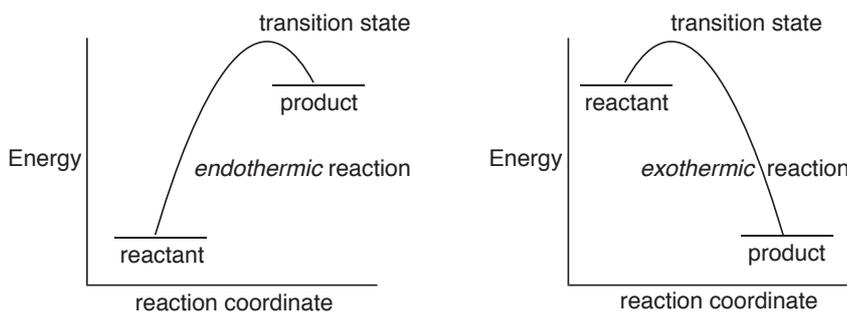


## LOCAL IONIZATION POTENTIAL MAPS AND LUMO MAPS: ELECTROPHILIC AND NUCLEOPHILIC REACTIVITIES

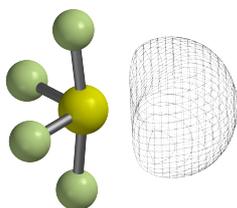
The Hammond Postulate states that the transition state in a (one-step) reaction will more closely resemble the side of the reaction that is higher in energy. Thus, the transition state of an *endothermic* reaction will more closely resemble the products, and the transition state of an *exothermic* reaction will resemble the reactants. One way to rationalize the Hammond postulate is to suggest that similarity in energy implies similarity in structure. That is, the transition state will resemble whichever reactants or products to which it is closer in energy. As seen in the reaction coordinate diagrams below this is the product in an *endothermic* reaction and the reactants in an *exothermic* reaction.



The Hammond Postulate provides a conceptual basis both for the Fukui-Woodward-Hoffmann rules (see the topic *Atomic and Molecular Orbitals*) and for the use of graphical models. Both consider the properties of reactants as an alternative to direct calculations of transition states and reaction pathways as a way to assess chemical reactivity and selectivity. In this context, two models stand out as being particularly useful: the local ionization potential map for electrophilic reactions and (with some caveats) the LUMO map for nucleophilic reactions.

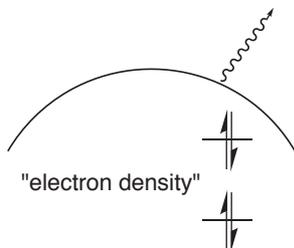
## Local Ionization Potential Maps and Electrophilic Reactivity

The local ionization potential provides a measure of the relative ease of electron removal (ionization) at any location around a molecule. For example, a surface of low local ionization potential for sulfur tetrafluoride demarks the areas which are most easily ionized, and is clearly recognizable as a lone pair on sulfur.

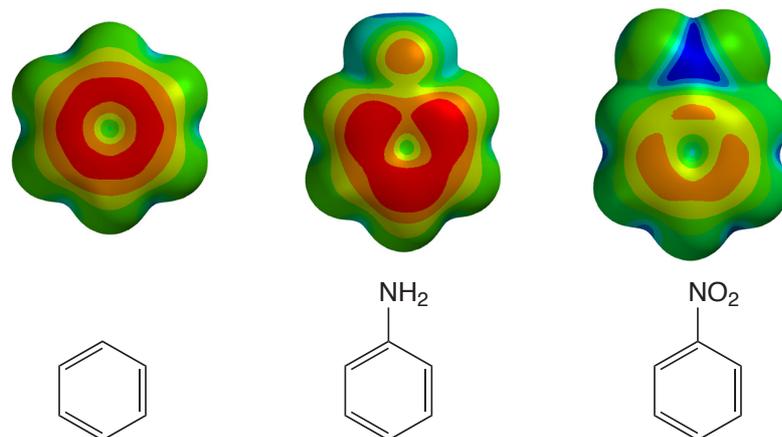


local ionization potential for sulfur tetrafluoride

While the local ionization potential by itself is not a particularly useful model, a map of the local ionization potential onto an electron density surface (a local ionization potential map) has proven to be of value in revealing regions from which electrons are most easily ionized and susceptible to electrophilic attack.



For example, they show both the positional selectivity in electrophilic aromatic substitution ( $\text{NH}_2$  directs *ortho/para*, and  $\text{NO}_2$  directs *meta*), and the fact that  $\pi$ -donor groups ( $\text{NH}_2$ ) activate benzene while electron-withdrawing groups ( $\text{NO}_2$ ) deactivate benzene.

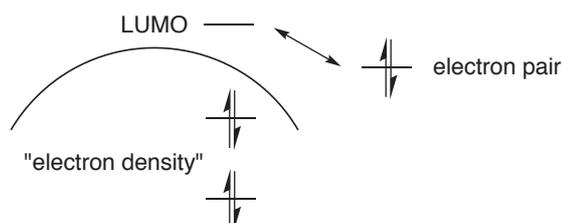


local ionization potential maps for benzene (left), aniline (center) and nitrobenzene (right)

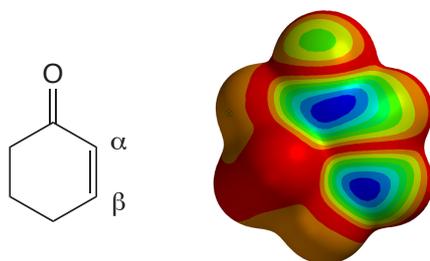
Open *benzene, aniline, nitrobenzene local ionization potential maps* in the *topics* directory. Here, the color red corresponds to regions of lowest ionization potential (most accessible to electrophiles). Note, that the  $\pi$  system in aniline is more accessible than the  $\pi$  system in benzene (the standard) and that the *ortho* and *para* positions are more accessible than *meta* positions. Note also, that the  $\pi$  system in nitrobenzene is less accessible than the  $\pi$  system in benzene and that here the *meta* positions are more accessible than the *ortho* and *para* positions, in accord with observation. Close *benzene, aniline, nitrobenzene local ionization potential maps* when you are finished.

## LUMO Maps and Nucleophilic Reactivity

As elaborated in the topic *Atomic and Molecular Orbitals*, the energies and shapes of the frontier molecular orbitals may anticipate chemistry of a molecule. Molecular orbital maps may also lead to informative models. The most common of these is the so-called LUMO map, in which the (absolute value) of the LUMO is mapped onto an electron density surface. This anticipates where an electron pair (a nucleophile) might attack.

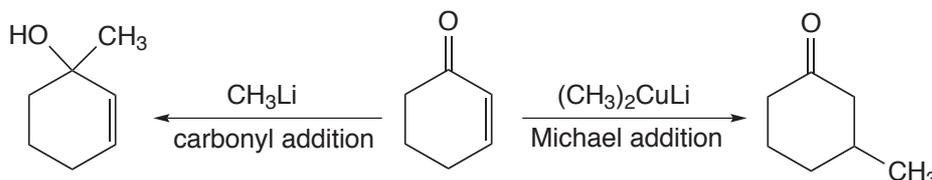


A good example is provided by the LUMO map for cyclohexenone.



LUMO map for cyclohexenone showing positions for nucleophilic attack in blue

The LUMO shows which regions of a molecule are most electron deficient, and hence most subject to nucleophilic attack. In this case, one such region is over the carbonyl carbon, consistent with the observation that carbonyl compounds undergo nucleophilic addition at the carbonyl carbon. Another region is over the  $\beta$  carbon, again consistent with the known chemistry of  $\alpha,\beta$ -unsaturated carbonyl compounds, in this case conjugate or Michael addition.



The buildup of positive charge on the  $\beta$  carbon leading to possibility of Michael addition could have been anticipated from resonance arguments, although the LUMO map, like an experiment, has the advantage of showing the result (“you don’t have to ask”).

Open *cyclohexenone LUMO map* in the *topics* directory and *click* on the resulting surface. Switch to a mesh or transparent surface in order to see the underlying skeletal model. On Windows, *click* on the graphic and select **Mesh** or **Transparent** from the menu which appears at the bottom right of the screen. On the Mac, position the cursor over the graphic, hold down on either the left or right button and select from the menu which appears alongside. Orient the molecule such that the two “blue regions” are positioned over the appropriate carbons and then switch back to a solid surface. Close *cyclohexenone LUMO map* when you are finished.

Some caution needs to be exercised. Specifically the LUMO may not be the important molecular orbital for the chemical reaction of interest, and it may be necessary to base the map on a higher-energy unoccupied molecular orbital (LUMO+1, LUMO+2, ...).