18.7: Observations on Orbitals and Orbital Energies

The Meaning of Orbital Energies

The physical content of the Hartree-Fock orbital energies can be seen by observing that $\hat{F}\phi = \epsilon_i\phi_i$ implies that ϵ_i can be written as:

$$\epsilon_i = \langle\phi_i|\hat{F}|\phi_i\rangle = \langle\phi_i|h|\phi_i\rangle + \sum_{j(\text{occupied})} \langle\phi_i|J_j - K_j|\phi_i\rangle = \langle\phi_i|h|\phi_i\rangle + \sum_{j(\text{occupied})} [\mathbf{J}_{i,j} - \mathbf{K}_{i,j}].$$

In this form, it is clear that ϵ_i is equal to the average value of the kinetic energy plus Coulombic attraction to the nuclei for an electron in ϕ_i plus the sum over all of the spin-orbitals occupied in Ψ of coulomb minus exchange interactions between ϕ_i and these occupied spin-orbitals.

- If ϕ_i itself is an occupied spin-orbital, the term $[\mathbf{J}_{i,i} - \mathbf{K}_{i,i}]$ disappears and the latter sum represents the coulomb minus exchange interaction of ϕ_i with all of the N-1 **other** occupied spin-orbitals.
- If ϕ_i is a virtual spin-orbital, this cancellation does not occur, and one obtains the coulomb minus exchange interaction of ϕ_i with all N of the occupied spin-orbitals.

In this sense, the orbital energies for occupied orbitals pertain to interactions which are appropriate to a total of N electrons, while the orbital energies of virtual orbitals pertain to a system with N+1 electrons. It is this fact that makes SCF virtual orbitals not optimal (in fact, not usually very good) for use in subsequent correlation calculations where, for instance, they are used, in combination with the occupied orbitals, to form polarized orbital pairs as discussed in Chapter 12. To correlate a pair of electrons that occupy a valence orbital requires double excitations into a virtual orbital that is not too dislike in size. Although the virtual SCF orbitals themselves suffer these drawbacks, the space they span can indeed be used for treating electron correlation. To do so, it is useful to recombine (in a unitary manner to preserve orthonormality) the virtual orbitals to 'focus' the correlating power into as few orbitals as possible so that the multiconfigurational wavefunction can be formed with as few CSFs as possible. Techniques for effecting such reoptimization or improvement of the virtual orbitals are treated later in this text.

Koopmans' Theorem

Further insight into the meaning of the energies of occupied and virtual orbitals can be gained by considering the following model of the vertical (i.e., at fixed molecular geometry) detachment or attachment of an electron to the original N-electron molecule:

1. In this model, **both** the parent molecule and the species generated by adding or removing an electron are treated at the single-determinant level.
2. In this model, the Hartree-Fock orbitals of the parent molecule are used to describe both the parent and the species generated by electron addition or removal. It is said that such a model neglects '**orbital relaxation**' which would accompany the electron addition or removal (i.e., the reoptimization of the spin-orbitals to allow them to become appropriate to the daughter species).

Within this simplified model, the energy difference between the daughter and the parent species can be written as follows (ϕ_k represents the particular spin-orbital that is added or removed):

1. For electron detachment:

$$E^{N-1} - E^N = \langle|\phi_1\phi_2\ldots\phi_{k-1}\ldots\phi_N|\mathbf{H}|\phi_1\phi_2\ldots\phi_{k-1}\ldots\phi_N|\rangle - \langle|\phi_1\phi_2\ldots\phi_{k-1}\phi_k\ldots\phi_N|\mathbf{H}|\phi_1\phi_2\ldots\phi_{k-1}\phi_k\ldots\phi_N|$$

$$= -\langle\phi_k|h|\phi_k\rangle - \sum_{j=(1,k-1,k+1,N)} [J_{k,j} - K_{k,j}] = -\epsilon_k;$$

2. For electron attachment:

$$E^N - E^{N+1} = \langle|\phi_1\phi_2\ldots\phi_N|\mathbf{H}|\phi_1\phi_2\ldots\phi_N|\rangle - \langle|\phi_1\phi_2\ldots\phi_N\phi_k\ldots\phi_N|\mathbf{H}|\phi_1\phi_2\ldots\phi_N\phi_k|\rangle$$

$$= -\langle\phi_k|h|\phi_k\rangle - \sum_{j=(1,N)} [J_{k,j} - K_{k,j}] = -\epsilon_k;$$

So, within the limitations of the single-determinant, frozen-orbital model set forth, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to

as Koopmans' theorem (T. Koopmans, Physica 1, 104 (1933)); it is used extensively in quantum chemical calculations as a means for estimating IPs and EAs and often yields results that are at least qualitatively correct (i.e., ± 0.5 eV).

> *Koopmans' theorem argues that the ionization potentials and electron affinities are given as the negative of the occupied and virtual spin-orbital energies, respectively.*

Orbital Energies and the Total Energy

For the N-electron species whose Hartree-Fock orbitals and orbital energies have been determined, the total SCF electronic energy can be written, by using the Slater-Condon rules, as:

$$E = \sum_{i(occupied)} \langle \phi_i | h | \phi_i \rangle + \sum_{i>j(occupied)} [J_{i,j} - K_{i,j}].$$

For this same system, the sum of the orbital energies of the occupied spin-orbitals is given by:

$$\sum_{i(occupied)} \epsilon_i = \sum_{i(occupied)} \langle \phi_i | h | \phi_i \rangle + \sum_{i,j(occupied)} [J_{i,j} - K_{i,j}].$$

These two seemingly very similar expressions differ in a very important way; the sum of occupied orbital energies, when compared to the total energy, double counts the coulomb minus exchange interaction energies. Thus, within the Hartree-Fock approximation, the sum of the occupied orbital energies is **not** equal to the total energy. The total SCF energy can be computed in terms of the sum of occupied orbital energies by taking one-half of $\sum_{i(occupied)} \epsilon_i$ and then adding to this one-half of $\sum_{i(occupied)} \langle \phi_i | h | \phi_i \rangle$:

$$E = \frac{1}{2} \left[\sum_{i(occupied)} \langle \phi_i | h | \phi_i \rangle + \sum_{i(occupied)} \epsilon_i \right].$$

The fact that the sum of orbital energies is not the total SCF energy also means that as one attempts to develop a qualitative picture of the energies of CSFs along a reaction path, as when orbital and configuration correlation diagrams are constructed, one must be careful not to equate the sum of orbital energies with the total configurational energy; the former is higher than the latter by an amount equal to the sum of the coulomb minus exchange interactions.

> *The sum of orbital energies is not the total SCF energy.*

The Brillouin Theorem

The condition that the SCF energy be stationary with respect to variations $\delta\phi_i$ in the occupied spin-orbitals (that preserve orthonormality) can be written

$$\langle |\phi_1 \ldots \delta\phi_i \ldots \phi_N | \mathrm{H} | \phi_1 \ldots \phi_i \ldots \phi_N | \rangle = 0.$$

The infinitesimal variation of ϕ_i can be expressed in terms of its (small) components along the other occupied ϕ_j and along the virtual ϕ_m as follows:

$$\delta\phi_i = \sum_{j=\infty} U_{ij}\phi_j + \sum_m U_{im}\phi_m.$$

When substituted into $|\phi_1 \ldots \delta\phi_i \ldots \phi_N$, the terms $\sum_{j'=occ} |\phi_1 \ldots \phi_j \ldots \phi_N| U_{ij}$ vanish because ϕ_j already appears in the original Slater determinant $|\phi_1 \ldots \phi_N|$,so $|\phi_1 \ldots \phi_j \ldots \phi_N|$ contains ϕ_j twice. Only the sum over virtual orbitals remains, and the stationary property written above becomes

$$\sum_m U_{im} \langle |\phi_1 \ldots \phi_m \ldots \phi_N | H | \phi_1 \ldots \phi_i \ldots \phi_N | \rangle = 0.$$

The Slater-Condon rules allow one to express the Hamiltonian martix elements appearing here as

$$\langle |\phi_1 \ldots \phi_m \ldots \phi_N | \mathrm{H} | \phi_1 \ldots \phi_i \ldots \phi_N | \rangle = \langle \phi_m | h | \phi_i \rangle + \sum_{j=occ,\neq i} \langle \phi_m | [J_j - K_j] | \phi_i \rangle,$$

which (because the term with j=i can be included since it vanishes) is equal to the following element of the Fock operator: $\langle \phi_m | F | \phi_i \rangle = \epsilon_i \delta_{im} = 0$. This result proves that Hamiltonian matrix elements between the SCF determinant and those that are singly excited relative to the SCF determinant vanish because they reduce to Fock-operator integrals connecting the pair of orbitals involved in the 'excitation'. This stability property of the SCF energy is known as the Brillouin theorem (i.e., that $|\phi_1 \phi_i \phi_N|$ and $|\phi_1 \ldots \phi_m \ldots \phi_N|$ have zero Hamiltonian matrix elements **if** the ϕs are SCF orbitals). It is exploited in quantum chemical calculations in two manners:

1. *When multiconfiguration wavefunctions are formed from SCF spin-orbitals, it allows one to neglect Hamiltonian matrix elements between the SCF configuration and those that are 'singly excited' in constructing the secular matrix.*
2. *A so-called generalized Brillouin theorem (GBT) arises when one deals with energy optimization for a multiconfigurational variational trial wavefunction for which the orbitals and CI mixing coefficients are simultaneously optimized. This GBT causes certain Hamiltonian matrix elements to vanish, which, in turn, simplifies the treatment of electron correlation for such wavefunctions. This matter is treated in more detail later in this text.*