

## 18.3: The Unrestricted Hartree-Fock Spin Impurity Problem

As formulated above in terms of spin-orbitals, the Hartree-Fock (HF) equations yield orbitals that do not guarantee that  $\Psi$  possesses proper spin symmetry. To illustrate the point, consider the form of the equations for an open-shell system such as the Lithium atom Li. If  $1s\alpha$ ,  $1s\beta$ , and  $2s\alpha$  spin-orbitals are chosen to appear in the trial function  $\Psi$ , then the Fock operator will contain the following terms:

$$F = h + J_{1s\alpha} + J_{1s\beta} + J_{2s\alpha} - [K_{1s\alpha} + K_{1s\beta} + K_{2s\alpha}].$$

Acting on an  $\alpha$  spin-orbital  $\phi_{k\alpha}$  with  $F$  and carrying out the spin interfrations, one obtains

$$F\phi_{k\alpha} = h\phi_{k\alpha} + (2J_{1s} + J_{2s})\phi_{k\alpha} - (K_{1s} + K_{2s})\phi_{k\alpha}.$$

In contrast, when acting on a  $\beta$  spin-orbital, one obtains

$$F\phi_{k\beta} = h\phi_{k\beta} + (2J_{1s} + J_{2s})\phi_{k\beta} - (K_{1s})\phi_{k\beta}.$$

Spin-orbitals of  $\alpha$  and  $\beta$  type **do not** experience the same exchange potential in this model, which is clearly due to the fact that  $\Psi$  contains two  $\alpha$  spin-orbitals and only one  $\beta$  spin-orbital.

One consequence of the spin-polarized nature of the effective potential in  $F$  is that the optimal  $1s\alpha$  and  $1s\beta$  spin-orbitals, which are themselves solutions of  $F\phi_i = \epsilon_i\phi_i$ , do not have identical orbital energies (i.e.,  $\epsilon_{1s\alpha} \neq \epsilon_{1s\beta}$ ) and are not spatially identical to one another (i.e.,  $\phi_{1s\alpha}$  and  $\phi_{1s\beta}$  do not have identical LCAO-MO expansion coefficients). This resultant spin polarization of the orbitals in  $\Psi$  gives rise to spin impurities in  $\Psi$ . That is, the determinant  $|1s\alpha 1s'\beta 2s\alpha|$  is not a pure doublet spin eigenfunction although it is an  $S_z$  eigenfunction with  $M_s = \frac{1}{2}$ ; it contains both  $S = \frac{1}{2}$  and  $S = \frac{3}{2}$  components. If the  $1s\alpha$  and  $1s'\beta$  spin-orbitals were spatially identical, then  $|1s\alpha 1s'\beta 2s\alpha|$  would be a pure spin eigenfunction with  $S = \frac{1}{2}$ .

The above single-determinant wavefunction is commonly referred to as being of the **unrestricted Hartree-Fock** (UHF) type because no restrictions are placed on the spatial nature of the orbitals which appear in  $\Psi$ . In general, UHF wavefunctions are not of pure spin symmetry for any open-shell system. Such a UHF treatment forms the starting point of early versions of the widely used and highly successful Gaussian 70 through Gaussian- 8X series of electronic structure computer codes which derive from J. A. Pople and coworkers (see, for example, M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohling, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whitehead, D. J. Fox, E. M. Fleuder, and J. A. Pople, Gaussian 86, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA (1984)).

The inherent spin-impurity problem is sometimes 'fixed' by using the orbitals which are obtained in the UHF calculation to subsequently form a properly spin-adapted wavefunction. For the above Li atom example, this amounts to forming a new wavefunction (after the orbitals are obtained via the UHF process) using the techniques detailed in Section 3 and Appendix G:

$$\Psi = \frac{1}{\sqrt{2}} [|1s\alpha 1s'\beta 2s\alpha| - |1s\beta 1s'\alpha 2s\alpha|].$$

This wavefunction is a pure  $S = \frac{1}{2}$  state. This prescription for avoiding spin contamination (i.e., carrying out the UHF calculation and then forming a new spin-pure  $\Psi$ ) is referred to as **spin-projection**.

It is, of course, possible to first form the above spin-pure  $\Psi$  as a trial wavefunction and to then determine the orbitals  $1s$ ,  $1s'$  and  $2s$  which minimize its energy; in so doing, one is dealing with a spin-pure function from the start. The problem with carrying out this process, which is referred to as a **spin-adapted** Hartree-Fock calculation, is that the resultant  $1s$  and  $1s'$  orbitals still do not have identical spatial attributes. Having a set of orbitals ( $1s$ ,  $1s'$ ,  $2s$ , and the virtual orbitals) that form a non-orthogonal set ( $1s$  and  $1s'$  are neither identical nor orthogonal) makes it difficult to progress beyond the singleconfiguration wavefunction as one often wishes to do. That is, it is difficult to use a spinadapted wavefunction as a starting point for a correlated-level treatment of electronic motions.

Before addressing head-on the problem of how to best treat orbital optimization for open-shell species, it is useful to examine how the HF equations are solved in practice in terms of the LCAO-MO process.

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