Screening and Chemical Shifts

OCEAN Tutorial, Session 2

Screening and Chemical Shifts

- What is screening?
- Converging the screening in OCEAN
- Chemical shifts

But first, get the example running

- We'll be looking at NH_4NO_3
  - (Not the room-temperature phase)
- Go back to your directory in scratch

1. > cd /hpcgpfs01/scratch/jtv3
   - but your username, not mine!

2. > cp -r /hpcgpfs01/work/workshop/ocean_tutorial/session2 .
   - (try hitting the tab key after you've typed a few letters)

3. > sbatch runit

Screening in the Bethe-Salpeter Eqn.

- Two interaction terms in the BSE
  1. Bare exchange
     - Repulsive
     - Mixes L_2/L_3 and t_{2g}/e_g ratios
  2. Screened direct
     - Responsible for exciton binding
     - Screened by the electrons

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Screening

- System
  - Electrons and ions in the ground state
  - Excited electron and hole
- Electrons and ions will react to external potentials
  - (In this case the presence of the electron or hole)
  - Reaction is frequency dependent
    - Too fast for ions
  - Charge density changes
  - $\chi = \delta n / \delta v_{\mathrm{ext}}$

Major Approximations

- Random Phase Approximation (RPA)
  - $\chi_0(1,2) = -iG_0(1,2)G_0(2,1^+)$

Major Approximations

- Random Phase Approximation (RPA)
- Static Screening

Static screening

- Dielectric response should be frequency dependent
- Important energy scales for ϵ^{-1}
  - Band gap
  - Plasmon energy
- Energy scale for exciton is pair binding energy
  - Difference between interacting and non-interacting
  - Not the core-level binding
  - Not the excitation energy above the edge
- Strinati PRL **49**, 1519 (1982); PRB **29**, 5718 (1984)

Static screening

- Core and valence BSE both use static screening
  - Few exceptions in literature
- Exciton binding tends to be smaller than band gap

OCEAN methodology

Eric Shirley, Ultramicroscopy **106**, 986 (2006)

OCEAN methodology

- Screening with OCEAN:
  - Generate DFT orbitals
  - Short-range – long-range partition

Eric Shirley, Ultramicroscopy **106**, 986 (2006)

DFT orbitals

- $\chi_0(1,2) = -iG_0(1,2)G_0(2,1^+)$

$$G_0(E) = \sum_{n\mathbf{k}} \frac{\psi^\dagger_{n\mathbf{k}}\psi_{n\mathbf{k}}}{E - \varepsilon_{n\mathbf{k}} \pm i\eta}$$

- Get our orbitals from DFT
- Sum over bands and k-points
  - Use finite number of both
  - Convergence covered later

Dividing the screening problem

- Linear superposition
  - Can break problem into pieces
- Step 1 is core-valence partition
  - Core electrons will screen core hole
  - Core orbitals not available from DFT calculation
  - Use atomic DFT program
  - Allow spectator core orbitals to relax: $V_C(\mathbf{r})$
    - Ex. Ti 1s hole will be screened by 2s & 2p core-level orbitals

Short/long-range partitioning

- Need valence response to core-screened potential $V_C(\mathbf{r})$
- Use linear superposition
  - $V_C(\mathbf{r}) = V_1(\mathbf{r}) + V_2(\mathbf{r})$
- Place a neutralizing shell at R
  - $V_1(\mathbf{r}) = V_C(\mathbf{r}) - \Theta(R-r)/R - \Theta(r-R)/r$
  - $V_2(\mathbf{r}) = \Theta(R-r)/R + \Theta(r-R)/r$

Short/long-range partitioning

- $V_1(\mathbf{r}) = V_C(\mathbf{r}) - \Theta(R-r)/R$
  $-\Theta(r-R)/r$
  - V_1 is zero outside of R

Short/long-range partitioning

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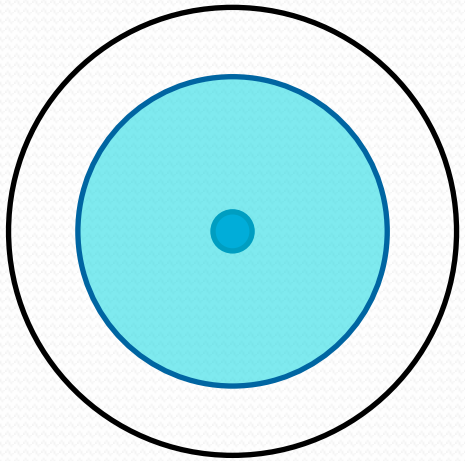
  $-\Theta(r-R)/r$
  - V_1 is zero outside of R
  - Only need screening for inside sphere s; s > R



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  - Constant and small (1/R) inside R
  - Exciton is strongly localized

Short/long-range partitioning

- $V_1(\mathbf{r}) = V_C(\mathbf{r}) - \Theta(R-r)/R$
  $-\Theta(r-R)/r$
  - V_1 is zero outside of R
  - Only need screening for inside sphere s; s > R
  - Use RPA for space within sphere s
- $V_2(\mathbf{r}) = \Theta(R-r)/R + \Theta(r-R)/r$
  - V_2 has infinite extent
  - Constant and small (1/R) inside R
  - Exciton is strongly localized
  - Use model screening

Short/long-range partitioning

- Use of model
  - Exciton is localized where V_2 is small: $V_2(\mathbf{r}) \approx 1/R$
  - Controllable parameter R
  - Long-ranged behavior of screening is simple: ϵ_0^{-1}/r

- Model derived from Levine-Louie dielectric function
  - Z.H. Levine & S.G. Louie, Phys. Rev. B **25**, 6310 (1982)
  - E.L. Shirley, Ultramicroscopy **106**, 986 (2006)

Short/long-range partitioning

- Typical R is 3.5 – 5.5 Bohr
  - This is screen.shells { }
  - Also cnbse.rad { }
    - Can run many screen.shells, choose a single one for
- Typical s is 8 Bohr
  - Need χ [G(r,r')] within the sphere s

Results

- ropt – the screening potential from the valence
  - Column 1: radius
  - Column 2: V_2 (modeled screened potential of shell)
  - Column 3: V_1 (RPA screened hole – shell)
  - Column 4: $V_1 + V_2$
- rpot – the total, screened, core-hole potential
- SCREEN/zF_0001/n01l00/
  - Element & index
  - Principle and angular quantum numbers of edge

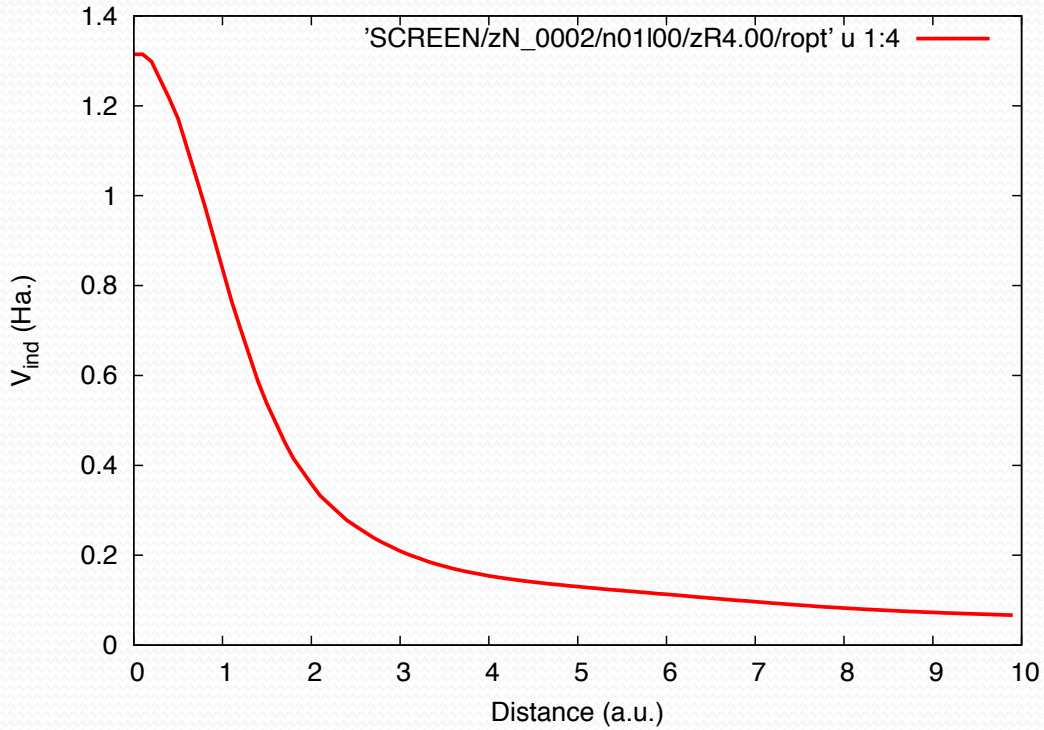
Converging the screening

Converging the screening

- Defaults are pretty good
- Look at changes to ropt
- Things to check
  1) Number of bands (and sometimes k-points)
  2) R – the shell radius for the local RPA

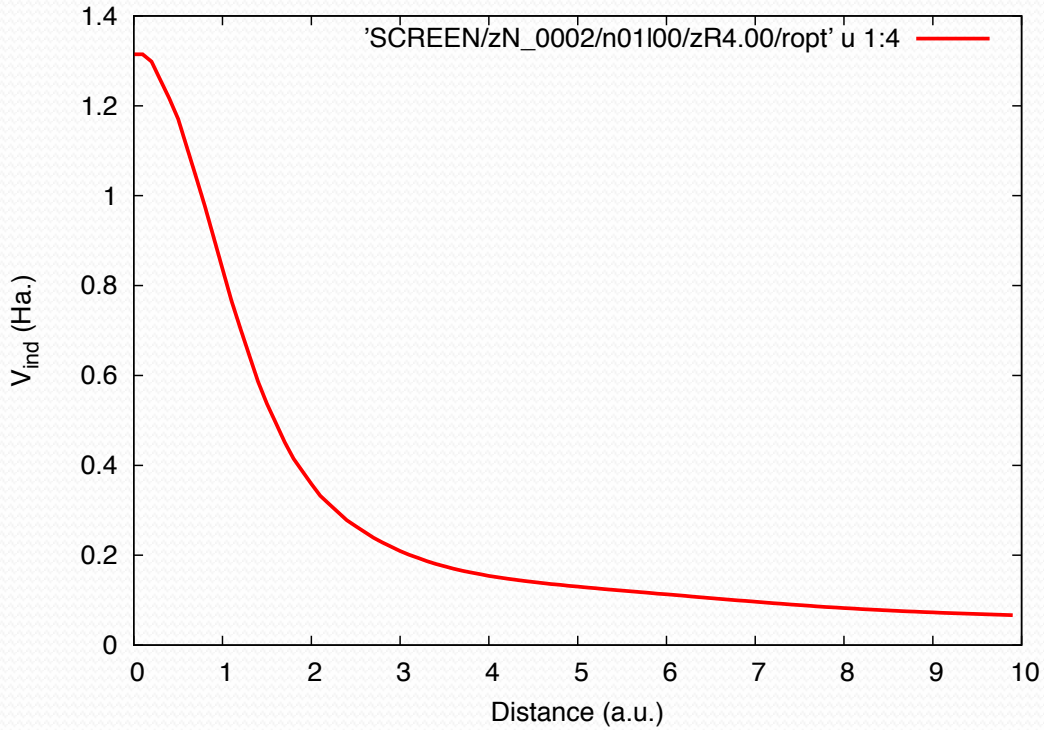
Plot the screening potential

- Screening is in SCREEN
- Each atomic site gets a directory
  - zN_0001 & zN_0002
  - The NO_3 nitrogen is the 2nd
- Separated by core level
  - n01l00 = 1s (n02l01 = 2p)
- Separated by short/long partition
  - zR4.00 = 4 Bohr



Plot the screening potential

- p ‘SCREEN/zN_0002/n01l00/zR4.00/ropt’ u 1:4
  - 1: the radial grid
  - 2: long-range model
  - 3: short-range RPA
  - 4: total



Converge the screening

- Start the next run, then explain
- Save both screening and spectra
  - > mv SCREEN SCREEN.1
  - > mv CNBSE CNBSE.1
- Edit AN.in
  - screen.nbands 200
- > sbatch runit

Converging the screening

$$\chi_0(1,2) = -iG_0(1,2)G_0(2,1^+) \qquad G_0(E) = \sum_{n\mathbf{k}} \frac{\psi^\dagger_{n\mathbf{k}}\psi_{n\mathbf{k}}}{E - \varepsilon_{n\mathbf{k}} \pm i\eta}$$

- Use finite number of bands and k-points
- Remarkably few k-points
  - 2x2x2 grid works for most systems
  - More for metals, very small unit cells
  - Advantage of local approach
  - screen.nkpt { }

Converging the screening

$$\chi_0(1,2) = -iG_0(1,2)G_0(2,1^+)$$

$$G_0(E) = \sum_{n\mathbf{k}} \frac{\psi^\dagger_{n\mathbf{k}}\psi_{n\mathbf{k}}}{E - \varepsilon_{n\mathbf{k}} \pm i\eta}$$

- Use finite number of bands and k-points
- Remarkably few k-points
- Aim for about 100 eV worth of bands
  - screen.nbands

Converging the screening

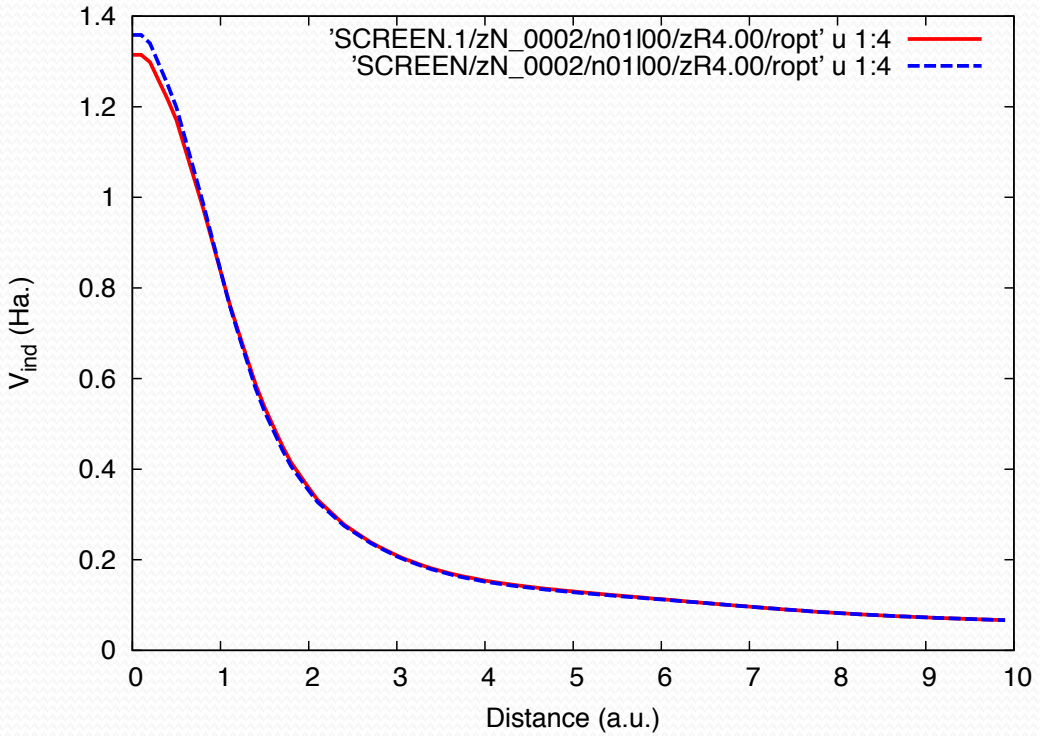
$$\chi_0(1,2) = -iG_0(1,2)G_0(2,1^+)$$

$$G_0(E) = \sum_{n\mathbf{k}} \frac{\psi^\dagger_{n\mathbf{k}}\psi_{n\mathbf{k}}}{E - \varepsilon_{n\mathbf{k}} \pm i\eta}$$

- Use finite number of bands and k-points
- Remarkably few k-points
- Aim for about 100 eV worth of bands
- Re-run calculation to check
  - Which is what we just did

Converge the screening potential

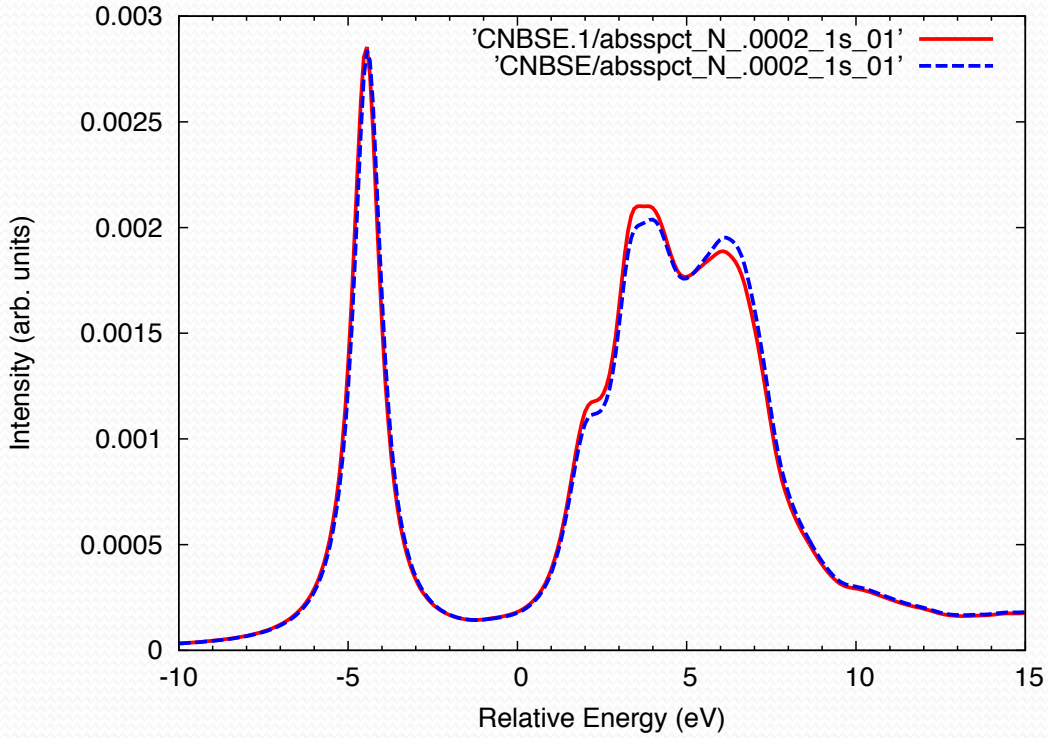
- Plot the two potentials
  - > gnuplot
  - > plot ‘SCREEN.1/zN_0002/n01l00/zR4.00/ropt’ u 1:4 w l
  - > replot ‘SCREEN/zN_0002/n01l00/zR4.00/ropt’ u 1:4 w l
- Close
- More bands = more screening



Converge the screening potential

- Plot the spectra
  - CNBSE.1/absspct_N_.0002_1s_01
  - CNBSE/absspct_N_.0002_1s_01

- More screening
  - Less exciton binding
  - Spectral weight shifts higher
- Only slight changes
  - Probably close to converged



Converging the screening

- Short/long-range partitioning radius R
- Screened potential should be independent of R
  - Is ϵ_0^{-1} correct?
  - Is R large enough?
- Can run several radii
  - screen.shells { }
  - Bohr, rounded to 2 decimal places
  - Only 1 is used in BSE (cnbse.rad)

Core-level Shifts

Core-level (chemical) shifts

- First we'll kick off the next run

- Edit AN.in
- Change "calc xas" to "calc xes"
  - Absorption → Emission
- > sbatch runit

- I'll probably go too fast here, but slides will be available later

Core-level (chemical) shifts

- Core-level binding energies depend on chemical environment
  - Discovered in the 1920s by group of Manne Siegbahn
  - Foundation of XPS/ESCA
    - Correlate binding energy with oxidation state
- Previously (earlier sessions) showed relative energy
  - Spectral shape comparable to experiment
  - Absolute energy scale **offset** to match

Core-level (chemical) shifts

- How much fitting is acceptable?
- Relative shifts needed for most systems
  - Imperfect crystals
    - Vibrational disorder
    - Amorphous samples or liquids
  - Multiple oxidation states
    - Explicitly, e.g., NH_4NO_3
    - Surfaces or interfaces
- OCEAN needs 1 fit factor per edge & pseudopotential

Core-level (chemical) shifts

- OCEAN needs 1 fit factor per edge & pseudopotential
  - Ti 1s, Ti 2s, and Ti 2p → 3 different shifts
  - Good between Ti metal, TiO_2, TiS_2, or $Li_xTi_yO_z$
- Works ok
  - Water: Phys Rev B **85**, 045101 (2012) & Nano Letters **17**, 1034 (2017)
  - Battery cathodes: J. Am. Chem. Soc. **139**, 16591 (2017)
  - NH_4NO_4: Phys Rev B **90**, 205207 (2014); **94**, 035163 (2016)
  - Cu_2O surfaces: Chem Mater **30**, 1912 (2018)
- More benchmarks/stress tests are in progress

Core-level shifts with OCEAN

- Once again, no core orbitals with pseudopotential DFT
- DFT total energies for core orbitals are unreliable anyway

Core-level shifts with OCEAN

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1) Assume the core orbital is independent of environment
   - Ti 1s is the same in metal as the oxide as the …

Core-level shifts with OCEAN

- Once again, no core orbitals with pseudopotential DFT
- DFT total energies for core orbitals are unreliable anyway

1) Assume the core orbital is independent of environment
   - Ti 1s is the same in metal as the oxide as the …
2) Energy of orbital
   - $\varepsilon_{1s} = \langle \psi_{1s} | \hat{H} | \psi_{1s} \rangle$
   - $\varepsilon_{1s} = \langle \psi_{1s} | \hat{H}' | \psi_{1s} \rangle + \langle \psi_{1s} | \hat{v}_{\mathrm{ext}} | \psi_{1s} \rangle$
   - External is everything that changes, i.e., total Kohn-Sham potential
   - $\varepsilon_{1s} = X_{1s} + \langle \psi_{1s} | \hat{v}_{\mathrm{KS}} | \psi_{1s} \rangle$

Core-level shifts with OCEAN

1) Assume the core orbital is independent of environment
2) Energy of orbital: $\varepsilon_{1s} = X_{1s} + \langle \psi_{1s} | \hat{v}_{\mathrm{KS}} | \psi_{1s} \rangle$
3) Systems relaxes/screens
   - Remove charge to infinity
   - $\Delta = {}^{1}/_{2} W$
   - Depends on screened Coulomb

Core-level shifts with OCEAN

1) Assume the core orbital is independent of environment
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3) Systems relaxes/screens
   - Remove charge to infinity
   - $\Delta = {}^{1}/_{2} W$
   - Depends on screened Coulomb
4) Evaluate both terms at the atomic coordinate τ
   - Assuming the core orbital is small

- $\Delta\varepsilon_{1s} = X_{1s} + \hat{v}_{\mathrm{KS}}(\tau) - {}^{1}/_{2} W(\tau)$

Core-level shifts with OCEAN

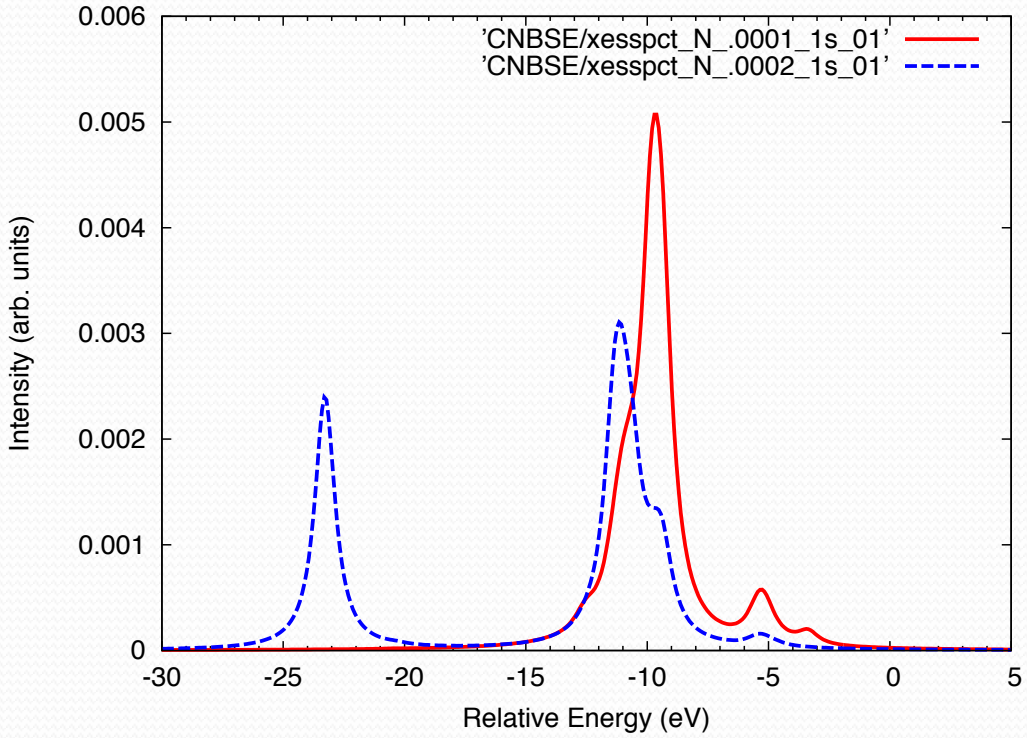
- $\Delta\varepsilon_{1s} = X_{1s} + \hat{v}_{\mathrm{KS}}(\tau) - {}^{1}/_{2}W(\tau)$

- Accurate enough to combine
  - Different molecular dynamics snapshots
  - Different chemical valences

XES of NH_4NO_3

- > gnuplot
- > p ‘CNBSE/xesspct_N_.0001_1s_01’
- rep ‘CNBSE/xesspct_N_.0002_1s_01’

- This assumes NO_3 and NH_4 have same N 1s binding energy
  - But one N is oxidized, one reduced
  - Need core-level shifts



XES of NH_4NO_3

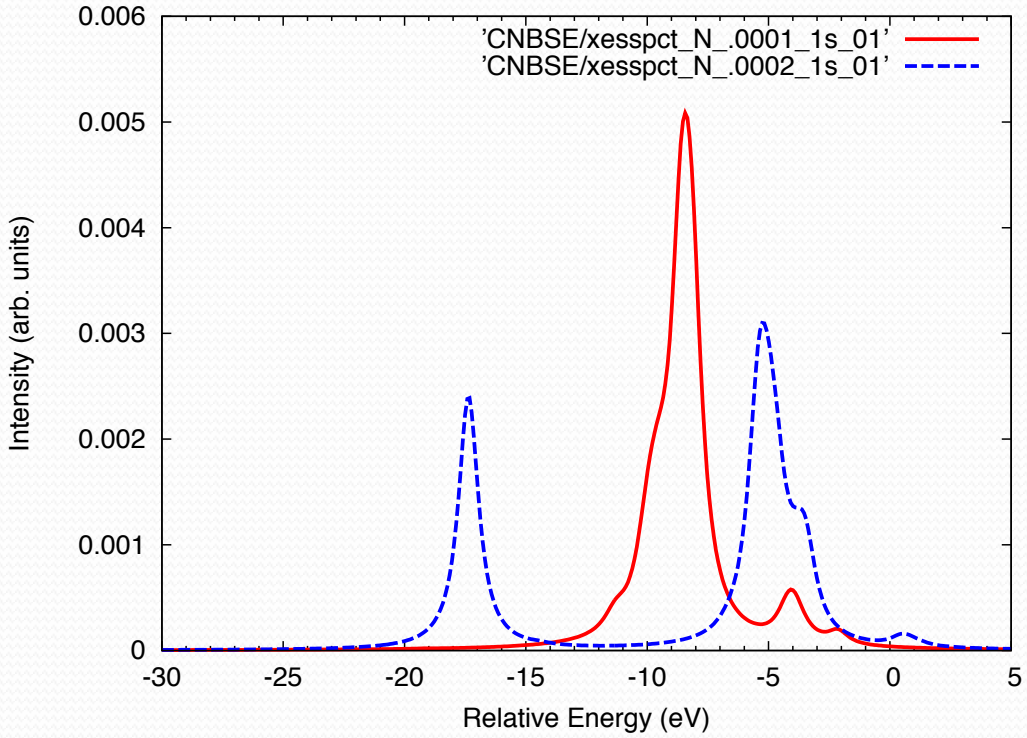
- Edit AN.in again
- Remove the ‘#’ from in front of “core_offset .true.”
  - A ‘#’ is a comment
  - The code won’t read anything that follows a ‘#’

- > sbatch runit

XES of NH_4NO_3

- > gnuplot
- > p ‘CNBSE/xesspct_N_.0001_1s_01’
- rep ‘CNBSE/xesspct_N_.0002_1s_01’

- Now the code calculates shifts
  - 4 eV shift between the two N’s
  - Previously 0 eV was the conduction band minimum
  - Now it is the 0 of the DFT calculation



Core-level shifts with OCEAN

- 3 options for core_offset flag
  - .false. – Default, no shifts
  - .true. – Calculate an average shift of 0
  - Any number – Use this as X for calculating the shift
- Using a number for core_offset
  - Depends on pseudopotential and edge
  - Need to use to compare between cells
    - MD calculations
    - Chemical reactions

Core-level shifts with OCEAN

- Using a number for core_offset
  - Run **one** system with “core_offset .true.”
  - OCEAN will give you the number
- > less SCREEN/core_shift.log

```
Radius = 4.00 Bohr
  core_offset was set to true. Now set to 120.254571918243
Site index    Total potential   New potential    1/2 Screening      core_offset       total offset
                    (eV)             (eV)              (eV)             (eV)              (eV)
         1     -137.711172094    -135.652088470     17.737967620    120.254571918        -2.3404511
         2     -143.388560093    -141.076373295     18.481350309    120.254571918         2.3404511
```

- Use “core_offset 120.25457” in subsequent runs