Appendix E: Multiconfigurational methods

This chapter is adapted from Chapters 8 and 9 of the book 'Multiconfigurational Quantum Chemistry' by Björn Roos et al., published by Wiley.

1 Why multiconfigurational wave functions?

We start with a more detailed analysis of the H_2 molecule. We use a minimal basis set in this study with one 1s function on each atom: $\psi_A \equiv 1s_A$ and $\psi_B \equiv 1s_B$ on the atoms A and B, respectively. From these atomic functions, we can construct bonding and antibonding spatial molecular orbitals (MO)

$$\sigma = N(\psi_A + \psi_B) \tag{1}$$
$$\sigma^* = N(\psi_A - \psi_B) \tag{2}$$

by taking their symmetric and antisymmetric combinations, respectively. The bonding orbital is in the RHF model assumed to be doubly occupied leading to a total wave function of the form

$$|\Phi_0\rangle = |\sigma\bar{\sigma}\rangle = \sigma(\mathbf{r}_1)\sigma(\mathbf{r}_2)\Theta_{2,0}, \tag{3}$$

which we shall simply denote as $(\sigma)^2$ and where

$$\Theta_{2,0} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \tag{4}$$

is the singlet (S = 0) antisymmetric spin function for two electrons.

The exact ground state wave function for H_2 is at the equilibrium geometry strongly dominated by a single electronic configuration, $(\sigma)^2$. The (σ) orbital is a bonding orbital with an increased electron density in the region between the two atoms. The double occupation of this orbital corresponds to the Restricted Hartree–Fock (RHF) approximation for the H_2 molecule. The RHF model leads to a reasonably accurate description of H_2 around the equilibrium geometry: computed bond distance is 0.735 Å (Experiment 0.746 Å) and the bond energy is 84 kcal/mol (Experiment 109 kcal/mol). It is typical for the HF model that it is able to describe closed-shell systems around their equilibrium geometry rather well. The correlation energy is only a small fraction of the total energy, but it is strongly distance dependent, which explains the error in the computed bond energy (there is no correlation energy at all for two separated hydrogen atoms).

The bond energy given above has been obtained by subtracting from the RHF energy for H_2 the energy of two separated hydrogen atoms (-627.5 kcal/mol). Suppose instead that we would use the RHF model to compute the potential curve for the dissociation of H_2, then the first thing to note is that the form of the MOs (see Eqs. 1, 2) are independent of the internuclear distance. The same form of the wave function

(see Eq. 3) is thus obtained also for the separated atoms. Let us expand this wave function as products of the atomic orbitals ψ_{A} and ψ_{B}

$$|\Phi_0\rangle = N^2 \left(\psi_{\mathrm{A}}(\mathbf{r}_1)\psi_{\mathrm{A}}(\mathbf{r}_2) + \psi_{\mathrm{A}}(\mathbf{r}_1)\psi_{\mathrm{B}}(\mathbf{r}_2) + \psi_{\mathrm{B}}(\mathbf{r}_1)\psi_{\mathrm{A}}(\mathbf{r}_2) + \psi_{\mathrm{B}}(\mathbf{r}_1)\psi_{\mathrm{B}}(\mathbf{r}_2)\right) \Theta_{2,0}. \tag{5}$$

We note that this wave function contains the so-called ionic terms, contributions where both electrons are located at the same atom. These terms are clearly unphysical at large separations, since they correspond to the dissociation to $\mathrm{H}^+ + \mathrm{H}^-$, which has an energy around 320 kcal/mol above $\mathrm{H}\cdot + \mathrm{H}\cdot$. It is only the second and third term in the wave function above that describe correctly the dissociated homolytic products.

It is a typical feature of the RHF model to include these "ionic structures" in fixed proportions into the wave function. Consequently, the model cannot in general be used to describe dissociation processes, in particular not homolytic processes. The potential curve corresponding to this wave function, Φ_0, will actually end up with an energy around 160 kcal/mol above the true energy at the limit of infinite separation.

Is there a remedy to this problem? We shall look for a formulation in terms of orthogonal molecular orbitals. We introduce in addition to Φ_0, the doubly excited Slater determinant (SD)

$$|\Phi_1\rangle = N^2 \left(\psi_{\mathrm{A}}(\mathbf{r}_1)\psi_{\mathrm{A}}(\mathbf{r}_2) - \psi_{\mathrm{A}}(\mathbf{r}_1)\psi_{\mathrm{B}}(\mathbf{r}_2) - \psi_{\mathrm{B}}(\mathbf{r}_1)\psi_{\mathrm{A}}(\mathbf{r}_2) + \psi_{\mathrm{B}}(\mathbf{r}_1)\psi_{\mathrm{B}}(\mathbf{r}_2)\right) \Theta_{2,0}, \tag{6}$$

corresponding to the electronic configuration $(\sigma^*)^2$. In terms of Φ_0 and Φ_1, we can now write our wave function as

$$|\Psi_{\mathrm{MC}}\rangle = C_0|\Phi_0\rangle + C_1|\Phi_1\rangle. \tag{7}$$

This is the multiconfigurational (MC) molecular orbital formulation of the wave function for the chemical bond in H_2, which will correctly describe the entire potential surface. Close to equilibrium $C_0 \approx 1$ and $C_1 \approx 0$, while at large separations $C_0 \approx -C_1$. The quantum chemical description of a chemical bond thus involves both the bonding and the antibonding orbital. Another way of viewing the multiconfigurational wave function, Eq. 7, is to note that the two configurations Φ_0 and Φ_1 are degenerate at infinite separation. Since the interaction between them is different from zero, strong mixing will occur with $C_0 = \pm C_1$. It is clear that the RHF model will not work in cases where more than one electronic configuration have the same, or nearly the same, energy.

Apart from dissociation, there are several situations, where near degeneracy occurs between different electronic configurations. A multiconfigurational treatment is then needed in order to obtain a qualitatively correct description of the electronic structure.

2 Dynamic and static correlation

Electron correlation is customarily divided into dynamic and static (non-dynamic), but there is no strict definition of these terms. In the context of quantum chemistry calculations, these terms are mainly used to describe the different ability of different methods to capture significant correlation effects. To take account of static correlation then means that energetically close or degenerate electronic state are given an evenhanded description by using several (or many) SD to describe them; the simplest example would be for an atomic or diatomic radical, where the multiplet structure requires several determinants for its description. This can be done already by SCF procedures, if a predetermined electronic structure with more than one determinant is optimized by only adjusting the orbitals, as is done by so-called open-shell Hartree–Fock that has been extensively used in atomic physics. But in general, a similar situation is at hand when such electronic structure occur, for example, toward dissociation, "accidental" near degeneracy, open

d-shells, reactions that are Hartree–Fock forbidden or whose description by single-orbital methods require symmetry breaking, or cause multiple local minima in the orbital optimization when single-determinant methods are attempted. In photochemistry, such effects are rule rather than exception.

By contrast, the dynamic correlation describes a situation where double (or higher) excitations from strongly occupied shells to weakly occupied correlating orbitals can adequately describe the stabilizing effect of allowing electrons to avoid coming too close, when the orbital density in a mean field picture would allow such close encounters. Dynamic correlation can also be described without correlating orbitals, for example, adding a correlation potential to the mean field (bare Coulomb or including exchange) using a density functional, or in some highly accurate methods where the wave functions contain terms that depend directly on the interelectronic distances.

3 Methods for static correlation

Correlation effects in molecules are normally partitioned into near-degeneracy effects (static correlation) and dynamic correlation that qualitatively differ in the way they separate the electrons. Static correlation leads to a large separation in space of the two electrons in a pair, for example, on two different atoms in a dissociation process. Dynamic correlation, on the other hand, deals with the interaction between two electrons at short interelectronic distance, the cusp region. It should be emphasized that multiconfigurational SCF (MCSCF) methods deal primarily with the near-degeneracy effects. Other methods are used to treat dynamical correlation. These include large-scale configuration interaction methods, coupled cluster methods, and perturbation theory.

There is normally no need for orbital optimization in calculations of dynamical correlation effects, since the electron density is only weakly affected. This is, however, a rule with several exceptions that we are not going to mention here.

Multiconfigurational SCF

Let us start by writing down the MCSCF wave function

$$|\Psi(\mathbf{c},\mathbf{C})\rangle = \sum_I C_I |\Phi_I(\mathbf{c})\rangle \tag{8}$$

where C_I are the expansion coefficients and $|\Phi_I(\mathbf{c})\rangle$ the SD with MOs parametrized by a set of coefficients $\mathbf{c}$. This wave function is then optimized by varying both sets of parameters, i.e. orbital coefficients $\mathbf{c}$ and CI coefficients $\mathbf{C}$ until the energy functional

$$E(\mathbf{c},\mathbf{C}) = \frac{\langle\Psi(\mathbf{c},\mathbf{C})|H|\Psi(\mathbf{c},\mathbf{C})\rangle}{\langle\Psi(\mathbf{c},\mathbf{C})|\Psi(\mathbf{c},\mathbf{C})\rangle} \tag{9}$$

becomes stationary.

Complete active space

In more complex situations than a simple dissociation of an H_2 molecule, it may be difficult to make a priori judgments about the most important electronic configurations to include in the MCSCF wave function. This problem can be, at least partly, solved by the Complete Active Space (CAS) method. Here, the problem is reduced to defining a set of active orbitals, which describe the near-degeneracy effects. The

choice of active orbitals requires an insight into the electronic structure, which is often rather obvious, but, not always. There are many cases where the choice is not at all clear, and several trials have to be made before the best choice has been found. This is far from black box situation, and the procedure is not easily automatized.

The CASSCF method is based on a partitioning of the occupied molecular orbitals into subsets, corresponding to how they are used to build the wave function. We define for each symmetry block of MOs the following subsets: *inactive* (occupied), *active*, and *external* (virtual). The inactive and active orbitals are occupied in the wave function, while the external orbitals span the rest of the orbital space, defined from the basis set used to build the MOs. The inactive orbitals are kept doubly occupied in all configurations that are used to build the CASSCF wave function. The number of electrons occupying these orbitals is thus twice the number of inactive orbitals. The remaining electrons occupy the active orbitals. We illustrate the active spaces for one CAS wave function in Figure 1, which shows a component of a CAS wave function with two electrons in three orbitals coupled to a singlet. Such a CAS would be denoted CAS(2,3), following the notation CAS(n,k) where n stands for the number of electrons in k orbitals comprising the active space.

The CASSCF method is an attempt to generalize the Hartree–Fock model to situations where near degeneracies occur, while keeping as much of the conceptual simplicity of the RHF approach as possible. Technically, the CASSCF model is by necessity more complex, since it is based on a MC wave function. The building blocks are, as in the RHF model, the occupied (inactive and active) orbitals. The number of electrons is, however, in general less than twice the number of occupied orbitals. The number of electron configurations generated by the orbital space is therefore larger than unity. The total wave function is formed as a linear combination of all SDs in the n-electron space that have the inactive orbitals doubly occupied. It is in this sense "complete" in the configurational space spanned by the active orbitals. The inactive orbitals represent an "SCF sea" in which the active electrons move. These orbitals have occupation numbers exactly equal to two, while the occupation numbers of the active orbitals varies between zero and two. It is obvious that the inactive orbitals should be chosen as the orbitals that are not expected to contribute to near-degeneracy correlation effects.

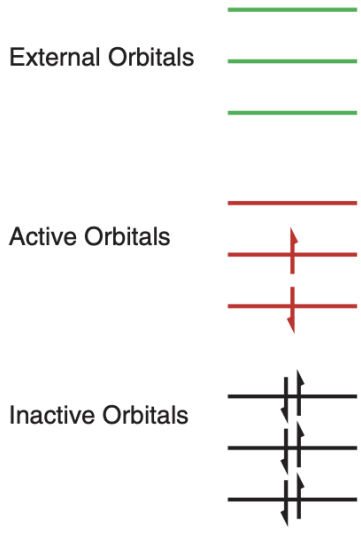

Figure 1: Illustration of the active orbitals for a CAS(2,3)