As formulated above in terms of spin-orbitals, the Hartree-Fock (HF) equations yield orbitals that do not guarantee that \(|\Psi\rangle\) 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 \(|1s\alpha\rangle\), \(|1s\beta\rangle\), \(|2s\alpha\rangle\) spin-orbitals are chosen to appear in the trial function \(|\Psi\rangle\), then the Fock operator will contain the following terms:

\[
\begin{align*}
[F &= h + J_{1s\alpha} + J_{1s\beta} + J_{2s\alpha} - \frac{1}{2}(K_{1s\alpha} + K_{1s\beta} + K_{2s\alpha})] \text{.} \\

\end{align*}
\]

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

\[
\begin{align*}
[F\phi_{k\alpha}] = h\phi_{k\alpha} + (2J_{1s} + J_{2s})\phi_{k\alpha} - (K_{1s} + K_{2s})\phi_{k\alpha} \text{.} \\

\end{align*}
\]

In contrast, when acting on a \(|\beta\rangle\) spin-orbital, one obtains

\[
\begin{align*}
[F\phi_{k\beta}] = h\phi_{k\beta} + (2J_{1s} + J_{2s})\phi_{k\beta} - (K_{1s} + K_{2s})\phi_{k\beta} \text{.} \\

\end{align*}
\]

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

One consequence of the spin-polarized nature of the effective potential in F is that the optimal \(|1s\alpha\rangle\) spin-orbitals, which are themselves solutions of \((F \phi_{k\alpha} = \epsilon_{k\alpha} \phi_{k\alpha})\), do not have identical orbital energies (i.e., \(|\epsilon_{1s\alpha} - \epsilon_{1s\beta}| \neq |\epsilon_{1s\beta} - \epsilon_{1s\beta}|\)) and are not spatially identical to one another (i.e., \(|\phi_{1s\alpha} - \phi_{1s\beta}| \neq |\phi_{1s\alpha} - \phi_{1s\beta}|\)). This resultant spin polarization of the orbitals in \(|\Psi\rangle\) gives rise to spin impurities in \(|\Psi\rangle\). That is, the determinant \(|1s\alpha\rangle\) \(|1s\beta\rangle\) \(2s\alpha\rangle\) \(|2s\beta\rangle\) is not a pure doublet spin eigenfunction although it is an \(|S_z = 0\rangle\) eigenfunction with \((M_s = \frac{1}{2})\); it contains both \(|S = \frac{1}{2}\rangle\) and \(|S = \frac{1}{2}\rangle\) components. If the \(|1s\alpha\rangle\) \(|1s\beta\rangle\) \(|2s\alpha\rangle\) \(|2s\beta\rangle\) spin-orbitals were spatially identical, then \(|1s\alpha\rangle\) \(|1s\beta\rangle\) \(|2s\alpha\rangle\) \(|2s\beta\rangle\) would be a pure spin eigenfunction with \(|S = \frac{1}{2}\rangle\).

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 \(|\Psi\rangle\). 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, C. C. 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:
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 \( |\Psi\rangle \)) is referred to as \textbf{spin-projection}.

It is, of course, possible to first form the above spin-pure \( |\Psi\rangle \) 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 \textbf{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 single-configuration wavefunction as one often wishes to do. That is, it is difficult to use a spin-adapted 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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