Absorbance

Inputs

*.fdf (aten o script)
*.psf
someter

Outputs
*.EPSIMG

Optical
/usr/share/sim/agl/SIESTA_APPS/siesta-4.0.1/Util/Optical
input.f -o input
./input < SiH-O-Aptms1.EPSIMG
./optical
*.out (absorp_coef.out)
graficar con
gnuplot(C:\Users\tgdia\Documents\Silicio-SiH\scripts\Optical\Optical\Optical\SiOH-Aptes-AM)

Input *.fdf

1. System Information

- SystemName: A label for the system (Si-O-APTES), likely a silicon oxide surface functionalized with APTES (aminopropyltriethoxysilane).
- NumberOfAtoms (703): A large system, suggesting a slab model (periodic surface) or nanostructure.
- NumberOfSpecies (5): Atoms involved are Si, O, C, N, H, typical for organosilane-modified surfaces.

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2. DFT & Electronic Structure Settings

Exchange-Correlation Functional

- XC.functional GGA & XC.authors PBE:
    - Uses PBE-GGA, a standard choice for solids and molecules.

    - Physical Implication: PBE slightly underestimates band gaps but gives good structural properties.

Spin & Convergence

- SpinPolarized .false.:
    - No spin polarization → closed-shell system (no unpaired electrons).
- MeshCutoff 150 Ry:
    - Real-space grid cutoff → higher values improve accuracy but increase cost.
    - Rule of thumb: 150–200 Ry is typical for GGA.
- ElectronicTemperature 298 K:
    - Fermi-Dirac smearing at room temperature → helps SCF convergence in metals/semiconductors.

SCF (Self-Consistent Field)

- DM.MixingWeight 0.01:
    - Small mixing → slow but stable convergence (useful for difficult systems).
- DM.Tolerance 1.d-4:
    - Stops SCF when max density change < 10^{-4} → moderately tight tolerance.

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3. Lattice & Atomic Structure

Supercell Dimensions

- LatticeVectors:
    - 10.99 Å × 60.445 Å × 60.445 Å → Slab geometry (short in x, extended in y/z).
    - Physical Implication: Models a surface with vacuum spacing (~60 Å) to avoid periodic interactions.

Atomic Positions

- AtomicCoordinatesFormat Ang: Positions in Ångstroms.
- ChemicalSpeciesLabel:
    - Maps atomic numbers to labels (e.g., Si (Z=14), O (Z=8), etc.).
- SlabDipoleCorrection .true.:
    - Corrects artificial electric fields in slab calculations due to periodic boundary conditions.

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4. Basis Set

- PAO.BasisSize SZ: Single-zeta (minimal basis) → Fast but less accurate.

- PAO.EnergyShift 200 meV:
    - Determines basis size → lower shift = larger basis.
    - Physical Implication: 200 meV is moderate (typical: 50–300 meV).
- PAO.SplitNorm 0.15:
    - Adds polarization orbitals → improves bonding description.

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5. K-Point Sampling

- kgrid_Monkhorst_Pack 1×2×2:
    - Sparse grid → Used for large systems (703 atoms).
    - Physical Implication: Balances accuracy vs. cost; fine for structural relaxation.
- KgridCutoff 10.0 Ang:
    - Alternative k-point sampling → 10 Å cutoff ensures sufficient Brillouin zone sampling.

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6. Optical Properties

- OpticalCalculation .true.:
    - Computes dielectric function (for UV-Vis spectra).
- Optical.Broaden 0.25 eV:
    - Lorentzian broadening → mimics experimental spectra.
- Optical.Mesh 5×5×5:
    - Denser k-grid for optical properties → needed for accurate transitions.

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7. Population Analysis

- WriteMullikenPop:
    - Mulliken charges → qualitative atomic charges.
- WriteHirshfeldPop:
    - Hirshfeld charges → more robust partitioning.
- SaveBaderCharge:
    - Bader analysis → topological charge partitioning (accurate but expensive).

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8. Molecular Dynamics (MD) & Relaxation

- MD.TypeOfRun cg:
    - Conjugate-gradient relaxation → finds nearest local minimum.
- MD.MaxForceTol 0.05 eV/Å:
    - Force convergence threshold → tight tolerance for precise geometry.
- MD.MaxCGDispl 0.1 Å:

- Limits step size → avoids large, unstable moves.

The last part… OPTICAL

Resumen de relaciones clave

- $\varepsilon'' = 2n\kappa$
- $\kappa = \dfrac{\varepsilon''}{2n}$
- $A = \left(\dfrac{4\pi}{\lambda} \cdot \dfrac{\varepsilon''}{2n}\right) d = \left(\dfrac{2\pi\varepsilon''}{n\lambda}\right) d$

1. OpticalCalculation .true.

Physics:

- Enables the calculation of the **optical response** of the system, i.e., how light (photons) interacts with the material.
- Computes the **dielectric function**
- ϵ(ω)
- $\epsilon(\omega)$, which describes:
  - **Light absorption** (imaginary part,
  - Im[ϵ(ω)]
  - Im[$\epsilon(\omega)$]).
  - **Refraction** (real part,
  - Re[ϵ(ω)]
  - Re[$\epsilon(\omega)$]).

Example:

- For **SiO_2**, this predicts its transparency in the visible range or UV absorption.

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2. Optical.Broaden 0.25 eV

Physics:

- Introduces a **Lorentzian broadening** of 0.25 eV to mimic experimental effects:
  - **Finite lifetime of excitons** (electron-hole pairs).
  - Material imperfections (disorder, impurities).
  - Limited resolution of measurement instruments.

Why 0.25 eV?

- Typical for **semiconductors/insulators** (e.g., silicon).
- For **metals**, use smaller values (e.g., 0.1 eV) due to abrupt electron response near the Fermi level.

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3. Optical.Mesh 5 5 5

Physics:
- Defines a **specific k-point grid** for optical calculations, separate from the ground-state calculation.
- **Why denser than the SCF grid?**
    - Optical transitions depend on **small energy differences** between bands, requiring finer sampling of the Brillouin zone.

Example:
- In a semiconductor like GaAs, a direct bandgap transition needs a dense grid to capture the gap accurately.

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4. Optical.OffsetMesh .true.

Physics:
- Shifts the k-point grid **away from the Γ-point** (center of the Brillouin zone).
- **Purpose**:
    - Critical transitions in some materials occur **away from Γ** (e.g., silicon's indirect gap between Γ and X).
    - Avoids **underestimating absorption** if only Γ is sampled.

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5. Optical.PolarizationType polycrystal

Physics:
- Averages the optical response over **all polarizations** (x, y, z).
- **Useful for**:
    - **Amorphous materials** (glasses).
    - **Powders or non-oriented samples** (as in real experiments).
- **Alternatives**:
    - x, y, z: For anisotropic crystals (e.g., graphene absorbs differently in-plane vs. out-of-plane).

Output of the Calculation

1. **Absorption spectrum**:
    - Im[ϵ(ω)]
    - Im[$\epsilon(\omega)$] vs. energy (eV). Shows which light wavelengths the material absorbs.

2. **Refractive index**:
    - Re[ϵ(ω)]
    - Re[$\epsilon(\omega)$] relates to
    - n
    - n (how much light bends).

Practical example:

- For **TiO_2**, you'd see an absorption peak near 3 eV (UV), explaining its use in sunscreens.

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1. K-Point Sampling (KgridCutoff)
KgridCutoff 10.0 Ang
What it does:
Defines the k-point grid density based on a real-space cutoff distance (10.0 Å).

Physics:

Larger cutoff → sparser k-grid (fewer k-points).

Smaller cutoff → denser k-grid (more k-points).

10.0 Å is a moderate value, balancing accuracy and computational cost.

Why use it?
Alternative to manual kgrid_Monkhorst_Pack specification. Useful for automatically adapting k-points to cell size.

2. Optical Properties Calculation
OpticalCalculation .true.
Purpose:
Enables calculation of the frequency-dependent dielectric function (for UV-Vis spectra, absorption, etc.).

Key Parameters:
a) Broadening (Optical.Broaden)
Optical.Broaden 0.25 eV
What it does:
Adds a Lorentzian broadening (0.25 eV) to simulate experimental spectra.

Physics:

Accounts for lifetime effects and instrumental resolution.

0.25 eV is typical for solids (resembles room-temperature broadening).

b) Energy Range (Commented Out)

###Optical.EnergyMinimum 0.0 eV
###Optical.EnergyMaximum 20.0 eV
Default behavior:

If not specified, SIESTA calculates spectra over a default range (usually 0–20 eV).

Why comment it?
User may prefer defaults or later post-processing adjustments.

c) k-Mesh for Optical Properties (Optical.Mesh)
%block Optical.Mesh
  5 5 5
%endblock Optical.Mesh
What it does:
Uses a 5×5×5 k-point grid for dielectric calculations.

Physics:

Optical transitions require denser k-grids than ground-state calculations.

5×5×5 is a minimum for qualitative spectra; higher (e.g., 10×10×10) improves accuracy.

d) Offset Mesh (Optical.OffsetMesh)
Optical.OffsetMesh .true.
Purpose:
Shifts the k-mesh away from Γ-point (origin) to avoid symmetry-related artifacts.

Why?

Some systems (e.g., metals) need off-Γ sampling for accurate optical transitions.

e) Polarization Type (Optical.PolarizationType)
Optical.PolarizationType polycrystal
What it does:
Averages dielectric response over all polarizations (isotropic approximation)