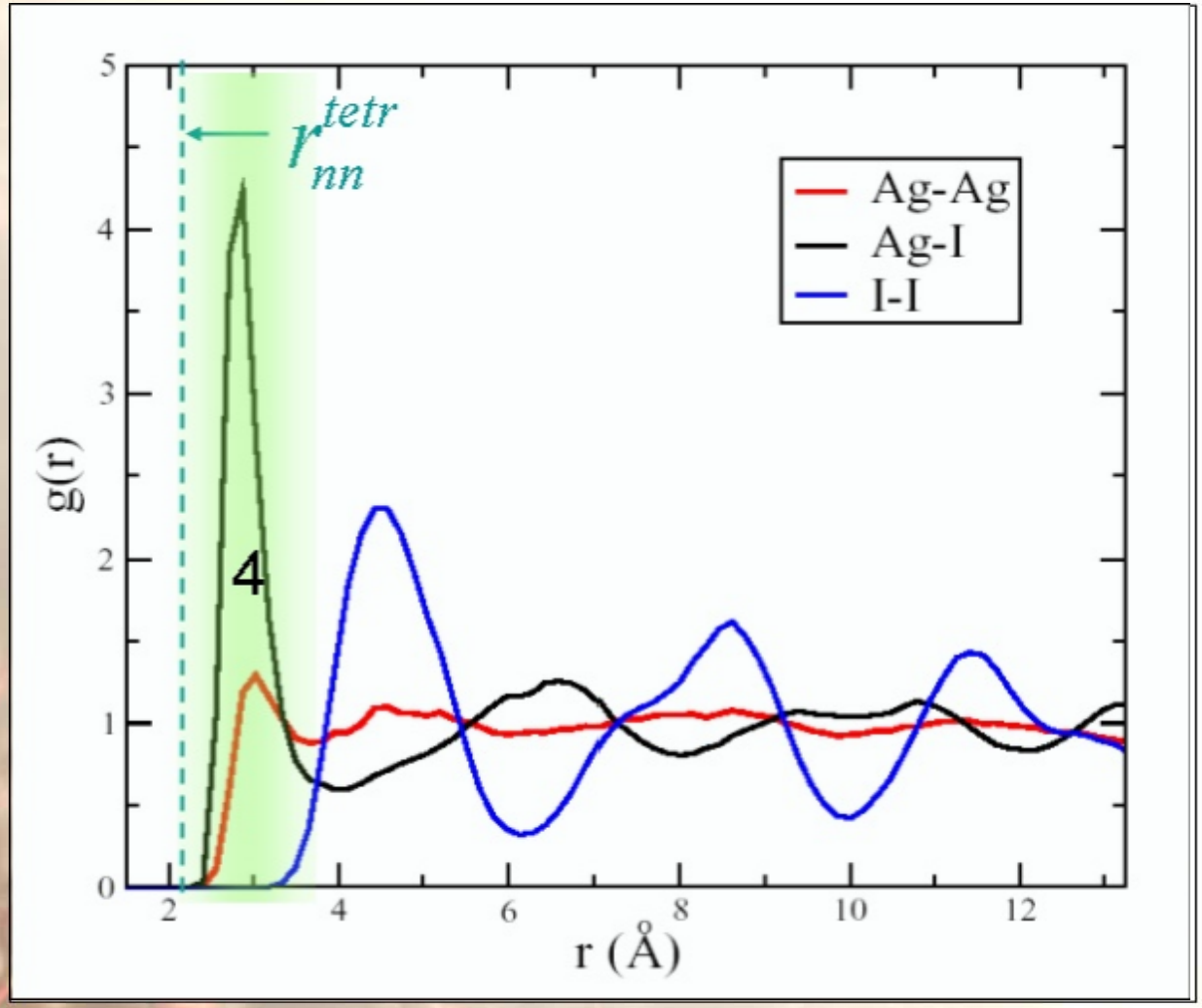
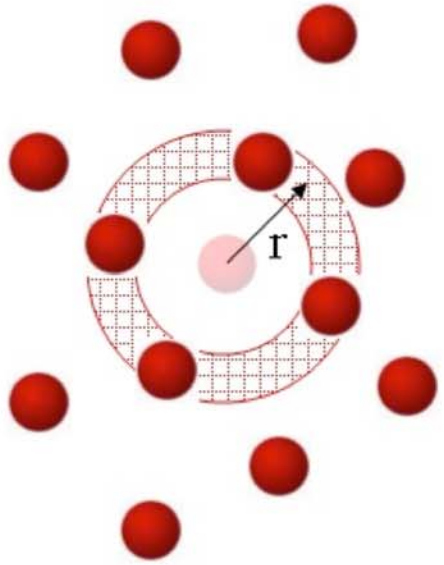
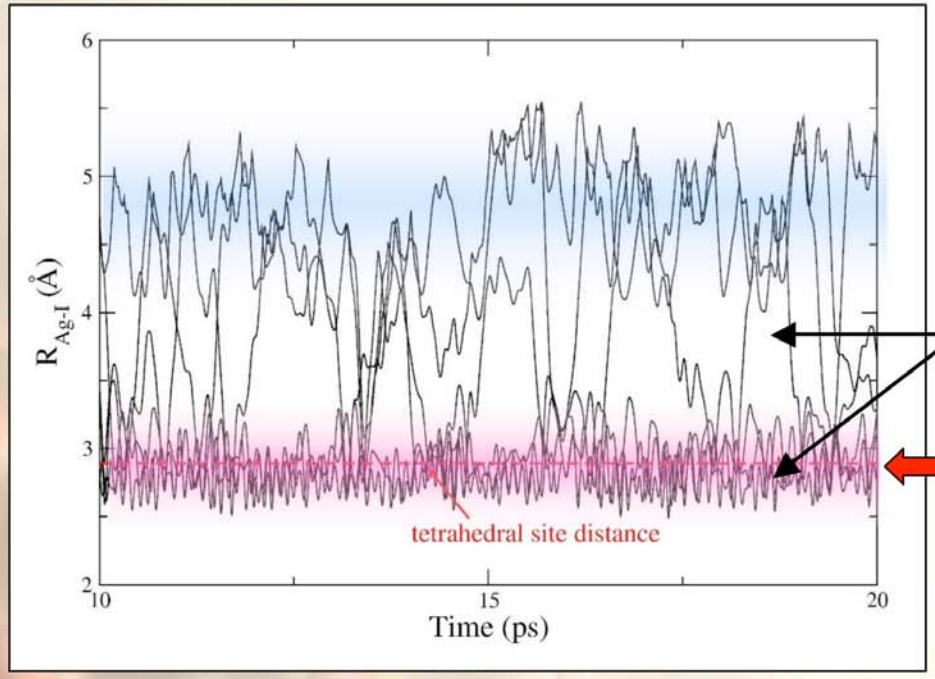
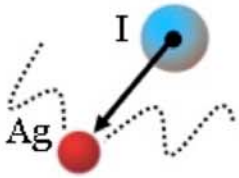




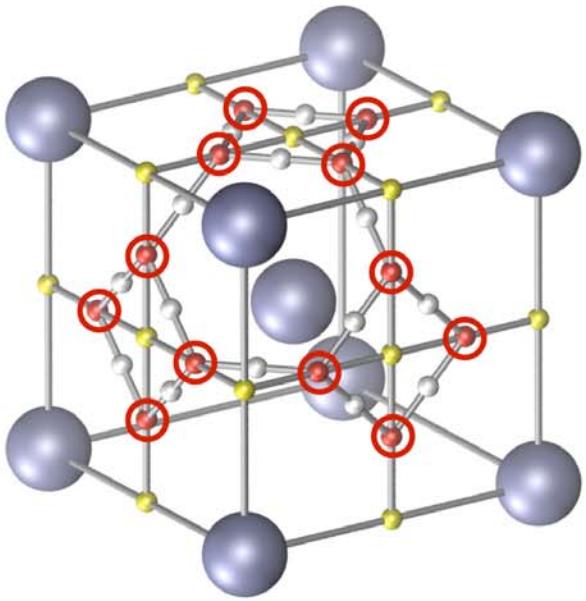
Instantaneous dynamical structure (II)





1:3

68-75% occ.



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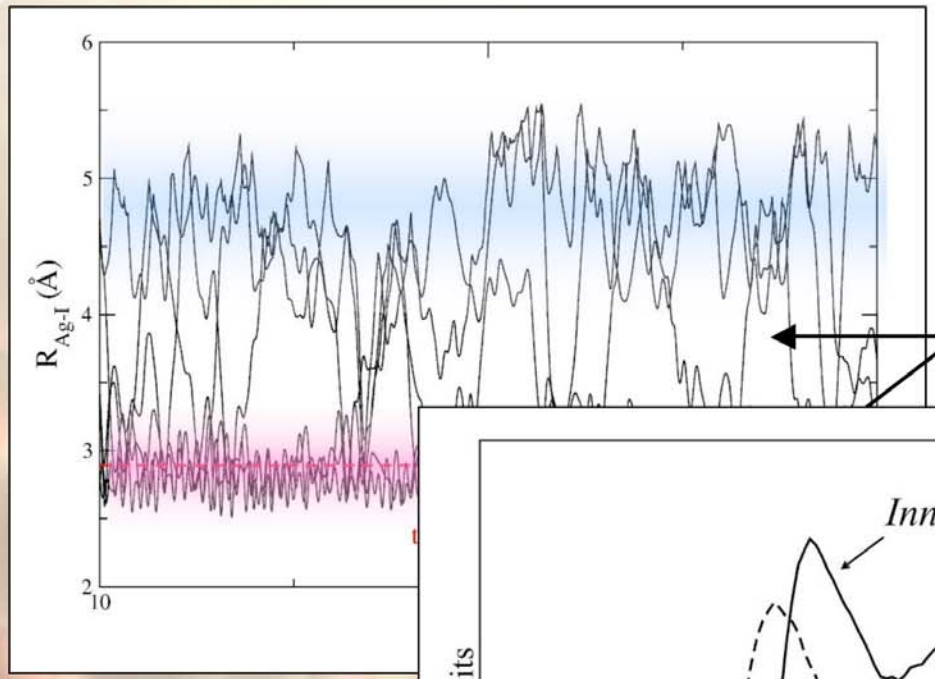

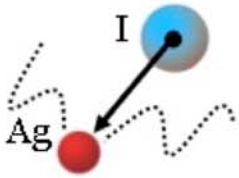

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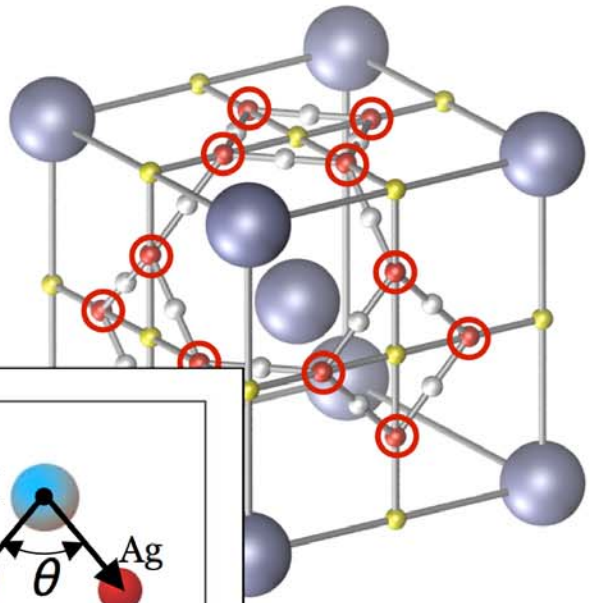
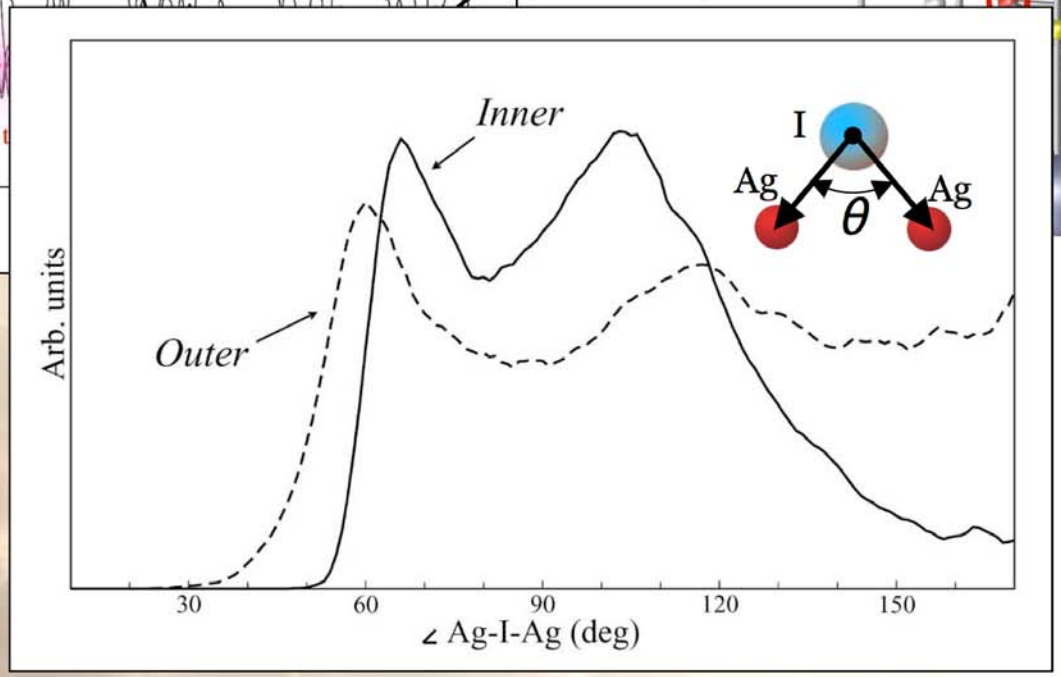
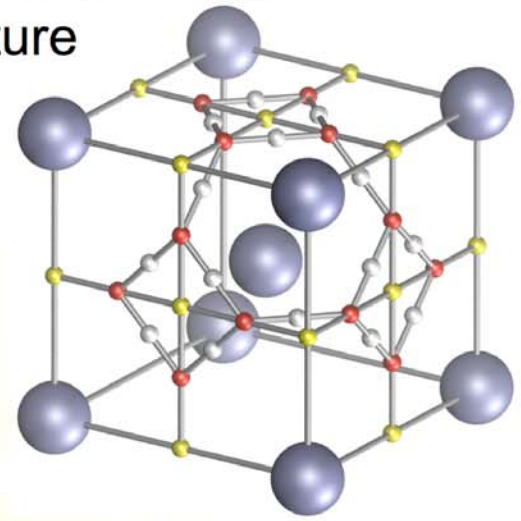


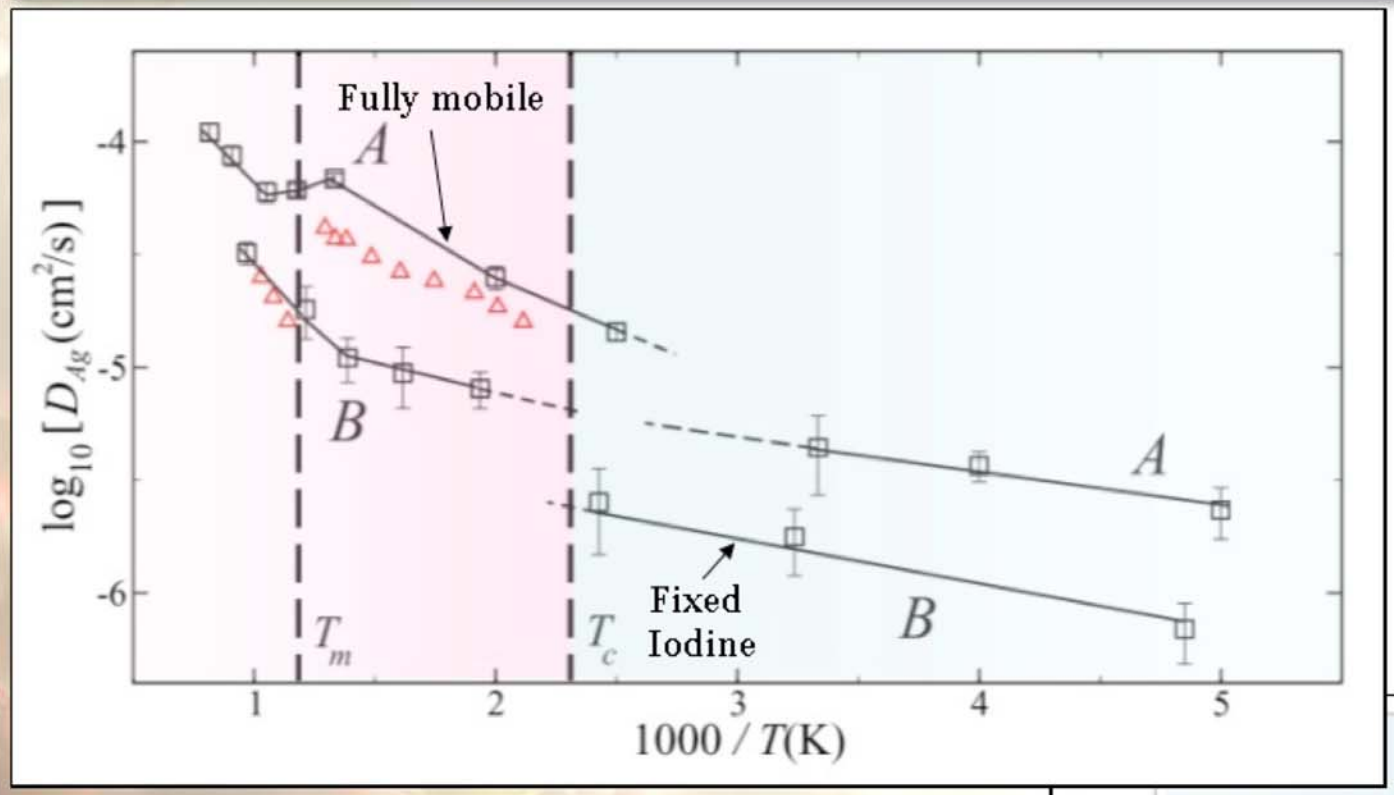


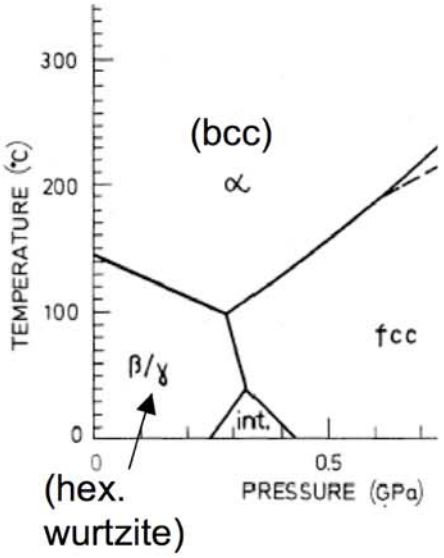
Silver ion ordering rules

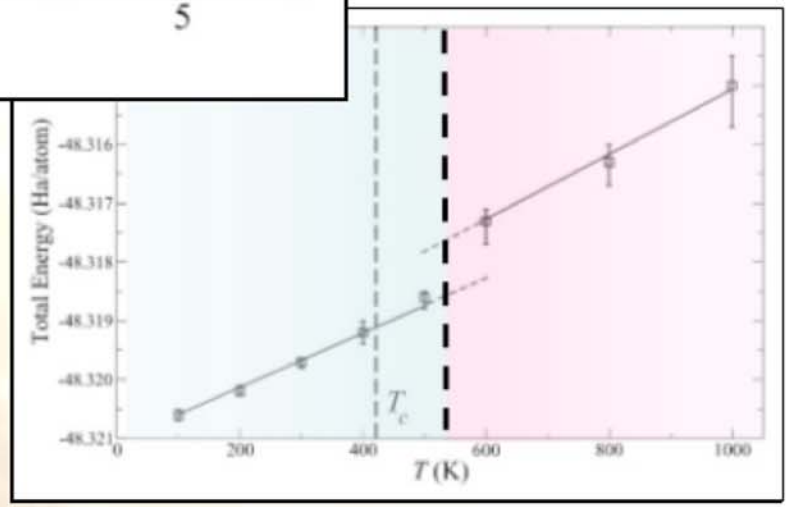
1. Four silver ions populate the first cationic shell surrounding an iodine.
2. No two ions occupy neighboring tetrahedral sites.
3. On average, three Ag^+ ions surround an iodine at a radius of R_{AgI} = 2.6 Å, the tetrahedral interstitial distance.
4. A fourth Ag^+ transitions between that shell and a second shell of $R_{AgI} \approx 4.2$ Å, associated with a neighboring iodine; the transition rate between the two is temperature dependent and disappears below T_c.
5. The angular positions of the three inner silvers are correlated, whereas the fourth (outer) silver is relatively unconstrained.



An independent transition of the diffusing species? (I)







Experiment: Kvist et al., *Z. Naturforsch.* **25a**, 257 (1970); Araki et al., *J. Phys. Soc. Japan* **68**, 134 (1999).

An independent transition of the diffusing species? (II)

$$\Delta U \xrightarrow{?} \Delta U_{\mathrm{Ag}} + \Delta U_{\mathrm{I}}$$

$$\int_{\mathbf{r}_1}^{\mathbf{r}_2} \mathbf{F} \cdot d\mathbf{l} = U(r_1) - U(r_2)$$

$$k_B T^2 C_V = \left| \langle U^2 \rangle - \langle U \rangle^2 \right|$$

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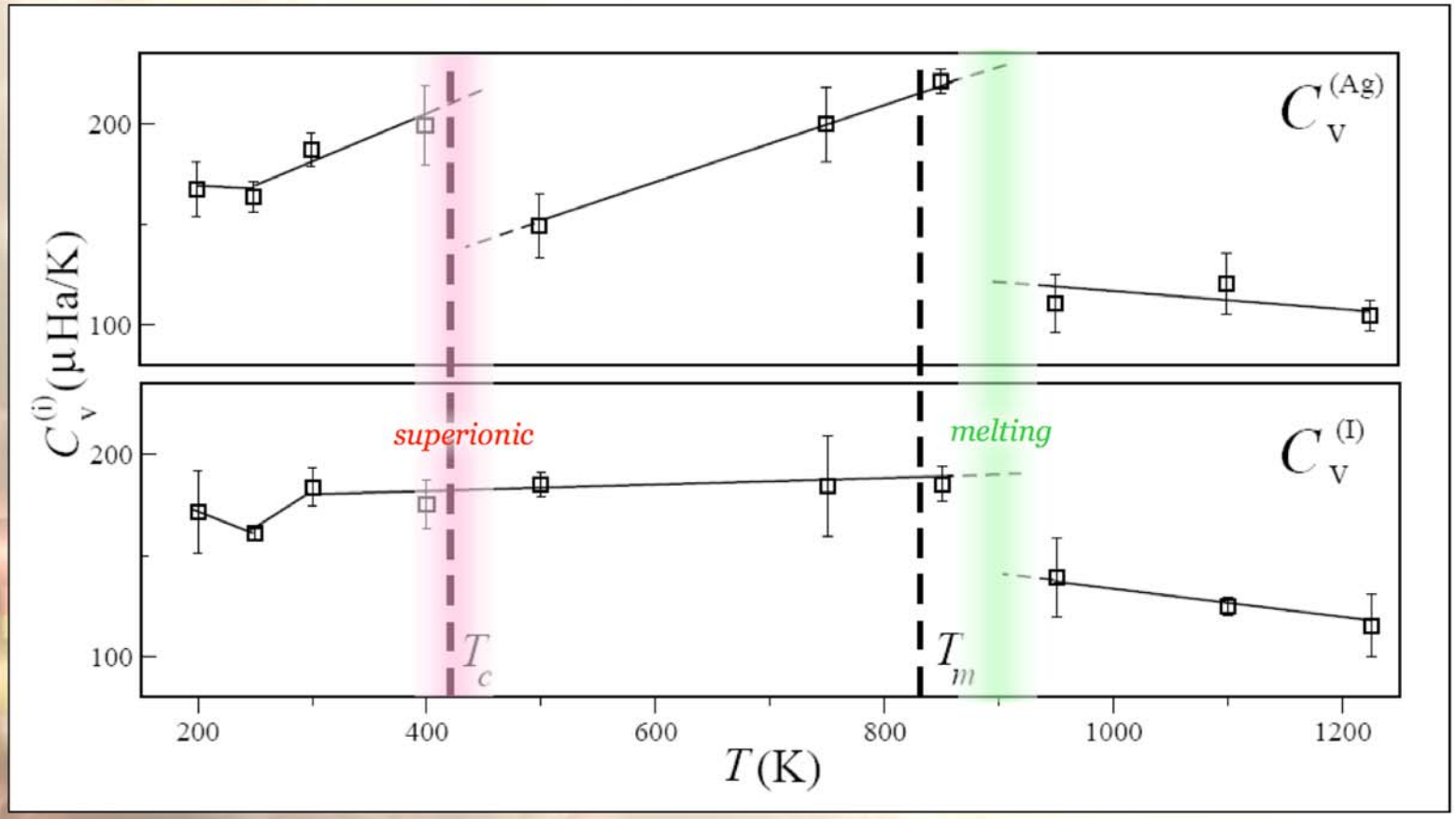
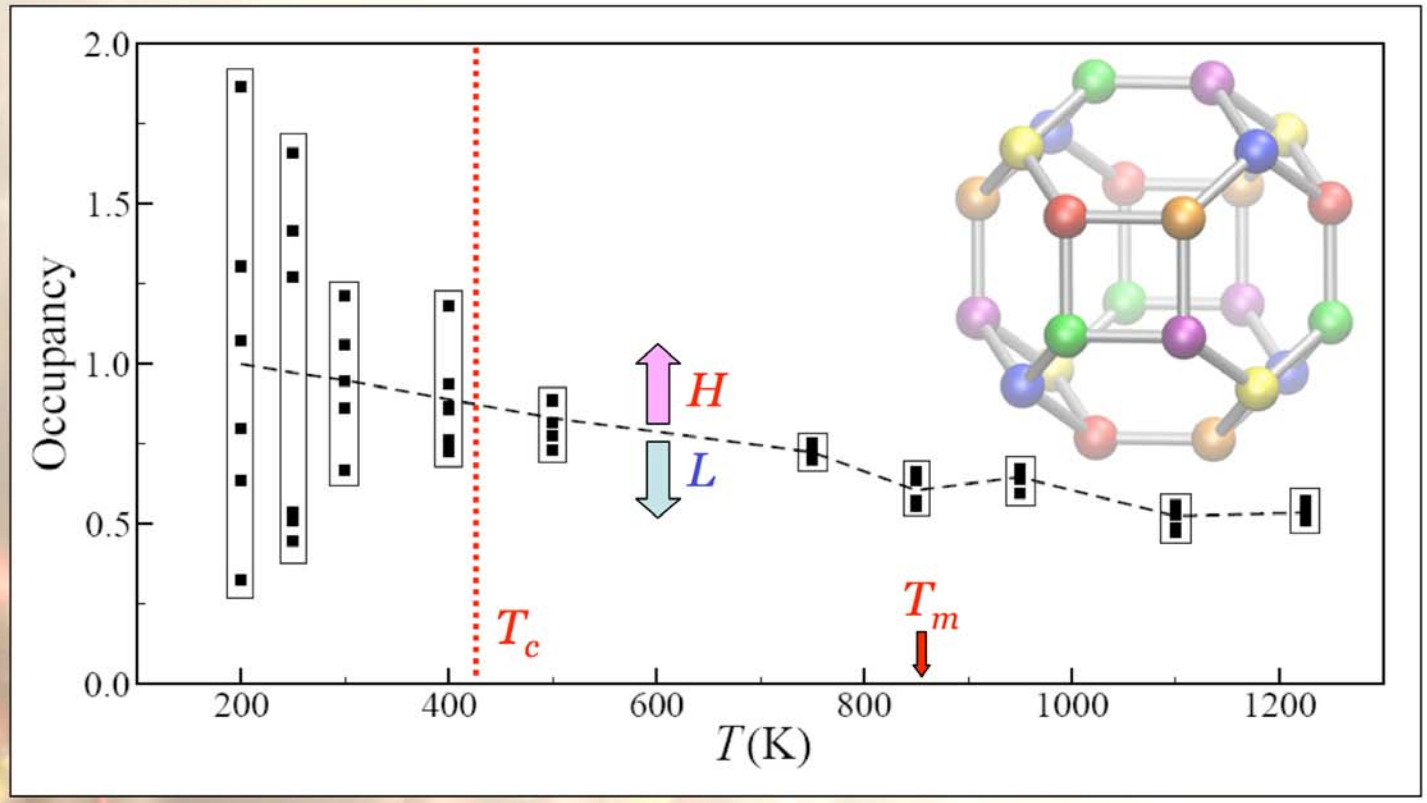
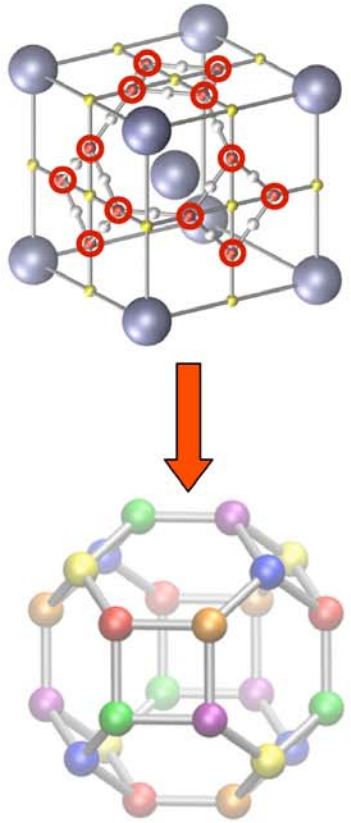


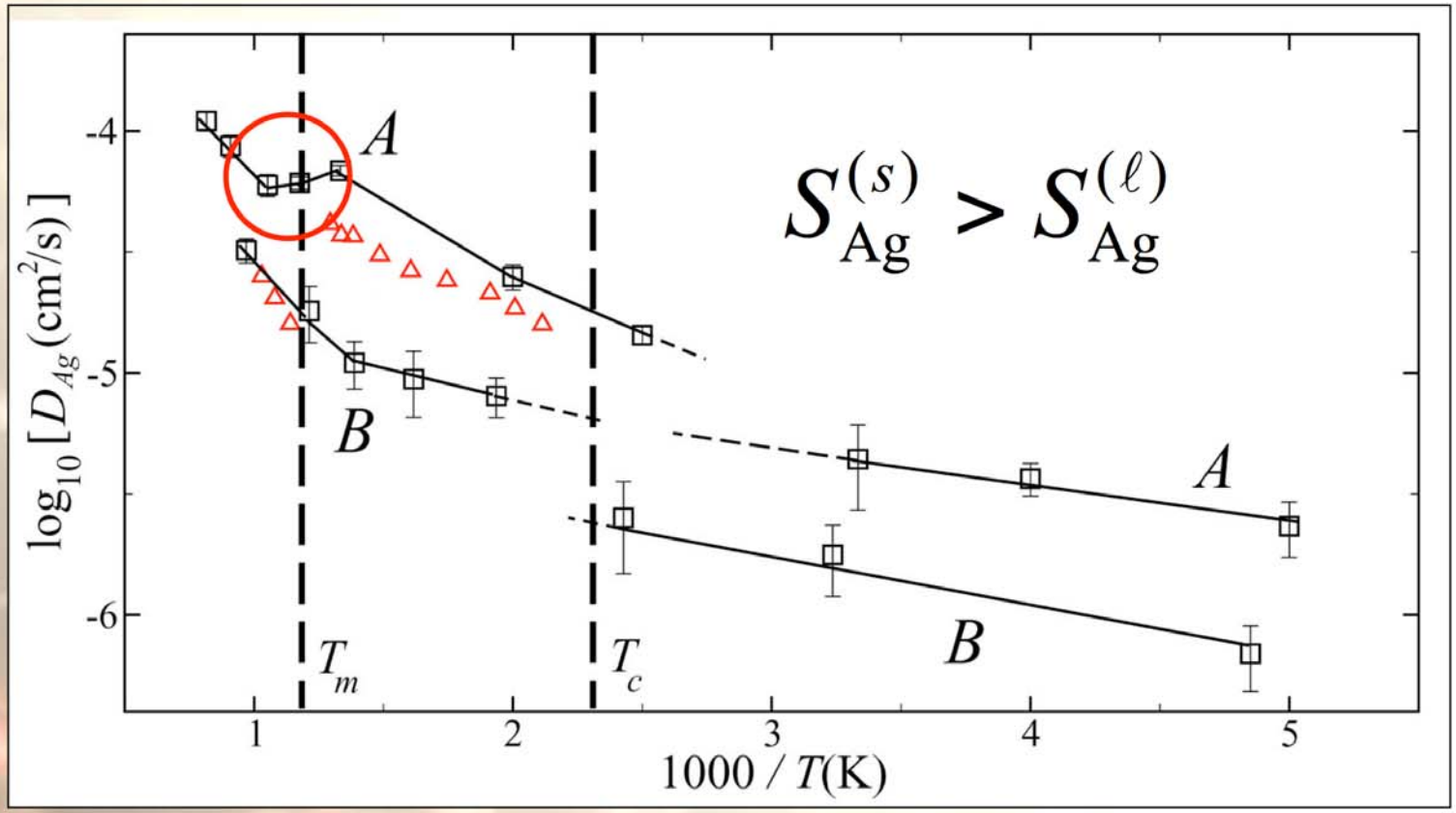
An order-disorder transition?





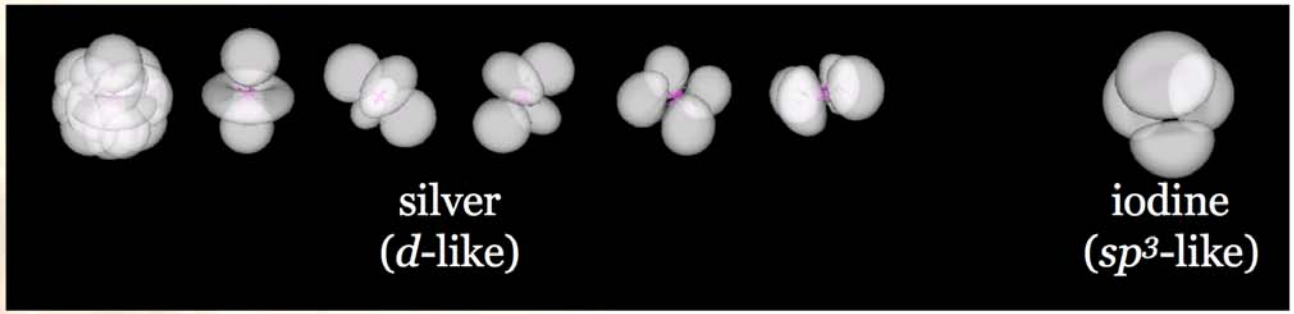
Madden et al., PRB 45, 10206 (1992); Seok and Oxtoby, PRB 58, 5146 (1998).

A phase between a solid and a liquid?



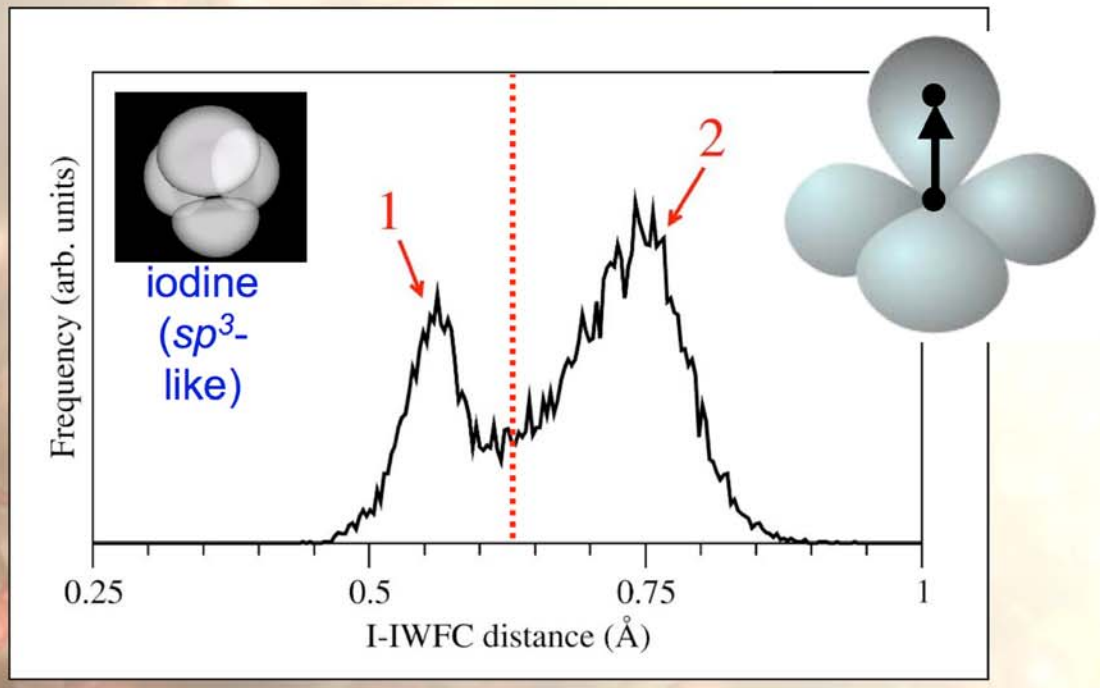
A unique chemical signature

Maximally localized Wannier functions



N.Marzari and D.Vanderbilt, *Phys.Rev.B* **56**, 12847 (1997)

A unique chemical signature



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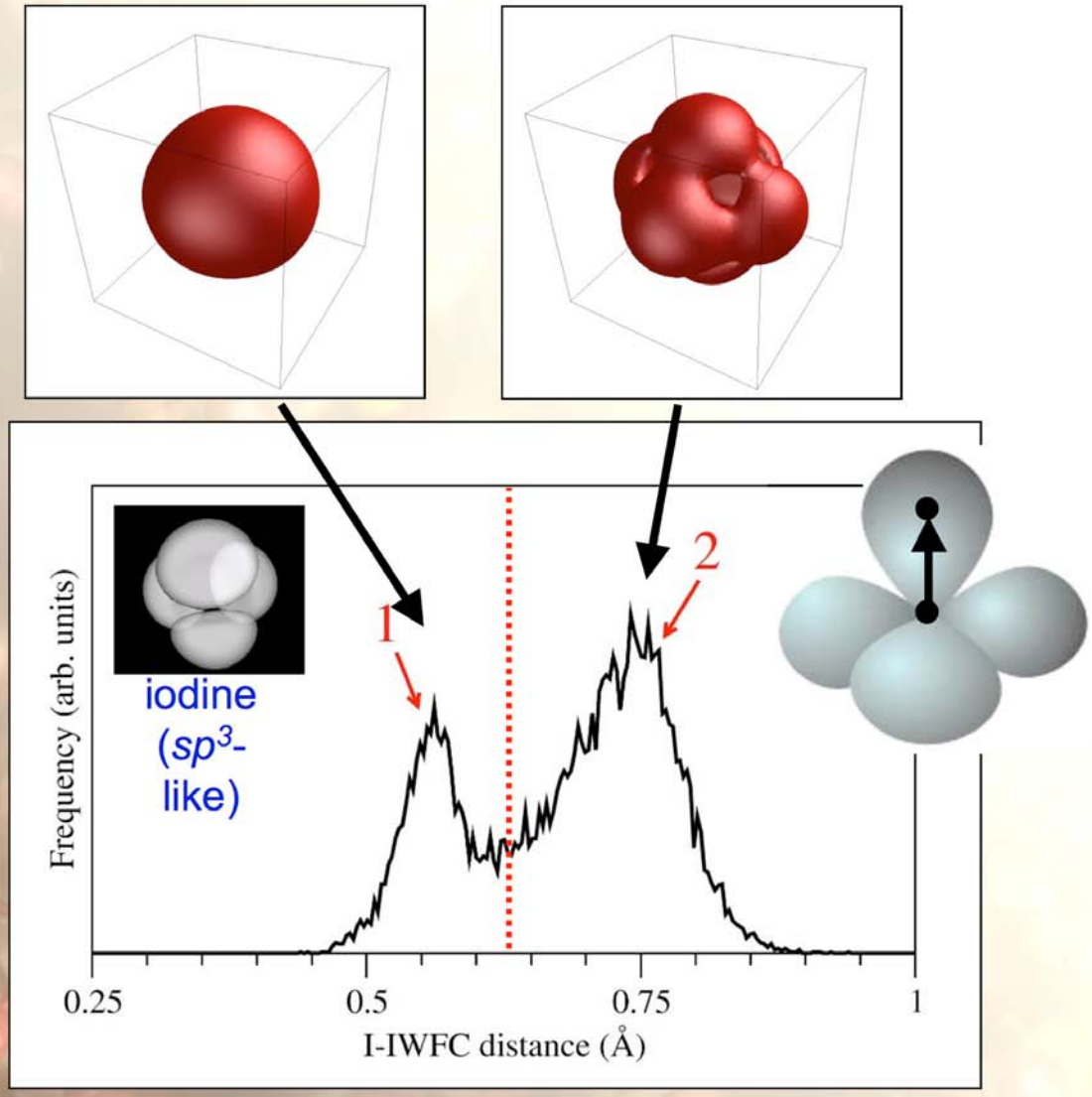

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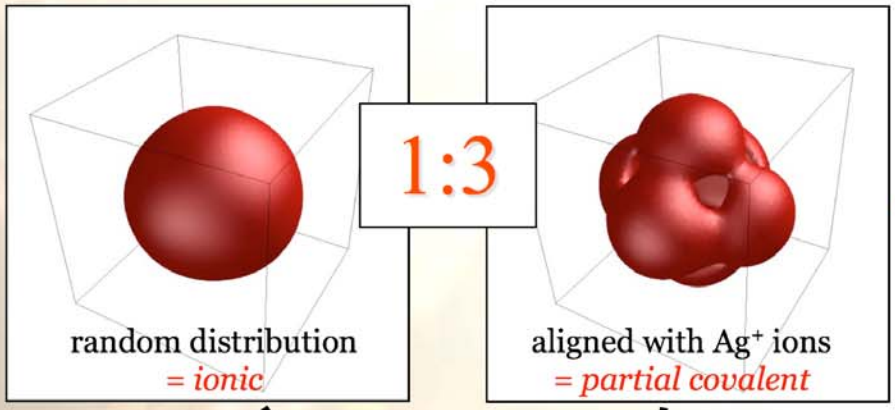
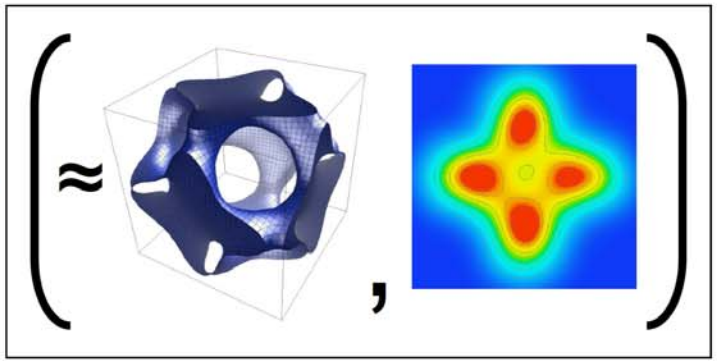
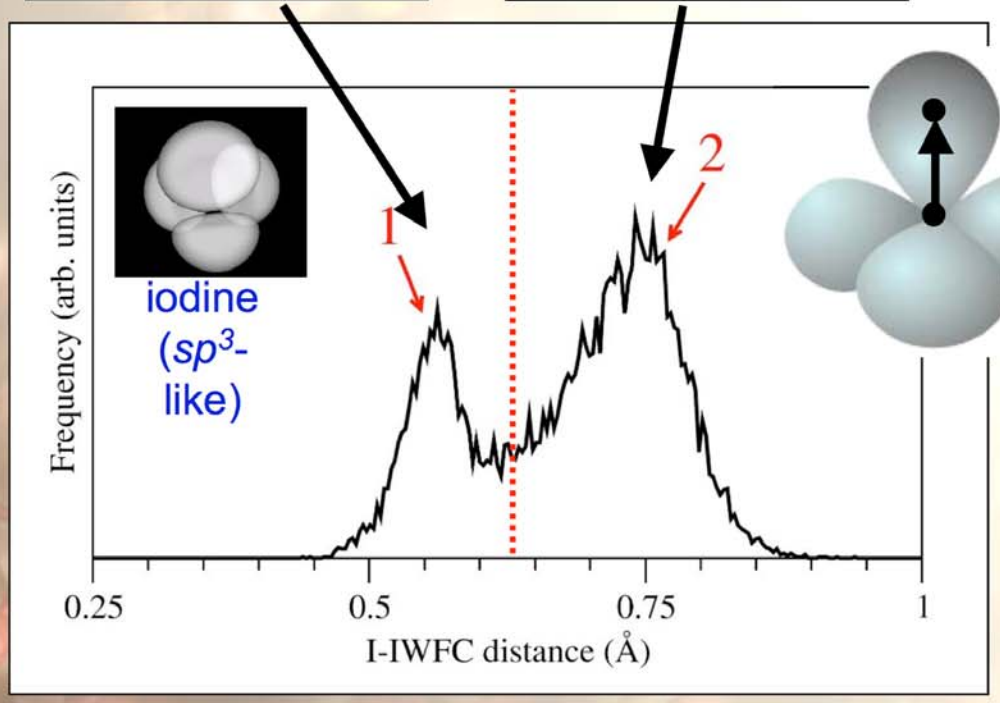
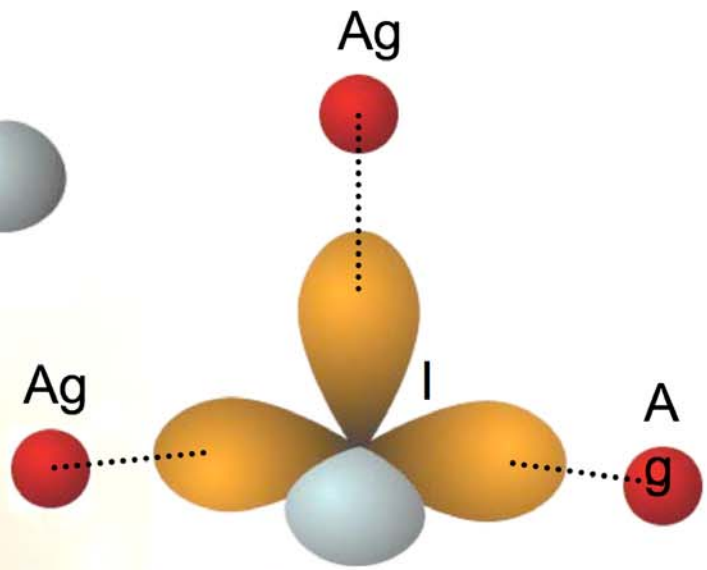
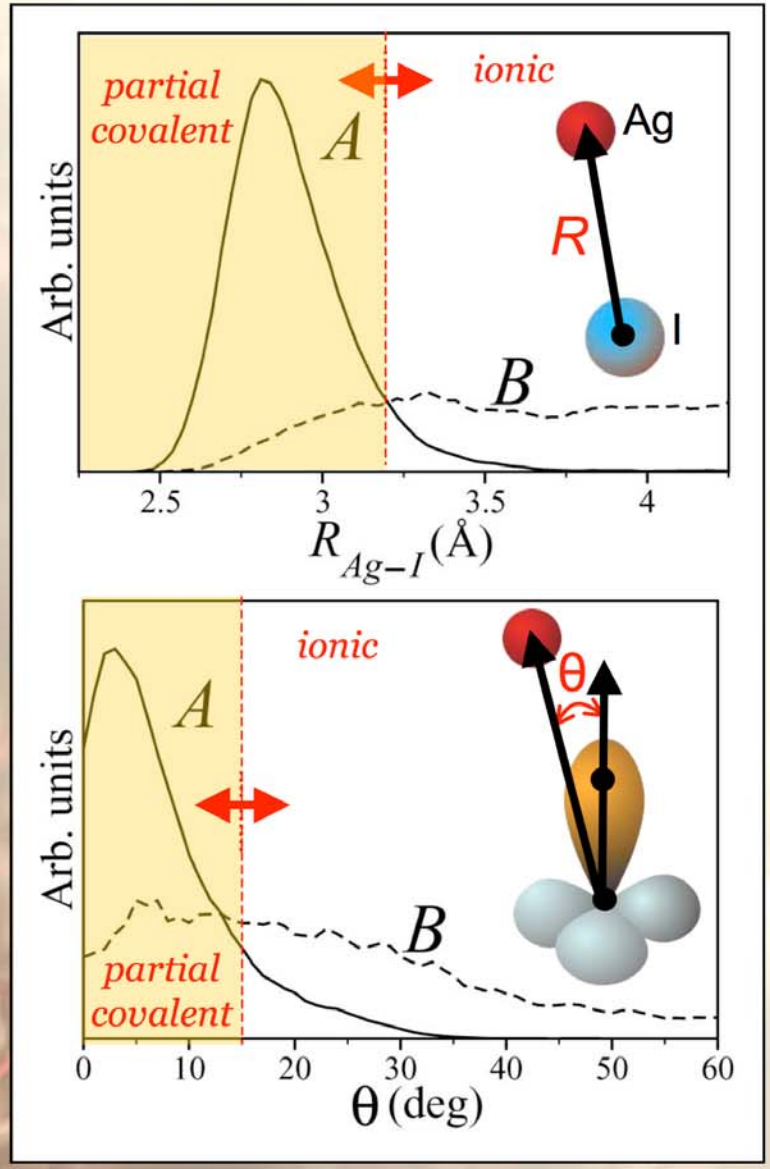


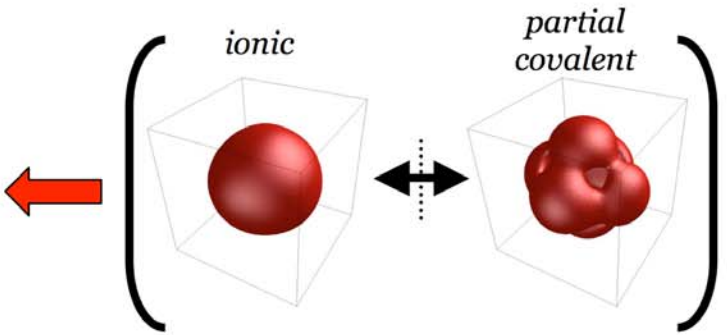


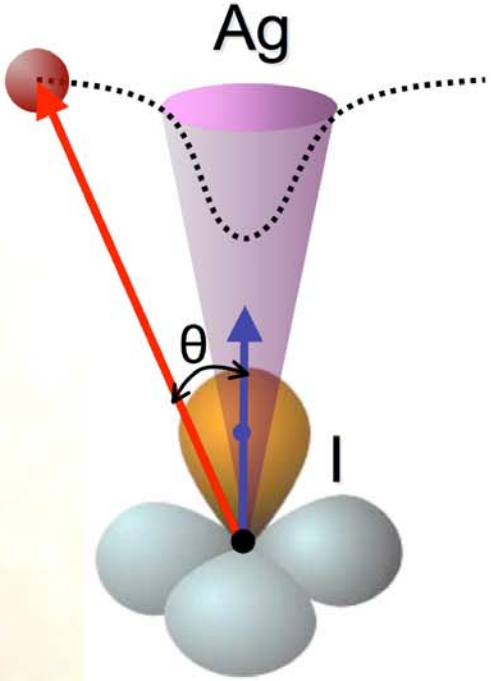




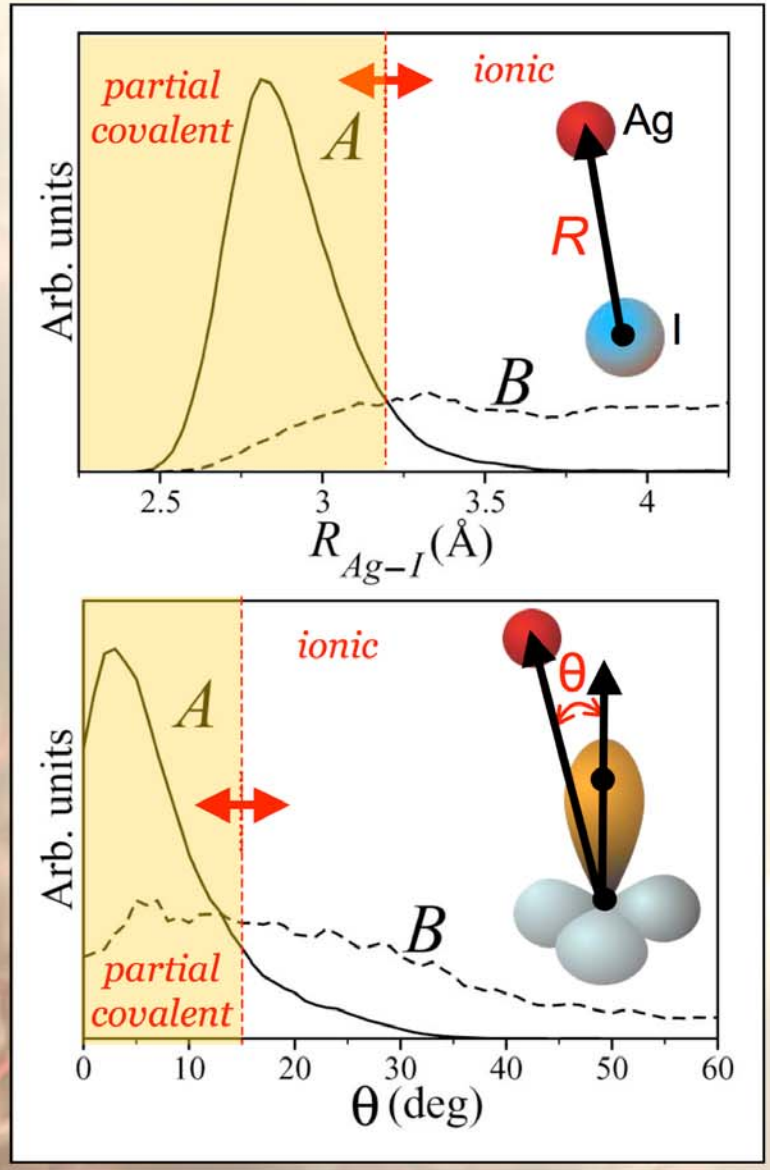
Chemical picture of the conduction mechanism

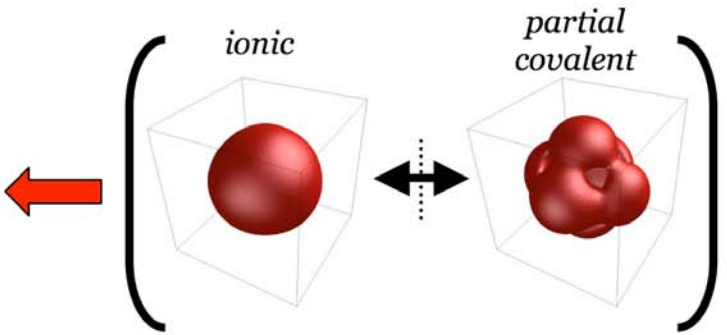


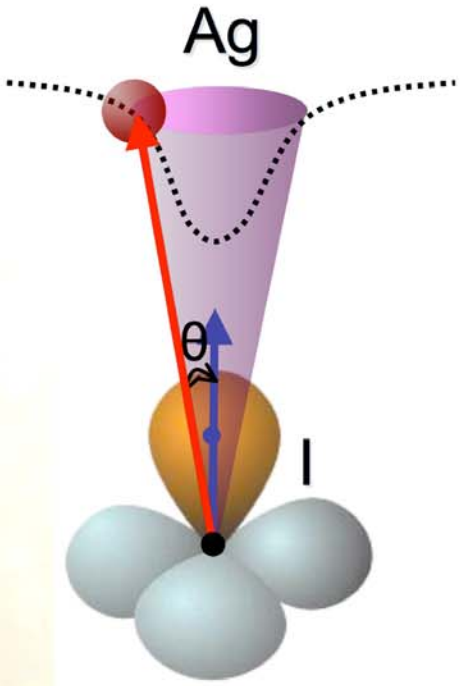




Chemical picture of the conduction mechanism







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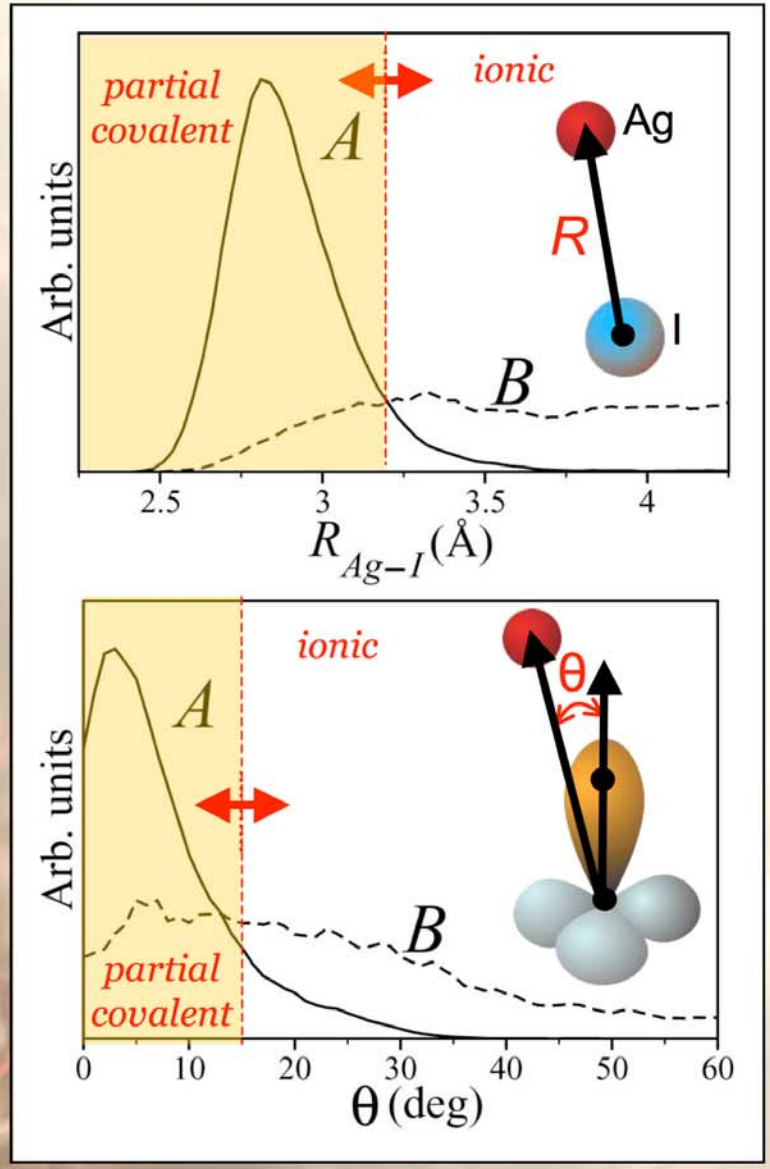

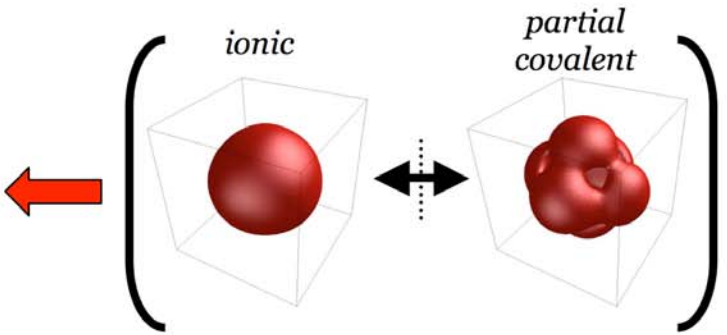

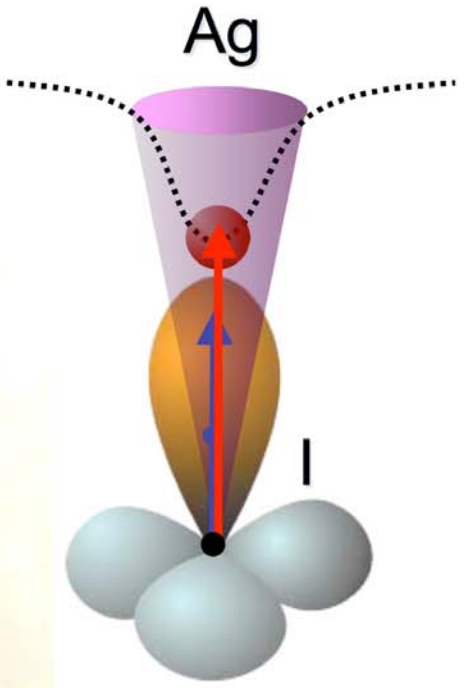

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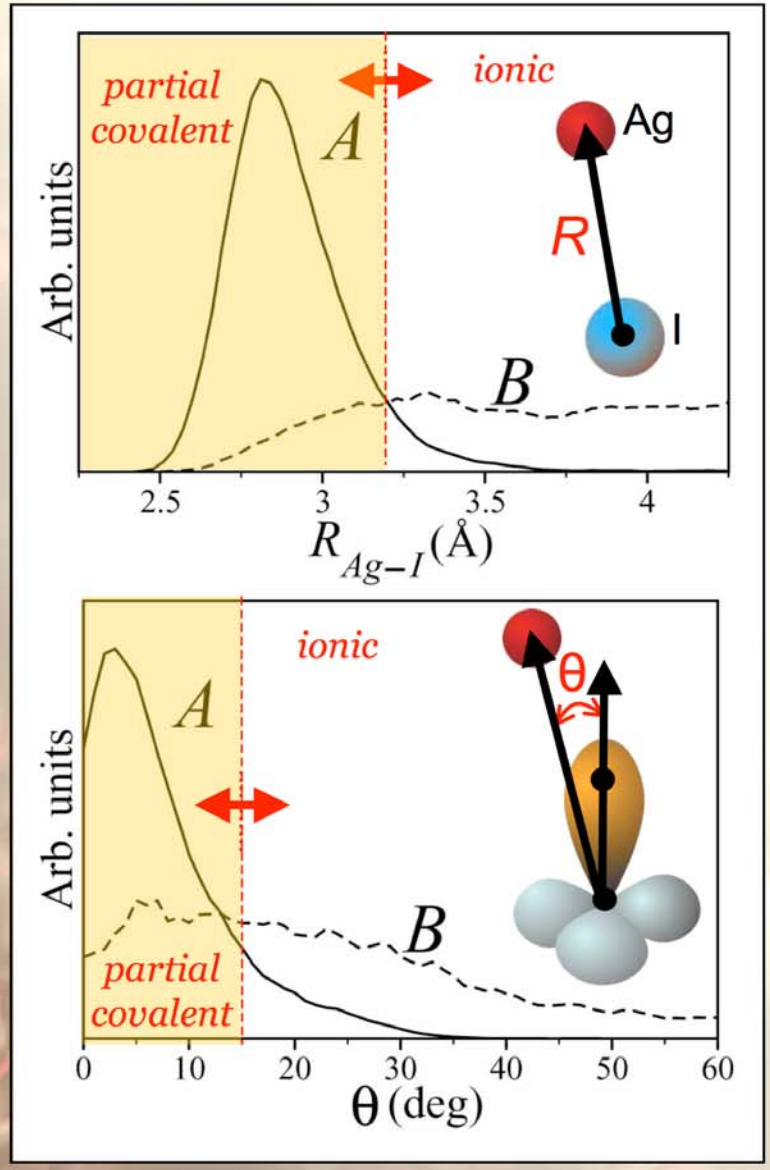

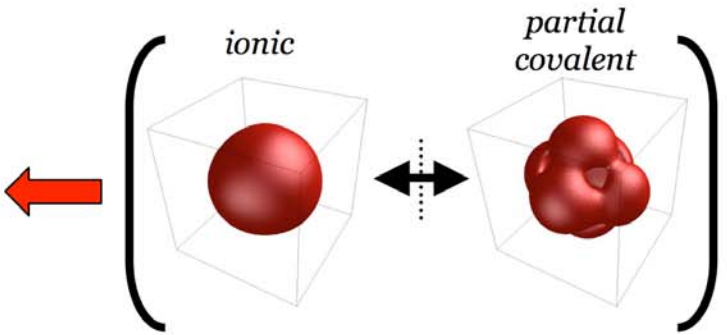

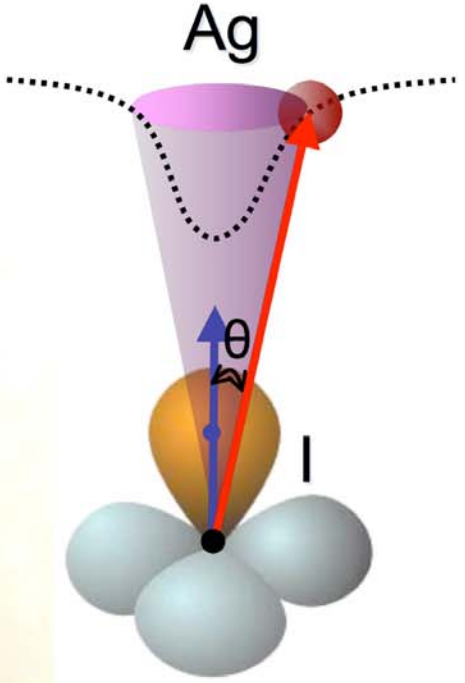

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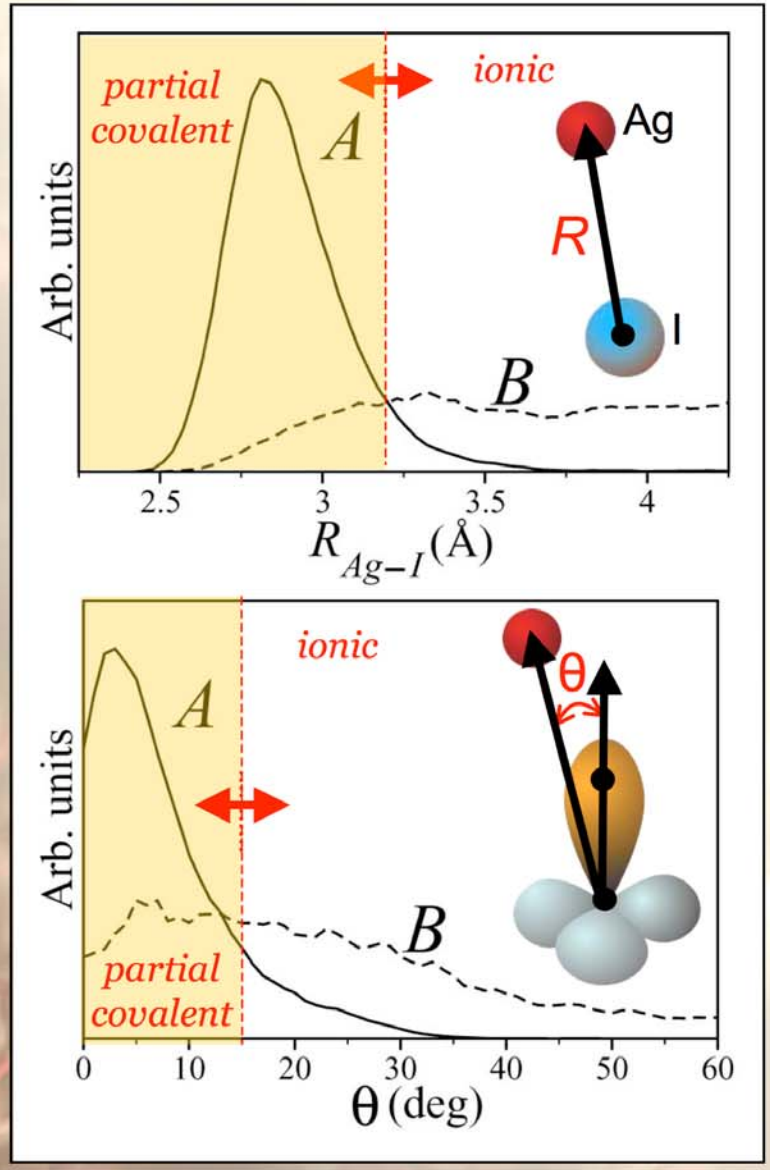
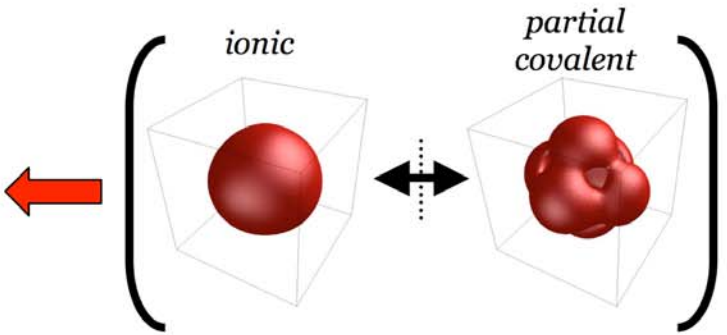
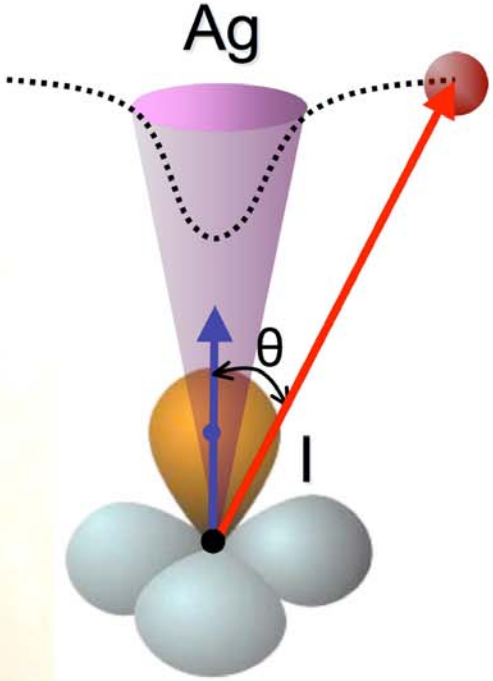
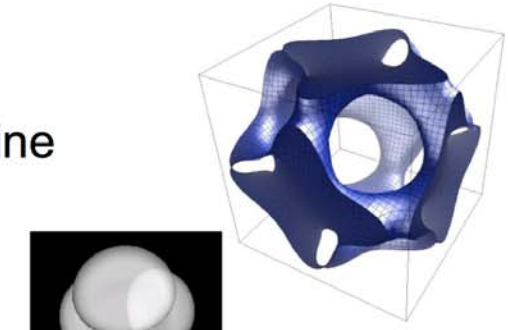






Motivations for superionicity

- Superionic phase is stabilized by Ag^+ entropic effect (thermodynamics)
- Geometric frustration (sterics)
  - Frustration between symmetries of closed-shell iodine orbitals and nearest-neighbor silvers (4-fold) and distribution of occupied interstitial sites (6-fold)
  - All four iodine orbitals cannot chemically bond with silvers instantaneously (usually only three)
  - Remaining silver(s) is ionically bonded (interacts via a weaker Coulombic potential) and may become mobile until captured by a neighboring iodine orbital



- Ordering tendency disappears when energetic barriers to mobility can be overcome (kinetics)
  - Capture mechanism resulting from chemical transition

Steric, thermodynamic, chemical, and kinetic effects all play a role

Summary and conclusions

- ✓ Presented results for dynamical simulations of α-AgI
- ✓ First-principles MD offers unique insights into atomistic diffusion processes in superionic conductors
- ✓ *Nuclear motion:* can resolve atomic trajectories in time and by ion
- ✓ *Statistical mechanics:* can examine the nature of the superionic transition by decoupling the ionic sublattices
- ✓ *Electronic behavior:* can directly observe chemical bonding behavior, including a sharply defined transition to partial covalency
- ✓ Superionic behavior in AgI can be attributed to a combination of thermodynamic, structural, chemical, and kinetic effects

B.C. Wood and N.Marzari, "Dynamical structure, bonding, and thermodynamics of the superionic sublattice in α-AgI," *Physical Review Letters* **97**, 166401 (2006).

Computational details

DFT with PBE-GGA XC

Plane-wave pseudopotential framework (ultrasoft and Troullier-Martins)

Periodic boundary conditions

Car-Parrinello MD at T = 200 K to 1225 K

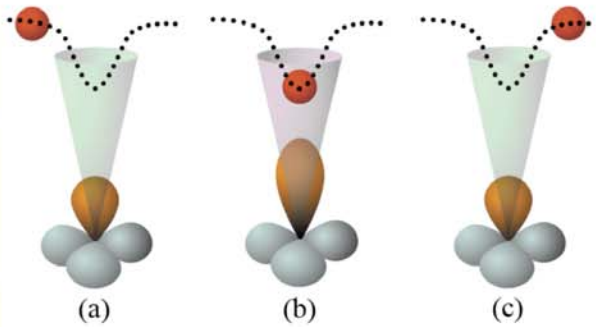
50-ps + 5 ps of equilibration

54-atom supercell

Cutoffs = 22 Ry (ψ); 176 Ry (ρ)

Canonical *NVT* ensemble

Δt = 20 au; μ = 700 au



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- *The Marzari research group* (http://quasiamore.mit.edu)
- *Quantum-ESPRESSO software package* (http://www.quantum-espresso.org)
- *DOE CSGF and the Krell Institute* ($$$)

It is unworthy of excellent men to lose hours like slaves in the labor of calculation which could be relegated to anyone else if machines were used.

-- Gottfried Wilhelm von Leibnitz (1646-1716)