In summary, for the small molecules considered here, SDCI improves SCF results considerably, but even using extended basis sets the agreement with experiment is not completely satisfactory. It is difficult to ascertain whether this is primarily due to the inadequacy of the basis sets or the SDCI approach itself. As will be discussed in the Section 4.6, for larger systems SDCI becomes increasingly poor due to inherent limitations of this method.

4.4 NATURAL ORBITALS AND THE ONE-PARTICLE REDUCED DENSITY MATRIX

Up to this point we have focused on determinants and configurations formed from a set of canonical Hartree-Fock orbitals. The resulting CI expansion unfortunately turns out to be rather slowly convergent. It is clear, however, that one can perform a CI calculation using N-electron configurations formed from *any* one-electron basis. Therefore, it is of interest to ask whether one can find a one-electron basis for which the CI expansion is more rapidly convergent than it is with the Hartree-Fock basis, and thus be able to obtain equivalent results with a smaller number of configurations. The set of *natural orbitals*, introduced by P.-O. Löwdin,[1] forms such a basis.

In order to define natural orbitals, we now consider the first-order reduced density matrix of an N-electron system. Given a normalized wave function, Φ, then $\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \Phi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N) \, d\mathbf{x}_1 \cdots d\mathbf{x}_N$ is the probability that an electron is in the space-spin volume element $d\mathbf{x}_1$ located at $\mathbf{x}_1$, while simultaneously another electron is in $d\mathbf{x}_2$ at $\mathbf{x}_2$ and so on. If we are interested only in the probability of finding an electron in $d\mathbf{x}_1$ at $\mathbf{x}_1$, independent of where the other electrons are, then we must average over all space-spin coordinates of the other electrons, i.e., integrate over $\mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N$ to obtain

$$\rho(\mathbf{x}_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \, \Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N)\Phi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N) \qquad (4.33)$$

$\rho(\mathbf{x}_1)$ is called the *reduced density function* for a single electron in an N-electron system. The normalization factor N is included so that the integral of the density equals the total number of electrons,

$$\int d\mathbf{x}_1 \, \rho(\mathbf{x}_1) = N \qquad (4.34)$$

We now generalize the density function $\rho(\mathbf{x}_1)$ to a density matrix $\gamma(\mathbf{x}_1, \mathbf{x}_1')$ defined as

$$\gamma(\mathbf{x}_1, \mathbf{x}_1') = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \, \Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\Phi^*(\mathbf{x}_1', \mathbf{x}_2, \ldots, \mathbf{x}_N) \qquad (4.35)$$

The matrix $\gamma(\mathbf{x}_1, \mathbf{x}_1')$, which depends on two continuous indices, is called the *first-order reduced density matrix* or alternatively, the *one-electron re-*

duced density matrix or simply the *one-matrix*. Note that the diagonal element of the continuous representation of the one-matrix is the density of electrons

$$\gamma(\mathbf{x}_1, \mathbf{x}_1) = \rho(\mathbf{x}_1) \tag{4.36}$$

Since $\gamma(\mathbf{x}_1, \mathbf{x}_1')$ is a function of two variables, it can be expanded in the orthonormal basis of Hartree-Fock spin orbitals $\{\chi_i\}$ as

$$\gamma(\mathbf{x}_1, \mathbf{x}_1') = \sum_{ij} \chi_i(\mathbf{x}_1)\gamma_{ij}\chi_j^*(\mathbf{x}_1') \tag{4.37}$$

where

$$\gamma_{ij} = \int d\mathbf{x}_1 \, d\mathbf{x}_1' \, \chi_i^*(\mathbf{x}_1)\gamma(\mathbf{x}_1, \mathbf{x}_1')\chi_j(\mathbf{x}_1') \tag{4.38}$$

The matrix γ formed from the elements $\{\gamma_{ij}\}$ is a discrete representation of the one-matrix in the orthonormal basis $\{\chi_i\}$.

Exercise 4.4 Show that γ is a Hermitian matrix.

Exercise 4.5 Show that $\operatorname{tr} \gamma = N$.

Exercise 4.6 Consider the one-electron operator

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

a. Show that

$$\langle \Phi | \mathcal{O}_1 | \Phi \rangle = \int d\mathbf{x}_1 \, [h(\mathbf{x}_1)\gamma(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1' = \mathbf{x}_1}$$

where the notation $[\ ]_{\mathbf{x}_1' = \mathbf{x}_1}$ means that $\mathbf{x}_1'$ is set equal to $\mathbf{x}_1$ after $h(\mathbf{x}_1)$ has operated on $\gamma(\mathbf{x}_1, \mathbf{x}_1')$.

b. Show that

$$\langle \Phi | \mathcal{O}_1 | \Phi \rangle = \operatorname{tr} \mathbf{h}\gamma$$

where

$$h_{ij} = \langle i|h|j \rangle = \int d\mathbf{x}_1 \, \chi_i^*(\mathbf{x}_1)h(\mathbf{x}_1)\chi_j(\mathbf{x}_1)$$

Thus the expectation value of any one-electron operator can be expressed in terms of the one-matrix.

In the special case that Φ is the Hartree-Fock ground state wave function Ψ_0, it can be shown from the definition (Eq. (4.35)) that

$$\gamma^{HF}(\mathbf{x}_1, \mathbf{x}_1') = \sum_{a} \chi_a(\mathbf{x}_1)\chi_a^*(\mathbf{x}_1') \tag{4.39}$$

where the sum runs over only the spin orbitals contained in Ψ_0. Thus the discrete representation of the HF one-matrix is particularly simple—γ^{HF} is diagonal with ones along the diagonal for those elements corresponding to occupied spin orbitals and zeros for unoccupied spin orbitals,

$$\gamma_{ij}^{HF} = \delta_{ij} \qquad i, j \in \text{occupied}$$
$$= 0 \qquad \text{otherwise} \tag{4.40}$$

The diagonal elements of γ^{HF} can be regarded as occupation numbers: one for occupied spin orbitals and zero for unoccupied spin orbitals.

Exercise 4.7 Recall that in second quantization a one-electron operator is

$$\mathcal{O}_1 = \sum_{ij} \langle i|h|j\rangle a_i^\dagger a_j$$

a. Show that

$$\gamma_{ij} = \langle\Phi|a_j^\dagger a_i|\Phi\rangle.$$

b. Show that the matrix elements of γ^{HF} are given by Eq. (4.40).

In general, when Φ is not Ψ_0, the discrete representation of the one-matrix in the basis of HF spin orbitals is *not* diagonal. However, since γ is Hermitian, it is possible to define an orthonormal basis $\{\eta_i\}$, related to $\{\chi_i\}$ by a unitary transformation, in which the matrix representation of the one-matrix is diagonal. The elements of the orthonormal set in which γ is diagonal are called *natural spin orbitals*. To make the above explicit, we start with the relation between two orthonormal bases $\{\eta_i\}$ and $\{\chi_i\}$ (see Eqs. (1.63) and (1.65))

$$\chi_i = \sum_k \eta_k(\mathbf{U}^\dagger)_{ki} = \sum_k \eta_k U_{ik}^* \tag{4.41}$$

$$\eta_i = \sum_k \chi_k U_{ki} \tag{4.42}$$

where $\mathbf{U}$ is a unitary matrix. Substituting Eq. (4.41) into Eq. (4.37), we have

$$\gamma(\mathbf{x}_1, \mathbf{x}_1') = \sum_{ijkl} \eta_k(\mathbf{x}_1) U_{ik}^* \gamma_{ij} U_{jl} \eta_l^*(\mathbf{x}_1')$$

$$= \sum_{kl} \eta_k(\mathbf{x}_1)\left(\sum_{ij} (\mathbf{U}^\dagger)_{ki}\gamma_{ij}U_{jl}\right)\eta_l^*(\mathbf{x}_1')$$

$$= \sum_{kl} \eta_k(\mathbf{x}_1)(\mathbf{U}^\dagger\gamma\mathbf{U})_{kl}\eta_l^*(\mathbf{x}_1')$$

$$= \sum_{kl} \eta_k(\mathbf{x}_1)\lambda_{kl}\eta_l^*(\mathbf{x}_1') \tag{4.43}$$

where we have defined the matrix λ as

$$\lambda = U^{\dagger}\gamma U \tag{4.44}$$

Now since γ is a Hermitian matrix, it is possible to find a unique unitary matrix U which diagonalizes γ, i.e.,

$$\lambda_{ij} = \delta_{ij}\lambda_i \tag{4.45}$$

The corresponding spin orbitals $\{\eta_i\}$ given by Eq. (4.42) are the natural spin orbitals. In terms of the natural spin orbitals, we can write Eq. (4.43) as

$$\gamma(\mathbf{x}_1, \mathbf{x}_1') = \sum_i \lambda_i\eta_i(\mathbf{x}_1)\eta_i^*(\mathbf{x}_1') \tag{4.46}$$

In analogy to the HF result of Eq. (4.39), λ_i is called the occupation number of the natural spin orbital η_i in the wave function Φ.

The importance of natural orbitals is that, in a certain sense, they give the most rapidly convergent CI expansion. That is, to obtain a given accuracy one requires fewer configurations formed from natural orbitals than configurations formed from any other orthonormal basis. It turns out that only configurations that are constructed from natural orbitals with large occupation numbers make significant contributions to the energy. Thus a natural spin orbital with a negligible occupation number may be omitted from the CI expansion without appreciably affecting the accuracy.

We shall not mathematically show why the use of natural orbitals is expected to improve the convergence of the CI expansion. Rather, we illustrate this point using a numerical example. Shavitt and coworkers performed the following interesting study for H_2O using the 39-STO basis described in Section 4.3. First, they performed a CI calculation containing all 4120 symmetry- and spin-adapted singly and doubly excited configurations constructed from the canonical HF basis. From this wave function they obtained the one-matrix and diagonalized it to determine the natural orbitals within the SDCI approximation. Then they performed a parallel series of truncated SDCI calculations using both the canonical and natural orbitals in order to answer the question, what is the minimum number of configurations needed to recover a given percent of the SDCI correlation energy? The answers are shown in Table 4.12. The faster convergence of the CI expansion based on natural orbitals is apparent. To obtain 60% of the SDCI correlation energy, one needs only 50 configurations formed from natural orbitals, as compared with 140 canonically based configurations. However, it can be also seen that the advantage of natural orbitals over canonical Hartree-Fock orbitals is only for relatively short expansions. It must be emphasized that these results are basis-set dependent, and it is expected that the differences between natural orbitals and Hartree-Fock orbitals are even greater for larger basis sets.

Table 4.12 The number of symmetry- and spin-adapted configurations required to recover given fractions of the SDCI correlation energy of H_2O within the 39-STO basis when canonical SCF (MO) and natural orbitals (NO) are used[a]

Percent of E_{corr}(SDCI)	Number of Configurations	
	MO	NO
20	14	6
40	52	18
60	140	50
80	351	147
90	617	362
99	1760	1652

[a] I. Shavitt, B. J. Rosenberg, and S. Palalikit, *Int. J. Quantum Chem.* S10: 33 (1976).

Exercise 4.8 For the special case of a two-electron system, the use of natural orbitals dramatically reduces the size of the full CI expansion. If ψ_1 is the occupied Hartree-Fock spatial orbital and ψ_r, $r = 2, 3, \ldots, K$ are virtual spatial orbitals, the normalized full CI singlet wave function has the form

$$|{}^1\Phi_0\rangle = c_0|1\bar{1}\rangle + \sum_{r=2}^{K} c_1^r|{}^1\Psi_1^r\rangle + \frac{1}{2}\sum_{r=2}^{K}\sum_{s=2}^{K} c_{11}^{rs}|{}^1\Psi_{11}^{rs}\rangle$$

where the singly and doubly excited spin adapted configurations are defined in Subsection 2.5.2.

a. Show that $|{}^1\Phi_0\rangle$ can be cast into the form

$$|{}^1\Phi_0\rangle = \sum_{i=1}^{K}\sum_{j=1}^{K} C_{ij}|\psi_i\bar{\psi}_j\rangle$$

where C is a symmetric $K \times K$ matrix.

b. Show that

$$\gamma(x_1, x_1') = \sum_{ij} (CC^\dagger)_{ij}(\psi_i(1)\psi_j^*(1') + \bar{\psi}_i(1)\bar{\psi}_j^*(1')).$$

c. Let U be the unitary transformation which diagonalizes C

$$\mathbf{U}^\dagger \mathbf{C} \mathbf{U} = \mathbf{d}$$

where $(\mathbf{d})_{ij} = d_i \delta_{ij}$. Show that

$$\mathbf{U}^\dagger \mathbf{C} \mathbf{C}^\dagger \mathbf{U} = \mathbf{d}^2.$$

d. Show that

$$\gamma(\mathbf{x}_1, \mathbf{x}_1') = \sum_i d_i^2 \left(\zeta_i(1)\zeta_i^*(1') + \bar{\zeta}_i(1)\bar{\zeta}_i^*(1') \right)$$

where

$$\zeta_i = \sum_k \psi_k U_{ki}$$

Thus U diagonalizes the one-matrix, and hence ζ_i are natural spatial orbitals for the two-electron system.

e. Finally, since C is symmetric, U can be chosen as real. Show that in terms of the natural spatial orbitals, $|^1\Phi_0\rangle$ given in part (a) can be rewritten as

$$|^1\Phi_0\rangle = \sum_{i=1}^K d_i |\zeta_i \bar{\zeta}_i\rangle$$

and note that this expansion contains only K terms.

Now that we have seen that the use of natural orbitals improves the convergence of the CI expansion, we are faced with the problem of how to exploit this in actual calculations. The difficulty is that the one-matrix and hence the CI wave function is required to calculate natural orbitals. Thus we can obtain the natural orbitals only after the CI calculation is complete. However, we clearly would like to have them before we start the calculation. Fortunately, it turns out that approximate natural orbitals are almost as good as the exact ones. There are several schemes that take advantage of this; here we only mention the iterative natural orbital method of Bender and Davidson.[2] In this approach one performs a series of small CI calculations. The configurations used in a given calculation are constructed from natural orbitals obtained from the wave function of the previous calculation. Thus one starts with a CI calculation involving a small number, say 50, of the most important configurations constructed from canonical Hartree-Fock orbitals. Using the resulting wave function, the one-matrix is calculated and then diagonalized to yield a set of approximate natural orbitals. Using the most important of these natural orbitals (i.e., those with the largest occupation numbers), one constructs a new set of 50 configurations; the procedure is repeated until the natural orbitals and/or the energy has converged. In practice, only a few iterations are performed and, in fact, the process often begins to diverge after several iterations.[3]