OCEAN and AI2NBSE postprocessors of ABINIT for Core and Valence Spectra

J.J. Rehr\textsuperscript{1}, John Vinson\textsuperscript{1}, E.L. Shirley\textsuperscript{2}

J.J. Kas\textsuperscript{1} and F. Vila\textsuperscript{1}

\textsuperscript{1}U. of Washington Seattle, WA
\textsuperscript{2}N.I.S.T. Gaithersburg, MD
aka SKWIGGLiE

Spectra from K-space Wave-functions with Interactions, Gradually Getting Like Experiment
1. OCEAN*

Obtaining Core Excitation spectra using ABINIT and NBSE

- Hybrid approach to core spectroscopy
- GW/BSE for XAS, NRIXS, EELS, …
- PAW Pseudo-potential / planewave DFT
- Includes self energy damping, multiplets …

2. Optical-UV Spectra

**AL2NBSE* (ABINIT + NIST BSE)**

PHYSICAL REVIEW B 78, 205108 (2008)

Optical to UV spectra and birefringence of SiO₂ and TiO₂:
First-principles calculations with excitonic effects

H. M. Lawler,1 J. J. Rehr,1 F. Vila,1 S. D. Dalosto,1,2 E. L. Shirley,2 and Z. H. Levine2
1Department of Physics, University of Washington, Seattle, Washington 98195, USA
2National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
(Received 11 July 2008; revised manuscript received 13 October 2008; published 12 November 2008)

A first-principles approach is presented for calculations of optical, ultraviolet spectra including excitonic effects. The approach is based on Bethe-Salpeter equation calculations using the NBSE code combined with ground-state density-functional theory calculations from the electronic structure code ABINIT. Test calculations for bulk Si are presented, and the approach is illustrated with calculations of the optical spectra and birefringence of α-phase SiO₂ and the rutile and anatase phases of TiO₂. An interpretation of the strong birefringence in TiO₂ is presented.

*Phys. Rev. B 78, 205108 (2008)*
Bethe-Salpeter Equation

\[ H = E_0 + V_c + W \]

**Particle-Hole Hamiltonian**

- **Bubble** \( V_c \) is unscreened
- **Ladder** \( W \) is screened
Bethe-Salpeter Equation

\[ H_{BSE} = H_h + H_e + H_{eh} \]

\[ H_h = -\epsilon_h + L \cdot S \]

\[ H_e = H_{KS} \]

\[ H_{eh} = V(r) + g(i, j) \]

Central term

Multiplets
Dielectric Response < BSE

\[ -\text{Im} \varepsilon^{-1}(q, \omega) = \frac{4\pi}{q^2} \text{Im} \langle \Psi_0 | \hat{D}^\dagger \frac{1}{E_0 + \omega - \hat{H} + i\gamma} \hat{D} | \Psi_0 \rangle \]

\( H \) particle-hole Hamiltonian including:

many-pole GW self-energy \( \Sigma \)

Algorithm: Haydock recursion
Ground-state

- Standard Density-Functional Theory
  - Pseudopotential, Plane-wave, LDA
  - ABINIT (www.abinit.org)
- Well-documented shortcomings; improvements:
  - GW
  - XC + U
- Core to pseudo transitions with PAW
  - Following Blöchl, PRB 50, 17953 (1994)
**Kohn-Sham Wave-Functions**

- **ABINIT** (Plane-wave, pseudo-potential)*
  - LDA (Ceperley-Alder) $V_{xc}$
  - Zero Temp / Frozen lattice

- Regular grid in $k$-space
  - Size required varies with BZ volume

- Core states from NIST HF atomic code

*Other PW/PP DFT codes may also work*
Electron-hole pair approximation

\[-\text{Im} \epsilon^{-1}(q, \omega) = \frac{4\pi}{q^2} \text{Im} \langle \Psi_0 | \hat{D}^\dagger \frac{1}{E_0 + \omega - \hat{H} + i\gamma} \hat{D} | \Psi_0 \rangle\]

\[\cdots \sum_{\phi, \chi} \text{Im} \left[ \langle \Psi_0 | \hat{D}^\dagger | \phi, \chi \rangle \times \langle \phi, \chi | \frac{1}{\omega - \hat{H}_{\text{eff}} + i\gamma} | \Psi_0 \rangle \right] \cdots\]

\[\phi = \phi_{n,k}(r)\] Conduction electron

\[\chi = \chi_{\alpha,r}(r)\] Core hole

\[\hat{D} = \begin{cases} \hat{e} \cdot r & \text{XAS} \\ e^{i\mathbf{q} \cdot \mathbf{r}} & \text{NRIXS} \end{cases}\]
PAW Matrix Elements

\[ \phi_{n,k}(r) = \sum_{G} C_{G}^{n,k} e^{i(k+G)\cdot r} \]

\[ F^{ps} \equiv F^{ae} \]

\[ \phi_{n,k}(r + \tau) = \sum_{\nu lm} A_{\nu lm}^{nk} F_{\nu l}^{ps}(r) Y_{lm}(\hat{r}) \]

\[ A_{\nu lm}^{nk} = 4\pi i^{l} \sum_{G} C_{G}^{nk} e^{i(k+G)\cdot \tau} Y_{lm}^{*}(\hat{k}) \int_{0}^{\infty} dr r^{2} j_{l}((k + G)r) F_{\nu l}^{ps}(r) \]

\[ \langle \phi_{n,k} | \hat{D}^{(1)} | \chi_{\alpha} \rangle = \int d^{3}r \sum_{\nu lm} A_{\nu lm}^{*nk} F_{\nu l}^{ae}(r) Y_{lm}^{*}(\hat{r}) \hat{D}^{(1)} \chi_{\alpha}(r) \]
Core-Hole Screening

\[ W(r) = V_\alpha(r) + \Delta V_\alpha(r) + \Delta V_{val}(r) \]

- Core response from self-consistent HF
- Use neutralizing shell to divide valence
  - RPA for short range
  - Model dielectric for long range

\[ \Delta V_{val}(r) = \int d^3r' \left[ \epsilon^{-1}(r, r') - \delta^3(r - r') \right] \times \left[ V_\alpha(r') + \Delta V_\alpha(r') \right] \]

GW Many-pole self-energy

- Extension of Hedin-Lundqvist plasmon-pole

- MPSE (Kas et al. *)
  - Calculate loss function with AI2NBSE
  - Model as a series of (many) poles
  - Apply as convolution

J.J. Kas et. al, Phys Rev B 76, 195116 (2007)
OCEAN Package

Structure → DFT/ABINIT

$G_0$ → $\epsilon_{\text{RPA}}^{-1}$ → $E_i; \psi_i$ → $\langle \chi | \hat{o} | \psi \rangle$ → $\chi$ → HFAtom

$\langle \chi | \hat{o} | \psi \rangle$ → BSE

Spectra
Example: Li K-edge XAS of LiF

1000 k-points
100 Ha. cut-off

Expt. data from K. Handa et. al, Memoires Sr. Center Ritsumeika Univ 7 (2005)
Example: Li K-edge XAS of LiF
Comparison with EXCITING* (NO MPSE)

*W. Olovsson et. al, Phys Rev B 79, 041102(R) (2009)
Example: F K-edge XAS in LiF


1000 k-points
100 Ha. cut-off
Ice: O K edge XAS


8 molecule cells
216 k-points
50 Ha. cut-off
Example: \( L \)-edge Spectra – Multiplet effects

\[ \text{Ti} \ L_{2,3} \text{edge} \quad \text{SrTiO}_3 \]

Bethe–Salpeter treatment of X-ray absorption including core-hole multiplet effects

Eric L. Shirley*


alá E. Shirley:  BSE + KS crystal potential
ab initio – no parameters

\[
H_{BSE} = H_h + H_e + H_{eh}
\]

\[
H_h = -\epsilon_\alpha + L \cdot S(p)
\]

\[
H_e = \frac{p^2}{2m} + L \cdot S(d) + H_{KS}^{xtal}
\]

\[
H_{eh} = V_\alpha(r) + g(i, j)
\]

cf. De Groot et al – Atomic model + crystal-field parameters

\[
H_{at} = H_{av} + L \cdot S(p)
\]

\[
+ L \cdot S(d) + H_{xtal field} + g(i, j)
\]
V L₂₃  Ni L₂₃

L₂₃ Transition Elements

PRL 45, 397 (1980)
3. *Ab initio* XAS Debye Waller Factors $e^{-2\sigma^2 k^2}$

*An Initio* Determination of Extended X-Ray Absorption Fine Structure Debye-Waller Factors

Fernando D. Vila, G. Shu, and John J. Rehr  
*Department of Physics, University of Washington, Seattle, WA 98195*

H. H. Rossner and H. J. Krappe  
*Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany*  
(Dated: August 23, 2005)

\[
\sigma^2 = \frac{\hbar}{\mu_i} \int_0^\infty \rho(\omega^2) \coth \frac{\beta \hbar \omega}{2} d\omega
\]

\[
\rho(\omega^2) = \langle Q_i | \delta(\omega^2 - D) | Q_i \rangle = \{6 - step Lanczos recursion\}
\]

**Many Pole model for phonons**

*VDOS $\rho$

**Dynamical matrix $D$ from ABINIT**

Example: XAFS Debye-Waller Factor of Ge


Expt: Dalba et al. (1999)
Conclusions

- Core & Valence BSE+GW packages
  OCEAN & AI2NBSE

- NRIXS, EELS, XAS,

- Includes GW self-energy, multiplets, ..

- Future: RIXS, XPS, DW factors, etc.
Acknowledgments

Rehr Group  & collaborators

- J. Vinson (UW)
- J. Kas (UW)
- F. Vila (UW)
- K. Jorissen (UW)
- H. Lawler (Vanderbilt)
- E. Shirley (NIST)

Thanks to

- X. Gonze, UC de Louvain
- A. Soininen (U. Helsinki)
- L. Reining (E. Polytechnique)
- C. Ambrosch-Draxl (U. Leobon)
- T. Ahmed (UW)

Supported by DOE BES Grant DEFG03-97ER45623
& DOE Computational Materials Science Network