

### 3. Discussion of the Hartree-Fock Equations

#### I. Solving the Hartree-Fock Equations

We summarize the results of the preceding derivation. Given a set of orthogonal and normalized spin-orbitals that form a complete set,  $\{\psi_i\}_{i=1}^{\infty}$ , we label the orbitals that are included in the Slater determinant of interest,  $\Phi_{sl} \equiv |\psi_1 \dots \psi_N|$  as the occupied orbitals. The other orbitals we refer to as *unoccupied* or *virtual* orbitals—virtual because an orbital represents the state of an electron, and so an unoccupied state is, indeed, not a real state of an electron, but only a “virtual” one. So that we can describe the stationary states—both the ground and excited states—of the system using Slater determinants, we force the energy to be stationary with respect to the variation of the occupied orbitals; this gave us the Hartree-Fock equations,

$$\begin{aligned} \left\{ -\frac{\nabla^2}{2} + v(\mathbf{r}) + j \left[ \{\psi_i\}_{i=1}^N; \mathbf{r} \right] - \hat{k} \left[ \{\psi_i\}_{i=1}^N; \mathbf{z} \right] \right\} \psi_{\alpha}(\mathbf{z}) &\equiv \varepsilon_{\alpha} \psi_{\alpha}(\mathbf{z}) \\ \hat{f} \left[ \{\psi_i\}_{i=1}^N; \mathbf{z} \right] \psi_{\alpha}(\mathbf{z}) &= \varepsilon_{\alpha} \psi_{\alpha}(\mathbf{z}) \end{aligned} \quad (3.1)$$

where  $\hat{f}$  denoted the Fock operator. Note that all of the key contributions to the energy of an electronic system are represented: the kinetic energy of the electron, the nuclear-electron attraction, the Coulomb repulsion between orbitals, and the favorable “exchange” effects for same-spin electrons endowed by virtue of the Pauli exclusion principle. Note that there is no detailed dependence on the distance between the electrons: the repulsion potential felt by an electron in the  $\alpha^{th}$  orbital due to an electron in the  $\beta^{th}$  orbital,  $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$ , has been replaced by its average value,  $\int \frac{|\psi_{\beta}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$ . For this reason, Hartree-Fock theory is said to be a *mean-field theory*. (A similar mean-field theory is used to derive the van der Waal’s equation of state for an imperfect gas.) Because electrons in a Slater determinant are uncorrelated, they can be considered to move independently. Hartree-Fock theory, then, is also an example of an *independent-particle model*.

Compared to the full Schrödinger equation for a many-electron system, the Hartree-Fock equations look very simple indeed. In fact, the Hartree-Fock equations look very similar to the Schrödinger equation for a one-electron system, which is the advantage we glean from using a very simple approximate wavefunction—the Slater determinant—to model our system. However, solving the Hartree-Fock equations for the occupied (and, if

desired, the unoccupied) orbitals is more difficult than finding the eigenvalues and eigenvectors of a one-electron system because the Hamiltonian for the  $\alpha^{th}$  orbital depends on the values of the other orbitals in the system,  $\psi_{i \neq \alpha}(\mathbf{r})$ , through the Coulomb and exchange potentials.

How does one solve an eigenvalue problem like the Hartree-Fock equations,

$$\hat{f}[\{\psi\}; \mathbf{r}] \psi_\alpha(\mathbf{z}) = \varepsilon_\alpha \psi_\alpha(\mathbf{z}) ? \quad (3.2)$$

You may recall a similar situation (van der Waal's equations; fixed point iteration).

The usual method is to

1. “Guess” an initial Slater determinant of orbitals,  $\Phi^{(in)} \equiv |\psi_1^{(in)} \dots \psi_N^{(in)}|$ .
2. Construct the Coulomb,  $j[\{\psi^{(in)}\}; \mathbf{r}]$ , and exchange,  $\hat{k}[\{\psi^{(in)}\}; \mathbf{z}]$ , potentials using the orbitals from this Slater determinant.
3. Construct the Fock operator. Now the Hartree-Fock equations are just a series of one-electron eigenvalue problems, Eq. (3.1), and we can solve them. One obtains a new set of orbitals,  $\{\psi_i^{(out)}\}$ , since

$$\hat{f}[\{\psi^{(in)}\}; \mathbf{r}] \psi_\alpha^{(out)}(\mathbf{z}) = \varepsilon_\alpha^{(out)} \psi_\alpha^{(out)}(\mathbf{z}) \quad (3.3)$$

4. There are two possibilities.
  - It could be that the “new” orbitals and the “old” orbitals are the same—or at least similar enough that we can consider the problem to be “solved.” That is, if

$$\psi_\alpha^{(in)}(\mathbf{z}) \approx \psi_\alpha^{(out)}(\mathbf{z}) \quad (3.4)$$

for all  $\alpha$ , then substitution of Eq. (3.4) into Eq. (3.3) implies that

$$\hat{f}[\{\psi^{(out)}\}; \mathbf{r}] \psi_\alpha^{(out)}(\mathbf{z}) \approx \varepsilon_\alpha^{(out)} \psi_\alpha^{(out)}(\mathbf{z}) \quad (3.5)$$

(or, if you prefer,  $\hat{f}[\{\psi^{(in)}\}; \mathbf{r}] \psi_\alpha^{(in)}(\mathbf{z}) \approx \varepsilon_\alpha^{(in)} \psi_\alpha^{(in)}(\mathbf{z})$ ). But this implies that we actually have solved the Hartree-Fock equations, Eq. (3.2), to the desired accuracy.

- The second possibility is that the difference between the “output” orbitals,  $\{\psi_i^{(out)}\}$ , and the “input” orbitals,  $\{\psi_i^{(in)}\}$ , is unacceptably large. In this case, we know that the Hartree-Fock equations are not solved by the “input” orbitals, and we should try to improve the orbitals in some way. The simplest method—not a very good method at all—is to simply take the “output” orbitals and use them the revised “guess” for the “input” orbitals,

$$\psi_i^{(in)}(\mathbf{z}) \leftarrow \psi_i^{(out)}(\mathbf{z}). \quad (3.6)$$

then one goes back to step 2, and repeats the process until eventually the “input” and “output” orbitals are “close enough” for our purposes.

When the process converges, we say that the orbitals,  $\{\psi_i^{(out)}\}$  and the potential,  $v(\mathbf{r}) + j[\{\psi^{(in)}\}; \mathbf{r}] + \hat{k}[\{\psi^{(in)}\}; \mathbf{z}]$  are “self-consistent” or non-contradictory. Recalling that the electric field is simply the negative gradient of the potential, Hartree-Fock is thus said to be a *self-consistent field* (SCF) method: *at convergence, the field induced by the orbitals,  $-\nabla\left(v(\mathbf{r}) + j[\{\psi^{(in)}\}; \mathbf{r}] + \hat{k}[\{\psi^{(in)}\}; \mathbf{z}]\right)$  and the orbitals induced by the field through Eq. (3.3), are one and the same or, to use the technical term, consistent.*

Once the Hartree-Fock equations have been solved, we can construct the Hartree-Fock wave function by forming a determinant of the occupied Hartree-Fock orbitals,  $\Phi_{HF} \equiv |\psi_1^{(HF)} \dots \psi_N^{(HF)}|$ . The energy of this Slater determinant is given by

$$E_{HF}[\Phi_{HF}] \equiv \sum_{i=1}^N \left( h_i + \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij}) \right). \quad (3.7)$$

(Because they are eigenfunctions of a one-electron Hamiltonian, Eq. (3.2), we always choose the Hartree-Fock orbitals to be orthogonal and normalized.)

## II. Interpreting the Hartree-Fock Orbitals and Orbital Energies

Two of the most useful concepts in chemistry are the concept of orbitals and their energies. We may rightly ask, then: What do the Hartree-Fock orbitals and orbital energies mean? We address this question here, dispelling some prevalent myths as we go along.

### A. The total energy is not the sum of the orbitals’ energies

If you put  $N$ -electrons in  $N$ -orbitals to model a system, you might suspect that the energy of the system is just the sum of all the orbital energies. This is true for some *very* primitive models, but not in Hartree-Fock theory. Comparing the energy formula, Eq. (3.7), with the expression for the sum of orbital energies obtained from the definition,

$$\sum_{i=1}^N \varepsilon_i \equiv \sum_{i=1}^N \left( h_i + \sum_{j=1}^N (J_{ij} - K_{ij}) \right). \quad (3.8)$$

we see that

$$E_{HF} = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}). \quad (3.9)$$

The reason is because there is a “double counting” of electron-electron repulsions in Eq. (3.8): the energy of an orbital is the kinetic energy plus electron-nuclear attraction energy plus the electron-electron repulsion (with exchange corrections) to all the other orbitals in the system. However, *in the total energy formula, we count the electron repulsion between orbitals  $i$  and  $j$  only once—not once for  $\psi_i(\mathbf{r})$  interacting with  $\psi_j(\mathbf{r})$  and a second time for  $\psi_j(\mathbf{r})$  interacting with  $\psi_i(\mathbf{r})$ , as in Eq. (3.8).*

Based on the preceding argument, and using the fact  $J_{ij} > K_{ij}$ , we see that *if you assume the total energy is the sum of the orbital energies, you obtain an energy that is too big.* Indeed, the energy so computed is usually *extremely* poor.

At first, the result in Eq. (3.9) may be counterintuitive: shouldn’t the electronic energy of a molecule be the sum of the energies of the composing electrons? Equation (3.9) says this is not the case, but gives us little insight into *why* it is not the case. To make this a bit more clear, suppose his kind students enroll your professor in the local chapter of Misanthropes Anonymous.

## **B. The energy it takes to excite an electron from an occupied orbital, $\psi_i(z)$ , to a unoccupied orbital, $\psi_a(z)$ , is not equal to the difference in the orbital energies, $\varepsilon_a - \varepsilon_i$ .**

We can approximate the Hartree-Fock wave function for an excited state of the system by replacing an occupied orbital with an unoccupied orbital in the Hartree-Fock wave function, obtaining the Slater determinant

$$\Phi_i^a \equiv |\psi_1 \dots \psi_{i-1} \psi_a \psi_{i+1} \psi_{i+2} \dots \psi_N|. \quad (3.10)$$

Note that this Slater determinant is not stationary with respect to the energy: because of the self-consistency requirement, exciting an electron changes the Fock operator, which causes the orbitals to change. When we skip the self-consistent procedure that produces this “revision” in the orbitals due to the excitation, we say that we have neglected *orbital relaxation*. Neglecting orbital relaxation, the excitation energy can be approximated with

$$E_{exc.}^{i \rightarrow a} \approx \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle - \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle \quad (3.11)$$

and, using the formula for the energy of a Slater determinant, Eq. (3.7), we obtain

$$\begin{aligned}
E_{exc}^{i \rightarrow a} &\approx E_i^a - E_{HF} \\
&\approx \left( \overbrace{\sum_{\substack{k=1 \\ k \neq i}}^N h_k + \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N \sum_{\substack{l=1 \\ l \neq i}}^N (J_{kl} - K_{kl})}^{k \neq i; l \neq i} + h_a + \frac{1}{2} \overbrace{\sum_{\substack{l=1 \\ l \neq i}}^N (J_{al} - K_{al})}^{k=a, l \neq i} + \frac{1}{2} \overbrace{\sum_{\substack{k=1 \\ k \neq i}}^N (J_{ka} - K_{ka})}^{k \neq i; l=a} \right) \\
&\quad - \left( \sum_{k=1}^N h_k + \frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (J_{kl} - K_{kl}) \right) \\
&= \left( h_a + \frac{1}{2} \left( \sum_{l=1}^N (J_{al} - K_{al}) - (J_{ai} - K_{ai}) \right) + \frac{1}{2} \left( \sum_{k=1}^N (J_{ka} - K_{ka}) - (J_{ia} - K_{ia}) \right) \right) \\
&\quad - \left( -h_i - \frac{1}{2} \overbrace{\sum_{\substack{k=1 \\ k \neq i}}^N (J_{ki} - K_{ki})}^{l=i} - \frac{1}{2} \overbrace{\sum_{\substack{l=1 \\ l \neq i}}^N (J_{il} - K_{il})}^{k=i} - \overbrace{(J_{ii} - K_{ii})}^{k=l=i} \right) \\
&= \left( h_a + \sum_{k=1}^N (J_{ka} - K_{ka}) - (J_{ai} - K_{ai}) \right) \\
&\quad - \left( -h_i - \sum_{k=1}^N (J_{ki} - K_{ki}) - 0 \right) \\
&= \varepsilon_a - \varepsilon_i - (J_{ai} - K_{ai})
\end{aligned} \tag{3.12}$$

The excitation energy is less than the difference in orbital energies because exciting an electron from an occupied orbital leaves a “vacancy” in the electron distribution the system—a place where electrons are well stabilized (as evidenced by the occupied orbital in that vicinity) but which is, in the excited state, vacant. The excited state orbital is “attracted” to this region, which accounts for the  $J_{ai} - K_{ai}$  term:

$$-(J_{ia} - K_{ia}) \equiv - \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_a(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \delta_{\sigma_a \sigma_i} \iint \frac{\psi_a^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \psi_a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{3.13}$$

Note that because  $K_{ai} > 0$  unless the spins of the orbitals,  $\psi_a(\mathbf{z})$  and  $\psi_i(\mathbf{z})$ , are different, we conclude that if the  $\alpha$ -spin and  $\beta$ -spin orbitals are the same, as they are for a triplet state, then flipping the spin of the electron (to form a triplet excited state) gives a smaller excitation energy. This predicts that triplet excited states will be more stable than singlet excited states, which is consistent with Hund’s maximum multiplicity rule.

### C. The orbital energy of occupied orbitals are approximations to the ionization potentials of the system.

We can approximate the Hartree-Fock wave function for the stationary states of the cation by removing an occupied orbital from the Hartree-Fock wave function,

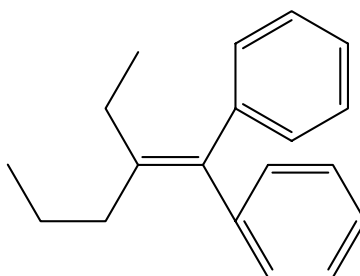
$$\Phi_i^{free} \equiv |\psi_1 \dots \psi_{i-1} \psi_{i+1} \psi_{i+2} \dots \psi_N| \tag{3.14}$$

where the notation indicates that an electron in an occupied orbital,  $\psi_i(\mathbf{r})$  is removed from the system, becoming a “free” (unbound) electron. Neglecting the subsequent relaxation of the remaining occupied orbitals in the cation, we can approximate the ionization of the neutral system to form the excited state of the cation by

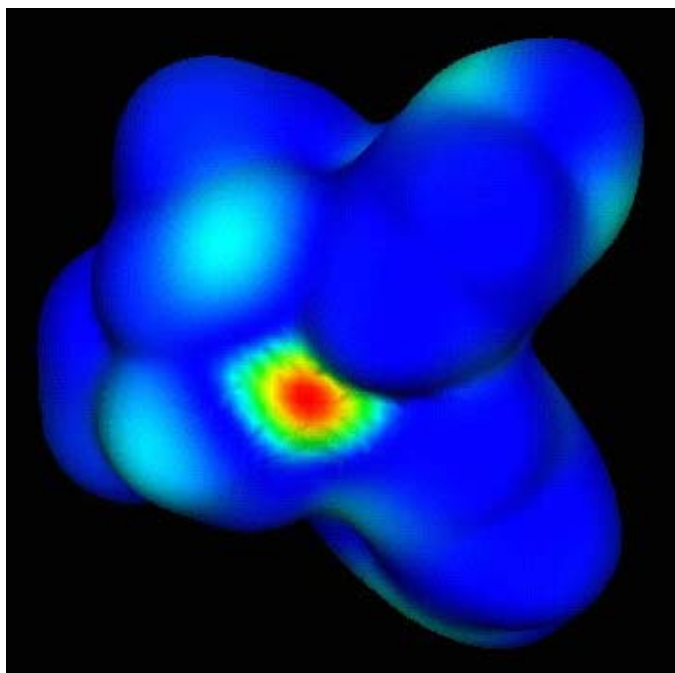
$$\begin{aligned}
I_i &\approx E_i^{free} - E_{HF} \\
&\approx \sum_{\substack{k=1 \\ k \neq i}}^N h_k + \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N \sum_{\substack{l=1 \\ l \neq i}}^N (J_{kl} - K_{kl}) - \left( \sum_{k=1}^N h_k + \frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (J_{kl} - K_{kl}) \right) \\
&= \left( -h_i - \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N (J_{ki} - K_{ki}) - \frac{1}{2} \sum_{\substack{l=1 \\ l \neq i}}^N (J_{il} - K_{il}) - (J_{ii} - K_{ii}) \right) \\
&= - \left( h_i + \sum_{\substack{k=1 \\ k \neq i}}^N (J_{ki} - K_{ki}) \right) - 0 \\
&= -\varepsilon_i
\end{aligned} \tag{3.15}$$

The fact that the orbital energies in Hartree-Fock theory approximate the negative of the ionization potentials is called *Koopmans’ theorem*. We can approximate the “way” the electron is removed from the molecule by noting that the electron has been removed from the orbital  $\psi_i(\mathbf{z})$ .

Particularly important for chemical purposes is the highest occupied molecular orbital (HOMO), because  $I_{HOMO} = -\varepsilon_{HOMO}$  is the ground state ionization potential: the minimum amount of energy it takes to remove an electron from a molecule. Molecules with large highest-occupied orbital energies (small ionization potentials) are good electron donors/nucleophiles/Lewis bases/reducing agents. The shape of the highest-occupied orbital controls the regioselectivity of the nucleophile: if  $|\psi_{HOMO}(\mathbf{r})|^2 \approx 0$  at a point, then we observe that it is difficult to remove an electron from the molecule at this point because most of the electron density at this point is associated with electrons in orbitals that are more tightly bound,  $\varepsilon_i < \varepsilon_{HOMO}$ . For example, the electrophilic attack of borane in the hydroboration reaction of 1,1-diphenyl-2-ethyl-1-butene occurs not on the negatively charged aromatic rings, but at the double bond.



Plotting the square of the highest-occupied orbital energy reveals that this, in fact, is where the most easily ionized electron is localized



**Figure.** The square of the HOMO orbital for 1,3-diphenyl-2-ethyl-1-butene

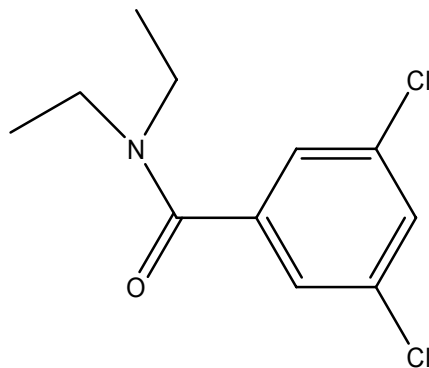
#### D. The orbital energy of unoccupied orbitals are approximations to the electron affinities of the system.

A similar analysis leads to the conclusion that the orbital energies of unoccupied orbitals corresponding to energy gained when an electron is added to the neutral system to form a stationary state (ground or excited) of the anion. That is

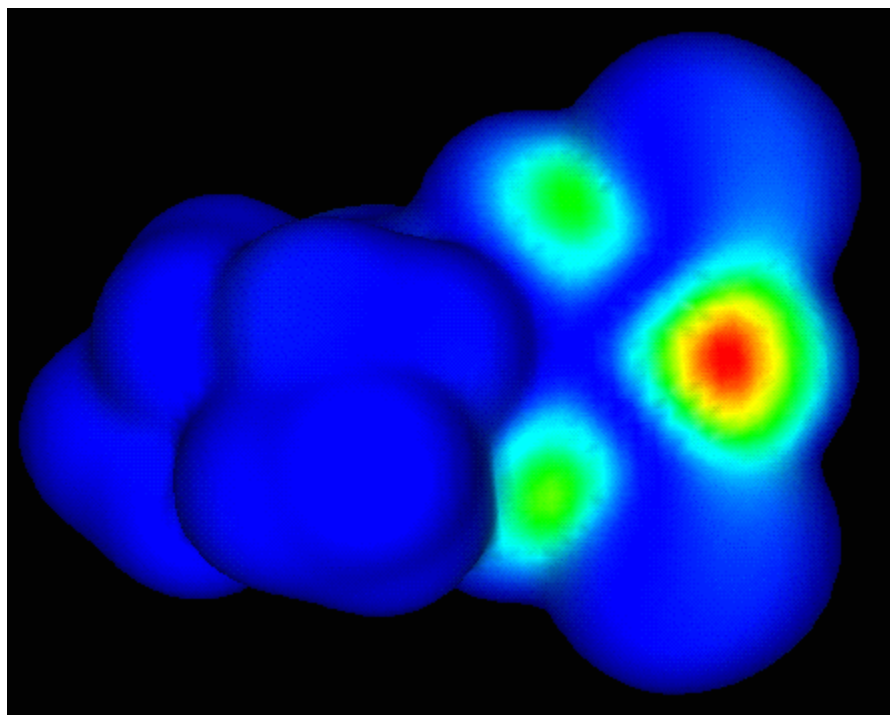
$$\begin{aligned} A_{free}^a &\approx E_{HF} - E_{free}^a \\ &\approx -\varepsilon_a \end{aligned} \tag{3.16}$$

Koopmans' theorem tends to be much less accurate for electron affinities than ionization potentials but, qualitatively accurate information is often obtained from the unoccupied Hartree-Fock orbitals. This is especially true of the lowest unoccupied orbital, which

represents the best way to add an electron to a molecule. Molecules with small lowest unoccupied orbital energies (large electron affinities) tend to be good electron acceptors/electrophiles/Lewis Acids/oxidizing agents. The shape of the lowest-unoccupied orbital controls the regioselectivity of the electrophile: if  $\psi_{LUMO}(\mathbf{r}) \approx 0$ , then adding an electron to the molecule near the point  $\mathbf{r}$  is less energetically favorable, because most of the vacant orbitals in that region have higher orbital energy than the LUMO. For example, one would expect, based on the fact that the carboxamide substituents is a powerful ortho-directing group, that a 3,5-dichloro-tertiary benzamide like the following



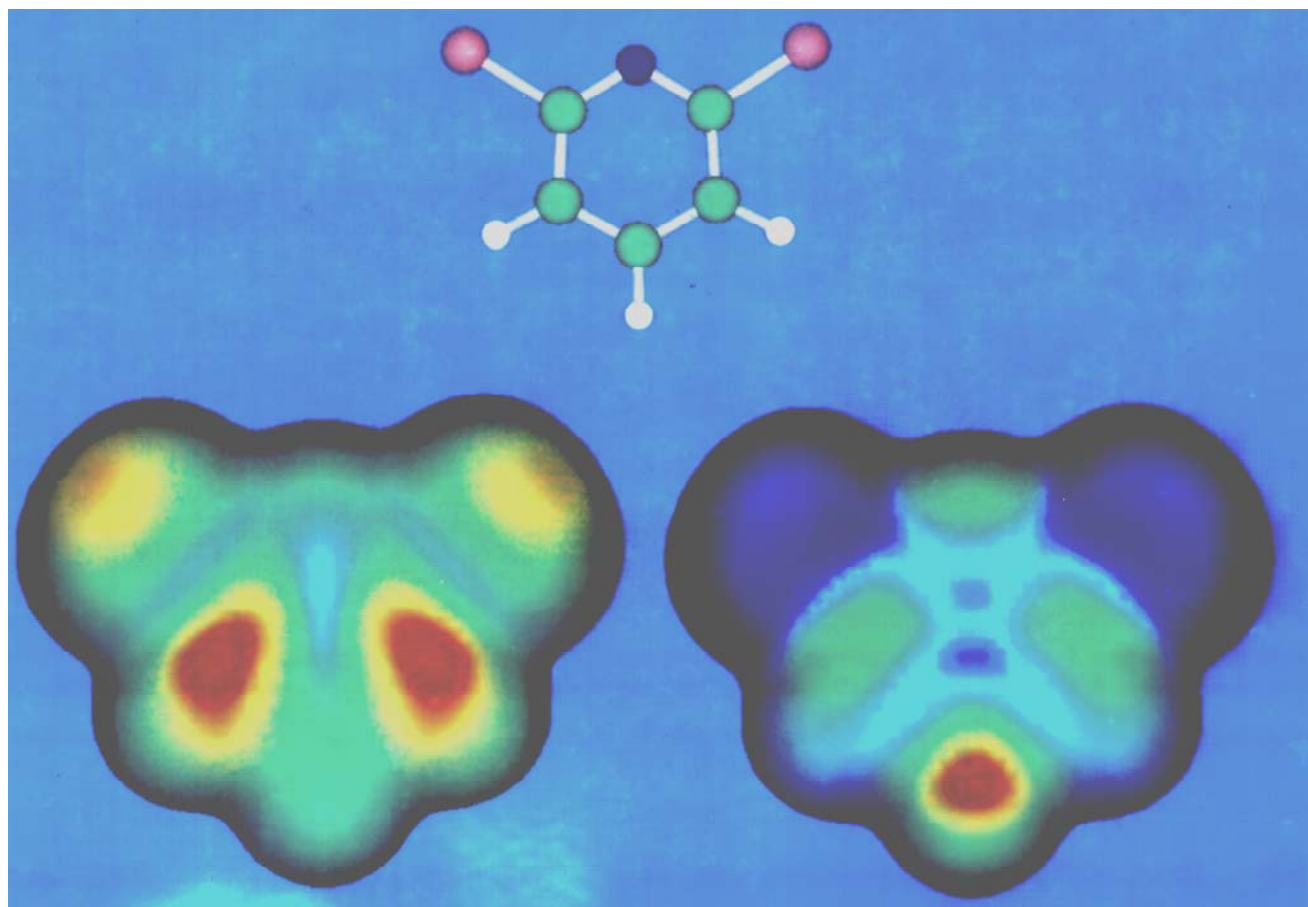
would be subject to metallation (nucleophilic attack) ortho to the carboxamide moiety. However para attack is observed, and this is consistent with the rule that electron donors will attack a complex where the amplitude of the LUMO orbital is largest.



**Figure.** Plot of  $|\psi_{LUMO}(\mathbf{r})|^2$  for a 3,5-dihalogenated benzamide.



There aren't many compounds that are subject to both nucleophilic and electrophilic attack. One of my favorites is 2,6-dichloropyridine. Most pyridines are not subject to electrophilic attack because electrophilic substitution is usually carried out in rather acidic conditions (electrophiles are Lewis Acids), wherein pyridines are protonated. Because it is difficult to take electrons from a positive species, protonated pyridines are relatively inert to electrophilic attack, and electrophilic aromatic substitution onto pyridines is quite difficult. However, the  $pK_a$  of 2-6 dichloropyridine is -2.86, so this compound usually exists in its unprotonated state. We observe electrophilic attack at the "meta" position and nucleophilic attack (which is much more common, owing to the electronegativity of nitrogen and Chlorine) at the "para" position. These trends are confirmed by the following plots of the LUMO (left) and HOMO (right) orbitals squared, respectively.

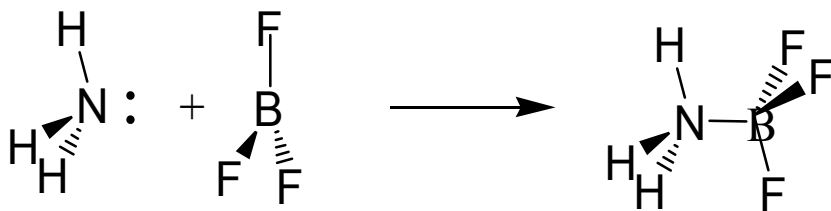


**Figure:**  $|\psi_{LUMO}(\mathbf{r})|^2$  and  $|\psi_{HOMO}(\mathbf{r})|^2$  for 2,6-dichloropyridine.

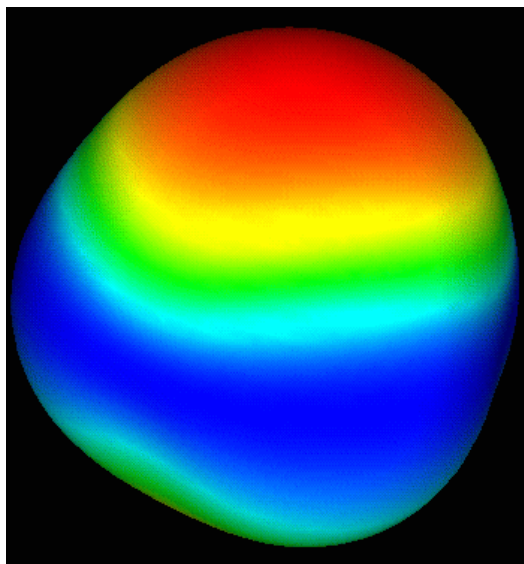
The preceding analysis is very typical of the utility of the orbital model in chemistry, and Koopmans' theorem can be considered the primary justification for the use of orbitals for describing chemical reactions: most chemical reactions are a combination between

electron transfer (ionic binding) and electron sharing (covalent binding) between different molecules. Insofar as this requires “taking electrons” from one molecule and “putting them on another” (and then, if the binding is covalent, replenishing the deficit), the orbitals and orbital energies give an accurate and useful representation of the energetics of chemical processes. For acid-base reactions, the situation is extremely simple. Electrons are removed from the base (from a high-energy occupied orbital) and put on the base (in a low-energy unoccupied orbital). The electrophilic reagent (acid) attacks the nucleophile (base) where the base has “high-energy electrons it is willing to give up”, which is exactly those locations where the orbital amplitudes of the high-energy orbitals are large. The site with which the acid attacks the base is exactly that site at which it can best stabilize the addition electrons: where the orbital magnitude of the vacant orbital is large. This is the essence of the elegantly simple, Nobel-prize-winning insights of Kenichi Fukui.

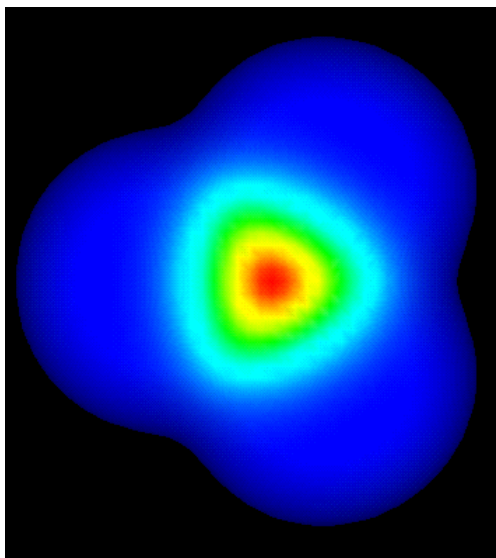
As an example, we can examine the reaction



and note that, as expected, the highest-occupied orbital of ammonia is concentrated on the nitrogen atom while the lowest unoccupied orbital of Boron trifluoride is concentrated on the Boron center.



**Figure.**  $|\psi_{HOMO}(\mathbf{r})|^2$  for ammonia. The red region represents the peak density, and the molecule is oriented with the nitrogens pointed down and slightly behind the plane of the paper.



**Figure.**  $|\psi_{LUMO}(\mathbf{r})|^2$  for  $\text{BF}_3$ . The boron atom is the central atom.