Fock-space coupled-cluster method

A study of the electronic spectra of model π-electron systems

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Summary. A generalization of the single-reference coupled-cluster method, employing the algebraic properties of the fermionic Fock space, is presented. This Fock-space coupled-cluster (FSCC) method is capable of providing not only the ground-state energy of an N-electron system, but also an important fraction of system's excitation spectrum, including ionization potentials, electron affinities, and excitation energies corresponding to N-electron singlet and triplet states. The FSCC method is applied to study the electronic spectra corresponding to the Pariser–Parr–Pople model of butadiene, hexatriene, and benzene, with the full configuration-interaction results taken as the reference. The problem of intruder states is discussed.

1. Introduction

The coupled-cluster (CC) method [1] is presently the most effective computational tool for performing size-extensive energy calculations for many-electron systems [2–4]. This method uses the exponential Ansatz to generate the correlated wave function of a given N-electron state, with the reference wave function Φ taken most often in the form of a single-determinantal Hartree–Fock (HF) function. Generalizations of the single-reference CC approach usually consider a manifold of reference states (the model space), and are capable of simultaneous determination of several energy levels. These multi-reference CC (MRCC) methods can be divided into two classes [5]: (i) the valence-universal MRCC methods [5–11], which require performing calculations for states with different numbers of electrons (N, $N-1, \ldots, N-n$, where n is the number of valence electrons), and (ii) the state-universal MRCC methods [12–17], in which the model space is contained entirely within the space of N-electron wave functions. Approaches (i) and (ii) are often referred to as the Fock-space and Hilbert-space MRCC approaches, respectively. This terminology is somewhat misleading, however. Since all the MRCC methods are expressed in the second-quantization language, they are implicitly defined in a Fock space (this is a vector space

spanned by all Slater determinants constructed from a given set of spin orbitals; for M spin orbitals the corresponding Fock space is of the dimensions 2^M). On the other hand, a finite- or infinite-dimensional Fock space has the structure of a Hilbert space.

There is a wealth of algebraic structures associated with a Fock space of dimension 2^M, including the unitary group $U(M)$, the special orthogonal groups of $SO(2M)$ and $SO(2M + 1)$, and the Clifford algebra C_{2M} (see [18], and references therein). The $U(M)$ group plays a very important role of the invariance group of the second-quantization formalism. In the usual approach, see [19], $U(M)$ appears as the invariance group only when the vacuum state corresponds to the state with no electrons (this state will be hereafter referred to as the physical vacuum); a smaller invariance group, $U(N) \otimes U(M - N)$, emerges when a Slater determinant built of N spin orbitals is used as the vacuum state. In each case, the amplitudes of Fock-space operators behave as the components of tensors under the transformations from the relevant invariance group. It is customary to represent these amplitudes by diagrams; this compact graphical notation is, in various mutations, ubiquitous in the theory of many-particle systems. The diagrammatic language, reflecting the tensor character of operators' amplitudes, made possible to formulate the linked-cluster theorem [20]. This theorem associates the property of size-extensivity of a physical quantity (e.g., energy) with the requirement that unlinked (or, in general, disconnected) diagrams are absent from the equations that define such a quantity, see [21] for a general discussion concerning the MRCC methods. From that point of view, the computational methods for many-particle systems which allow for the appearance of disconnecting diagrams have to be dismissed as being non-size-extensive. The MRCC formalisms [5–17] are not $U(M)$-invariant (although some of them, for instance [8a–d], are $U(N) \otimes U(M-N)$-invariant); moreover, the tensor structures of the corresponding MRCC equations have not been made very transparent, making considerations of their size-extensivity quite involved [12, 16, 21]. In the case of the state-universal MRCC methods [12–17], the difficulties stem primarily from the use of the projector operators associated with the model space (in particular, in the case of the so-called incomplete model spaces). We would like to note that the appearance of projection operators in the second quantization is rather awkward, since these operators usually contain terms with up to $2M$ fermion (i.e., creation and annihilation) operators. It is, therefore, customary to circumvent the explicit use of these operators, but this is usually done at the expense of obscuring the tensor structure of the formalism.

In 1985 two of the present authors (LZS and HJM) proposed a generalization of the single-reference CC method [22a,b] (see also later papers [22c,d]) which makes an extensive use of the algebraic structure of the Fock space; this method, called the generalized CC method in [22], will be hereafter referred to as the Fock-space coupled-cluster (FSCC) method. Below we summarize the characteristic features of the FSCC method, stressing differences with the MRCC methods [5–17]:

(1) A quasiparticle formalism is used, with the reference wave function Φ playing the role of the quasiparticle vacuum. In quantum-chemical applications the quasiparticles are simply "particles" and "holes", but more general types of quasiparticles, defined through the Bogoliubov–Valatin (BV) [23] or the Fukutome–Yamamura–Nishiyama (FYN) [24] transformations, may also be considered. The quasiparticle formalism introduced in [22a] is different from the usual second-quantization formalism based on the N-product concept [19].

(2) The electronic Hamiltonian $\hat{H}$ (defined in the Fock space) is subject to a similarity transformation yielding the quasiparticle Hamiltonian $\hat{G} = \hat{\Omega}^{-1}\hat{H}\hat{\Omega}$. By writing the wave operator as $\hat{\Omega} = \hat{\Omega}_{ex}\hat{\Omega}_{dx}$, this similarity tranformation is performed in two steps, where each of the component wave operators $(\hat{\Omega}_{ex}, \hat{\Omega}_{dx})$ is written in the exponential form. This *bi-exponential* Ansatz ensures a complete decoupling of the excitation and the de-excitation amplitudes of the wave operator $\hat{\Omega}$. The wave operator $\hat{\Omega}$ is not subject to the intermediate normalization, and we thus avoid the problems discussed at length in [21] (see also [8h]).

(3) In general, $\hat{H}$ does not commute with the quasiparticle-number operator $\hat{N}_q$, whereas $\hat{G}$ *is explicitly required* to commute with $\hat{N}_q$. This condition is the cornerstone of the FSCC model of electronic structure, and provides a definition for the notion of quasiparticles in this model – there is a one-to-one correspondence between the FSCC quasiparticles and certain eigenstates of the Hamiltonian $\hat{H}$. In general, the number of quasiparticles becomes a quantum number labeling the eigenstates of $\hat{H}$.

(4) The wave operator $\hat{\Omega}$ is multiplicatively separable, and there are *finite* (and independent of M) connected-diagram expansions defining the amplitudes of the quasiparticle Hamiltonian $\hat{G}$. Because of (3), a certain subset of these amplitudes must vanish, a condition that defines the set of basic equations of the FSCC method (the FSCC equations). An advantage of using the quasiparticle formalism is that the FSCC equations are explicitly invariant with respect to the unitary group $U'(M)$ which transforms *the single-quasiparticle states* among themselves.

(5) There is no model space, and the associated projector, in the FSCC theory, since operator $\hat{G}$ is defined in the *whole* Fock space. Therefore, we prefer to see the FSCC method as a natural extension of the single-reference CC method [1] (one recovers the usual CC equations as a subset of the FSCC equations), rather than a method originating from a MRCC concept. For the sake of comparison with the MRCC methods, the $U'(M)$-invariant subspaces of the Fock space [in the case under consideration these are the (*m*-particle)-(*n*-hole) spaces, (*mp-nh*) spaces, in short] may be treated as "model spaces".

(6) The diagonalization of the quasiparticle Hamiltonian $\hat{G}$ in the $U'(M)$-invariant subspaces of the Fock space corresponding to the number of quasiparticles equal to 0, 1, and 2 furnishes the energy of the N-electron ground state, as well as the excitation energies corresponding to certain classes of $(N \pm n)$-electron states ($n = 0, 1, 2$). Because of (4), the FSCC method is size-extensive, also when usual approximations (see [2–4]) are applied.

Our Fock-space approach [22] is different from that introduced by Kutzelnigg in the series of papers entitled "Quantum chemistry in Fock space" [25]. The main difference lies in our using the quasiparticle formalism which *is not* explicitly invariant with respect to the particle-number [$U(1)$] and spin [$SU(2)$] symmetries. These, and other relevant symmetries, can be taken into account by performing a symmetry-adaptation of the algebraic equations of the FSCC method. This procedure is very simple in the case of the particle-number symmetry, see [22b,c]. The general formulation of the FSCC method [22a] allows for the choice of a broken-symmetry quasiparticle vacuum Φ – a very useful concept when applications to extended systems are considered [26]. Let us make a general remark that insisting on the explicit enforcement of the particle-number and spin symmetries restricts one in the exploitation of the full algebraic potential of the second-quantization formalism. We would like also to point out

a difference between the unitary Ansatz of Kutzelnigg and Koch [25c] (see also [27]) and our bi-exponential Ansatz [22a] employing nilpotent algebras.

A concise presentation of the FSCC method is given in Sect. 2 of this paper. In Sect. 3 we discuss applications of the simplest non-trivial variant of the FSCC method. This variant is similar to the valence-universal MRCC methods [7, 8, 10, 11] with special choices of the model spaces (with all the "particles" and "holes" considered active). In our study we use the Pariser–Parr–Pople (PPP) model [28] for simple hydrocarbons: butadiene, hexatriene, and benzene, and compare the FSCC results with those of the full configuration-interaction (FCI) method. Numerical results are given for the ground-state energies, ionization energies and electron affinities, and for singlet and triplet excitation energies. Section 4 contains a discussion of the results for the excitation energies, with a special emphasis put on the problem of "intruder states" [29]. We end with concluding remarks in Sect. 5.

2. The Fock-space coupled-cluster method

The theory presented below follows that of paper [22a], including some refinements introduced in [22c]. We consider a problem of finding energy levels of an electronic system, e.g. a molecule described in the Born–Oppenheimer approximation. The algebraic approximation is used: an M-element (orthornormal) set of spin orbitals, $\{\phi_i : i = 1, \ldots, M\}$, generates the 2^M-dimensional fermionic Fock space for our problem. The electron annihilation operators, $\hat{a}_i$, and creation operators, $\hat{a}^i \equiv (\hat{a}_i)^\dagger$, corresponding to this spin-orbital basis are defined as in [30]. The physical vacuum, Φ_0, fulfills the condition: $\hat{a}_i \Phi_0 = 0$, for $i = 1, \ldots, M$. The Fock basis corresponding to vaccum Φ_0, $\{\Phi_0, \hat{a}^i \Phi_0, \hat{a}^j \hat{a}^i \Phi_0, \ldots\}$, spans the Fock space. Linear operators in the Fock space can be expressed as linear combinations of the so-called normal products of electron annihilation and creation operators, as exemplified by the electron-number operator:

$$\hat{N} = \delta_i^j \hat{a}^i \hat{a}_j, \tag{1}$$

and the electronic Hamiltonian for our molecule:

$$\hat{H} = W + h_i^j \hat{a}^i \hat{a}_j + \tfrac{1}{4} v_{ij}^{kl} \hat{a}^j \hat{a}^i \hat{a}_k \hat{a}_l. \tag{2}$$

In Eqs. (1) and (2) the Einstein summation convention is used. In Eq. (2), h_i^j and v_{ij}^{kl} are one-electron and (antisymmetrized) two-electron integrals, respectively; W is a constant term equal to the nuclear repulsion in the molecule. The formulas (1) and (2) are invariant with respect to the unitary transformations of the spin-orbital basis; these transformations form the unitary group $U(M)$. Parameters W, h_i^j, and v_{ij}^{kl} (the amplitudes of operator $\hat{H}$) may be treated as $U(M)$-tensors.

Operator (2) is the Fock-space Hamiltonian for our molecule, its spectrum consists of 2^M eigenvalues corresponding to states with the number of electrons ranging from 0 to M. This spectrum, and the corresponding eigenfunctions (in the present paper often referred to as "exact" or "correlated" wave functions for our molecule), are obtainable by applying a FCI procedure. For obvious reasons FCI calculations become prohibitively difficult for larger M, even for single levels, and other, approximate, techniques have to be developed. In practice one is interested only in a very small fraction of the spectrum of $\hat{H}$, including the

energy of the N-electron ground state of the molecule, and energies of some N-, $(N \pm 1)$-, $(N \pm 2)$-, ... electron states which may be considered as "excited states" with respect to the ground state. It is, therefore, convenient to introduce a new parametrization of the Fock space, based on a new vacuum state Φ approximating the correlated wave function of the N-electron ground state, Ψ. In general, Φ can be obtained by applying a unitary transformation in the Fock space:

$$\Phi = \hat{U}\Phi_0. \tag{3}$$

Now we can define the so-called quasiparticle annihilation operators corresponding to Φ:

$$\hat{b}_1 = \hat{U}\hat{a}_i\hat{U}^\dagger, \tag{4}$$

and the usual definition of the creation operators, $\hat{b}^i \equiv (\hat{b}_i)^\dagger$, follows. Φ is now the quasiparticle vacuum, since $\hat{b}_i\Phi = 0$, for $i = 1, \ldots, M$ (in [22] Φ was called the model vacuum). The largest group of operators $\hat{U}$ providing manageable algebraic expressions for b-operators in terms of a-operators is the $SO(2M + 1)$-group of the FYN transformations [24]; these transformations can mix states with even and odd numbers of electrons. An important subgroup of the FYN transformations [24] is the $SO(2M)$-group corresponding to the BV transformations [23]. When acting on the physical vacuum [see Eq. (3)], a BV-operator $\hat{U}$ (of the general form) produces a mixture of the Slater determinants with different numbers of electron pairs.

In the present paper we restrict our considerations to a special class of the BV transformations – the particle-hole transformations:

$$\hat{b}_i = \hat{a}^i, \tag{5a}$$

for $i = 1, \ldots, N$, and

$$\hat{b}_i = \hat{a}_i, \tag{5b}$$

for $i = N + 1, \ldots, M$. In this case Φ is the Slater determinant built of spin orbitals ϕ_i, $i = 1, \ldots, N$ (we assume that both N and M are even). The quasiparticles corresponding to the annihilation operators (5a) are called "holes", whereas those corresponding to operators (5b) are called "particles" (following [31] we prefer to use quotation marks to avoid the impression that the particles are quasiparticles). Our Fock space can now be parametrized by using a new Fock basis $\{\Phi, \hat{b}^i\Phi, \hat{b}^j\hat{b}^i\Phi, \ldots\}$, and linear operators can be expressed in terms of operators $\hat{b}_i$ and $\hat{b}^i$. For instance, the Hamiltonian (2) now reads:

$$\hat{H} = \eta + \eta_i{}^j\hat{b}^i\hat{b}_j + \tfrac{1}{2}\eta_{ij}\hat{b}^i\hat{b}^j + \tfrac{1}{2}\eta^{ij}\hat{b}_i\hat{b}_j + \tfrac{1}{4}\eta_{ij}{}^{kl}\hat{b}^i\hat{b}^j\hat{b}_k\hat{b}_l$$
$$+ \tfrac{1}{6}\eta_{ijk}{}^l\hat{b}^k\hat{b}^j\hat{b}^i\hat{b}_l + \tfrac{1}{6}\eta_i{}^{jkl}i\hat{b}^i\hat{b}_j\hat{b}_k\hat{b}_l + \tfrac{1}{24}\eta_{ijkl}\hat{b}^l\hat{b}^k\hat{b}^j\hat{b}^i + \tfrac{1}{24}\eta^{ijkl}\hat{b}_i\hat{b}_j\hat{b}_k\hat{b}_l, \tag{6}$$

where the η-amplitudes (antisymmetric with respect to the permutations among the upper and lower indices) are in a simple way related to parameters W, $h_i{}^j$, and $v_{ij}{}^{kl}$ of Eq. (2) (see [22a]). One finds that $\eta = \langle\Phi|\hat{H}\Phi\rangle$, and, when Φ is chosen as a Hartree–Fock (HF) wave function, $\eta_{ij} = \eta^{ij} = 0$. Equation (6) is invariant with respect to the group $U'(M)$ of the unitary transformations of the single-quasiparticle states, $\Phi^i \equiv \hat{b}^i\Phi$. The groups $U(M)$ and $U'(M)$ are different subgroups of the group $SO(2M)$ corresponding to the BV transformations [23].

The form of Eq. (6) of the Hamiltonian (2) is exactly the same as obtained by using the general BV transformation (in that case only the formulas for the η-amplitudes need to be generalized). Of course, the particle-number operator (1) and the Hamiltonian (2) commute, but this property is not obvious when the Hamiltonian is written in the form of Eq. (6). It is important to note that in the case of the general BV transformation operators (1) and (6) commute, but *not term-by-term*; the term-by-term commutation of these operators is retained only in the case of the particle-hole transformations (5). The "particles" and the "holes" correspond to different eigenvalues of the pseudocharge operator [22a] [related to the particle-number operator (1)]; this property is used for the symmetry-adaptation of the FSCC method [22b,c].

It is seen that Hamiltonian $\hat{H}$ written in the form of Eq. (6) does not commute with the quasiparticle-number operator:

$$\hat{N}_q = \delta_i{}^j \hat{b}^i \hat{b}_j. \tag{7}$$

It means that the number of quasiparticles is not conserved during the time evolution of the system which was initially in the state described by the quasiparticle vacuum Φ. The basic idea behind our FSCC method is to find a similarity transformation:

$$\hat{G} = \hat{\Omega}^{-1} \hat{H} \hat{\Omega}, \tag{8}$$

yielding a transformed Hamiltonian $\hat{G}$ which commutes with operator $\hat{N}_q$. The operator $\hat{G}$ which fulfills this condition can be written in the following form:

$$\hat{G} = g + g_i{}^j \hat{b}^i \hat{b}_j + \tfrac{1}{4} g_{ij}{}^{kl} \hat{b}^i \hat{b}^j \hat{b}_k \hat{b}_l + \cdots . \tag{9}$$

In Ref. [22], operator $\hat{G}$ was called the effective Hamiltonian; however, since this name is most often used for a Hamiltonian restricted to some model space, in the present paper the name quasiparticle Hamiltonian is used for $\hat{G}$. Due to a well-known property of similarity transformations, the spectra of operators $\hat{H}$ and $\hat{G}$ are identical. We choose the wave operator $\hat{\Omega}$ such that $\hat{\Omega}\Phi = \Psi$; in this case one finds from Eq. (9) that $g = \langle \Phi | \hat{G} \Phi \rangle = E$, where E is the energy of our N-electron ground-state wave function Ψ. In general, the spectrum of the quasiparticle Hamiltonian (9) can be found step-by-step by diagonalizing this operator in subspaces corresponding to the number of quasiparticles equal to $0, 1, 2, \ldots, M$ [these subspaces are the $U'(M)$-invariant subspaces of the Fock space]. When the quasiparticles are defined through transformation (5), operator (9) can be diagonalized in the mp-nh subspaces, where m and n correspond to the number of "particles" and "holes" respectively. Operator $(\hat{G} - g)$ supplies directly the excitation spectrum of our system, including excitations changing the number of electrons in the system. The interpretation of the g-amplitudes of this operator is as follows: matrix $\{g_i{}^j\}$, after diagonalization, gives the quasiparticle energies. In the case when our quasiparticles are simply "particles" and "holes", this matrix is block-diagonal, with the $1p$-$0h$ and $0p$-$1h$ blocks corresponding to certain electron affinities and ionization energies of the system, respectively. Matrix $\{g_{ij}{}^{kl}\}$ describes the two-body quasiparticle interactions; it splits into three submatrices corresponding to $2p$-$0h$, $0p$-$2h$, and $1p$-$1h$ subspaces. The matrix elements of the last block are necessary for calculating the excitation energies corresponding to the "singly excited" states. One should note that, in general, n-body quasiparticle-interaction terms $(2 \leqslant n \leqslant M)$ are present in the quasiparticle Hamiltonian (9). However, the first three terms on the rhs of Eq. (9), if known exactly, are sufficient to generate the ground-state energy and a part of

molecular excitation spectrum which is important from the point of view of molecular spectroscopy. The "renormalization" procedure transforming the electronic Hamiltonian (2, 6) into the quasiparticle Hamiltonian (9) is the essence of the FSCC method introduced in [22a]. As seen, this method effectively converts the many-electron problem associated with Hamiltonian $\hat{H}$ into a few-quasiparticle problem of Hamiltonian $\hat{G}$.

The universal [25b] wave operator $\hat{\Omega}$ of the FSCC method is constructed as follows:

$$\hat{\Omega} = \hat{\Omega}_{ex}\,\hat{\Omega}_{dx}, \tag{10}$$

where

$$\hat{\Omega}_{ex} = \exp(\hat{\Theta}), \tag{11}$$

$$\hat{\Omega}_{dx} = \exp(\hat{\Xi}), \tag{12}$$

and

$$\hat{\Theta} = \tfrac{1}{2}\theta_{ij}\hat{b}^j\hat{b}^i + \tfrac{1}{6}\theta_{ijk}{}^l\hat{b}^k\hat{b}^j\hat{b}^i\hat{b}_l + \tfrac{1}{24}\theta_{ijkl}\hat{b}^l\hat{b}^k\hat{b}^j\hat{b}^i + \cdots, \tag{13}$$

$$\hat{\Xi} = \tfrac{1}{2}\xi^{ij}\hat{b}_i\hat{b}_j + \tfrac{1}{6}\xi_i{}^{jkl}\hat{b}^i\hat{b}_j\hat{b}_k\hat{b}_l + \tfrac{1}{24}\xi^{ijkl}\hat{b}_i\hat{b}_j\hat{b}_k\hat{b}_l + \cdots. \tag{14}$$

Operators $\hat{\Theta}$ and $\hat{\Xi}$ are called the CC excitation and de-excitation operators, respectively. Operator $\hat{\Theta}$, by design, contains only terms in which the number of the creation operators is greater than that of the annihilation ones; the opposite rule applies to operator $\hat{\Xi}$. Because of the definition (10), it is convenient to perform transformation (8) in two steps. In the first one, the auxiliary quasiparticle Hamiltonian:

$$\hat{\Gamma} = \hat{\Omega}_{ex}^{-1}\hat{H}\hat{\Omega}_{ex}, \tag{15}$$

is obtained, and then, in the second step, the proper quasi-particle Hamiltonian, $\hat{G}$, is calculated:

$$\hat{G} = \hat{\Omega}_{dx}^{-1}\hat{\Gamma}\hat{\Omega}_{dx}. \tag{16}$$

In Ref. [22a] we found that in order to obtain operator $\hat{G}$ in the form of Eq. (9), the amplitudes of operator:

$$\begin{aligned}
\hat{\Gamma} = \gamma &+ \gamma_i{}^j\hat{b}^i\hat{b}_j + \tfrac{1}{2}\gamma_{ij}\hat{b}^j\hat{b}^i + \tfrac{1}{2}\gamma^{ij}\hat{b}_i\hat{b}_j \\
&+ \tfrac{1}{4}\gamma_{ij}{}^{kl}\hat{b}^j\hat{b}^i\hat{b}_k\hat{b}_l + \tfrac{1}{6}\gamma_{ijk}{}^l\hat{b}^k\hat{b}^j\hat{b}^i\hat{b}_1 + \tfrac{1}{6}\gamma_i{}^{jkl}\hat{b}^i\hat{b}_j\hat{b}_k\hat{b}_l \\
&+ \tfrac{1}{24}\gamma_{ijkl}\hat{b}^l\hat{b}^k\hat{b}^j\hat{b}^i + \tfrac{1}{24}\gamma^{ijkl}\hat{b}_i\hat{b}_j\hat{b}_k\hat{b}_1 + \cdots,
\end{aligned} \tag{17}$$

should fulfill the following conditions:

$$\gamma_{ij} = 0, \tag{18a}$$

$$\gamma_{ijkl} = 0, \qquad \gamma_{ijk}{}^l = 0, \tag{18b}$$

$$\gamma_{ijklm} = 0, \qquad \gamma_{ijklm}{}^n = 0, \qquad \gamma_{ijkl}{}^{mn} = 0, \tag{18c}$$

etc. We would like to note that the conditions (18) involve only the γ-amplitudes with the number of the lower indices *greater* than the number of the upper ones. In [22a] we also proved that when Eqs. (18) are satisfied, one automatically gets:

$$g = \gamma = E, \tag{19a}$$

$$g_i{}^j = \gamma_i{}^j, \tag{19b}$$

$$g_{ij}{}^{kl} = \gamma_{ij}{}^{kl}, \tag{19c}$$

etc. Thus, the quasiparticle Hamiltonian $\hat{G}$ of the form given in Eq. (9) can be directly obtained from the auxiliary quasiparticle Hamiltonian (17). Therefore, as far as the energy spectrum of the Hamiltonian $\hat{H}$ is concerned, there is no need to know that de-excitation operator $\hat{\Xi}$ of Eq. (14). This general result [22a] has been later found valid also in applications of valence-universal MRCC methods [8h, 11b]. However, the knowledge of operator $\hat{\Xi}$ is necessary to calculate molecular properties such as expectation values and transition moments [22d]. The bi-exponential Ansatz (10–14) provides an explicit decoupling of the excitation and de-excitation CC amplitudes in the FSCC method. This Ansatz offers a convenient solution to the problem of finding a proper normalization of the wave operator in the MRCC methods. This problem is far from being trivial, since some normalization conditions (including the most popular intermediate normalization) are not compatible with the requirement of the size-extensivity of MRCC formalisms [21].
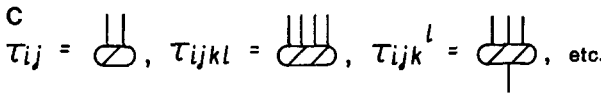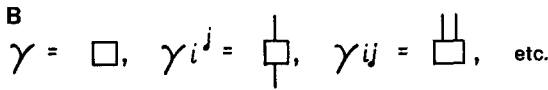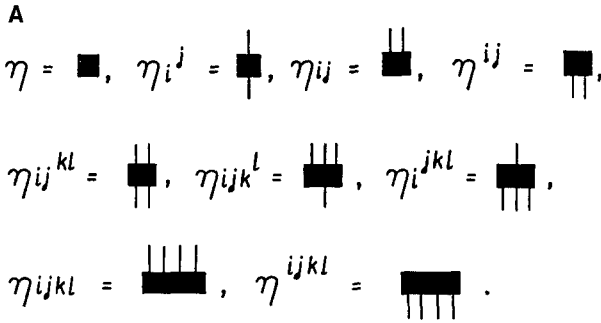
To calculate operator $\hat{\Gamma}$ one has to find the CC excitation operator $\hat{\Theta}$ of Eq. (13), with the θ-amplitudes chosen such that conditions (18) are satisfied. In [22a] (and, in a more detailed form, in Ref. [22c]) we developed an algebraic-diagrammatic technique for performing similarity transformations in Fock space, such as that defined in Eqs. (15) and (11). To apply this technique, one first expresses operator (11) using the Lindgren exponential Ansatz [9a]:

$$\hat{\Omega}_{ex} = \{\exp(\hat{T})\}, \qquad (20)$$

where operator $\hat{T}$ has *exactly* the same structure as operator $\hat{\Theta}$, with τ-amplitudes of operator $\hat{T}$ replacing the θ-amplitudes of operator $\hat{\Theta}$. Actually, in [22c] (see also a preliminary formulation in [22a]) we used the formalism of Jeziorski and Paldus [5] which allows for a rigorous algebraic formulation of Ansatz (20), avoiding some ambiguities of the original Lindgren proposal [9a]. We showed in Refs. [22a,c] that there are finite, connected formulas expressing the τ-amplitudes of operator $\hat{T}$ in terms of the θ-amplitudes of operator $\hat{\Theta}$. We showed also how to express the γ-amplitudes of operator $\hat{\Gamma}$ directly through the η-amplitudes of operator $\hat{H}$, and the τ-amplitudes of operator $\hat{T}$; the resulting formulas have the form of (finite) connected-diagram expansions. Using the above results one finds that Eqs. (18) constitute a set of coupled nonlinear algebraic equations for (unknown) τ-amplitudes; we call these equations the FSCC equations. In [22, 26] we considered the θ-amplitudes as unknowns (the corresponding equations were called the generalized CC equations); however, such a formulation is less advantageous than the present one (see below). We would like also to note that in the approximate variants of the FSCC method considered in [22b,d] there is practically no difference between the τ- and θ-amplitudes.

The FSCC equations can be conveniently arranged in a triangular structure shown in Eqs. (18): the columns correspond to the number of the upper indices $(0, 1, 2, \ldots)$, and the rows to the total number of indices $(2, 4, 6, \ldots)$. It is to be noted that the number of these equations is equal to the number of unknowns (the τ-amplitudes). The replacement of the θ-amplitudes by the τ-amplitudes as the unknowns in the FSCC equations results in a more decoupled structure of these equations. For instance, the equations of the first column of Eq. (18) become decoupled from the remaining ones; these equations are equivalent to the T_1-, T_2-, T_3-, $\ldots$ equations of the single-reference CC method [2–4]. It can be shown in general that with the τ-amplitudes as the unknowns the equations in the m-th column of Eqs. (18) are decoupled from those in the n-th column, for $n > m$. When the first three columns of Eqs. (18) are solved exactly, the resulting

A

$$\eta = \blacksquare, \quad \eta_i{}^j = \blacksquare, \quad \eta_{ij} = \blacksquare, \quad \eta^{ij} = \blacksquare,$$

$$\eta_{ij}{}^{kl} = \blacksquare, \quad \eta_{ijk}{}^l = \blacksquare, \quad \eta_i{}^{jkl} = \blacksquare,$$

$$\eta_{ijkl} = \blacksquare, \quad \eta^{ijkl} = \blacksquare.$$

B

$$\gamma = \square, \quad \gamma_i{}^j = \square, \quad \gamma_{ij} = \square, \quad \text{etc.}$$

C

$$\tau_{ij} = \oslash, \quad \tau_{ijkl} = \oslash, \quad \tau_{ijk}{}^l = \oslash, \quad \text{etc.}$$

Fig. 1A–C. A diagrammatic representation of operators' amplitudes: **A** η-amplitude of Hamiltonian $\hat{H}$ [see Eq. (6)]; **B** γ-amplitudes of the auxiliary quasiparticle Hamiltonian $\hat{\Gamma}$ [see Eq. (17)]; **C** τ-amplitudes of the CC excitation operator $\hat{T}$ [see Eq. (20)]

τ-amplitudes are sufficient to calculate the exact values of the g-amplitudes corresponding to the first three terms on the rhs of Eq. (9).

The FSCC equations may be written in a compact diagrammatic form using Hughenholtz-type diagrams [20b] of Fig. 1 (for details the reader is asked to consult [22a,c]). In Fig. 2 we present the diagrammatic FSCC equations (18a) and (18b). These equations correspond to a special choice of the reference wave function Φ as the Brueckner (maximum overlap) determinant with respect to the exact ground-state wave function Ψ (for iterative determination of Brueckner orbitals within the CC method, see [32] and [22b]). By optimizing Φ to become the Brueckner determinant one gets:

$$\theta_{ij} = \tau_{ij} = 0, \tag{21}$$

thus eliminating many terms in the FSCC equations. The γ-amplitudes which determine the first three terms of the quasiparticle Hamiltonian (9) [see Eqs. (19)] are shown in Fig. 3.

In the simplest non-trivial approximate variant of the FSCC method [22b] one solves the FSCC equations depicted in Fig. 2. In order to decouple these equations from the rest of the FSCC equations, one has to neglect the terms with the numbers enclosed in the square brackets; this leaves the τ-amplitudes τ_{ijkl} and $\tau_{ijk}{}^l$ as the only unknowns. In principle, one has also to adjust the occupied spin orbitals such that Eq. (18a) (see also Fig. 2A) is fulfilled. Once the FSCC equations of Fig. 2 are solved, the g-amplitudes of the quasiparticle Hamiltonian (9) are calculated according to equations depicted in Fig. 3 (again, the terms with the numbers in the square brackets are neglected). This variant of the FSCC method will be employed in the subsequent section.

Fig. 2A–C. A diagrammatic form of the FSCC equations: **A** $\gamma_{ij} = 0$ [Eq. (18a)]; **B** $\gamma_{ijkl} = 0$ [the first of Eqs. (18b)]; **C** $\gamma_{ijk}{}^{l} = 0$ [the second of Eqs. (18b)]
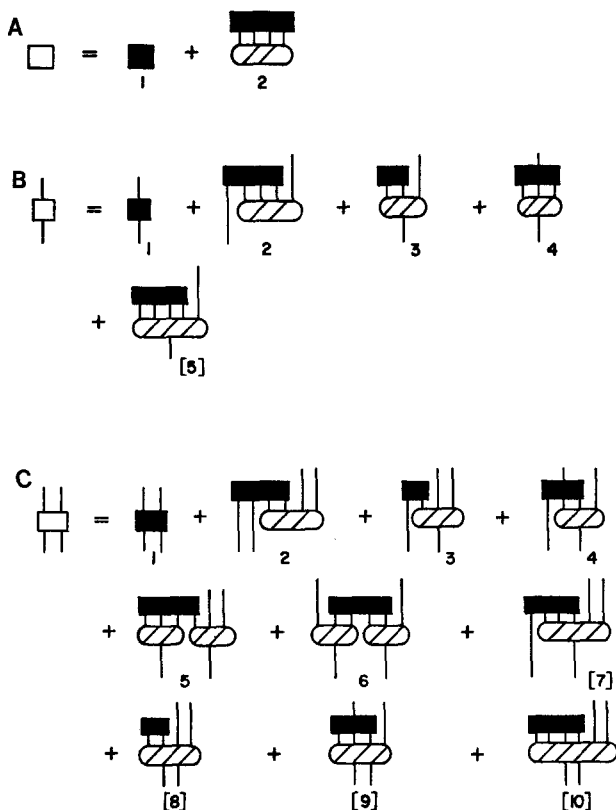
Fig. 3A–C. Diagrammatic expressions defining the g-amplitudes of the quasiparticle Hamiltonian $\hat{G}$ [see Eqs. (19)]: **A** γ ($=g=E$); **B** $\gamma_i^{\,j}$ ($=g_i^{\,j}$); **C** $\gamma_{ij}^{\,kl}$ ($=g_{ij}^{\,kl}$)

3. FSCC and FCI calculations for model π-electron systems

The PPP model [28] of π-electron systems provides a convenient testing ground for many-body theories (see, for instance, [33]). We performed calculations for *trans*-butadiene, *all-trans*-hexatriene, and benzene using the parametrization of Schulten et al. [34]. The resonance-integral formula:

$$\beta(r_{nn}) = \beta_0 + 3.21(r_{nn} - 1.397) \tag{22}$$

was used, where r_{nn} is a nearest-neighbor distance in Å, and the energy unit is eV. For the two-electron integrals the Mataga–Nishimoto (MN) formula [35] was used. The values of the carbon atom effective ionization potential I_0, the resonance integral β_0, the one-center two-electron integral γ_0, and the nearest-neighbor distances are collected in Table 1.

As indicated by the FCI results of [34b] (see also a previous discussion in [36]), the MN formula provides an enhancement of the electronic correlation effects in the PPP model (in comparison, e.g., with the Ohno formula [37]), a feature which is useful for our purpose of testing the performance of the FSCC method. The FCI energies for our π-electron systems were obtained by applying the unitary-group approach (UGA) in the atomic-orbital basis [38]. We used the variant of the FSCC method described in the last paragraph of the previous section, with the following additional simplifications:

Table 1. The parameters of the PPP model [34b]

I_0 (eV) a	β_0 (eV) b	γ_0 (eV) c	r_{nn} (Å) d	(C-C-C) e
11.16	−2.43	11.13	1.460 (i)	120°
			1.350 (ii)	
			1.397 (iii)	

[a] The carbon atom effective ionization potential
[b] The resonance integral
[c] The one-center two-electron integral
[d] The nearest-neighbor distances
 (i)   single bonds } butadiene, hexatriene
 (ii) double bonds }
 (iii) benzene
[e] The angles between angles carbon-carbon bonds

(S1) Equation (21) is assumed to hold, but Φ is in each case approximated by the HF determinant. It means that the T_1-equations [Eqs. (18a), see also Fig. 2A] are not satisfied.

(S2) In Fig. 2C, diagram 5, the γ-amplitude is replaced by the corresponding η-amplitude [see Fig. 3B, diagram 1]; in this case the corresponding FSCC equations become linear with respect to amplitudes $\tau_{ijk}{}'$ (the unknowns).

Let us introduce indices ϱ, σ, $\tau = 1, 2, \ldots, N$ for the "holes", and indices r, s, $t = N + 1, \ldots, M$ for the "particles" [see Eqs. (5)]. We can now rewrite Eqs. (18b) as:

$$\gamma_{\varrho\sigma rs} = 0, \tag{23}$$

$$\gamma_{\varrho\sigma r}{}^\tau = 0, \tag{24a}$$

$$\gamma_{\varrho rs}{}^t = 0, \tag{24b}$$

where only such combinations of the "particle" and "hole" indices appear which are allowed by the particle-number symmetry [22a–c]. Equations (23) correspond to the diagrammatic equation of Fig. 2B; the latter can be written in a more expanded form by using oriented lines (with arrows) to distinguish between "particles" and "holes". The procedure of line-orienting applied to the diagrammatic equation of Fig. 2C leads to two types of equations represented by Eqs. (24a,b). Equations (23) are identical with the CCD equations of the single-reference CC method [3], and their solution provides amplitudes $\tau_{\varrho\sigma rs}$ (identical with the T_2-amplitudes). Equations (24) are peculiar to the FSCC method; they provide amplitudes $\tau_{\varrho\sigma r}{}^\tau$ and $\tau_{\varrho rs}{}'$ which are necessary for calculating the g-amplitudes of the quasiparticle Hamiltonian (9) depicted in Fig. 3B and 3C. Because of the simplification (S2), Eqs. (24) are linear in the unknowns. We would like to add that the quasiparticle Hamiltonian (9) in non-Hermitian, and in the present implementation of the FSCC method we used a diagonalization procedure suitable for non-Hermitian matrices.

Below we present and discuss the results of the FCI and FSCC calculations for our π-electron systems:

Table 2. Ground state energies

	FCI	FSCC	HF	S^2_{FCI}
		Total electronic energy (eV)		
		[correlation energy (eV)]		a
Butadiene				
State ^1A_g	-78.156	-78.153	-76.775	0.88
	$[-1.381]$	$[-1.378]$	$[0.0]$	
Hexatriene				
State ^1A_g	-134.990	-134.982	-132.975	0.82
	$[-2.014]$	$[-2.006]$	$[0.0]$	
Benzene				
State $^1A_{1g}$	-144.880	-144.876	-143.363	0.87
	$[-1.517]$	$[-1.513]$	$[0.0]$	

[a] For definition, see Eq. (25)

3.1. Ground-state calculations

The FCI, FSCC, and HF total electronic energies and correlation energies for the ground states of the neutral molecules are given in Table 2. We provide also the values of quantity:

$$S^2_{FCI} = |\langle \Phi | \Psi \rangle|^2, \tag{25}$$

where Φ and Ψ are the ground-state HF and FCI wave functions, respectively (both are assumed to be normalized). As seen, the FSCC method (equivalent in this case to the CCD method [3]) performs very well, reproducing 99.8, 99.6, and 99.7% of the correlation energy for butadiene, hexatriene, and benzene, respectively. This supports the use of the simplification ($S1$), and indicates that diagrams 6–8 of Fig. 2B (corresponding to T_3- and T_4-amplitudes) are unimportant. We would like also to note that the values of parameter S^2_{FCI} are quite large, which indicates that a one-determinantal description of the ground states of our molecules is satisfactory.

3.2. Ionization energies

The ionization energies of our molecules are shown in Table 3. In addition to the FCI and FSCC results, we give also the results obtained by using the Koopmans approximation [39]. This approximation corresponds to neglecting in Fig. 3B all the diagrams except diagram 1. In Table 3 we list, for each ionized state (n), the value of parameter:

$$S^2_{max} = \sum_k C^2_k, \tag{26}$$

where C_k's are the coefficients of the FCI wave function $\Psi_{(n)}$, corresponding to the $0p$-$1h$ subspace of the Fock space spanned by configurations $\{\Phi_k\} = \{\hat{b}_\varrho \Phi; \varrho = 1, 2, \ldots, N\}$. Parameter (26) provides a measure of the con-

Table 3. Ionization energies

Eigenv. a	FCI			FSCC		Koopmans	
	ΔE (eV) b	S^2_{max} c		δ_{FCI} (eV) d	S^2_{FCI} e	δ_{FCI} (eV) d	S^2_{FCI} e
Butadiene							
State ^2B_g	(1)	10.415	0.94	−0.027	0.94	−0.671	0.94
State ^2A_u	(2)	12.402	0.72	−0.090	0.72	−0.051	0.72
Hexatriene							
States ^2A_u	(1)	9.819	0.88	−0.056	0.88	−0.649	0.88
	(4)	12.528	0.59	−0.145	0.59	0.294	0.59
State ^2B_g	(2)	11.427	0.66	−0.057	0.66	−0.117	0.66
Benzene							
States $^2E_{1g}$	(1, 2)	10.570	0.89	−0.040	0.89	−0.175	0.89
State $^2A_{2u}$	(3)	12.734	0.67	0.078	0.67	0.701	0.67

[a] Eigenvalue number in the FCI procedure
[b] The FCI ionization energy
[c] For definition, see Eq. (26)
[d] $\delta_{FCI} = \Delta E$(method) $- \Delta E$(FCI)
[e] For definition, see Eq. (27)

tainment of $\Psi_{(n)}$ in the "model space" spanned by $\{\Phi_k\}$. For the FSCC and Koopmans results we give also in Table 3 the values of parameters:

$$S^2_{FCI} = |\langle \Phi_{(n)} | \Psi_{(n)} \rangle|^2, \tag{27}$$

where $\Phi_{(n)}$ is a normalized wave function obtained by diagonalizing the quasiparticle Hamiltonian (9) in our "model space" [in the Koopmans approximation one replaces Hamiltonian (9) by Hamiltonian (6)]. Parameter (27) is an analog of that defined in Eq. (25). If, for a given state (n), the values of parameters (26) and (27) are very close to each other, then both the FCI and (FSCC or Koopmans) methods provide a very similar mixing of wave functions within the "model space". This is indeed the case for all the results presented in Table 3.

As seen in Table 3, the FSCC results for the ionization energies come very close to the FCI ones, the largest difference being less than 0.15 eV. We would like to point out that in the worst case (the second state ^2A_u of hexatriene) also the value of parameter S^2_{max} is small (0.59). This indicates that there is a strong admixture of excited ionized configurations from the outside of $0p$-$1h$ space, thus making the contribution of diagram 5 of Fig. 3B (neglected in our FSCC calculations) more important in this case.

We checked the validity of simplification (S2) by performing iterative calculations including the full diagram 5 of Fig. 2C, but the resulting FSCC ionization energies changed only slightly, and mostly for the worse.

The ionization energies calculated in the Koopmans approximation are not too bad, a fact which is usually attributed to a partial cancellation of the electronic-correlation and orbital-relaxation effects [40]. However, the orbital-relaxation effects are expected to be rather small for our molecules. A useful decomposition of an FCI ionization energy into interpretable contributions can

be provided by the diagrammatic equation in Fig. 3B (the corresponding
diagrams will be denoted below by $B1-B5$). For instance, by using the FSCC
results for the $^2A_{2u}$ ionized state of benzene we found: $B1 = 13.435$ eV,
$B2 = 0.363$ eV, $B3 = 0$ eV, $B4 = -0.987$ eV, and $B5 = 0.078$ eV. The value of $B1$
represents the ionization energy in the Koopmans approximation. The $B2$-
contribution may be called the "lost-correlation" term, since it corresponds to
the "breaking" of those pair-correlation contributions to the ground-state corre-
lation energy which involve the spin orbital missing in the ionized state; $B2$ is
always positive. Term $B3$ originates from the adjustment of the HF orbitals to
the Brueckner ones, and is expected to be small; due to the simplifications ($S1$)
in the present paper this term vanishes. Contribution $B4$ stems form two effects:
the orbital relaxation, and the "semi-internal" correlation [41] in the ionized
state. The latter effect corresponds to additional electronic correlations involving
scattering of electron pairs, in which one of the electrons fills the spin orbital
missing in the ionized state. Since term $B4$ is always negative, a partial cancella-
tion of the $B2$- and $B4$-contributions occurs. Term $B5$ corresponds to the change
of the pair-correlation energies for pairs of spin orbitals which are occupied in
the ground and the ionized state; the value of $B5$ given above was estimated as
a difference between the FSCC and FCI ionization energies.

3.3. Electron affinities

The electron affinities calculated for our molecules are shown in Table 4; the
form of presentation is the same as in the case of the ionization energies, see
Table 3. For parameters (26) and (27), the "model space" corresponds now to
the the $1p$-$0h$ space.
    There is no need to discuss the results contained in Table 4 in more detail,
since the differences between the FCI, and the FSCC and the Koopmans values

Table 4. Electron affinities

		FCI			FSCC		Koopmans	
	Eigenv. a	ΔE (eV) b	S^2_{max} c	δ_{FCI} (eV) d	S^2_{FCI} e	δ_{FCI} (eV) d	S^2_{FCI} e
Butadiene								
State ^2A_u	(1)	-0.775	0.94	-0.027	0.94	-0.671	0.94
State ^2B_g	(2)	1.212	0.72	-0.090	0.72	-0.051	0.72
Hexatriene								
States ^2B_g	(1)	-1.371	0.88	-0.056	0.88	-0.649	0.88
	(4)	1.338	0.59	-0.145	0.59	0.294	0.59
State ^2A_u	(2)	0.237	0.66	-0.057	0.66	-0.117	0.66
Benzene								
States $^2E_{2u}$	(1, 2)	-0.620	0.89	-0.040	0.89	-0.175	0.89
State $^2B_{2g}$	(3)	1.544	0.67	0.078	0.67	0.701	0.67

a, c, d, e See footnotes to Table 3
b The FCI electron affinity

Table 5. Butadiene, singlet excitation energies

State symmetry	FCI			FSCC		TDA	
	Eigenv. No.	ΔE (eV)	S^2_{max}	δ_{FCI} (eV)	S^2_{FCI}	δ_{FCI} (eV)	S^2_{FCI}
	a	b	c	d	e	d	e
^1A_g	(2)*	4.751	0.37	$\left\{\begin{array}{c}0.518\end{array}\right.$	$0.37\}$	$\left\{\begin{array}{c}2.115\end{array}\right.$	$0.37\}$
	(5)*	9.221	0.45	$\left.-3.952\right.$	$0.45\}$	$\left.-2.355\right.$	$0.45\}$
	(4)	8.774	0.92	-0.481	0.92	-0.507	0.92
^1B_u	(3)	6.731	0.96	0.050	0.96	-0.979	0.96
	(6)	10.514	0.89	-0.182	0.87	-0.624	0.86

a, c, d, e See footnotes to Table 3

b The FCI singlet excitation energy

* If there are two FCI states assigned to a given FSCC (and TDA) level, the corresponding values of δ_{FCI} and S^2_{FCI} are enclosed in curly brackets

of the electron affinities are the same as those for the ionization energies in Table 3. This fact is due to the so called alternancy symmetry [42] of the PPP model.

3.4. Singlet excitation energies

The excitation energies corresponding to singlet excited states of the neutral systems are collected in Tables 5 (budadiene), 6 (hexatriene), and 7 (benzene). Besides the FCI and FSCC results we give also the results obtained in the Tamm–Dancoff approximation (TDA) [8e, 11b, 43]. The TDA corresponds to performing a diagonalization of Hamiltonian (6) in the $1p$-$1h$ subspace of the Fock space. The $1p$-$1h$ space is a direct sum of two spaces spanned by the singlet and the triplet spin-adapted configurations, respectively; in the present case the former space plays the role of the "model space" in the definitions of the parameters (26) and (27).

As seen from Tables 5 and 6, the FSCC results for the non-aromatic systems (butadiene and hexatriene), although generally better than the TDA ones, are unsatisfactory. For instance, for the lowest excited ^1A_g state, the FSCC values for butadiene and hexatriene are off by 0.518 eV and 1.031 eV, respectively. In these cases the values of the parameter S^2_{max} are very small, being 0.37 (butadiene) and 0.30 (hexatriene) (in each of these cases it is also possible to find a FCI state with a higher value of S^2_{max}, but with a much worse energy match). The small values of S^2_{max} indicate that the lowest singlet excited states of linear hydrocarbons are dominated by configurations from outside the $1p$-$1h$ space. In fact, for butadiene as well as for hexatriene, the largest contribution to the FCI wave function of the lowest ^1A_g state comes from the doubly excited configuration of the lowest energy. There is no doubt that in this case the contributions of diagrams 7–10 of Fig. 3C, neglected in our FSCC calculations, become important (a closer analysis points to diagram 9 as the most important one). Similar problems occur for the lowest excited ^1B_u state of hexatriene. In addition, for higher states of this symmetry complex values of the FSCC energies appear; again, it is an indication that there is a serious misrepresentation of some

Table 6. Hexatriene, singlet excitation energies

State symmetry	Eigenv. No.	FCI ΔE (eV)	S^2_{max}	FSCC δ_{FCI} (eV)	S^2_{FCI}	TDA δ_{FCI} (eV)	S^2_{FCI}
	a	b	c	d	e	d	e
^1A_g	(2)*	3.882	0.30	1.031	0.30	1.958	0.30
	(7)*	7.864	0.45	−2.951	0.43	−2.024	0.45
	(6)	7.526	0.87	−0.179	0.87	−0.704	0.87
	(5)*	6.146	0.16	2.003	0.12	3.696	0.11
	(13)*	10.091	0.34	−1.941	0.27	−0.248	0.29
	(12)	10.018	0.84	−0.329	0.82	−0.614	0.84
^1B_u	(3)*	4.739	0.36	0.336	0.36	2.159	0.36
	(11)*	9.388	0.41	−4.312	0.41	−2.490	0.41
	(4)	5.784	0.92	−0.008	0.91	−1.084	0.92
	(8)	8.561	0.76	−0.168 +0.007i	0.33	−0.331	0.71
	(10)	8.965	0.77	−0.572 −0.007i	0.69	−0.278	0.66
	(16)	10.924	0.60	−0.535	0.52	−0.025	0.42

a, c, d, e See footnotes to Table 3
b See footnote to Table 5
* If there are two FCI states assigned to a given FSCC (and TDA) level, the corresponding values of δ_{FCI} and S^2_{FCI} are enclosed in curly brackets

Table 7. Benzene, singlet excitation energies

State symmetry	Eigenv. No.	FCI ΔE (eV)	S^2_{max}	FSCC δ_{FCI} (eV)	S^2_{FCI}	TDA δ_{FCI} (eV)	S^2_{FCI}
	a	b	c	d	e	d	e
$^1B_{2u}$	(2)	3.703	0.76	−0.066	0.76	1.284	0.76
$^1B_{1u}$	(5)	6.932	0.93	0.016	0.93	−0.646	0.92
	(15)	11.281	0.80	−0.762	0.77	0.436	0.78
$^1E_{2g}$	(3, 4)	5.979	0.48	0.312	0.48	2.657	0.48
	(10, 11)	9.520	0.88	−0.366	0.88	−0.294	0.88
$^1E_{1u}$	(6, 7)	7.138	0.89	−0.211	0.89	−0.027	0.89

a, c, d, e See footnotes to Table 3
b See footnote to Table 5

non-Hermitian contributions to the g-amplitudes (19c), due to the neglect of diagrams 7–10 of Fig. 3C.

The FSCC method performs better in the calculations of singlet excitation energies of benzene (Table 7), but in this case values of parameter S^2_{max} are generally greater than for butadiene and hexatriene. As an example, we make

below a decomposition of the FCI excitation energy ΔE corresponding to the lowest $^1B_{2u}$ state of benzene ($S^2_{max} = 0.76$) into diagrammatic contributions. ΔE can be expressed as a sum of the FCI ionization energy corresponding to the $^2E_{1g}$ state, equal to 10.570 eV (see Table 3), and the electron affinity corresponding to the $^2E_{2u}$ state (see Table 4), equal to -0.620 eV, plus the "particle"-"hole" interaction terms depicted in Fig. 3C (these terms will be hereafter denoted by $C1$–$C10$). The FSCC estimates give: $C1 = -4.614$ eV (this is a "bare" interaction term of the TDA), $C2 = -0.106$ eV, $C3 = 0$ eV, $C4 = -1.476$ eV, $C5 = 0$ eV, and $C6 = -0.036$ eV; an estimate of the $C7$–$C10$ contributions amounts to -0.015 eV in this case. It is seen that the largest correction to the TDA interaction term comes here from diagram $C4$ which depends on τ-amplitudes derived from Eqs. (24).

3.5. Triplet excitation energies

The excitation energies corresponding to triplet excited states of the neutral systems are shown in Tables 8 (butadiene), 9 (hexatriene), and 10 (benzene). As for the singlet excitation energies, the FCI, FSCC, and TDA results are given. Parameters (26) and (27) are defined with respect to the "model space" spanned by the triplet spin-adapted $1p$-$1h$ configurations.

For butadiene and hexatriene, the FSCC results for the lowest ^3B_u state are very good, with the errors equal to 0.073 eV and -0.036 eV, respectively; for the lowest ^3A_g states the errors are larger and amount to 0.373 eV and 0.328 eV, respectively. The FSCC result for the lowest $^3B_{1u}$ state of benzene is off by -0.337 eV. The magnitudes of the errors of the FSCC results for higher triplet excited states of our molecules vary, being usually smaller for larger values of parameter S^2_{max}.

Ending this section let us remark that for a PPP model of ethylene the results of the FSCC and FCI calculations coincide.

Table 8. Butadiene, triplet excitation energies

State symmetry	FCI			FSCC		TDA	
	Eigenv. No.	ΔE (eV)	S^2_{max}	δ_{FCI} (eV)	S^2_{FCI}	δ_{FCI} (eV)	S^2_{FCI}
	a	b	c	d	e	d	e
^3B_u	(1)	2.222	0.93	0.073	0.91	-0.695	0.93
	(3)*	5.748	0.29	{ 1.495	0.27}	{ 1.968	0.27}
	(5)*	9.920	0.70	{-2.677	0.67}	{-2.204	0.68}
^3A_g	(2)	3.585	0.92	0.373	0.92	-0.580	0.92
	(4)	8.609	0.97	-0.009	0.97	-1.203	0.97

a, c, d, e See footnotes to Table 3
b The FCI triplet excitation energies
* If there are two FCI states assigned to a given FSCC (and TDA) level, the corresponding values of δ_{FCI} and S^2_{FCI} are enclosed in curly brackets

Table 9. Hexatriene, triplet excitation energies

State symmetry	FCI			FSCC		TDA	
	Eigenv. No.	ΔE (eV)	S^2_{max}	δ_{FCI} (eV)	S^2_{FCI}	δ_{FCI} (eV)	S^2_{FCI}
	a	b	c	d	e	d	e
^3B_u	(1)	1.828	0.86	-0.036	0.84	-0.653	0.86
	(3)	3.767	0.85	0.528	0.80	-0.477	0.85
	(4)*	4.752	0.20	$\{$ 1.683	0.17$\}$	$\{$ 2.087	0.17$\}$
	(11)*	8.705	0.68	$\{-2.270$	0.60$\}$	$\{-1.866$	0.63$\}$
	(9)	7.976	0.88	-0.101	0.88	-1.078	0.88
	(6)*	6.621	0.17	$\{$ 2.345	0.11$\}$	$\{$ 3.470	0.10$\}$
	(19)*	10.953	0.48	$\{-1.986$	0.48$\}$	$\{-0.861$	0.48$\}$
^3A_g	(2)	2.946	0.86	0.328	0.85	-0.614	0.86
	(5)*	5.514	0.27	$\{$ 1.402	0.26$\}$	$\{$ 1.822	0.26$\}$
	(13)*	9.436	0.60	$\{-2.521$	0.58$\}$	$\{-2.101$	0.59$\}$
	(7)	7.009	0.89	0.046	0.89	-1.169	0.89
	(15)	9.640	0.55	-0.263	0.55	0.203	0.54

a, c, d, e See footnotes to Table 3.

b See footnote to Table 8.

* If there are two FCI states assigned to a given FSCC (and TDA) level, the corresponding values of δ_{FCI} and S^2_{FCI} are enclosed in curly brackets

4. FSCC results for neutral excited states – a discussion

We would like to make a few comments concerning the results of our FCI and FSCC calculations of the singlet and triplet excitation energies (Tables 5–10):

(i) The version of the FSCC method implemented in the present paper does not take into account those effects of the orbital relaxation and electron correlation which are due to the *simultaneous* presence of a "particle" and a "hole" in an electronic system (these effects were also neglected in the multi-reference CC calculations of excitation energies in [8e, 11a–d]). Essentially, our approach is to calculate corrections to the TDA "bare" interaction term (diagram 1 in Fig. 3C) by including only the contributions from the τ-amplitudes found in calculations for the ground state and $(N \pm 1)$-electron states (diagrams 2–6 in Fig. 3C). Since no convergence problems were encountered in solving Eqs. (23) and (24), the only source of errors can be attributed to the neglect of diagrams 7–10 of Fig. 3C in our present calculations. However, the inclusion of these diagrams would require solving additional FSCC equations, with a very large number of unknowns.

(ii) For the excited states with $S^2_{max} > 0.7$ the largest discrepancy between FCI and FSCC results does not exceed 0.8 eV, being often smaller (0.3–0.4 eV). In these cases the FSCC results are usually better than the TDA ones. Also the values of parameters S^2_{FCI} for the FSCC and TDA methods are in these cases usually very close to that of S^2_{max}.

(iii) In several cases it was difficult to make a proper assignment of an FCI level to an FSCC one: we had to choose between two FCI states, and the one

Table 10. Benzene, triplet excitation energies

State symmetry	FCI			FSCC		TDA	
	Eigenv. No.	ΔE (eV)	S^2_{max}	δ_{FCI} (eV)	S^2_{FCI}	δ_{FCI} (eV)	S^2_{FCI}
	a	b	c	d	e	d	e
$^3B_{1u}$	(1)	2.812	0.90	−0.337	0.90	−0.236	0.90
	(7)*	7.689	0.34	{ 1.472	0.34}	{ 3.078	0.34}
	(24)*	12.696	0.51	{−3.536	0.51}	{−1.930	0.51}
$^3B_{2u}$	(6)	6.113	0.97	−0.012	0.97	−1.126	0.97
$^3E_{1u}$	(2, 3)	3.851	0.79	0.450	0.79	0.232	0.79
$^3E_{2g}$	(4, 5)	5.120	0.68	0.492	0.68	0.489	0.68
	(9, 10)	8.683	0.80	−0.043	0.80	−0.046	0.80

[a, c, d, e] See footnotes to Table 3.
[b] See footnote to Table 8.
* If there are two FCI states assigned to a given FSCC (and TDA) level, the corresponding values of δ_{FCI} and S^2_{FCI} are enclosed in curly brackets

with the lower value of S^2_{max} gave a better energy match to the FSCC excitation energy. These cases provide a very clear illustration of the problem of "intruder states" ([29], see also examples discussed in [9b, 10h, 44, 45]). The two FCI states, say (m) and (n), affected by an "intruder state" can be written as:

$$\Psi_{(m)} = c_1 \Phi_{(m)} + c_2 \Lambda_{(m)}, \qquad (28a)$$

$$\Psi_{(n)} = c_3 \Phi_{(n)} + c_4 \Lambda_{(n)}, \qquad (28b)$$

where $\Psi_{(i)}$, $\Phi_{(i)}$, and $\Lambda_{(i)}$ $(i = m, n)$ are normalized, and the last two wave functions represent the parts of $\Psi_{(i)}$ from the "model space" and from its orthogonal complement, respectively. For instance, for the lowest ^1A_g state of butadiene (see Table 5, $m = 2$, $n = 5$) we found that:

$$\langle \Phi_{(2)} | \Phi_{(5)} \rangle = 1,$$

$$\langle \Lambda_{(2)} | \Lambda_{(5)} \rangle = 0.70,$$

and the coefficients in the linear combinations (28) read: $c_1 = 0.61$, $c_2 = 0.67$, $c_3 = 0.79$, $c_4 = -0.74$. The role of the "intruder state" is played in this case by the lowest doubly excited configuration; its projections onto $\Lambda_{(2)}$ and $\Lambda_{(5)}$ are equal to 0.70 and 0.74, respectively. It is seen that the "intruder state" effectively splits a state from the "model space" into two FCI states, and only one of them can be described within a FSCC or TDA approach. Sano and I'Haya [44] applied a multireference perturbation theory to a PPP model of butadiene, and found a poor convergence of perturbation expansions of excitation energies for states affected by "intruder states". The importance of doubly- and higher-excited configurations in the description of low-lying excited states in the PPP model was studied by Koutecký et al. [36], Schulten et al. [34], and Čížek et al. [46]. In the case of linear polyenes they found that strong mixing with doubly-excited configurations pushes the lowest excited level of symmetry ^1A_g below the lowest ^1B_u-level. Results of Refs. [34, 36, 44, 46] indicate that the PPP model puts

extreme demands on approximate methods devised for calculating the excitation spectra.

(iv) In the valence-universal MRCC methods [8d–f, j, 9, 10, 11], in order to avoid problems with "intruder states", one usually considers only a few active "particles" and "holes"; this requires calculating additional CC amplitudes to decouple the active part of the $1p$-$1h$ space from the remaining part (there is, however, a substantial net reduction in the number of the considered CC amplitudes). In the case of our molecules the choice of active "particles" and "holes" with lowest energies (i.e., corresponding to the lowest unoccupied and highest occupied orbitals, respectively) would lead to a considerable reduction of the number of excited states taken into account [for each molecule we give the symmetry label and the FCI eigenvalue number (in brackets) of the surviving states]: butadiene-$^1B_u(3)$ and $^3B_u(1)$, hexatriene-$^1B_u(4)$ and $^3B_u(1)$, benzene-$^1B_{2u}(2)$, $^1B_{1u}(5)$, $^1E_{1u}(6, 7)$, and $^3B_{2u}(6)$, $^3B_{1u}(1)$, $^3E_{1u}(2, 3)$. In the case of the butadiene (see Tables 5 and 8) and hexatriene states (see Tables 6 and 9) the FSCC results are excellent, indicating that the decoupling of the active part of the $1p$-$1h$ space is unimportant; in the case of benzene the active states are decoupled by symmetry. Therefore, our results could be compared with those of the MRCC methods employing the above choices of active spaces. We would like to note that there is no fundamental problem with modifying the FSCC formalism by introducing "active" and "inactive" quasiparticles. However, our calculations for linear hydrocarbons, butadiene and hexatriene, indicate that the procedure of limiting the number of active "particles" and "holes" does not provide a true remedy for the problem of "intruder states": too few excited levels are covered, and, moreover, the calculated ^1B_u-states are *not* the lowest singlet excited states for these molecules, see (iii).

(v) One may wonder to that extent the problem of "intruder states" discussed in (iii) reflects the physics of low-lying excited states in π-electron states in π-electron systems. It is well established [47] for octatetraene, as well as for longer linear polyenes, that the lowest excited singlet state corresponds to symmetry ^1A, and contains a significant admixture of $2h$-$2p$ configurations. After some confusion regarding the ordering of the lowest ^1A_g and ^1B_u levels in *trans*-butadiene and hexatriene (see a discussion in [48]), there is now experimental evidence [49] that also these molecules conform to the general pattern. Thus, the results of the CI PPP studies by Schulten et al. [34] are now validated, at least at a semi-quantitative level. Let us remark that various parametrizations of the PPP model, such as that used in the present paper (see also [34]), are known to give quite good a description of excitation spectra of polyenes already at the TDA level. However, it is true only for some excited states, mostly those corresponding to the allowed transitions from the ground state (the "new" ^1A-states do not belong to this category). The FCI treatment, while bringing the correct ordering of lowest excited states, destroys a good quantitative agreement reached at the TDA level. However, Schulten et al. [34b] demonstrated that the FCI PPP description can be improved by adjusting the β_0-parameter and switching to the Ohno formula [37]. Figures 7–9 of [34b] show that the parametrization employing the Mataga–Nishimoto formula [35] (the same as used in the present paper) uses to overdraw the effects of "intruder states". We conclude that the present FCI PPP model is realistic at the qualitative level, and exaggerated at the quantitative one.

(vi) It is important to note that the hierarchy of the FSCC equations need not be solved by following an order-by-order perturbation expansion: to the

contrary, it seems quite obvious that one would attempt to solve FSCC equations belonging to a given column of Eq. (18) *after* the pertinent subset of the FSCC equations from the preceding columns have been solved. In fact, in our FSCC calculations reported in this paper we first solved the CCD equations (23), then the converged amplitudes $\tau_{\varrho\sigma rs}$ were put into Eqs. (24), and finally the remaining τ-amplitudes were calculated. A more advanced variant of the FSCC method includes, in addition to Eqs. (18a) and (18b), also the FSCC equations (18c). For the ground state, this variant provides the description at the level of the CCSDT method [4b]; the FSCC ionization energies and electron affinities are also expected to improve because of the inclusion of diagram 5 in the formula depicted in Fig. 3B. For the excitation-energy calculations the new variant of the FSCC method supplies diagrams 7–9 of Fig. 3C, which should considerably improve the results in the case of excited states discussed in (ii). The description of the remaining excited states originating from $1p$-$1h$ configuration is also likely to improve, since the last set of Eqs. (18c) supplies the amplitudes $\tau_{\varrho\sigma rs}{}^{\tau t}$ which are responsible for changing the admixture of $2p$-$2h$ configurations, some of which play the role of "intruder states". Computational problems are expected at that point, since in the case of strong mixing the pertinent τ-amplitudes may become quite large, see an example of MRCC calculations for the $2p^2$ states of beryllium in [10h]. Moreover, a nonlinear character of the corresponding FSCC equations becomes important, because one will need *multiple* solutions to account for the "level-splitting" discussed in (iii). It seems that "intruder states" cannot (and should not) be avoided at any price, and that there is a potential in such methods as the FSCC one to deal with this problem.

5. Concluding remarks

The FSCC method introduced in [22a,b] provides a natural extension of the single-reference CC method [1–4]. The FSCC equations (18) have a structure similar to the usual CC equations (in fact, the latter ones are contained in the hierarchy of the FSCC equations), and a comparable numerical effort is required for their solution. However, in addition to the ground-state energy of a molecule, the FSCC method enables one to calculate also an important part of the molecular excitation spectrum. In the present paper we show that the FSCC method, in its simplest version involving the FSCC equations (23) and (24), performs very well in the calculations of the total energies, ionization energies, and electron affinities of our model π-electron systems: butadiene, hexatriene, and benzene. The FSCC calculations of the excitation energies (corresponding to the singlet and triplet excited states of the $1p$-$1h$ origin) give good results for states not affected by "intruder states" [29].

It is a peculiar property of the electronic structure of π-electron systems that many of low-lying excited states contain large contributions of doubly- and higher-excited configurations [34], which play a role of "intruder states" [44]. The present version of the FSCC method, although in general improves upon the TDA [8e, 11b, 43], is not sufficient to give a satisfactory description of such states. We suggest that a more elaborate version of the FSCC method, involving Eqs. (18c) from the hierarchy of the FSCC equations, might be capable to deal with the problem of "intruder states" in such cases. The electronic spectra of π-electron systems provide an example where the usual way of avoiding "intruder states" (by limiting the number of active "particles" and "holes") seem to be non-effective.

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