First-principles explorations of dynamics in materials - from attoseconds to nanoseconds - aided by X-ray spectroscopy

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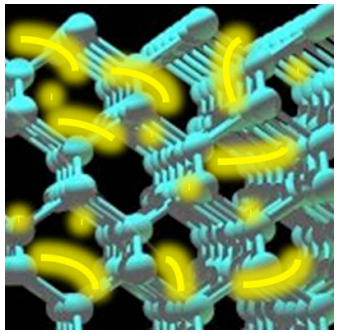
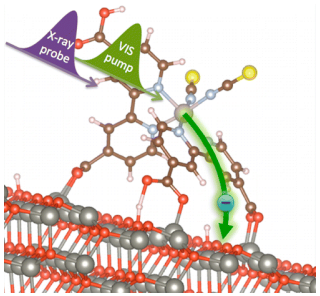
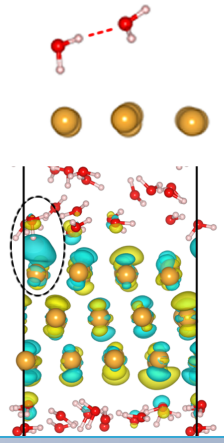
BERKELEY LAB

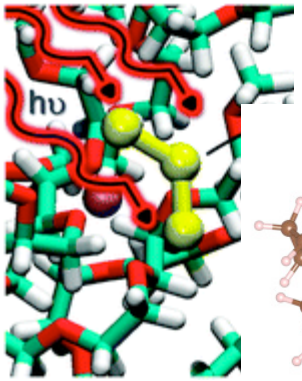
MOLECULAR FOUNDRY

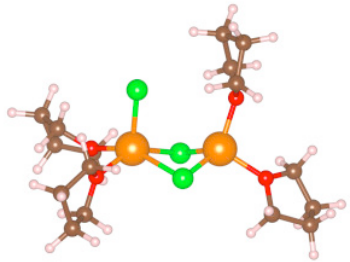
Materials in the Temporal Domain











1 as | 1 fs | 1 ps | 1 ns | time

electron-electron scattering

electron-phonon scattering

solvent dipole reorientation

chemical equilibration

Example 2: Laser-driven silicon

X-ray Probes

pump-probe / transient

(in situ) spectroscopy / static

Example 1: Biased water-gold interface (brief)

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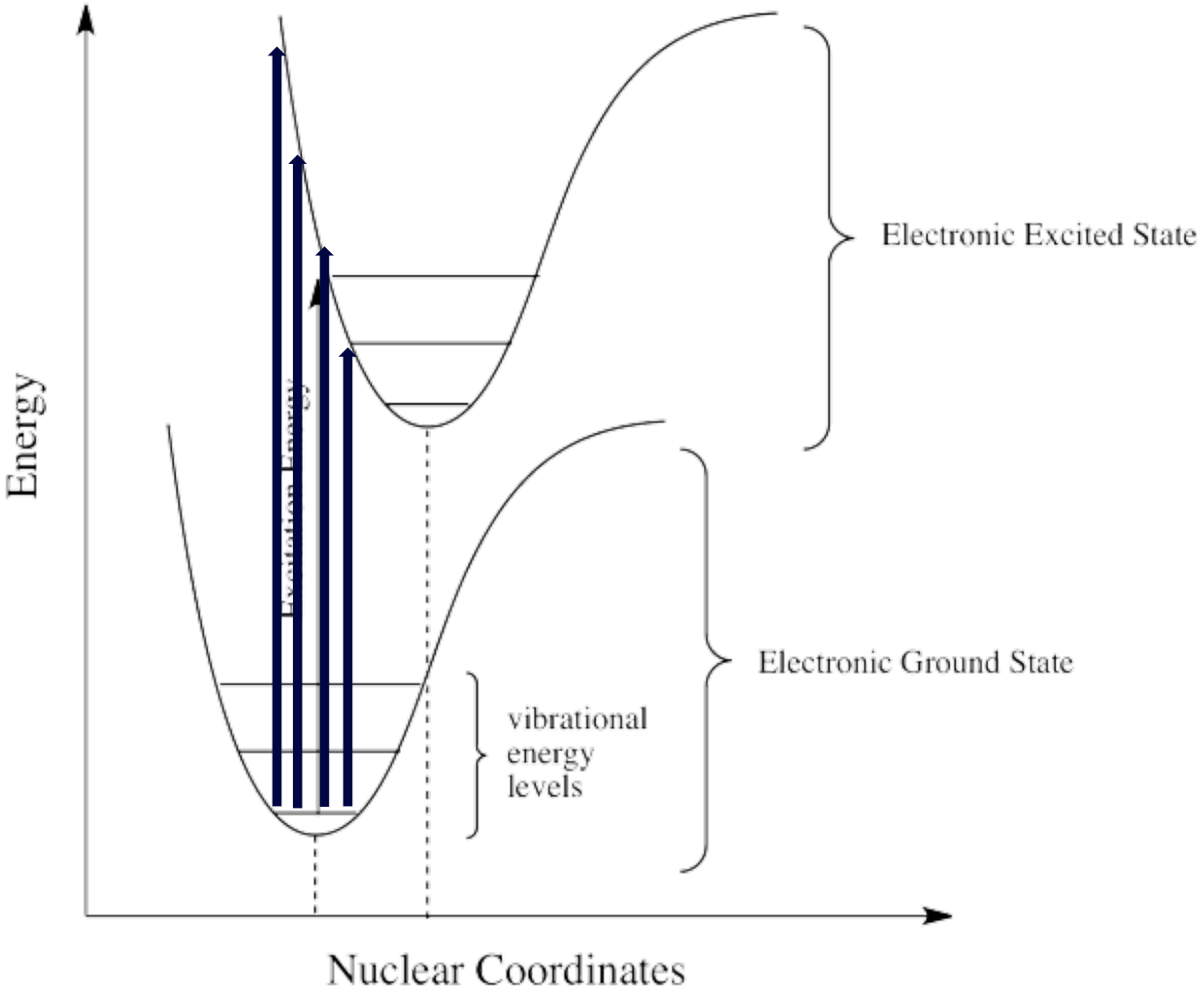
Vertical Excitations using X-rays



X-ray photons excite electrons on attosecond timescales

Continuous X-ray Excitation samples local potential energy surface

Individual excitations can collapse quantum states out of equilibrium

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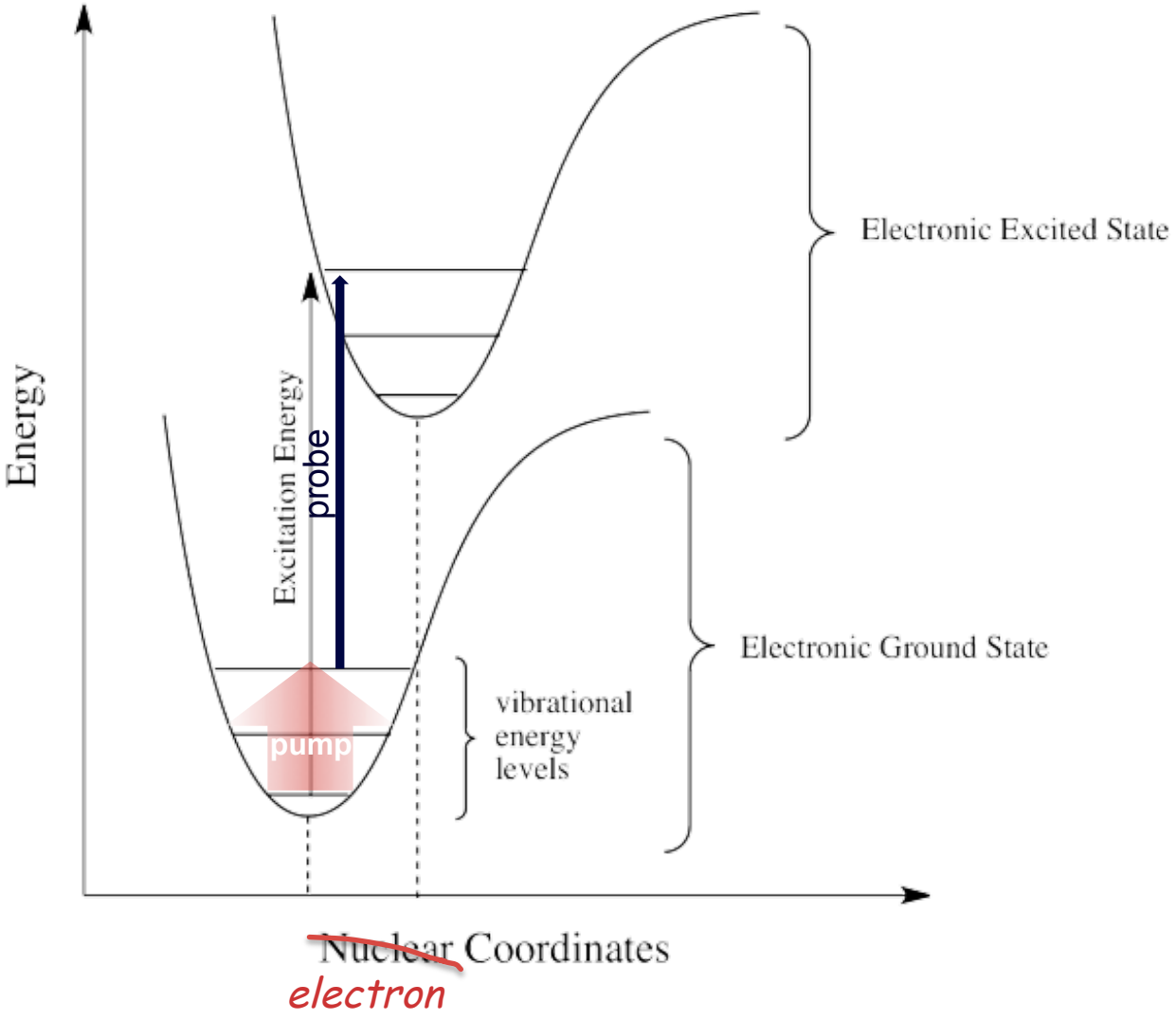
Vertical Excitations using X-rays



X-ray photons excite electrons on attosecond timescales

Continuous X-ray Excitation samples local potential energy surface

Individual excitations can collapse quantum states out of equilibrium

Pump-probe can explore excited states with lifetimes longer than X-ray probe

Could we probe dynamics on attosecond timescales?

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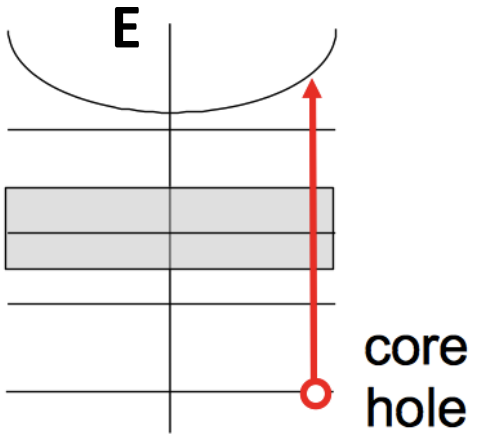
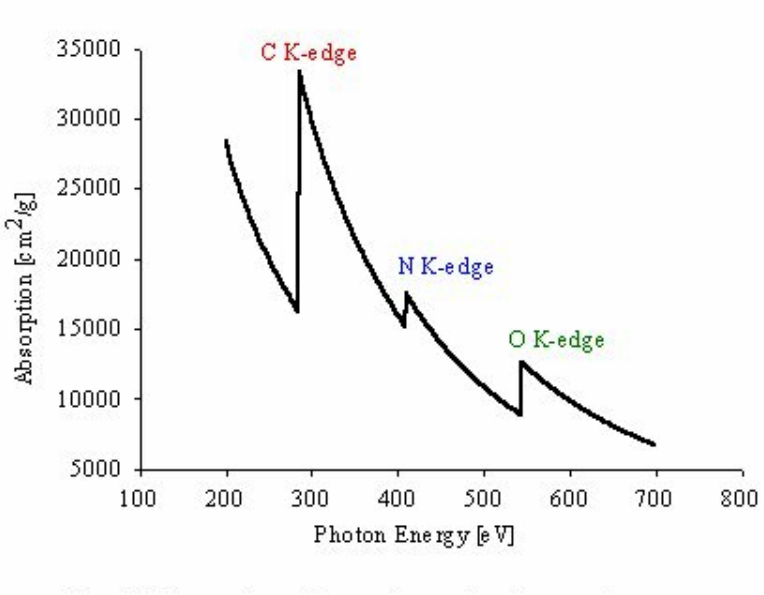
X-ray Absorption Cross Section (Fermi's Golden Rule):

$$\sigma(\omega) = 4\pi^2 \alpha_0 \hbar\omega \sum_f^{unocc} |\langle \Psi_f | \epsilon \cdot r | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$



1. probes unoccupied electronic structure

2. element-specific transitions

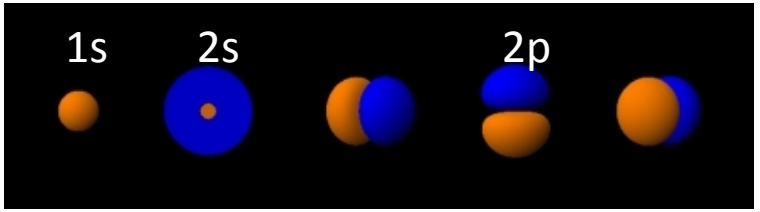


3. dipole selection rule

$$\Delta l = \pm 1$$

$$\left\langle \psi_f \middle| r \middle| \phi_{1s}^I \right\rangle = \sum_{l,m} \left\langle \psi_f \middle| p_{l,m}^I \right\rangle \left\langle \phi_{l,m}^I \middle| r \middle| \phi_{1s}^I \right\rangle$$

odd odd even



1s-> K-edge 2s,2p -> L-edge 3s,3p,3d -> M-edge …

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Fermi's Golden Rule for X-ray Absorption

X-ray Absorption Cross-section

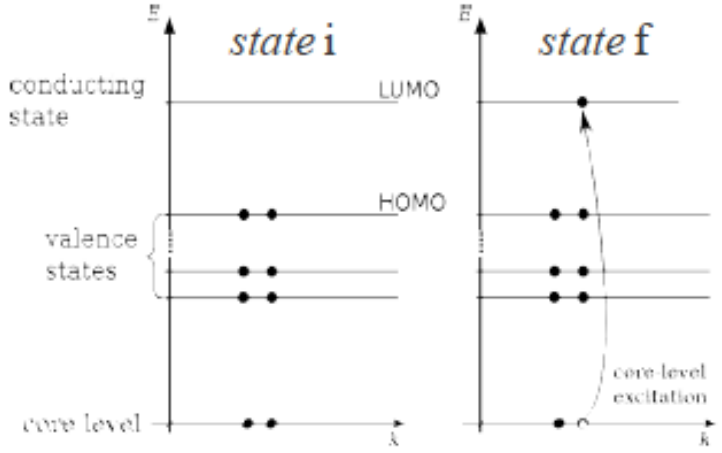
$$\sigma(\omega) = 4\pi^2 \alpha_0 \hbar\omega \sum_f |\langle \Psi_f | \hat{T} | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Dipole approximation

$\epsilon \cdot R$

polarization vector (photon)

position operator (electron)



~~non-interacting approximation~~

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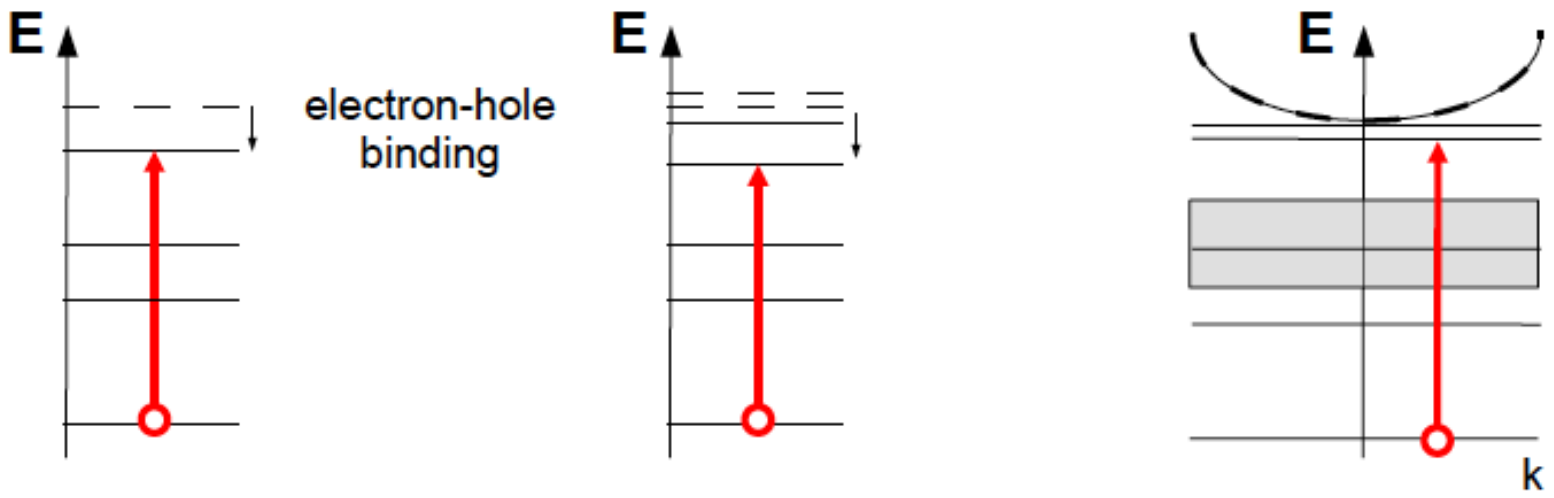
The Final State Rule

Fermi's Golden Rule links initial to final states – final state effects important

molecules

crystals



molecular orbital
character preserved

orbital mixing
mixed character exciton

strong band mixing
localized exciton
"impurity levels"

Stronger excitonic effects than for UV/vis valence excitations

Wannier << Frenkel << Core-Hole

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ΔSCF excited state calculations

Density functional theory

$$E_{GS} = min_{\rho} E[\rho]$$ Hohenberg and Kohn (1964)

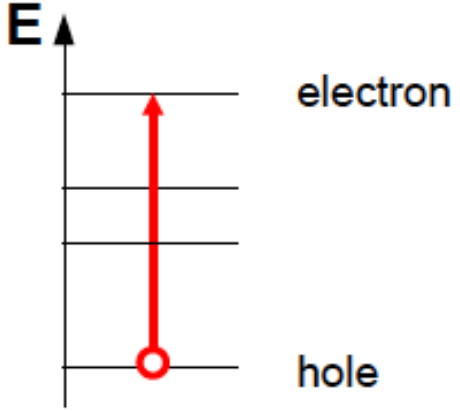
for fixed electron occupations

$$\rho = \sum_{n} \sum_{\sigma} f_{n\sigma} |\psi_{n\sigma}|^2$$ Kohn and Sham (1965)

approximate excited states by changing occupancies

$$[f_{n\sigma}] = [1\,1 \ldots 1\,1\,0\,0 \ldots]$$
$$[g_{n\sigma}] = [0\,1 \ldots 1\,1\,1\,0 \ldots]$$

core-hole excited electron



at self-consistency $\Delta E = min_{\rho} E[\rho; g] - min_{\rho} E[\rho; f] \approx E_{XS} - E_{GS}$

ΔE captures much of the electronic relaxation in the core-excitonic state

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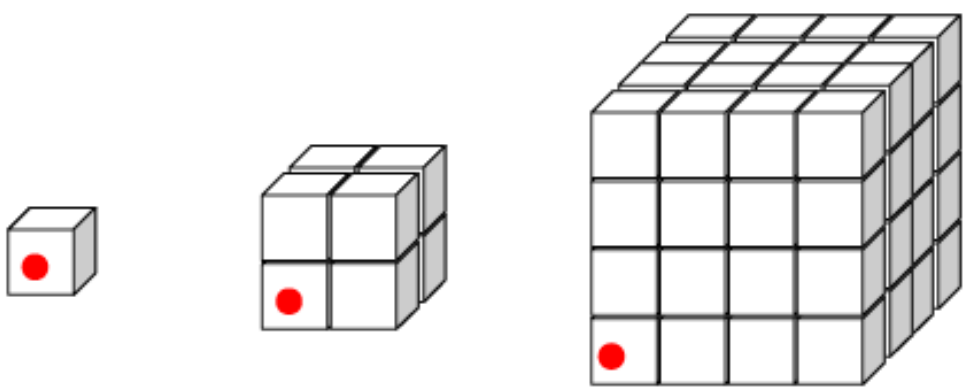
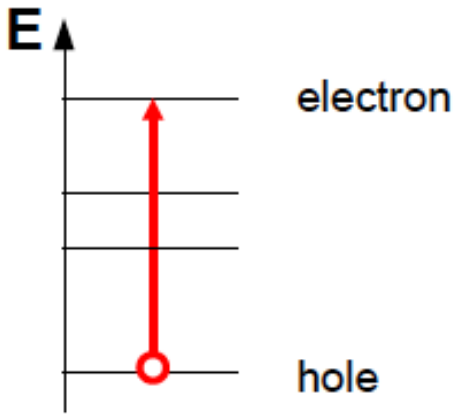
ΔSCF limitations

Intrinsically local approximation – good for finite/isolated systems

For crystalline systems or condensed phases – supercell approximation





1 excited atom per n x m x l primitive cells

Increase supercell size until excited electron density fully-contained
(or at least until spectrum/energy stops changing)

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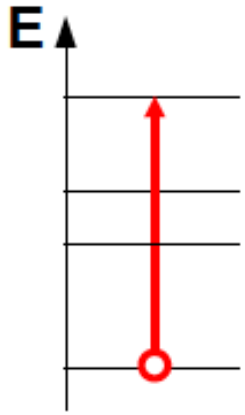
ΔSCF limitations

Only one excitation at a time...



... we need a full spectrum!!!

XCH Approximation

1. Generate SCF using both e**X**cited electron and **C**ore-**H**ole (XCH)
2. Use the unoccupied KS eigenstates of this SCF in Fermi's Golden Rule

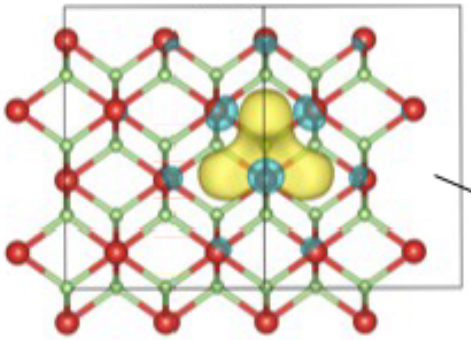
Only one SCF calculation necessary
Implementation with orthonormal basis
Accurate in practice

Potential problems for higher excitations
Especially if charge distribution very different from lowest excitation

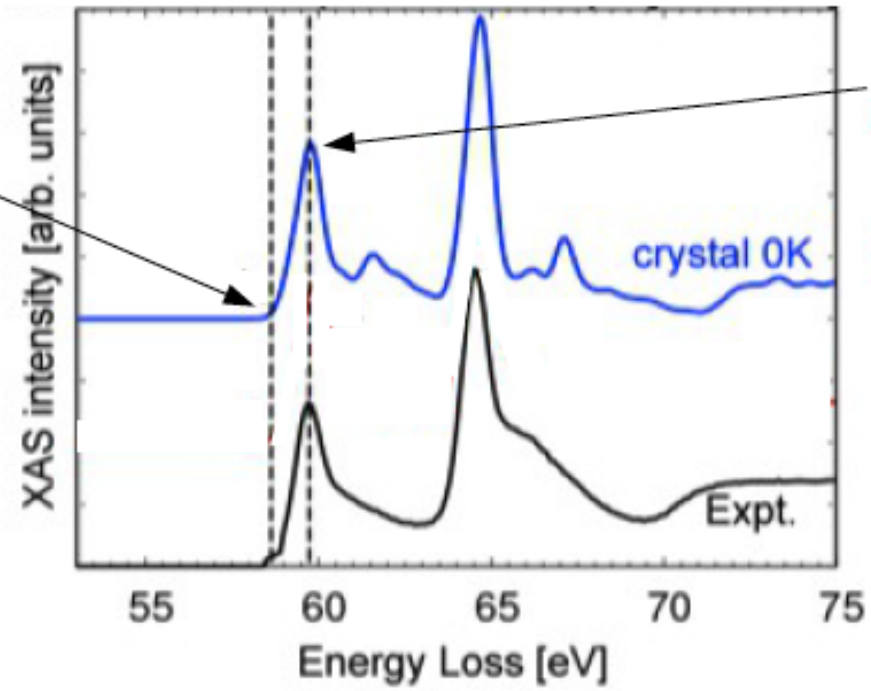
Mo and Ching, Phys Rev B (2000)
Prendergast and Galli, Phys Rev Lett (2006)

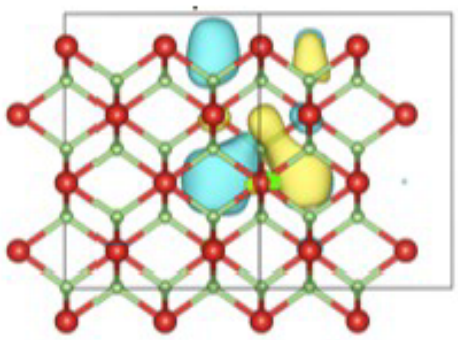
Example: Li K-edge XAS of Li_2O

Cubic lithium oxide has been measured at Li K-edge using X-ray Raman Spectroscopy



Li 1s→2s
core excited state





Li 1s→2p
core excited state

Simulations provide excellent agreement with experiment.

Also permit interpretation by analysis of individual core-excited states.

Pascal et al., J Chem Phys 140, 034107 (2014)

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Vibronic effects in optical transitions

Born-Oppenheimer:

$$|\Psi\rangle = |\psi\rangle \times |\chi\rangle$$

Electronic dipole transition:

$$\mu_{n_i \to n_f} = \langle \psi_{n_i} | r | \psi_{n_f} \rangle$$

Transition Amplitude (with vibrons):

$$M_{i \to f} = \mu_{n_i \to n_f} \langle \chi_{\nu_i} | \chi_{\nu_f} \rangle + \sum_{\nu=1}^{3N-6} \frac{\partial \mu_{n_i \to n_f}}{\partial Q_\nu} \langle \chi_{\nu_i} | Q_\nu | \chi_{\nu_f} \rangle + O(Q^2)$$

Franck-Condon effect

Herzberg-Teller effect

Dominant term for dipole-forbidden transitions

Look for what should be hidden…

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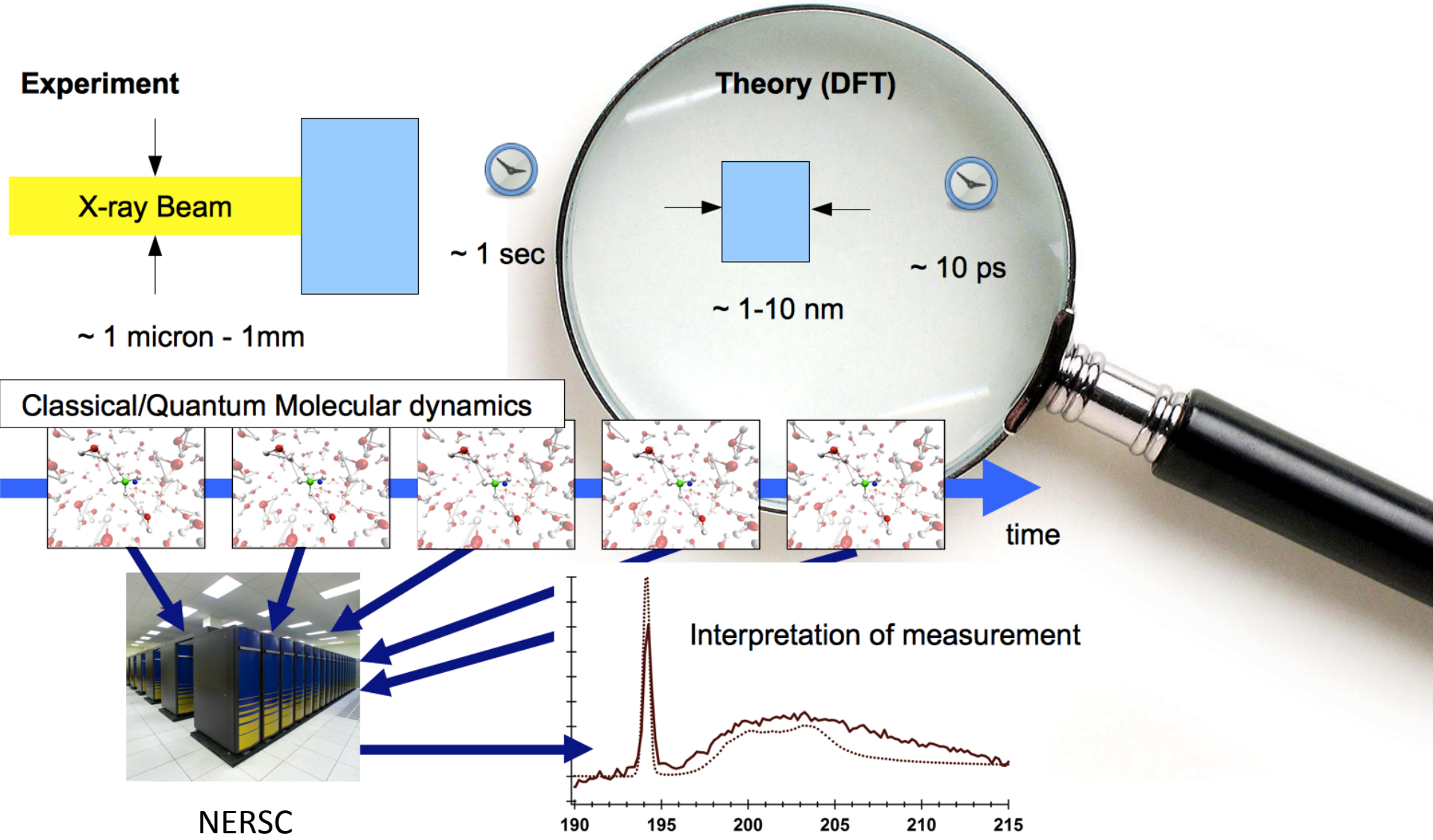
Sampling Vibrations and Conformations



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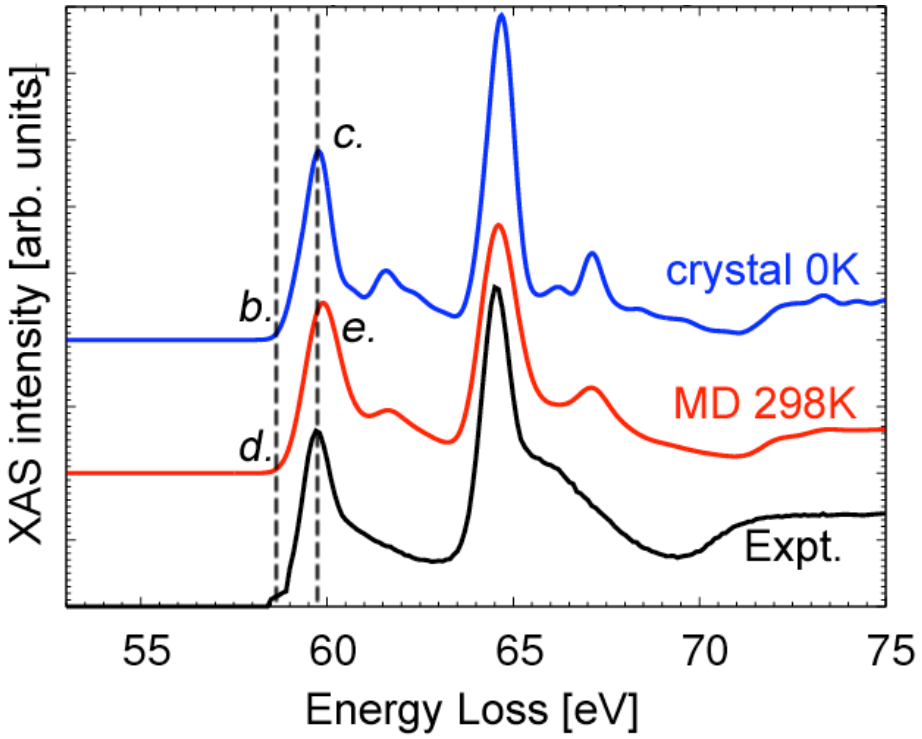
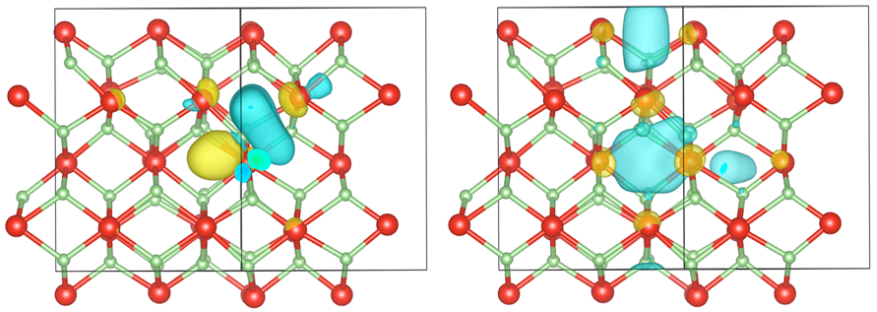
Converged **dynamic** XAS simulation – lithium oxide (Li_2O antifluorite)

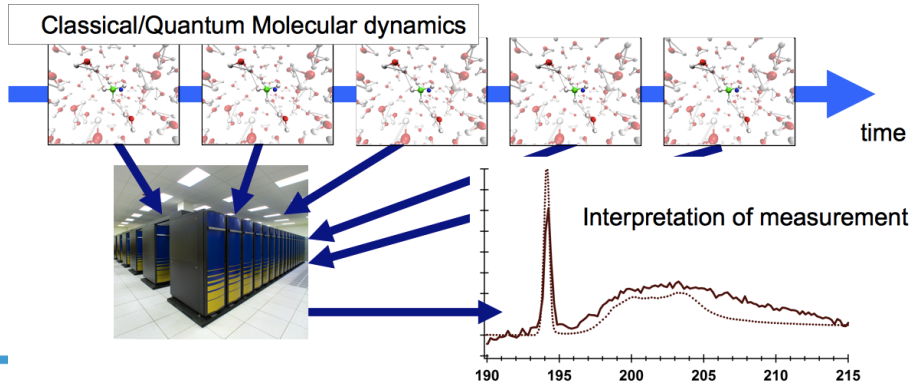


Molecular Dynamics

- nuclei evolve in time
- XCH electron density recalculated
- vibronic effects on states
- spectral line-shape modification



Reordering of states and character



sample (many) nuclear configurations at finite T and average

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What? No core electrons?

Model core-electron excitation using modified pseudopotential (PP)

- generate PP in excited electron configuration

$$N: 1s^2 2s^2 2p^3 \longrightarrow N^*: 1s^1 2s^2 2p^4$$

- valence electrons experience unscreened potential: V*

new atom type: N*
new pseudopotential: V*
include once per supercell

- substitute this modified atom for various atoms in different chemical environments/coordinations

- compare total energies for: chemical shifts; relative spectral alignment

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Energy alignment

Accurate core-excitation energies inaccessible with pseudopotentials

Atomic approximations sometimes reliable:

$$\Delta E = [E^{XS}_{tot}(PS) - E^{GS}_{tot}(PS)] - [E^{XS}_{atom}(PS) - E^{GS}_{atom}(PS)] + [E^{XS}_{atom}(AE) - E^{GS}_{atom}(AE)]$$

+ Δ_{expt}

Analogous to reaction/formation energy "Born-Haber cycle"

Hamann and Muller, Phys Rev Lett (2002)

England et al., Chem Phys Lett (2011)

Relative energies are simpler – chemical shifts

$$\Delta_{ij} = [E^{XS}_{tot}(i) - E^{XS}_{tot}(j)]$$

XPS: *Bianchettin et al. Phys Rev B (2006)*

For aligning Molecular Dynamics snapshots

$$\Delta^{(n)}_{i} = [E^{XS}_{tot}(i; R_n) - E^{XS}_{tot}(0; R_0)] - [E^{GS}_{tot}(i, R_n) - E^{GS}_{tot}(0, R_0)]$$

XAS: *Schwartz et al. J Chem Phys (2009)*

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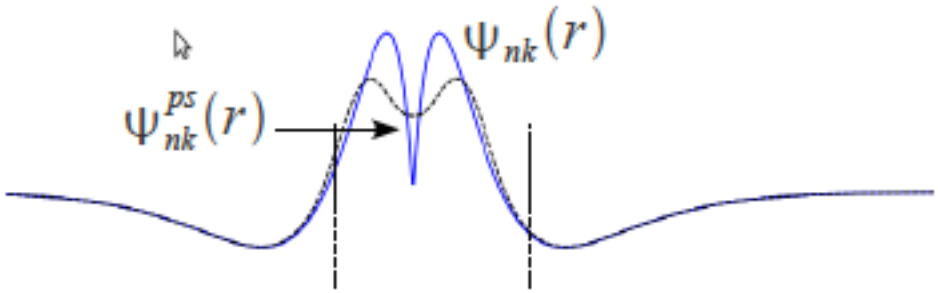
Matrix elements

$$\langle \Psi_{nk} | r | \Psi_{ik} \rangle$$



Pseudo wave functions may not have the correct symmetry at atomic cores

cut out pseudo-core
paste in atomic all-electron core

$$\Psi_{ik}(r) = \frac{1}{\sqrt{N}} \sum_R \sum_I e^{ik\cdot R} \Phi^I_i (r - \tau_I + R)$$

Projector-Augmented Wave formalism:
Blöchl Phys Rev B (1994)
Taillefumier et al. Phys Rev B (2002)

projectors of non-local potential, dual to atomic pseudowaves

$$\langle \Psi_{nk} | r | \Psi_{ik} \rangle \approx \sum_\lambda \langle \Psi^{PS}_{nk} | \beta^I_{\lambda k} \rangle \langle \Phi^I_\lambda | r | \Phi^I_i \rangle$$

all-electron atomic matrix elements

$$\sum_\lambda |\beta^I_{\lambda k}\rangle \langle \Phi^{I,PS}_\lambda| = 1_{\Omega_I}$$

$$V^{nl} = \sum_I \sum_{\lambda,\lambda'} |\beta^I_\lambda\rangle D^I_{\lambda\lambda'} \langle \beta^I_{\lambda'}|$$

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Spectral convergence

$$\sigma(\omega) = 4\pi^2 \alpha_0 \hbar\omega \sum_{nk} |\langle \psi_{nk} | \varepsilon \cdot r | \psi_{ik} \rangle|^2 \delta(\epsilon_{nk} - \epsilon_{ik} - \hbar\omega)$$

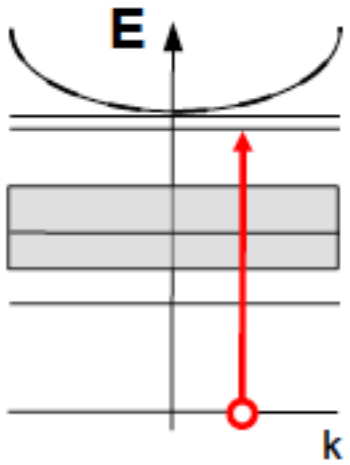
$$\langle \psi_{nk} | r | \psi_{ik} \rangle \approx \sum_{\lambda} \langle \psi_{nk}^{PS} | \beta_{\lambda k}^{I} \rangle \langle \phi_{\lambda}^{I} | r | \phi_{i}^{I} \rangle$$

Core-exciton confinement

- increase supercell size
- cost scales as N^3
- prohibitive for crystals with large dispersion

Brillouin zone integration gives reasonable DOS

It also works for X-ray excited states



Expensive k-point sampling

- spectral convergence requires many more k-points than SCF
- each calculation includes 100's to 1000's of empty states
- supercells still make this prohibitive
- use interpolation schemes for k-space (Shirley 1996)

Prendergast & Louie, Phys Rev B 80, 235126 (2009)

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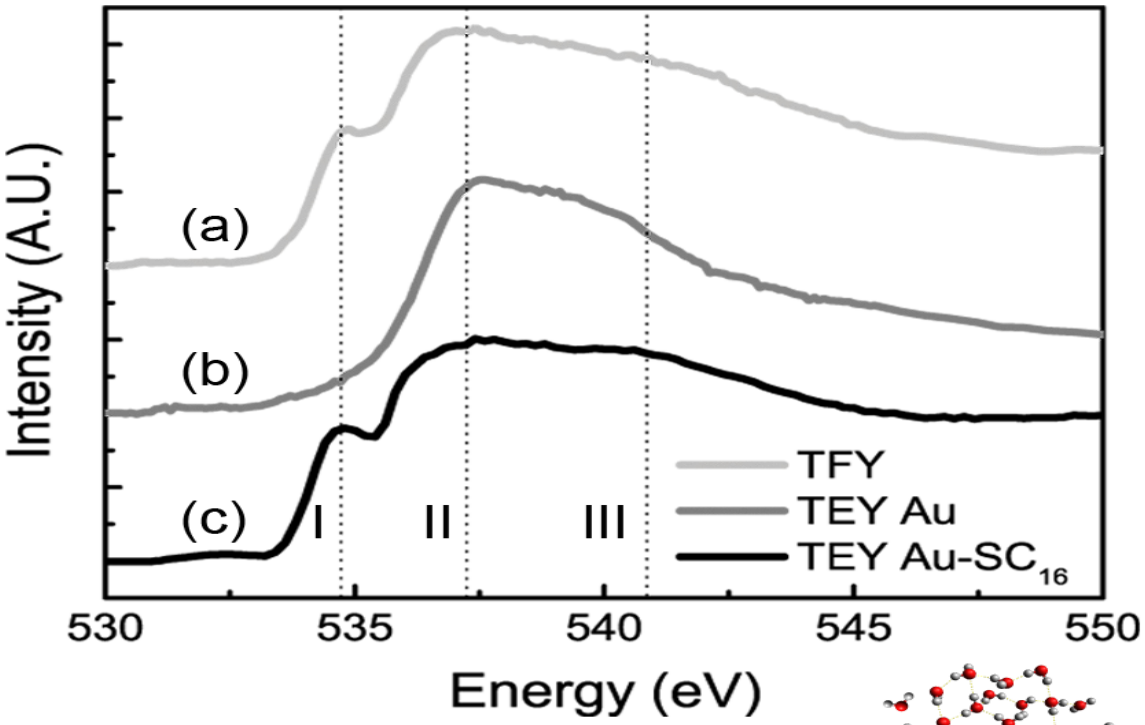
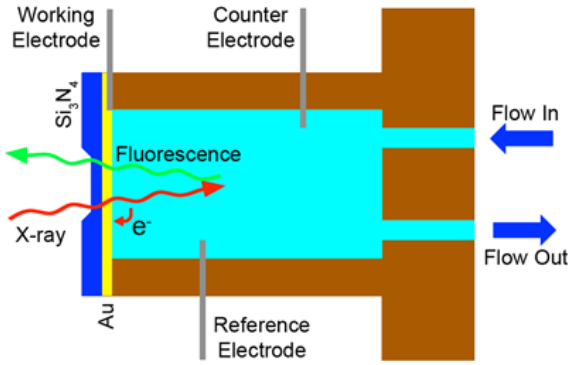
Example 1: Biased water-gold interface (brief)

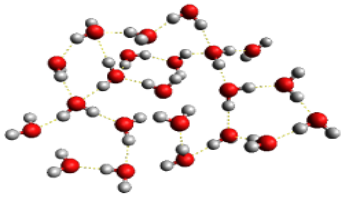
Interfacial water appears ice-like (at first glance)



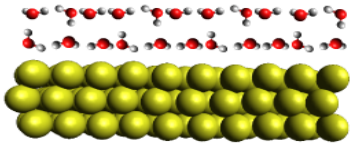


Water next to a gold electrode

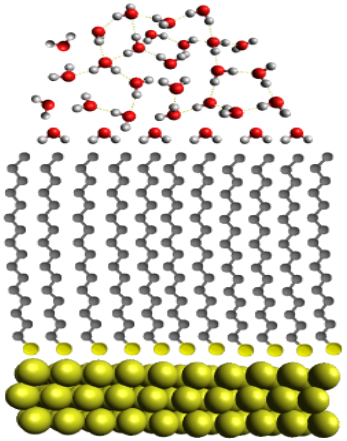
(a)



(b)



(c)



consistent with UHV (STM) understanding

Peak I : related to broken H-bond population

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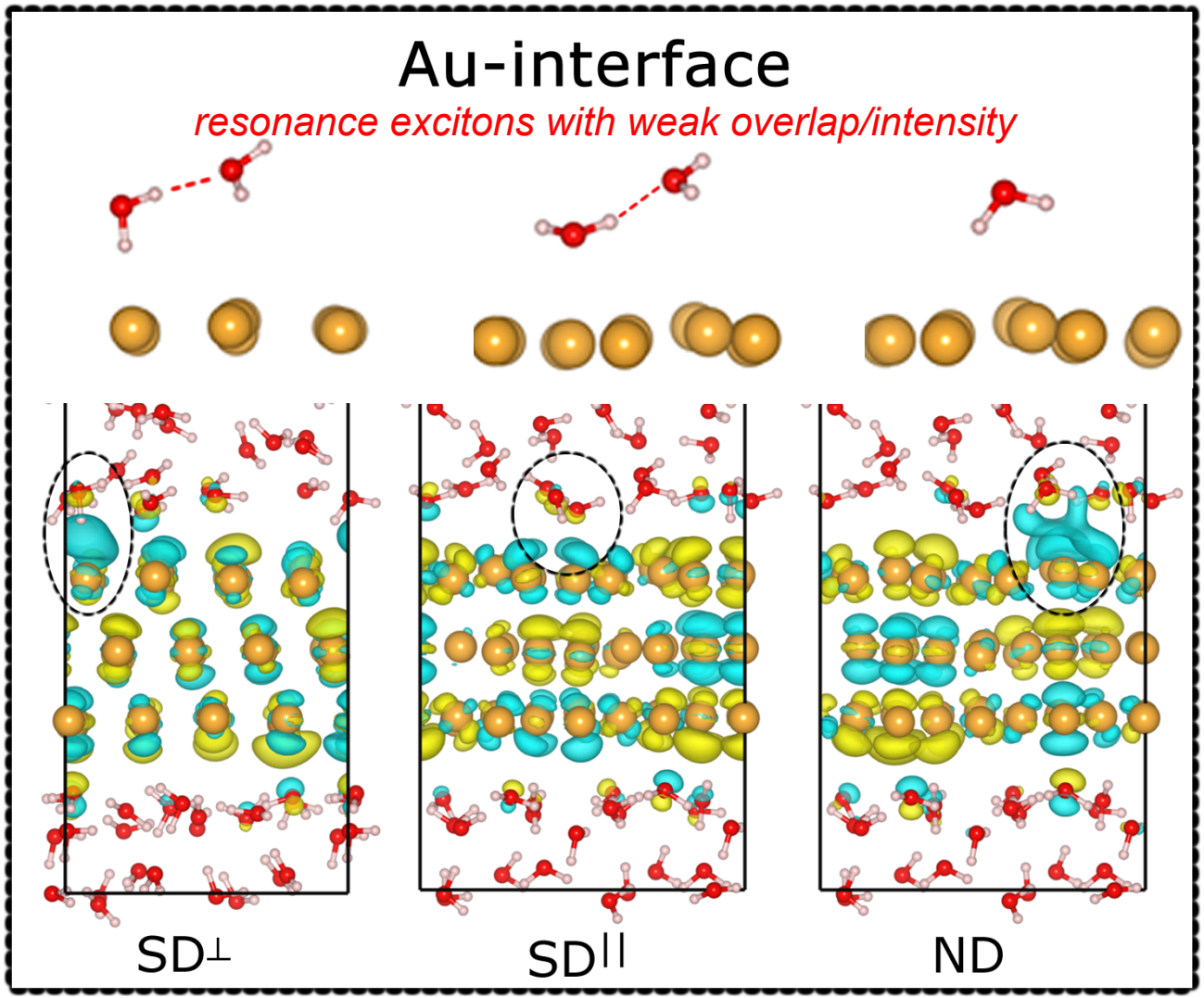
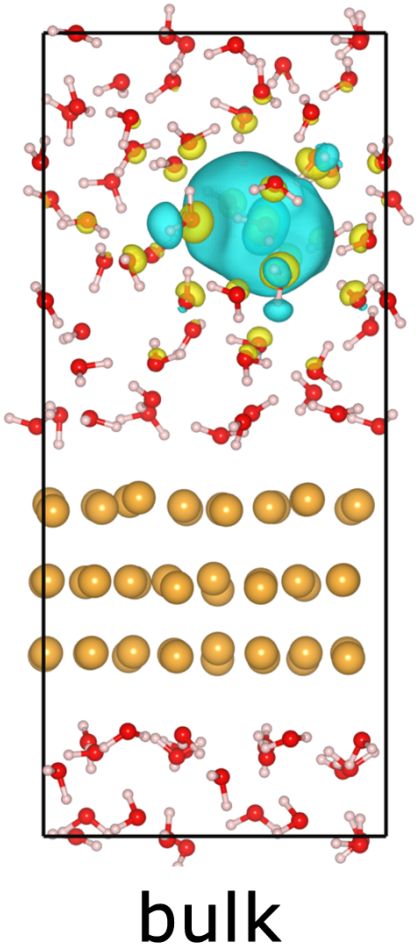
Strong anisotropic electronic coupling to Au surface





Velasco-Velez, Wu, Pascal, Wan, Guo, Prendergast & Salmeron, Science 346, 831 (2014)

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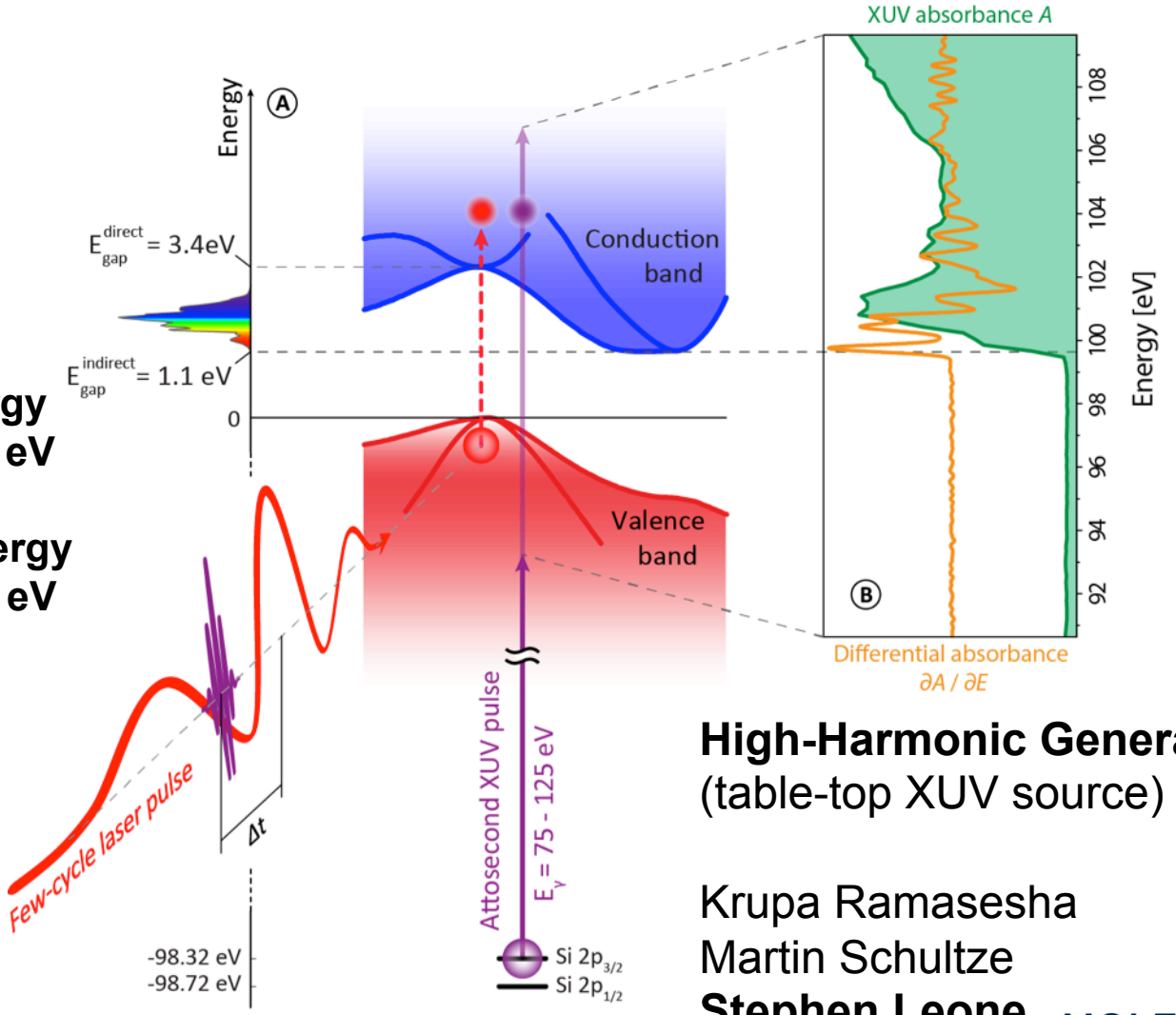
Example 2: Laser-driven silicon

Atto-second band-gap dynamics in Silicon

Vis pump energy
E_{pump} = 1.1-2.7 eV

XUV probe energy
E_{probe} = 75-125 eV



High-Harmonic Generation (HHG)
(table-top XUV source)

Krupa Ramasesha
Martin Schultze
Stephen Leone
UCB & LBNL

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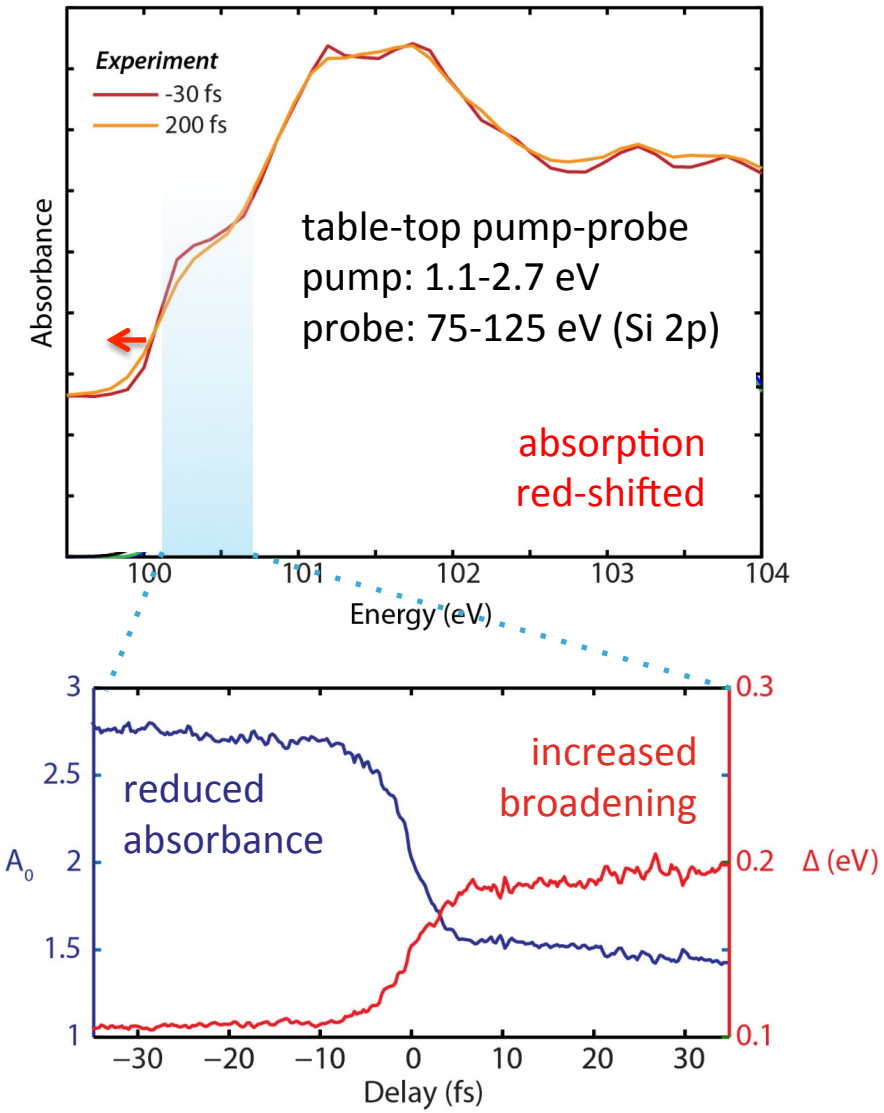
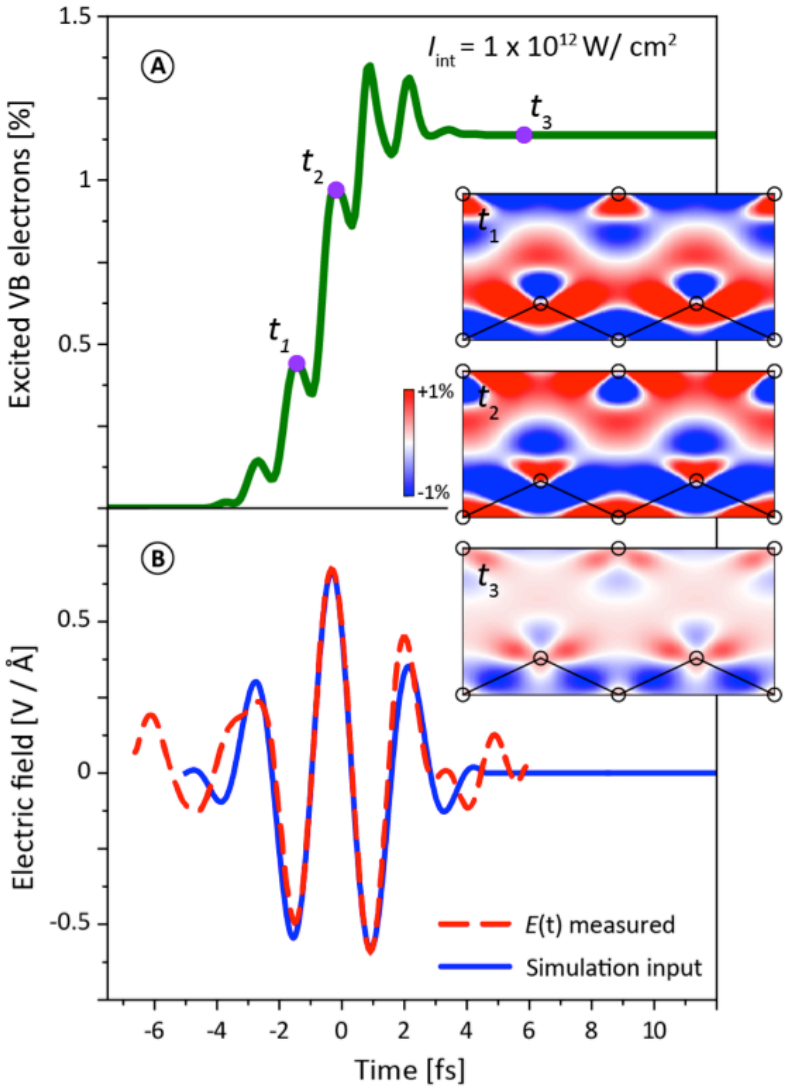
Attosecond band-gap dynamics in silicon – experimental observations



Action of the fs laser pulse from RT-TDDFT



During pulse passage:

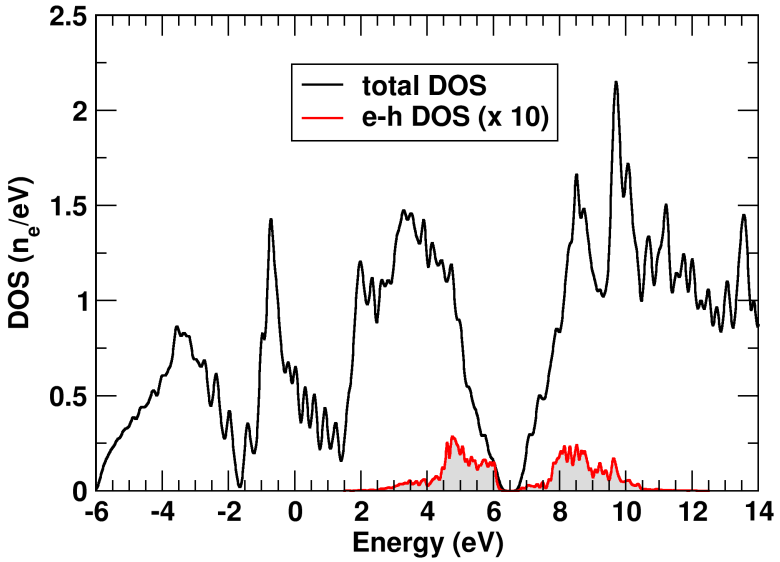
Field drives dipolar oscillations along Si-Si bonds

Excitation density exhibits steps in phase with field extrema

After pulse passage:

Electron density is depleted from the Si-Si bond and transferred to interstitial regions

~2.3 x 10^{21} cm^{-3} or ~1.2 % of electrons are excited to the CB



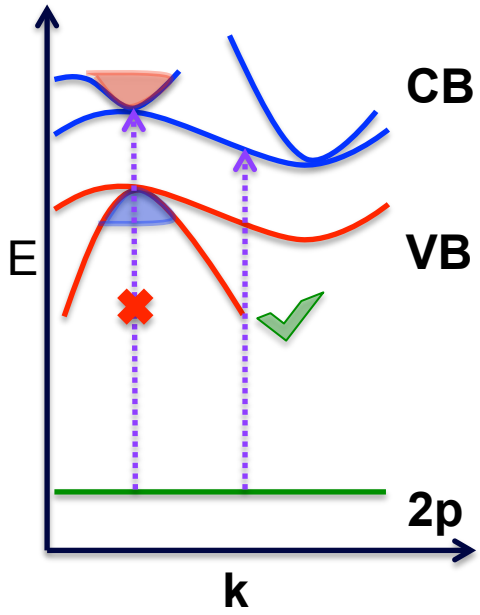
TDDFT for … crystalline solids
Yabana, Sugiyama, Shinohara, Otobe & Bertsch
Phys. Rev. B 85, 045134 (2012)

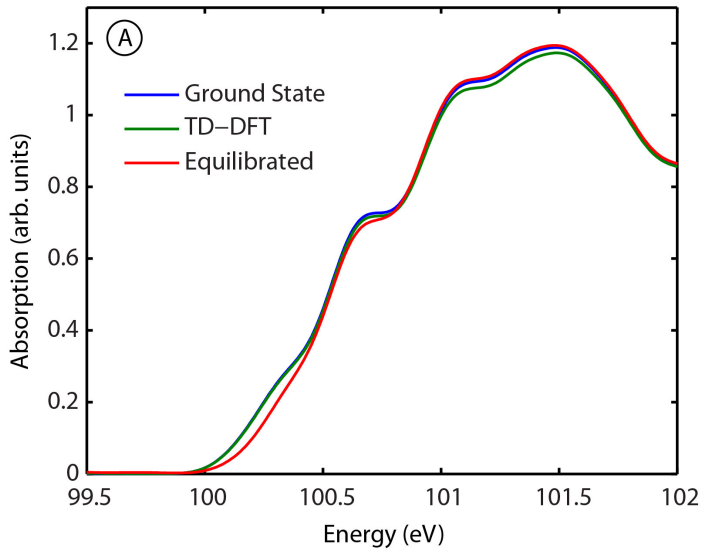
Pauli blocking

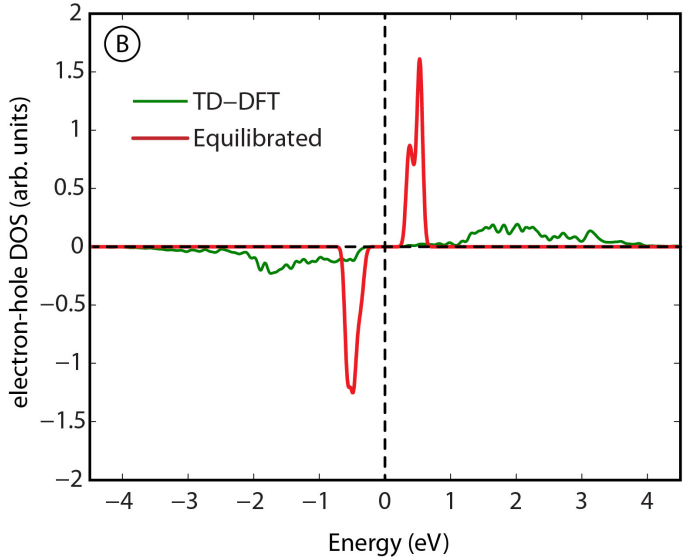
1-e basis ← XCH SCF KS basis

$$A(t, v_Z) \sim \sum_{\kappa_Z} \sum_{v,v'} \langle \phi_{\kappa_Z} | \hat{\mu}_e | \phi_v \rangle \langle \phi_v | \hat{\rho}_0(t) | \phi_{v'} \rangle \langle \phi_{v'} | \hat{\mu}_e | \phi_{\kappa_Z} \rangle$$

Time dependent 1-RDO*







- Investigated for real-time TD-DFT e-h distribution and thermalized distribution
- State-blocking is **insignificant** at short times following pump excitation
- Could be observed on longer time scales following e-h thermalization

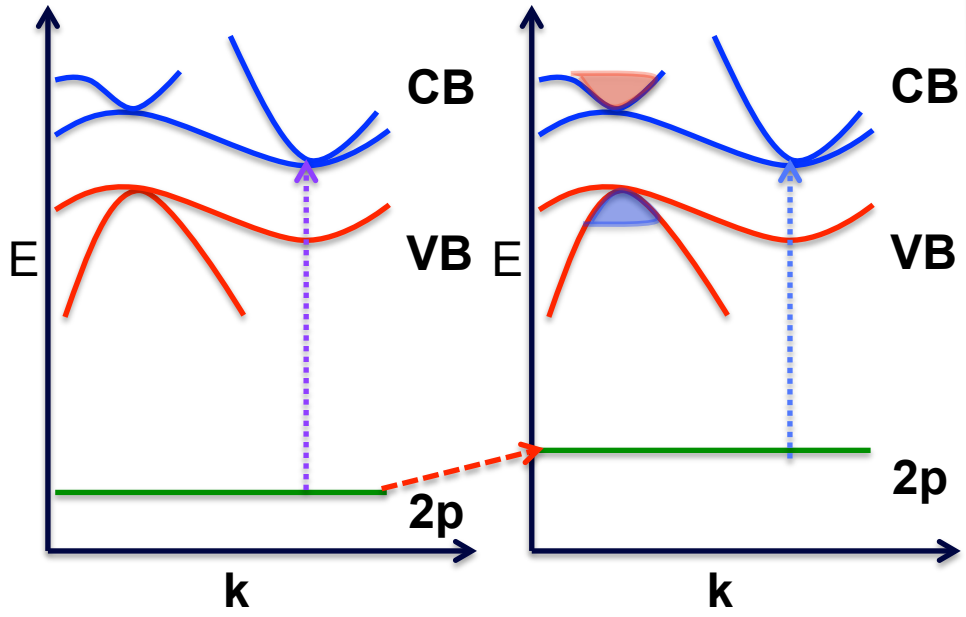
*Dutoi, Cederbaum et al., Phys. Rev. A. **88**, 013419 (2013)

MOLECULAR FOUNDRY

Red-shift of the absorption edge

Phys. Rev. B. **51**, 1527 (1995)

Core-level shift



Self-consistent occupation-constrained DFT approach

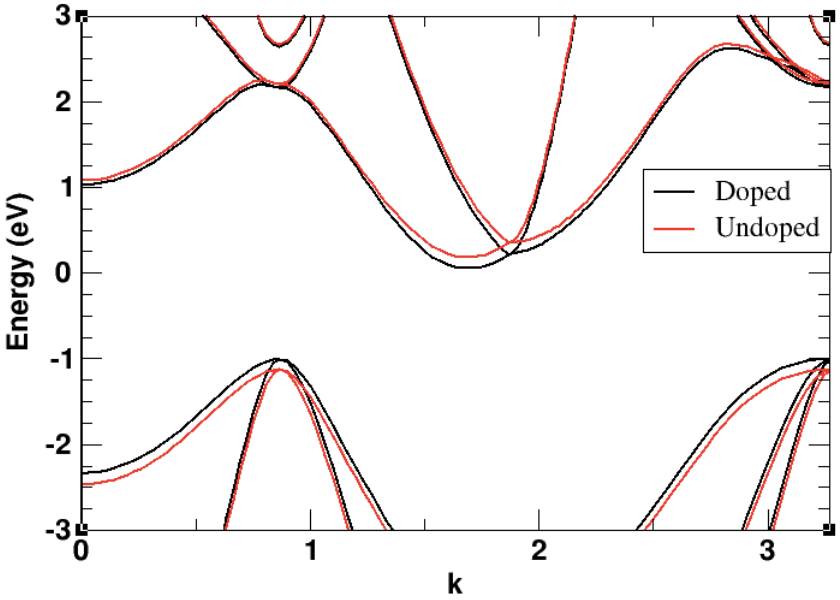
$$\Delta E_{CL} = \{(E_{XCH}^{e-h} - E^{e-h}) - (E_{XCH}^{GS} - E^{GS})\}$$

Thermalized e-h distribution: 1 % carrier density

ΔE_{CL} = 43 meV

Phys. Rev. Lett. **96**, 215502 (2006)

Band-gap reduction



GW approach

Comput. Phys. Commun. 183, 1269 (2012)

$$E_{n\boldsymbol{k}}^{QP} = E_{n\boldsymbol{k}} + \langle n\boldsymbol{k}|Re\Sigma(E_{n\boldsymbol{k}}^{QP}) - V_{XC}|n\boldsymbol{k}\rangle$$

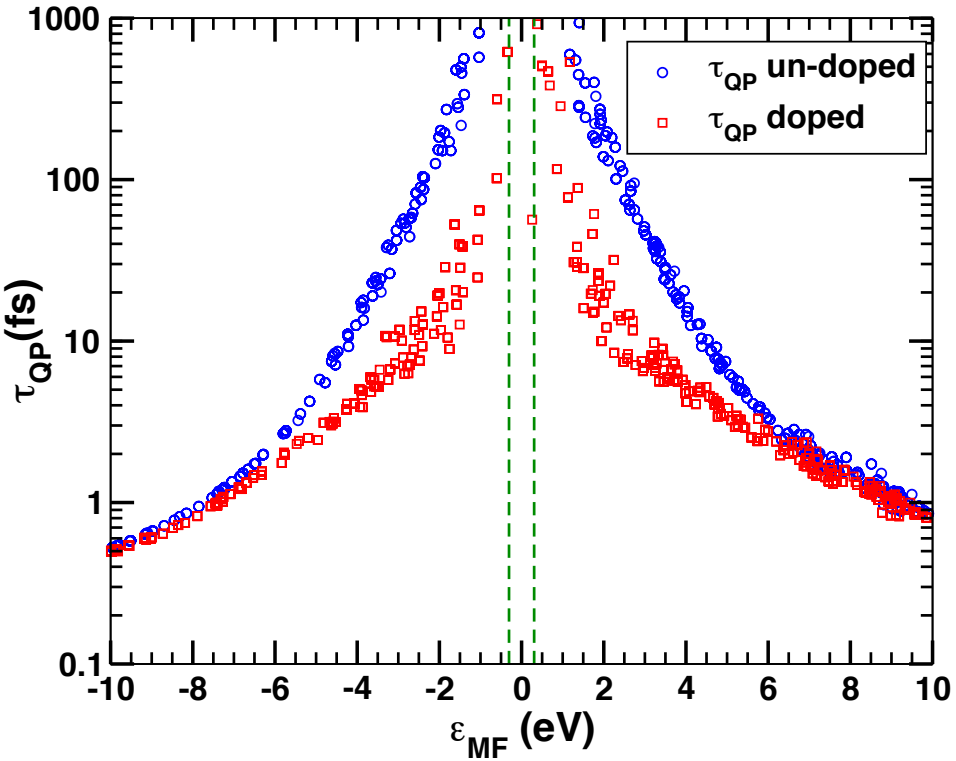
Electron doping at 1 % density

ΔE_{BGR} = 92 meV

MOLECULAR FOUNDRY

Scattering-induced spectral broadening

e-e scattering



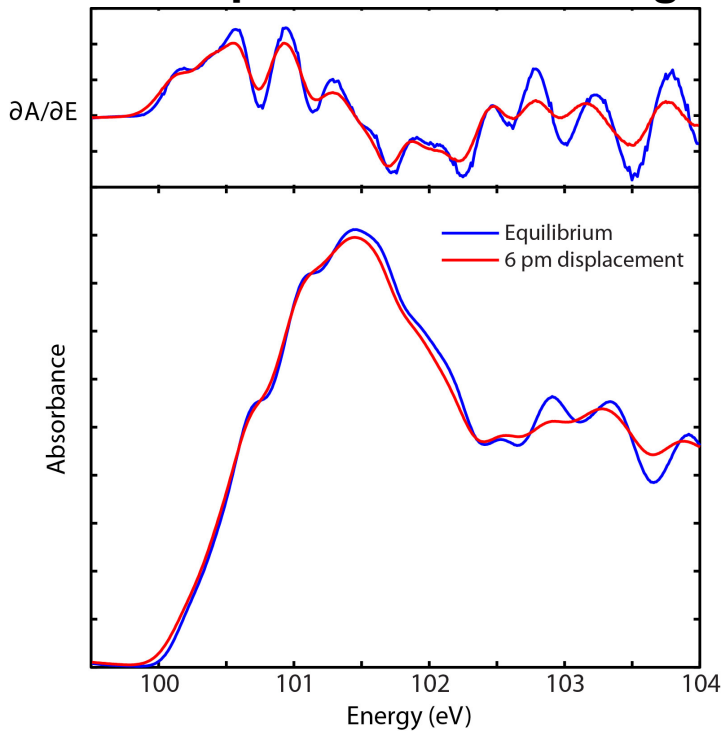
GW approach $\tau_{nk}^{-1} = -2\,\langle nk|\mathrm{Im}\Sigma(E_{nk})|nk\rangle$

Comput. Phys. Commun. 183, 1269 (2012)

Electron doping at 1 % density

Δσ > 65 meV at 1.6 eV and above

LO phonon broadening



Self-consistent DFT approach

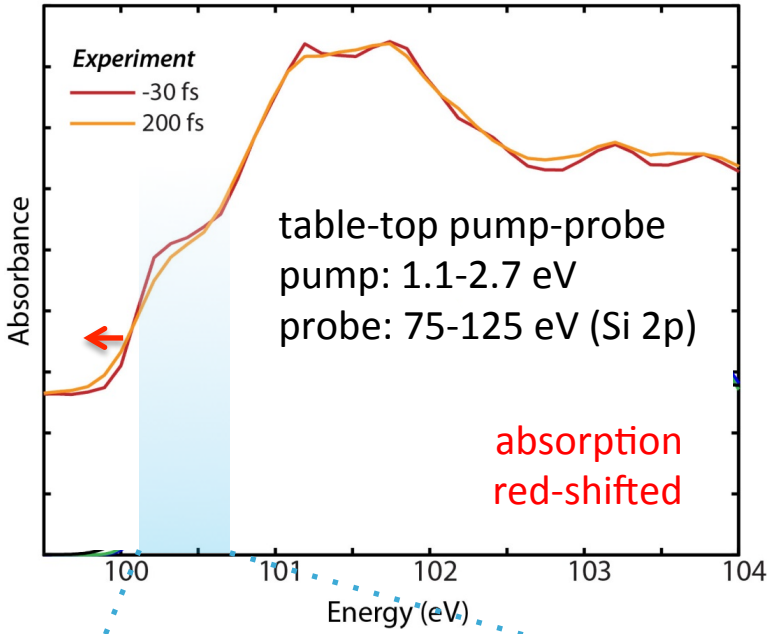
Chem. Phys. Lett. 514, 187 (2011)

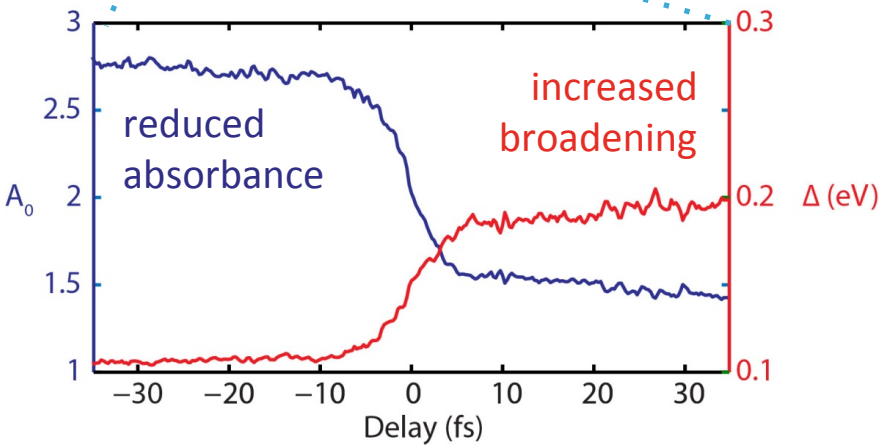
Frequency 15.6 THz
Amplitude: 6 pm (1 quantum)

Δσ ~ 26 meV

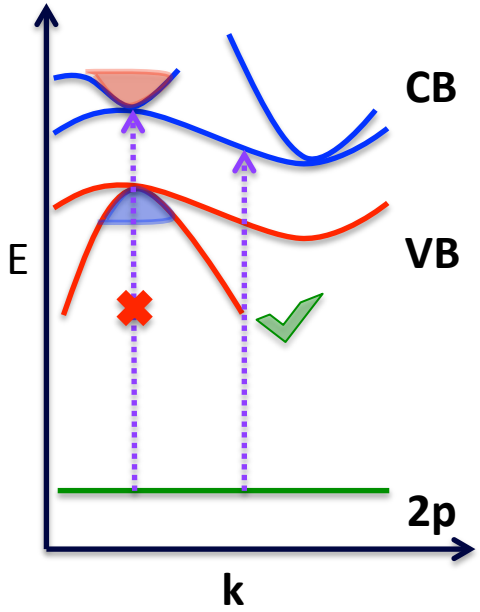
MOLECULAR FOUNDRY

Attosecond band-gap dynamics in silicon



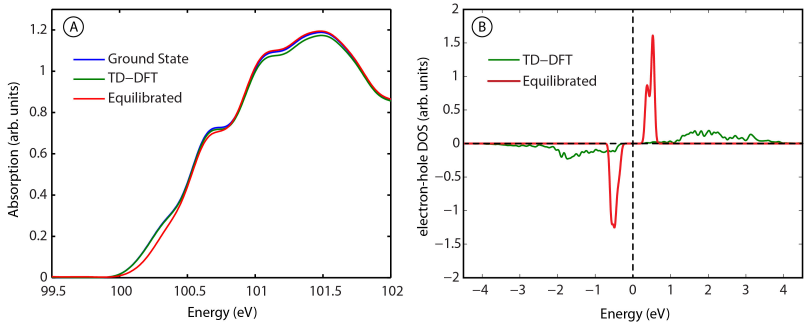


pump establishes non-equilibrium electron-hole population

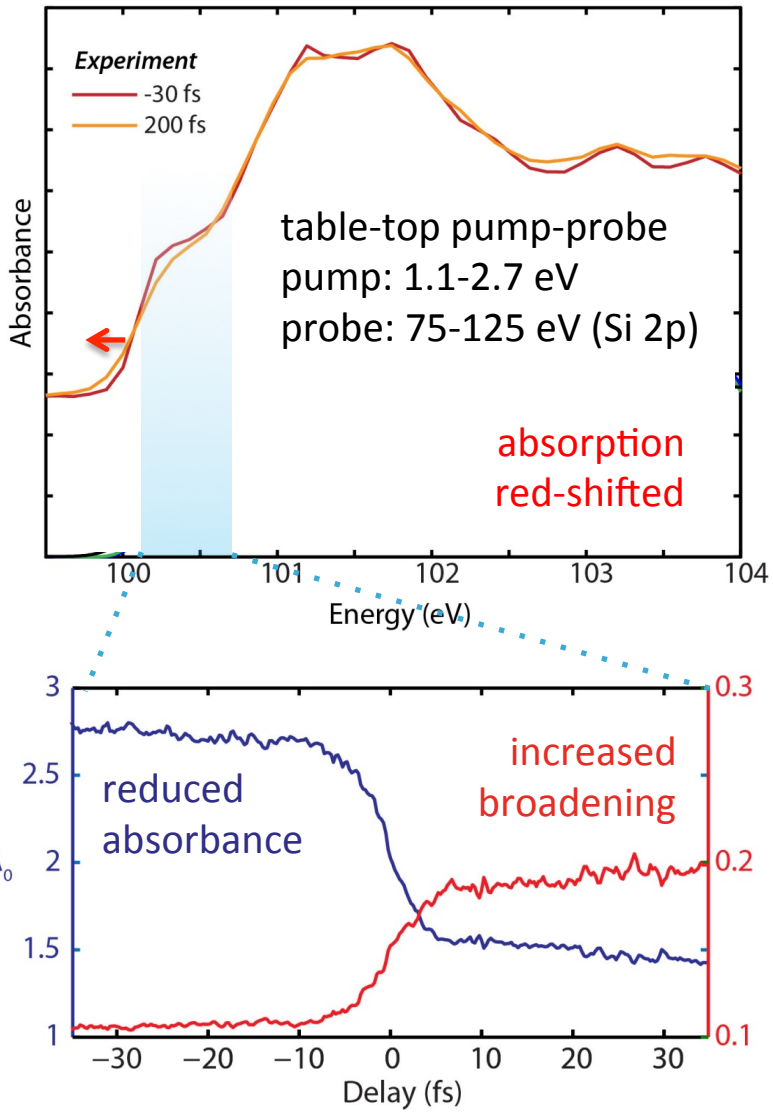


Pauli blocking

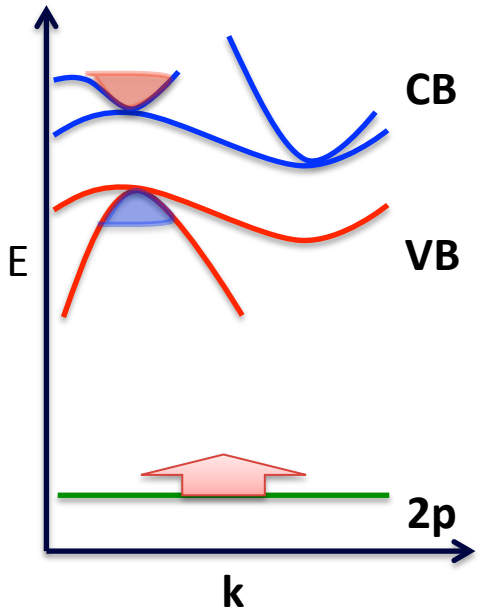
No spectral change vs. GS



Attosecond band-gap dynamics in silicon

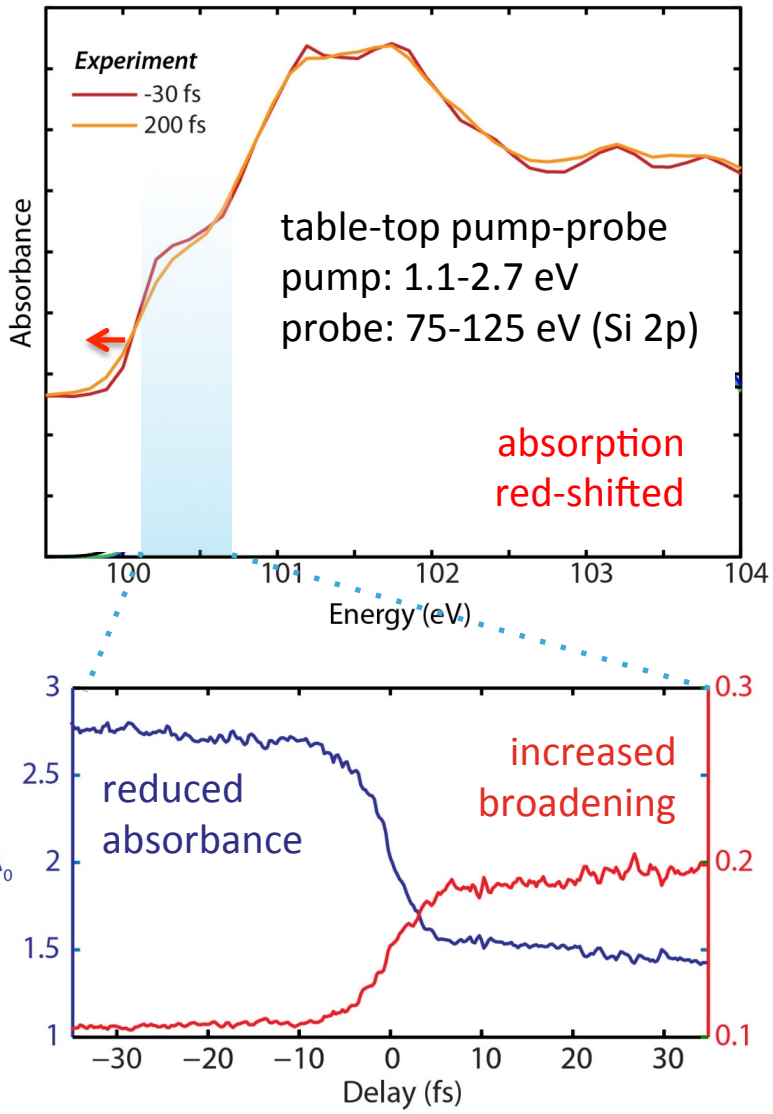


electronic screening due to pumped free-carriers

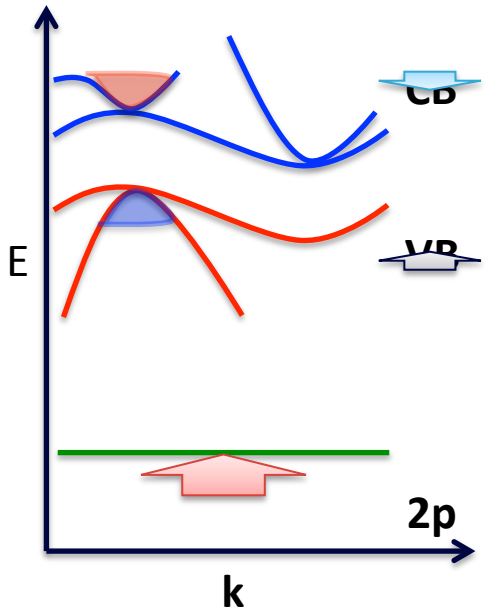


43 meV red-shift in core binding energy

Attosecond band-gap dynamics in silicon



electronic screening due to pumped free-carriers

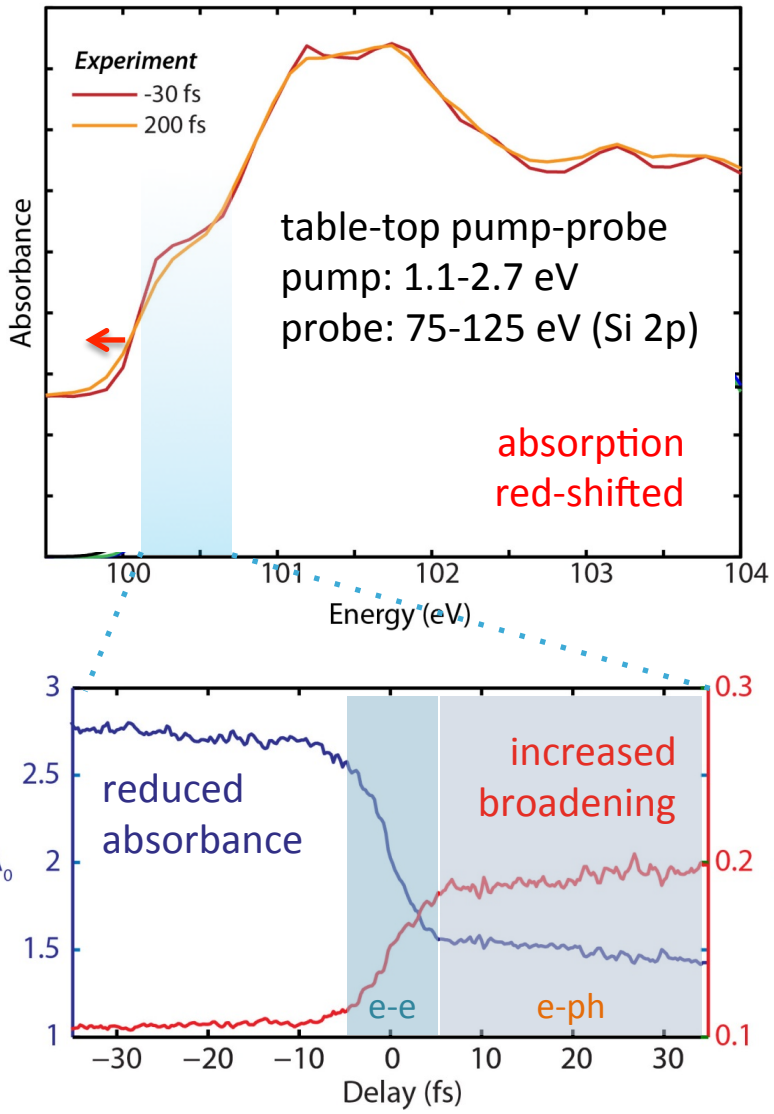


43 meV red-shift in core binding energy

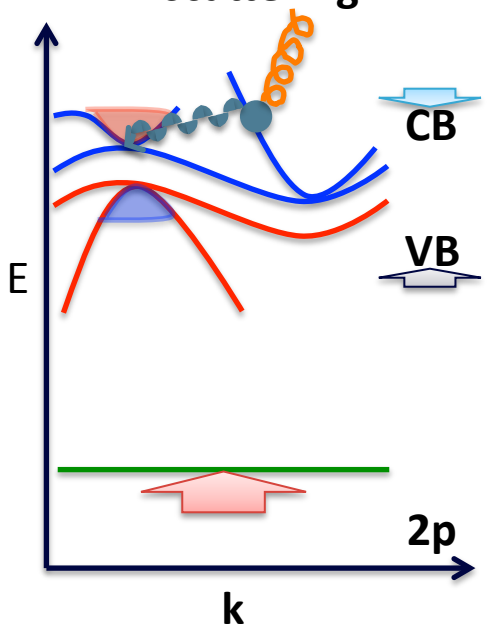
92 meV band gap reduction

121 meV measured red shift in absorption

Attosecond band-gap dynamics in silicon



life-time broadening due to scattering



43 meV red-shift in core binding energy

92 meV band gap reduction

121 meV measured red shift in absorption

65 meV electron-electron (~80 meV, < 5 fs)

26 meV electron-phonon (~20 meV, > 5 fs)

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Science 346, 1348 (2014)

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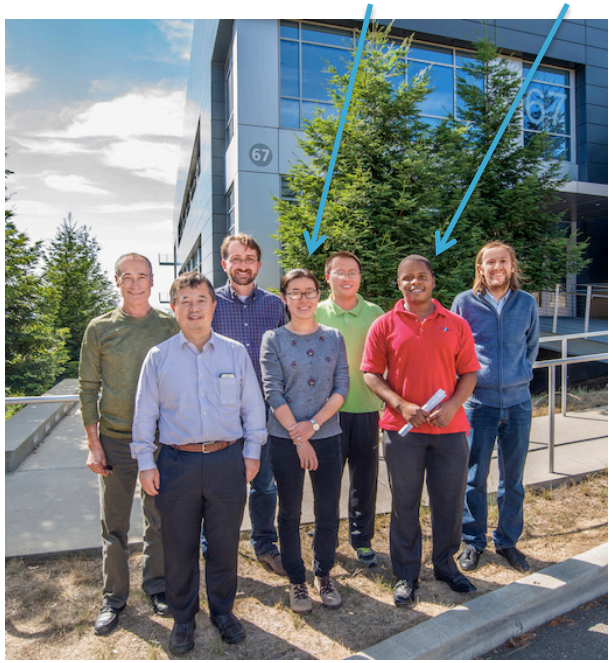

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Advanced Light Source:
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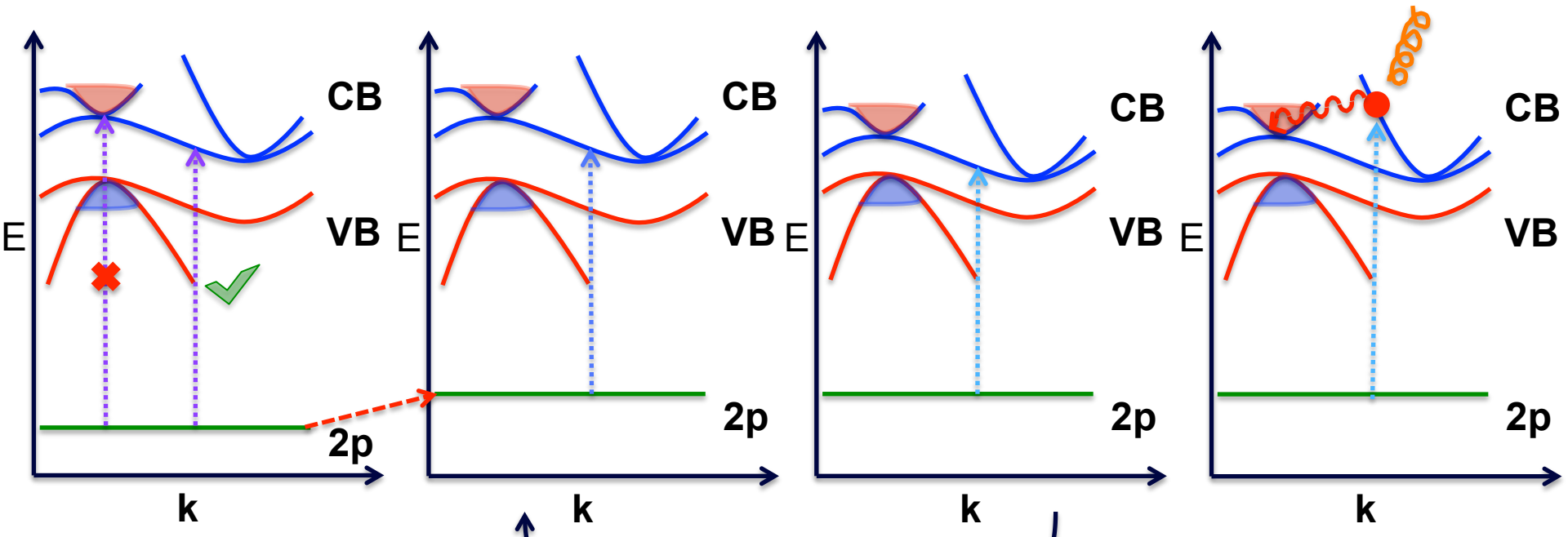
Science 346, 831 (2014)

MOLECULAR FOUNDRY

Effect of an e-h population on XUV absorption in Si



Modulation of absorption intensity

Red-shift of the absorption edge

Spectral broadening

Not significant

ΔE_{CL} = 43 meV

ΔE_{BGR} = 92 meV

e-e	e-ph
65 meV	26 meV
~80 meV	**~20 meV**

Experiment: 121 meV

Schultze, Ramasesha, Pemmaraju, Sato, Whitmore, Gandman, Prell, Borja, Prendergast, Yabana, Neumark, Leone, Science 346, 1348 (2014)