CONFIGURATION INTERACTION IN A NONORTHOGONAL
DETERMINANT BASIS

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A class of electron models which reduce to a superposition of nonorthogonal determinants is studied by methods of covariant quantum chemistry. A compact matrix representation is found which contains variational parameters only in the form of Fock-Dirac densities \( \rho_A, \ldots, \rho_B \) of separate determinants \( |\phi_A\rangle, \ldots, |\phi_B\rangle \). Non-orthogonality of the determinants is taken into account by means of additional projectors obtained by pseudo-inversion of the products of the form \( \rho_A \rho_B \). Orbital optimization is thus reduced to a clearly Hermitian eigenvalue problem. Inclusion in the initial model of configurations singly excited with respect to each of the determinants \( |\phi_A\rangle, \ldots, |\phi_B\rangle \) is discussed. This generalized Tamm-Dancoff model is studied in detail for the spin-symmetrized (half-projected) Hartree-Fock methods. Correlation effects in the excited states of model \( \pi \)-systems of the alternant type are analyzed within the framework of the model.

In the standard configuration interaction (CI) method one usually uses a basis consisting of orthogonal determinants which have all been constructed from the same orthonormal set of spin-orbitals. At the same time, nonorthogonal determinants constructed from different sets of orbitals form, generally speaking, a very flexible basis for the CI calculations [1]. In fact, determinant functions

\[
|\Phi_A\rangle = \sqrt{N!} A_N \psi_A^1(1) \ldots \psi_A^N(N),
\]

\[
|\Phi_B\rangle = \sqrt{N!} A_N \psi_B^1(1) \ldots \psi_B^N(N), \quad \langle \psi_A^l | \psi_B^m \rangle \neq \delta_{lj}
\]

eetc., can lead, with the help of CI

\[
|\Psi\rangle = c_A |\Phi_A\rangle + c_B |\Phi_B\rangle + \ldots + c_Z |\Phi_Z\rangle
\]

to physically correct results already with a small number of terms in Eq. (3). For example, the half-projected Hartree-Fock method [2, 3] corresponds to a two-determinant approximation (3) where \( |\phi_A\rangle \) is a determinant with different orbitals for different spins and \( |\phi_B\rangle \) is obtained from \( |\phi_A\rangle \) by replacing orbitals with the spin "up" by orbitals with the spin "down". Equation (3) can also represent the wave function in the complex MO method [4], where \( |\phi_B^*\rangle \) is obtained from \( |\phi_A\rangle \) by complex conjugation. In all such cases \( \langle \phi_A^* | \phi_B \rangle \neq 0 \).

A method for calculating matrix elements of the Hamiltonian \( H_N \) in the basis (1) and (2) was proposed a long time ago [5], but in terms of the minors of the overlap matrices \( \left| \langle \phi_A^* | \phi_B \rangle \right| \), which makes it very cumbersome to use. This method requires that the problem of orbital optimization in (3) be solved from the beginning every time (see, for example, [1, 3, 4]). A direct operator approach has been proposed for the half-projected Hartree-Fock method [6]. The approach is based on the replacement of orbitals which are being optimized by variational operators ("covariant quantum chemistry" [7]). In fact, an operator approach for arbitrary models of the type (3) was nonexplicitly outlined in [6].

In this paper we discuss an arbitrary superposition of nonorthogonal determinants (3) and a generalized Tamm-Dancoff model containing a mixture of singly excited configurations \( |\phi_A^1\rangle, |\phi_B^1\rangle, \ldots, \) (with respect to each of the determinants \( |\phi_A\rangle, |\phi_B\rangle, \ldots, \)) together with (1) and (2):

\[
|\Psi\rangle = \tilde{c}_A |\Phi_A\rangle + |\Phi_A^1\rangle + \tilde{c}_B |\Phi_B\rangle + |\Phi_B^1\rangle + \ldots
\]


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This allows us to find excited electronic states with effective accounting for interparticle
correlations and with a relatively small number ($\sim N^2$) of variational parameters.

**OPERATOR REPRESENTATION OF THE ELECTRON MODEL**

According to the general principles of covariant quantum chemistry [7, 8] the electron
model can be formulated from the very beginning purely in operator language. This means
that instead of $|\Psi\rangle$ one constructs a projector on $|\Psi\rangle$

$$
\rho_N^\Psi = |\Psi(1...N)\rangle \langle \Psi(1...N)|.
$$  

(5)

There exists an explicit algebraic expression of Eq. (5) in terms of certain variational
operators. These operators can be written in more general terms, for example, in terms of
orbitals which are being optimized or in terms of configuration coefficients.

For definiteness, we take $|\Psi\rangle$ in the form (3) with a two-term expansion on the RHS

$$
|\Psi\rangle = e^{in\alpha_A}|\Phi_A\rangle + e^{-in\alpha_B}|\Phi_B\rangle,
$$  

(6)

where $\alpha$ is a phase to be specified later, and the spin-orbitals in (1) and (2) are, in
general, constructed from complex MO. In multiconfiguration approximations of this kind
the complex nature of the variational parameters is essential [9]. In the case of a single
determinant $|\Phi_A\rangle$ the operator representation (5) is well known [5, 8]

$$
\rho_A^{\Phi_A} = |\Phi_A\rangle \langle \Phi_A| = \hat{\rho}_A[\rho_A],
$$  

(7)

where

$$
\hat{\rho}_A[X] = A_N X(1)...X(N), \quad \hat{\rho}_A[X] \hat{\rho}_A[Y] = \hat{\rho}_N[XY]
$$  

(8)
denotes an external product associated with the one-electron operator $X$. The Fock–Dirac
density matrix $\rho_A$ of the determinant (1)

$$
\rho_A = \sum_{i=1}^N |\psi_i^\alpha\rangle \langle \psi_i^\alpha|
$$  

(9)

plays the role of $X$ in Eq. (7). Similarly, for $|\Phi_B\rangle$ (2) we have

$$
\rho_B^{\Phi_B} = \rho_B[\rho_B], \quad \rho_B = \sum_{i=1}^N |\psi_i^\beta\rangle \langle \psi_i^\beta|.
$$  

(10)

The one-electron operators $\rho_A$ and $\rho_B$ can also be written as variational operators of the
approximation (6). Nevertheless, Eqs. (7) and (10) do not solve the problem of the operator
representation because the projector for $|\Psi\rangle$ (5) of the form (6), (7) and (10) contains
intermediate $N$-electron operators $|\Phi_A\times \Phi_B\rangle$, and these cannot be expressed in terms of the
densities $\rho_A$ and $\rho_B$ (which are quadratic in $\Phi_A$ and $\Phi_B$).

The problem is solved by a simple trick, similar to the one in [6]. We multiply and
divide $|\Phi_A\times \Phi_B\rangle$ by the overlap integral between (1) and (2)

$$
|\Phi_A\rangle \langle \Phi_B| = \xi e^{in}, \quad \xi = |\langle \Phi_A| \Phi_B\rangle|, \quad \eta = \arg \langle \Phi_A| \Phi_B\rangle.
$$  

(11)

Elementary transformations

$$
|\Phi_A\rangle \langle \Phi_B| = |\Phi_A\rangle \langle \Phi_A| \langle \Phi_B| e^{-in}\xi = \hat{\rho}_N[\rho_A \rho_B] e^{-in}\xi
$$  

(12)
give (after identification of the phase $\eta$ in (11) and (6)) the desired operator representa-
tion of the model (6)

$$
\rho_N^\Psi = |c_A| \hat{\rho}_N[\rho_A] + |c_B| \hat{\rho}_N[\rho_B] + (c_A^* c_B^* \hat{\rho}_N[\rho_A \rho_B] + c_A^* c_B \hat{\rho}_N[\rho_B \rho_A]) \xi.
$$  

(13)

In contrast to $\rho_A$ and $\rho_B$, the product $\rho_A \rho_B$ is not a projection operator. Nevertheless, one
can still construct a projector associated with a non-Hermitian operator $\rho_A \rho_B$. We denote
this operator by $W$ and require that