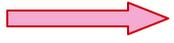


Some possible challenges for modeling soft x-ray spectra on the nanoscale

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Soft x-ray spectra: absorption or (resonant) inelastic scattering

insight into  {
- local atomic geometry for TM/RE ions,
- oxidation states of TM/RE atoms,
- well tuned to C 1s, O 1s, TM 2p edges,...
- vibrational effects, lifetimes...etc.

Discussion points:

- nanoscale systems: small or large?
large from a modeling viewpoint
- coupling to the outside world
*image charges, dipoles,
electron gain/loss to surroundings,
“truncation problem”*

need for large-scale computing, and *scalable* algorithms

need for “embedding” techniques to “place” the “crucial” part of a nanoscale system in its environment

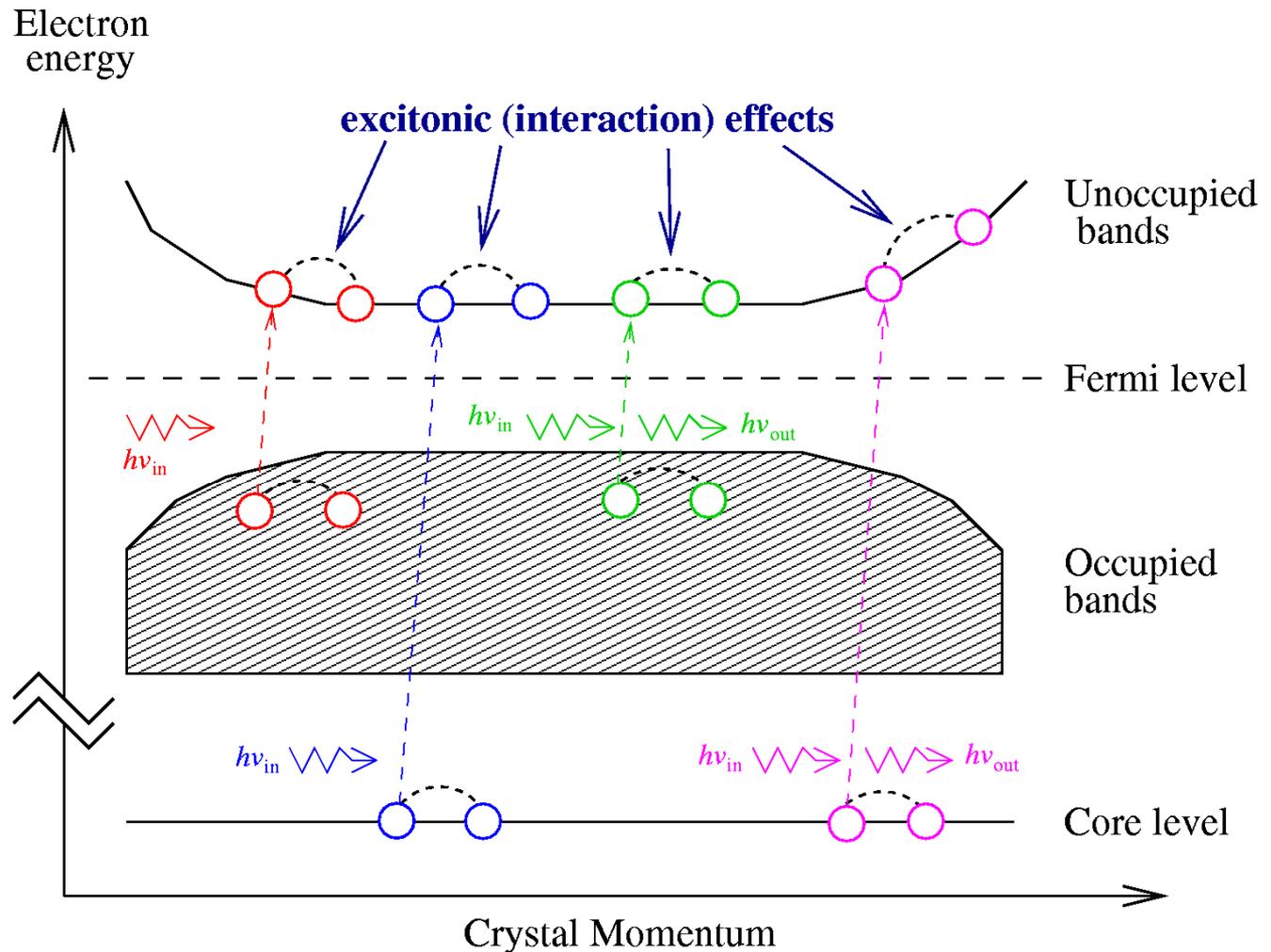
Examples:

- semiconductor nanocrystal (from G.W. Bryant, NIST)
- transition metal/rare-earth ions in ligand cages
- core hole screening in a complex system

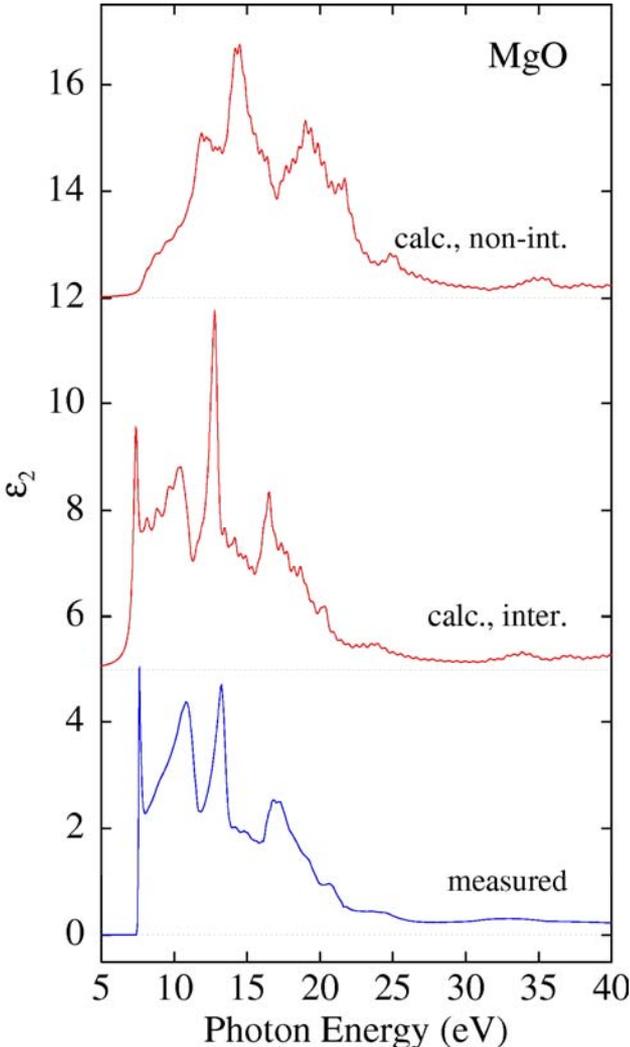
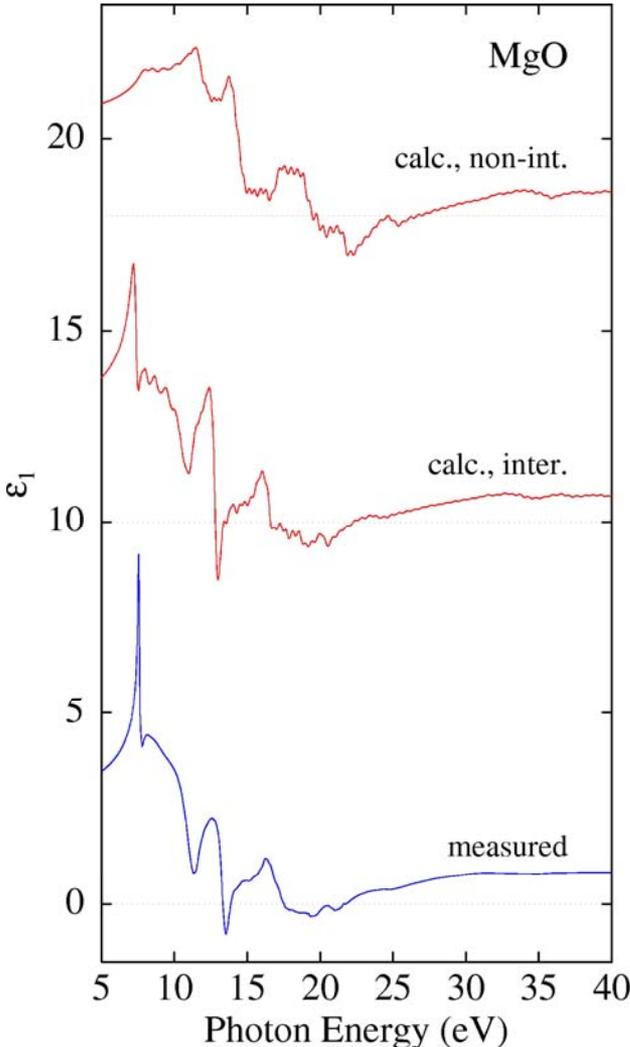
Strawperson conclusions:
(1) modeling will be hard
(2) we know strategic areas for development

Modeling of electronic/optical excitations:

- detailed band structure, many-body corrections to band structure
- electron/hole-state lifetime damping effects
- electron-hole interaction in excited state (\rightarrow 2-particle e.o.m.)

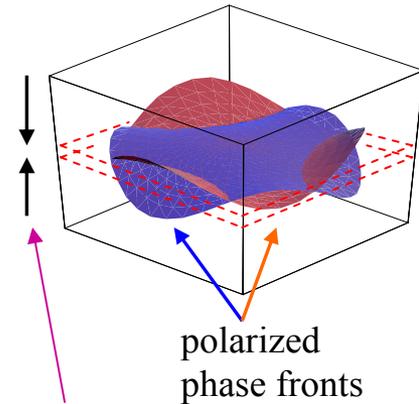
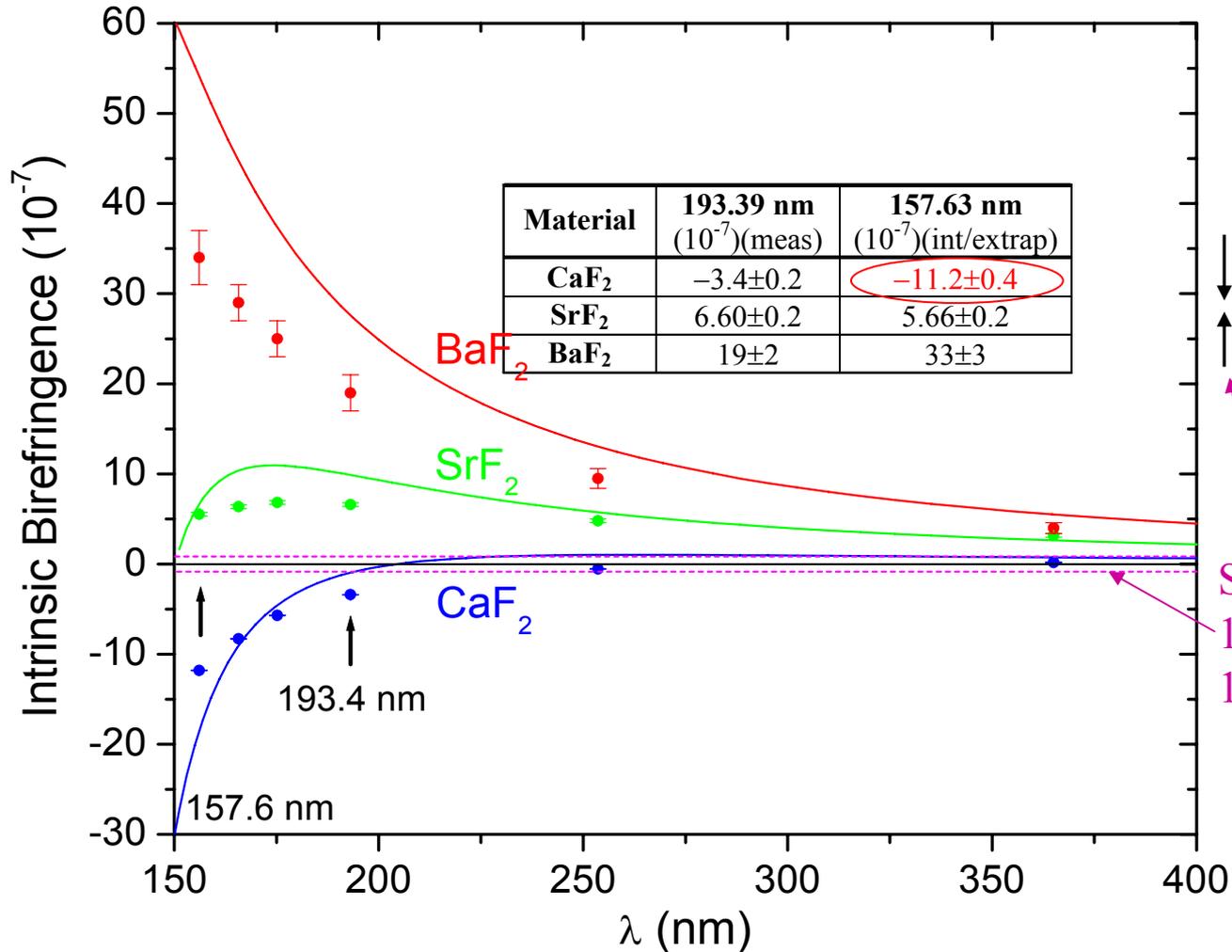


MgO optical constants:



Intrinsic Birefringence of CaF_2 , SrF_2 , and BaF_2

For light propagating along $(1,1,0)$ direction, refractive index difference for polarization along $(1,-1,0)$ vs. $(0,0,1)$



SEMATECH
157 nm target:
 $1 \times 10^{-7} = 1 \text{ nm/cm}$

- Values very small for CaF_2 in visible – why not observed previously.
- Large for $\lambda \approx 157 \text{ nm}$ ($\gg 157 \text{ nm}$ target and 193 nm target): $1/\lambda^2$ scaling + excitonic effects.
- Sign for CaF_2 opposite that for SrF_2 and BaF_2 (sign change for CaF_2).
- Remarkable agreement with first-principles calculation (curve).

Multiplet effects in 3d-oxide $L_{2,3}$ spectra:

Example: Ti $L_{2,3}$ in SrTiO_3 or $(\text{TiO}_6)^{4+}$ in a larger system

J. El. Spect. 144, 1187 (2005)

This work: Bethe-Salpeter *solid-state* calculation:

Generalize: $\{ |cn'\mathbf{k}(\mathbf{q})\rangle \} \rightarrow \{ | \alpha M_L M_S, n'\mathbf{k}\sigma; \mathbf{q} \rangle \}$

$$H_{\text{eff}} = H_{\text{BSE}} \approx H_h + H_e + H_{\text{eh}}$$

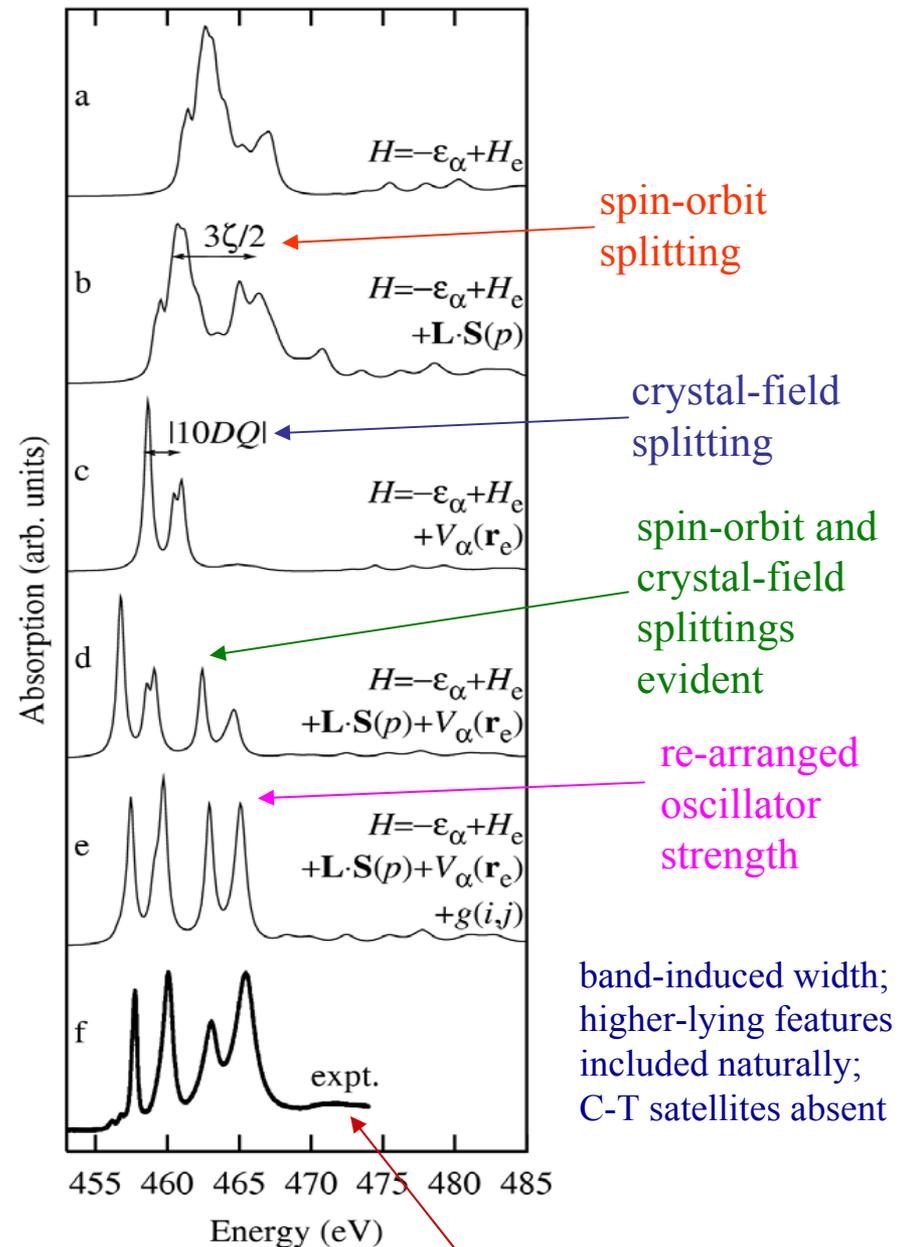
$$H_h = -\varepsilon_\alpha + \mathbf{L} \cdot \mathbf{S}(p)$$

$$H_e = \frac{p_e^2}{2m} + V_{\text{KS}}^{\text{xtal}} + \mathbf{L} \cdot \mathbf{S}(d)$$

$$H_{\text{eh}} = V_\alpha(\mathbf{r}_e) + g(i, j)$$

central part
screened
by RPA

Slater-type
integrals,
scaled by $\times 0.83$



charge-transfer satellites: how do we extend the calculation to include the environment without losing tractability?

Not necessarily nanoscale, but a new way of thinking:

Consider screening of an oxygen 1s core hole in HfO_2 .

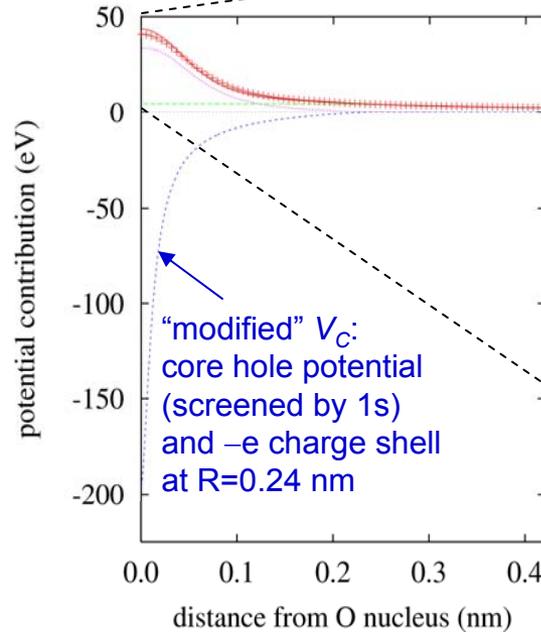
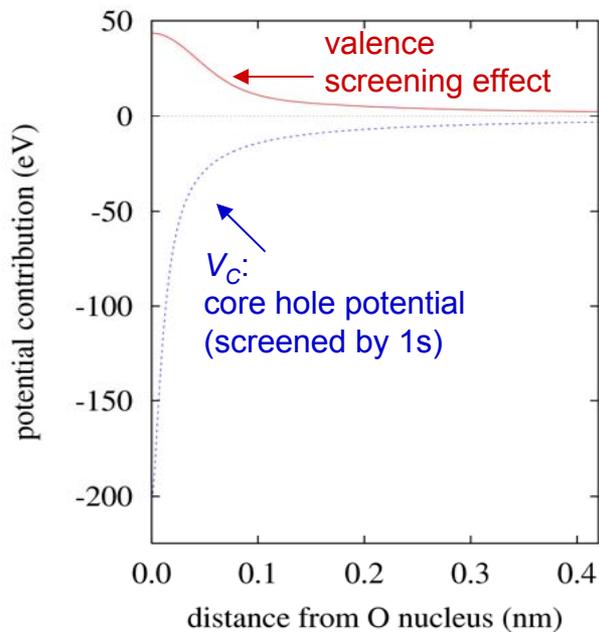
Traditional calculation: RPA screening

- * *Reciprocal-space*
- * *$O(N^3)$ calculation*
- * *double-sum over el. states for response function*
- * *Description of potential with same [poor] level of detail everywhere*

New calculation (in progress): RPA screening, but...

- * *Real-space method*
- * *$O(N^2)$ calculation*
- * *single-sum over el. states for response function (imaginary axis contour integral)*
- * *Detailed potential only on site*
- * *long-range effects treated in model dielectric function*

These types of innovation can help overcome the long-range, non-local effects of electron *wave functions*, and allow one to “truncate” or decouple a quantum subsystem from its environment.



Detail of screening:

