

3.021 Quantum Modeling Problem Set 5

PLEASE NOTE: For all calculations of gaps, use a “scissor shift” as we discussed in class, by adding **0.9 eV** to rigidly shift the unoccupied states higher in energy.

1. Efficiency of solar thermal fuels

In this problem, we will explore the energy density of two different solar thermal fuels candidate materials. For parts (b) and (c) we will assume that only the trans state is photoactive (i.e., can be made to switch upon light absorption).

(a) Download the coordinate files for the cis and trans states of two different candidate fuels, labeled creatively fuel1 and fuel2. Using the Siesta tool on the nanoHUB, compute the amount of energy that each fuel can store per molecule. Be sure to explain how you converged your results. Compute the maximum energy density of fuel1 and fuel2, either gravimetric or volumetric.

(b) Now download the solar spectrum data (file labeled “thesun”). Using only the values for the gaps that you computed, calculate the maximum amount of the sun’s energy each fuel can convert. Use the spectrum corresponding to the radiation at sea level.

from the nanoHUB simulations) to calculate the maximum amount of the sun’s energy each fuel can convert. Is this different than the values from part (b)? If yes, please explain.

2. Yield in solar thermal fuels

Now we learn that the cis state is also photoactive!

(a) Using only your computed values of the energy gap, compute the photostationary state for fuel1 and fuel2. What percentage of each fuel can be converted into the cis state? The equations from the end of lecture 5 will be useful here.

(b) Using your computed total density of states, now calculate the photostationary state (and thus the yields) for fuel1 and fuel2. If different than (a) please comment.

3. Optimizing the energy density in solar thermal fuels

Finally, we would like to make a general statement about the relationship between the amount of energy a candidate solar thermal fuel can store per molecule (ΔH) and its maximum efficiency (η_{\max}) at converting the sun’s energy into latent heat in order to design

a fuel with the largest possible energy density. The maximum efficiency is obtained when the longest wavelength of light that induces trans \rightarrow cis photoisomerization (λ_{max}) is equal to the HOMO-LUMO gap of the molecule (E_{gap}). For any candidate, E_{gap} must be equal to or larger than ΔH , so we can say that we obtain η_{max} when $hc/\lambda_{\text{max}} = \Delta H$.

(a) Explain why hc/λ_{max} must be larger than ΔH .

(b) Using the solar spectrum data plot the maximum efficiency of a solar thermal fuel for $0 < \Delta H < 3$ eV. [Hint: Use the spreadsheet to obtain numerical values for h_{max} at increments of, e.g., 0.2 eV.] Assume that only the trans state is photoactive.

(c) Assume you have enough molecules to absorb all of the solar photons over some time period. Given the efficiencies found in (b), determine the maximum "effective energy density" (i.e., energy density*efficiency) for the same range of ΔH . Assume a molecular weight of 200 g/mol. What is the value of ΔH that gives the largest effective energy density in this picture?

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