

Natural orbitals in CIS and singular-value decomposition

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Abstract

We prove that Mayer's recent proposition (*Chem.Phys.Letters, in press*) to consider the singular-value decomposition of the CIS coefficient matrix of an excited state leads to the natural orbitals of that state. It also follows that the CIS natural orbitals emerge by separate unitary transformations in the occupied and virtual Hartree-Fock subspaces.

In a recent paper[1], Mayer pointed out that by considering the singular-value decomposition (SVD) of the configuration interaction with single substitutions (CIS) coefficient matrix, the CIS wave function is simplified to contain only N determinants, N being the number of electrons. Here we show that the orbitals resulting from this SVD are the natural MOs of the corresponding wave function.

The structure of Mayer's CIS wave function[1] is

$$\Psi = \sum_k^N \lambda_k \psi_{N+k}^{v+} \psi_k^{o-} |0\rangle \quad (1)$$

where λ_k -s are the singular values, $|0\rangle$ is the Fermi vacuum (the Hartree-Fock ground state), N is the number of electrons (occupied spinorbitals), and the superscripts o and v on the creation/annihilation operators ψ^+/ψ^- indicate occupied and virtual MOs, respectively. We assume that the number of virtuals is not smaller than the number of occupied MOs, which is the case in any realistic calculations on excited states.

The first-order density matrix, by its definition and using the wave function of structure (1)

$$\begin{aligned}
P_{ab} &= \langle \Psi | \psi_b^+ \psi_a^- | \Psi \rangle \\
&= \sum_{k,l}^N \lambda_k \lambda_l \langle 0 | \psi_l^{o+} \psi_{N+l}^{v-} \psi_b^+ \psi_a^- \psi_{N+k}^{v+} \psi_k^{o-} | 0 \rangle
\end{aligned}$$

Evaluating the matrix element between the Fermi vacua, Wick's theorem gives 3 possible contractions

$$\begin{aligned}
P_{ab} &= \sum_{k,l}^N \lambda_k \lambda_l \left\{ \begin{aligned} & \langle 0 | \psi_l^{o+} \psi_{N+l}^{v-} \psi_b^+ \psi_a^- \psi_{N+k}^{v+} \psi_k^{o-} | 0 \rangle \\ & - \langle 0 | \psi_l^{o+} \psi_{N+l}^{v-} \psi_b^+ \psi_a^- \psi_{N+k}^{v+} \psi_k^{o-} | 0 \rangle \\ & + \langle 0 | \psi_l^{o+} \psi_{N+l}^{v-} \psi_b^+ \psi_a^- \psi_{N+k}^{v+} \psi_k^{o-} | 0 \rangle \end{aligned} \right\}
\end{aligned}$$

leading to three terms in P :

$$P_{ab} = \delta_{ab} n_a + \sum_{k,l}^N \lambda_k \lambda_l \left\{ -\delta_{la} \delta_{lk} \delta_{bk} n_a + \delta_{lk} \delta_{(N+l),b} \delta_{a,(N+k)} (1 - n_a) \right\}$$

where $n_a = 1, 0$ indicates whether orbital ψ_a is occupied or virtual in $|0\rangle$. Note that the first term is the ground state Hartree-Fock (HF) density matrix, and the third term is zero if $a > 2N$ or $b > 2N$, as a consequence of Mayer's SVD analysis[1]. Resolving the Kronecker deltas we find that

$$P_{ab} = \delta_{ab} n_a - \lambda_a^2 \delta_{ab} n_a + \lambda_a^2 \delta_{ab} (1 - n_a) \quad (a \leq 2N \text{ in the last term.}) \quad (2)$$

Here the first term is the HF density matrix, and the latter two are diagonal corrections to it. Thus we proved that in the SVD basis set the CIS first-order density matrix is diagonal, that is, the associated orbitals are natural orbitals of the system.

By Eq.(2), the CIS occupation numbers (eigenvalues of P) can be compactly given as

$$P_{aa} = \begin{cases} 1 - \lambda_a^2 & \text{if } a \leq N \text{ (occupied)} \\ \lambda_a^2 & \text{if } N < a \leq 2N \text{ (first } N \text{ virtuals)} \\ 0 & \text{if } a > 2N \text{ (higher virtuals)} \end{cases}$$

which obviously meet the requirement $\text{Tr}P = N$.

The above analysis sheds some light on the following points:

- (i) Among the CIS natural orbitals, the upper $(M - 2N)$ virtuals (M is the no. of basis functions) are not uniquely defined, since they belong to the degenerate occupation number 0.
- (ii) The CIS natural orbitals are obtained from a separate unitary transformation in the occupied and for the virtual subspace. This is a speciality of CIS and does not hold in general: occupied and virtual HF orbitals usually mix to form natural MOs.

Point (ii) is especially interesting in light of the controversial views about the correlation content of the CIS wave function. Many authors argue that no correlation effects can be described by single substitutions, thus "CIS completely neglects electron correlation" [2], and that CIS (and even the Random Phase Approximation, RPA[3,4]) are associated to linear response to (time-dependent)HF, so they are uncorrelated. On the other hand, we can consider the definition by Kutzelnigg and Mukherjee[5] of electron correlation. This says that a wave function is correlated if the cumulants of its density matrices are nonzero. The CIS wave function must be considered as correlated in this sense, since its first order density matrix is not idempotent which generates nonzero cumulants of higher density matrices. Although point (ii) indicates that the CIS natural MOs are essentially HF orbitals, being merely transformations of the canonical ones, the non idempotent property of the CIS P matrix (manifested in noninteger occupation numbers) suggests that the correlation content of the CIS wave function can be judged only based on the distribution of the singular values λ_k . If only a single λ_k dominates in Ψ , no correlation is described by CIS. However, in many cases there are a large number of nonzero λ_k -s indicating a correlated CIS excited state. This is in full accord with Mayer's analysis[1].

Naturally, the CIS P matrix can also be written down without using Mayer's SVD analysis. The result is [6-8]:

$$P_{ab} = n_a \delta_{ab} - n_a n_b \sum_k^{virt} C_{ak} C_{bk} + (1 - n_a)(1 - n_b) \sum_i^{occ} C_{ia} C_{ib} \quad (3)$$

where the CIS coefficients defined by $\Psi = \sum_{ij} C_{ij} j^+ i^- |HF\rangle$. Eq. (3) is nondiagonal in a general HF basis, and its diagonalization is equivalent to Mayer's SVD. Eq. (3) reflects also that the CIS P is blockdiagonal in a general HF basis, since no occupied-virtual matrix elements emerge – a fact which has been known for a long time[6], and which is again in agreement with point (ii) above.

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