

## EFFECTIVE HAMILTONIAN AND INTERMEDIATE HAMILTONIAN FORMULATIONS OF THE FOCK-SPACE COUPLED-CLUSTER METHOD

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Various aspects of the effective Hamiltonian and intermediate Hamiltonian formulations are discussed in the context of the Fock-space coupled-cluster method. Problems that occur when single-reference methods of solving the Schrödinger equation need to be generalized to the multireference (MR) cases are pointed out. These problems make the generalization nontrivial, especially in the case of the most powerful coupled-cluster (CC) method. It is shown how some specific features of one of the basic MR-CC schemes, the Fock-space CC method, can be used to obtain a simple, yet very effective version of the method. This requires, however, switching from the effective Hamiltonian to the intermediate Hamiltonian formulation. The intermediate Hamiltonian version of the Fock-space CC method is discussed in detail and all its advantages over the standard one are emphasized.

**Keywords:** *Ab initio* calculations; Multi-reference coupled-cluster; Fock-space coupled-cluster; Intermediate Hamiltonian.

The single-reference quantum chemical methods are now being used in routine calculations. Among them the coupled-cluster (CC) methods<sup>1</sup> have demonstrated to be the most promising tools for the treatment of electron correlation effects, especially if high accuracy results are required<sup>2</sup>. The success of the single-reference (SR) CC methods in describing closed-shell system has inspired an intensive research activity towards a generalization of the CC schemes to multireference (MR) cases<sup>3-19</sup>. That would allow application of CC methods to open-shell and quasi-degenerate states, which are characterized by a large component of nondynamic correlation. The nondynamic correlation is difficult or, in most cases, even impossible to handle by the single-reference methods. Thus the multireference schemes should introduce a distinction between descriptions of nondynamic and dynamic

correlation effects. This goal can be achieved by using the effective Hamiltonian formalism<sup>20,21</sup>, in which the dynamic correlation is represented by the so-called wave operator. The wave operator generates this component of the wave function for which an approximate description, like finite-order perturbation expansion or cluster expansion with the cluster operator truncated at some level of excitation, is sufficiently accurate. The wave operator is folded into the effective Hamiltonian, the action being restricted to a small space spanned by strongly interacting zero-order functions. The nondynamic contribution to the electron correlation is provided by diagonalization of the effective Hamiltonian. The diagonalization furnishes a subset of eigenvalues of the Hamiltonian. The distinction made by the effective Hamiltonian formalism in treating both types of electron correlation may be seen as an efficient way of providing information about dominant and less important components of the wave functions. However, the success of this kind of approach depends to a large extent on clear separation of both correlation effects, which may be difficult to achieve because of formal or practical reasons. Another problem caused by the effective Hamiltonian approach is the necessity of describing several states at a time even if we are interested only in one of them. Multidimensional reference spaces make also the Fermi vacuum choice nontrivial which resulted in development of two different types of MR-CC schemes<sup>8,15</sup>.

Because of their formal complexity, high numerical costs and problems caused by the so-called intruder states<sup>22</sup>, the MR-CC methods have not been very widely used in routine calculations. One of possible ways of making the MR-CC methods more attractive is to reformulate them by employing intermediate Hamiltonian techniques<sup>21,23</sup>. The idea underlying the intermediate Hamiltonian approach is to extend diagonalization as a way of providing contributions to the correlation energy. Now the diagonalization gives contributions not only from the reference space but also from an additional intermediate space which plays a role of a buffer between the reference space and the remaining part of the functional space. The intermediate space should contain all functions which can cause convergence problems. There have been many attempts to use the intermediate Hamiltonian technique with respect to both basic MR-CC schemes<sup>24-26</sup> including most recent ones<sup>27-29</sup>.

In this paper we would like to show why the intermediate Hamiltonian reformulation of the Fock-space (FS) CC method (one of the two basic MR-CC schemes) can be especially advantageous in removing most drawbacks of the standard effective Hamiltonian formulation and how some specific features of the FS-CC method can be used to obtain a simple, yet

very effective intermediate Hamiltonian scheme. We start with general remarks on the problem of solving the time-independent Schrödinger equation within an algebraic approximation focusing on the problem of extracting an eigenvalue problem corresponding to a single state. After introducing basic single-reference approaches we show why a direct generalization of such methods like the many-body perturbation theory or CC method to the multireference case leads to effective Hamiltonian formulations and thus to the necessity of considering several states at a time. Then we discuss the standard effective Hamiltonian formulation of the FS-CC method with one- and two-body part in the cluster operator in more detail emphasizing those specific features of the method which are important for our intermediate Hamiltonian reformulation. The effective and intermediate Hamiltonian versions of the FS-CC method are introduced by considering simple similarity transformations of the Hamiltonian<sup>21</sup>. That permits better understanding of many aspects of both approaches. We summarize with showing that advantages of the new approach like, first of all, its state-specific character and an efficient way of solving the equations indicate that the method can be potentially used in routine quantum chemical calculations.

#### SOLVING THE TIME INDEPENDENT SCHRÖDINGER EQUATION

Let us consider the time-independent Schrödinger equation

$$H\Psi = E\Psi, \quad (1)$$

assuming an algebraic approximation. The finite-dimension functional space used to represent  $\Psi$  is indirectly defined by a choice of the primitive orbital basis set. The functional space for an  $N$ -electron system is spanned by all possible determinants involving  $N$  spin orbitals out of all available. Having matrix representation of the Hamiltonian  $H$  in this space, all solutions of Eq. (1) can be found by its diagonalization. Diagonalization of the matrix representation of  $H$  is numerically demanding and it is easy to see that enlarging the orbital basis rapidly increases the dimension of the functional space. On the other hand, obtaining all solutions of the Schrödinger equation is usually not reasonable. First of all, in most cases we are interested in description of one or several states and, second, in practice it is not possible to get good quality results for all states due to limitations in choosing the orbital basis set. Thus, the problem is extraction of the eigenvalue

problem corresponding to one or several states we are interested in from the complete eigenvalue problem, Eq. (1). To do so, some initial approximate information of the system under investigation would be desirable. This information can be provided by a reasonable one-particle description. Let us assume for a while that we are interested in the closed-shell ground state of the system. Since Eq. (1) is invariant with respect to a unitary transformation of the orbitals we can proceed to a new orbital set satisfying some criterion. If we require that the orbital set should be such that the energy functional with the determinantal function gives a minimum, then one can obtain one of the most popular Hartree-Fock (HF) orbitals. It should be noted here that the HF orbitals are only one of possible choices of orbitals satisfying the requirement since the HF energy is invariant with respect to separate unitary transformations of the occupied and unoccupied orbitals in the HF determinant. The requirement introduces only a partitioning of the orbital space into two subspaces, which is known as the Brillouin condition. The HF determinant can be used as a reference to generate all other determinants spanning the functional space. They can be obtained by single, double, *etc.*, up to  $N$ -uple substitutions of occupied spin orbitals with unoccupied ones in the HF determinant  $\Phi$ ; so the ground state function can be expressed as

$$\Psi = (1 + X_1 + X_2 + \dots + X_N)\Phi, \quad (2)$$

where  $X_i$  is the operator of all possible  $i$ -uple substitutions (excitations) associated with the coefficients which should be determined from Eq. (1). Equation (2) introduces the so-called intermediate normalization for  $\Psi$

$$\langle \Phi | \Psi \rangle = \langle \Phi | \Phi \rangle = 1. \quad (3)$$

Assuming that the HF determinant  $\Phi$  is the best approximation to  $\Psi$  among functions having determinantal form, one can expect that coefficients contained in  $X_i$  should be relatively small and thus easy to determine from Eq. (1) in a self-consistent manner. A set of equations for  $X_i$  can be obtained by projecting Eq. (1) on the HF and excited determinants and the number of them is equal to the number of unknowns, *i.e.*, the ground state energy and the coefficients. Denoting by  $i, j, \dots$  and  $a, b, \dots$  indices of occupied and unoccupied spin orbitals in  $\Phi$ , one has

$$E = \langle \Phi | H(1 + X_2) | \Phi \rangle \quad (4)$$

$$\langle \Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} | H(X_{k-2} + \dots + X_{k+2}) - X_k E | \Phi \rangle = 0, \quad (X_0 = 1, X_i = 0, i < 0), \quad (5)$$

where  $\Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k}$  stands for excited determinants and two sets of indices indicate the substitution. Both the Brillouin theorem and at most two-particle character of  $H$  are used here. Only  $X_2$  contributes to the energy expression directly, all other  $X_i$  affect the energy through  $X_2$ . Following the Møller-Plesset partitioning of  $H$  into the diagonal zero-order part  $H^0$  and the perturbation  $V$ , and introducing perturbative expansion for  $E$ , it can be seen that up to and including the third order, only  $X_2$  contributes to the energy. Contributions from other excitations appear in the fourth and higher orders. Equation (5) can be rewritten in the form

$$\langle \Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} | X_k | \Phi \rangle = \frac{1}{\varepsilon_{i_1} + \varepsilon_{i_2} + \dots + \varepsilon_{i_k} - \varepsilon_{a_1} - \varepsilon_{a_2} - \dots - \varepsilon_{a_k}} \times$$

$$\langle \Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} | V(X_{k-2} + \dots + X_{k+2}) - X_k (E - E^0) | \Phi \rangle = 0, \quad (6)$$

where  $E^0 = \langle \Phi | H^0 | \Phi \rangle$  and  $\varepsilon_l$  is the orbital energy associated with the  $l$ -th spin orbital. Using this expression one can start iterative procedure with some initial guess used for  $X_2$ , for example, with its first-order estimate, and with putting all other  $X_i$  equal to zero on the right-hand side of Eq. (6). That produces the lowest, second-order contributions to  $X_1$ ,  $X_3$  and  $X_4$  which, when used in the next iteration in equation for  $X_2$ , give the third-order contributions to  $X_2$ , thus the fourth-order ones to  $E$ . The subsequent iterations produce contributions corresponding to higher and higher excitations. Assuming that the perturbation expansion is fast-converging, one can expect to reach convergence with a desired accuracy in several iterations. In this way one can extract the ground-state eigenvalue problem from the complete eigenvalue problem given by Eq. (1) and solve it. This is, of course, one of the simplest schemes; for example, one can find many more sophisticated ones built into single-root diagonalization procedures. In all of them the idea, however, is to obtain a state-specific algorithm.

The above considerations show how one can concentrate on a single state at a time and obtain the exact solution within the algebraic approximation. But even that is still numerically very demanding, which limits the dimension of the orbital space we can use. However, our perturbative analysis shows that the numerical effort can be drastically reduced if we include only doubly substituted determinants in the expansion (2). This is because of the specific role the double excitations play in the expansion which can be attributed to, at most, the two-particle character of the Hamiltonian. Namely, the doubly excited determinants span the first interacting space, meaning that the only nonzero matrix elements of the Hamiltonian with the HF determinant are those of doubly excited determinants. Thus, neglecting  $X_i$  for  $i \neq 2$  should give a reasonable approximation to the exact energy leading to a tremendous numerical savings. The method is known as the configuration interaction (CI) method with doubles (CID). The scheme which, in addition, includes single excitations (CISD) is one of the basic CI methods. The configuration interaction methods are variational since all of them can be obtained from a variational principle applied to the energy expectation value functional. The variational character of the CI approach guarantees obtaining an upper bound to the exact energy. The accuracy of CI schemes can be systematically improved by including additional excitations in the expansion reaching in the limit the exact solution for a given *ab initio* model. While the CI schemes are variational, they do not possess another property, which is nowadays considered very important, namely size-extensivity. The size-extensivity of a method guarantees that the energy of a supersystem consisting of noninteracting subsystems is a sum of the energies of the subsystems. This can be essential, for example, for description of the dissociation processes and for extended systems. Two other categories of approximate methods, many-body perturbation theory (MBPT) and coupled-cluster method, are size-extensive although, in general, they are not variational. In particular, the CC method provides a powerful computational scheme due to the exponential expansion used to represent the wave function

$$\Psi = \exp(T)\Phi \quad (7)$$

$$T = \sum_{i=1}^N T_i, \quad (8)$$

where  $T_i$  is the excitation operator defined in a way similar to that of  $X_i$ . The advantage of this expansion is that it introduces description of higher excitations *via* products of lower excitation-rank cluster operators. For example, the basic computational CC scheme, the CC method with singles and doubles (CCSD :  $T \approx T_1 + T_2$ ) provides a reliable approximation to quadruple excitations through  $(1/2)T_2^2$ , which significantly increases accuracy compared with CISD although the number of unknown coefficients is the same in both approaches. Because of that the CC methods have become one of the standard tools in high-accuracy quantum chemical calculations.

All the above approximate methods are based on the assumption that the wave function  $\Psi$  is dominated by a single determinant  $\Phi$ . Then  $\Phi$  serves as a single reference to generate a reliable approximation to  $\Psi$ . In many cases, however,  $\Psi$  cannot be well approximated by a single determinant. This is the case when we have to deal with open-shell or quasi-degenerate situations. The perturbative arguments indicating that double excitations out of  $\Phi$  should predominate the expansion, Eq. (2), are not valid when the importance of one or several determinants become comparable with that of  $\Phi$ . In such a case one can at least expect much slower convergence of the single-reference perturbation expansion and thus the importance of higher than double excitations can be significant. In spite of the fact that the CCSD method can quite efficiently deal with some low degree of quasi-degeneracy, the quality of the results deteriorates rapidly when this degree becomes higher. One of ways of improving the accuracy of the single-reference methods is the inclusion of higher than double excitations in the expansion. For example, within the CI framework, that would comprise first of all  $X_3$  (CISDT) and  $X_4$  (CISDTQ), which produce fourth-order contributions to the energy. However, that preserves the single-reference character of the method and does not take into account that the zero-order functions of approximately equal importance should be treated on the same footing. A natural solution to the problem is to replace the single-reference determinant  $\Phi$  with a multidimensional reference (or model) space  $M$  spanned by determinants  $\Phi^\alpha$  ( $\alpha = 1, \dots, m$ ) dominating the wave function. By taking a linear combination of the reference space functions and all other determinants which are singly or doubly substituted with respect to at least one of them to represent  $\Psi$ , we ensure equal treatment of all functions from the reference space. Note that the same excited determinant can be reached by excitation operators from different reference functions; so if one insisted on introducing excitation operators associated with each reference function ( $X_i^\alpha$ ,  $i = 1, 2, k = 1, \dots, m$ ), the number of unknown coefficients would exceed the dimension of the selected space and

to determine all of them, one would have to consider several ( $m = \dim M$ ) states at a time. This can be, however, avoided by taking a linear combination of the reference determinants and selected excited determinants, which makes coefficients in the expansion reference-function independent. In such a case  $X_i^\alpha$  ( $i = 1, 2$ ) are used to select the outer space only. The simplification is possible if the reference space and outer space determinants are treated in the same way in the expansion. Again the importance of single and double excitations out of the reference space can be justified by using perturbative arguments, this time, however, of a multireference character. The method is known as the multireference CISD (MR-CISD) and is much more effective than CISDT or CISDTQ. The approach is conceptually very simple and does not differ much from its single-reference counterpart. Again single-root diagonalization procedures can be used to solve the equations. The MR-CISD method is not size-extensive because of the linear expansion used to represent  $\Psi$ .

The situation might be not so simple if, assuming that  $X^\alpha = \sum_i X_i^\alpha |\Phi^\alpha\rangle\langle\Phi^\alpha|$  is relatively small for all  $\alpha = 1, \dots, m$ , one wants to use a perturbation or coupled-cluster expansion in the multireference context. The assumption can be considered justified if the reference space is energetically well separated from the orthogonal space. In order to use many-body techniques to represent  $X^\alpha$ , it is necessary to select a Fermi vacuum. In the single-reference case the choice was obvious, all excitation operators being defined as spin orbital replacement operators with respect to the reference HF determinant. Now we have several reference functions so there is no natural choice for the vacuum. Basically two strategies can be followed in such a case. The first one is to select a single Fermi vacuum<sup>30</sup> for all  $X^\alpha$  while the second one is to define  $X^\alpha$  with respect to  $\Phi^\alpha$  as a vacuum<sup>31</sup>. Obviously, within the first option different choices are possible<sup>32,33</sup>, which will be discussed later.

Since the excitation operators  $X_i^\alpha$  are doubly indexed, the number of unknowns is excessively large to be, as before, used for describing a single state. To calculate  $X_i^\alpha$  with a given excitation level and explore all the information they contain, we have to consider an eigenvalue problem for  $m$  states simultaneously. Indeed, taking a linear combination of the reference functions  $\Phi^\alpha$  to represent the zero-order function  $\Psi_0$

$$\Psi_0 = \sum_{\alpha=1}^m c^\alpha \Phi^\alpha, \quad (9)$$



using it to generate  $\Psi$

$$\Psi = (1 + \sum_{\alpha=1}^m X^\alpha) \Psi_0 = \sum_{\alpha=1}^m (1 + \sum_i X_i^\alpha) \Phi^\alpha c^\alpha, \quad (10)$$

inserting it into the Schrödinger equation, Eq. (1), and projecting on the model space with the projection operator  $P = \sum_\alpha P^\alpha = \sum_\alpha |\Phi^\alpha\rangle\langle\Phi^\alpha|$  and on the complementary space, we have

$$PH(1 + X)P\Psi_0 = EP\Psi_0 \quad (11)$$

$$\sum_{\alpha i} Q_i^\alpha [H(1 + X) - XE]P^\alpha \Psi_0 = 0 \quad (12)$$

$$X = \sum_{\alpha} X^\alpha, \quad (13)$$

where  $Q_i^\alpha$  is the projection operator on a subspace of the complementary space spanned by determinants of excitation level  $i$  with respect to  $\Phi^\alpha$ . By inserting Eq. (11) into Eq. (12)

$$\sum_{\alpha i} Q_i^\alpha [H(1 + X) - XPH(1 + X)]P^\alpha \Psi_0 = 0, \quad (14)$$

and assuming that eigenfunctions  $\Psi_0^k = P\Psi^k$  ( $k = 1, \dots, m$ ) (the so-called model functions) of the  $PH(1 + X)P$  operator are linearly independent, the coupling between two sets of equations can be removed

$$\sum_i Q_i^\alpha [H(1 + X) - XPH(1 + X)]P^\alpha = 0. \quad (15)$$

Equation (15) is a complete set of equations from which all  $X_i^\alpha$  can be determined. The  $PH(1 + X)P$  operator acts entirely in the model space and, in the limit of having all excitations included in  $X$ , its eigenvalues are a subset of the eigenvalues of  $H$ . Because of that the operator is called the effective Hamiltonian

$$H_{\text{eff}} = PH(1 + X)P. \quad (16)$$

One may say that one of the basic reasons for which we deal with the description of several states at a time is a different treatment of the so-called dynamic and nondynamic correlation. While the nondynamic correlation effects, which might be associated with the model space contributions to the wave function, due to their significance and dominant character should be determined “exactly”, *i.e.*, by diagonalization of some effective operator, the remaining, dynamic, part coming from the outer space, can be evaluated in an approximate way. Note that the MR-CISD method treats both effects in the same manner so the effective Hamiltonian formalism is not required.

As mentioned, the excessive number of unknowns in the doubly indexed operator  $X_7^\alpha$  is the main cause for having a formalism which is not state-specific. There have been some attempts to overcome the problem within the perturbation theory<sup>34,35</sup> and coupled-cluster<sup>36</sup> frameworks. Even within the MR-CI method, some further simplifications concerning effective dimension of the outer space are possible<sup>37</sup>. The basic idea underlying most of these approaches is to make the excitation operators in  $X = \sum_\alpha X^\alpha$  universal, *i.e.*, to release the restriction that  $X^\alpha$  can act only on  $\Phi^\alpha$ . That is possible assuming that  $X^\alpha$  is defined as a second-quantized operator. Then the  $(1 + X)$  operator acts directly on a linear combination of the reference functions with fixed (contracted) coefficients. Comparing with the previous definition of  $X$ , also internal (within the reference space) excitations must be admitted. Excitation operators generate functions which are, in general, linearly dependent, so the next step is to remove the linear dependence by eliminating some of the functions. Usually, the multiconfiguration self-consistent-field (MC SCF) function is used as the reference function in these approaches. All that has been directed towards formulating and implementing a multireference scheme that would be as close as possible to its single-reference counterpart. Another direction that should be mentioned is an attempt to extend applicability of the single-reference methods and make them more efficient in dealing with some significant degree of quasi-degeneracy. That includes the so-called state-specific multireference CCSD methods<sup>38,39</sup> in which the concept of the reference space is used within the standard single-reference framework only to select higher than doubly excited operators in  $T$  as those which represent single and double excitations with respect to other than HF reference determinants. The dynamic and nondynamic correlation effects are treated here in the same single-reference manner. An idea of separating calculation of dynamic and nondynamic correlation underlies the so-called externally corrected CCSD (ecCCSD)<sup>40,41</sup> and reduced multireference CCSD (RMR CCSD)<sup>42</sup> methods. The latter uses

the MR-CISD method to evaluate nondynamic correlation effects and then the information is transferred *via*  $T_3$  and  $T_4$  operators calculated from the MR-CISD coefficients to the SR-CC method which corrects the description of dynamic correlation. In a similar way, the SR-CC based corrections to MR-CISD are formulated<sup>43</sup>. The same goal of obtaining more reliable description of a system in quasi-degenerate situations led recently to formulation of the so-called renormalized CC corrections<sup>44,45</sup>. It seems, however, that all these and other similar approaches have their limitations; so further effort directed towards making genuine multireference formulations more attractive seems required. This is especially true with respect to the most effective CC schemes. Moreover, many times we are interested not only in the ground state but also in excited states, so a method capable of describing low-lying excited states in an efficient manner would be desirable. In the following we would like to show how the intermediate Hamiltonian technique can resolve many problems plaguing the original formulation of the Fock-space coupled-cluster method. The FS-CC method is one of the two basic MR-CC schemes, namely, that associated with the choice of a single Fermi vacuum for all reference determinants.

#### BASICS OF THE FOCK-SPACE COUPLED-CLUSTER METHOD

The effective Hamiltonian formalism leads to extraction of the eigenvalue problem corresponding to several states from the complete eigenvalue problem of  $H$ . While our previous considerations were focused on the wave function analysis, the separation problem can also be solved using simple similarity transformations<sup>21</sup>. Let us assume a partitioning of the functional space into the reference space  $M$  and its orthogonal complement  $M_{\perp}$  with the projection operators  $P$  and  $Q$ , respectively, and consider a similarity transformation of the Hamiltonian  $H$  within the entire space

$$\tilde{H} = e^{-X} H e^X \quad (17)$$

$$X = QXP. \quad (18)$$

Obviously, both,  $H$  and  $\tilde{H}$ , have the same eigenvalues. We require the transformed Hamiltonian  $\tilde{H}$  to fulfil

$$Q\tilde{H}P = 0, \quad (19)$$

and the number of the  $X$  parameters permits satisfying the condition. From Eq. (18), one has  $X^k = 0$  for  $k \geq 2$ , so Eq. (19) can be written as

$$Q(1 - X)H(1 + X)P = Q[H(1 + X) - XH(1 + X)]P = 0, \quad (20)$$

which is equivalent to Eq. (15) obtained within the wave function approach for the excitation operator  $X$ . The structure of the transformed Hamiltonian  $\tilde{H}$  shows that the eigenvalue problem of  $H$  has been separated into two subproblems. All eigenvalues of  $H$  can be now obtained by separate diagonalizations of  $P\tilde{H}P$  and  $Q\tilde{H}Q$  blocks. Indeed, if one performs subsequent transformation of  $H$

$$\tilde{\tilde{H}} = (1 - S)\tilde{H}(1 + S) \quad (21)$$

$$S = PSQ, \quad (22)$$

requiring

$$P\tilde{\tilde{H}}Q = 0, \quad (23)$$

then it is easy to see that

$$P\tilde{\tilde{H}}P = P\tilde{H}P \quad (24)$$

$$Q\tilde{\tilde{H}}Q = Q\tilde{H}Q \quad (25)$$

$$Q\tilde{\tilde{H}}P = Q\tilde{H}P = 0. \quad (26)$$

So the second transformation, which leads to a block diagonal structure, changes only the  $PQ$  block by putting it equal to zero. Since diagonal blocks are identical, then all eigenvalues of  $\tilde{\tilde{H}}$  can be obtained by separate diagonalizations of  $P\tilde{H}P$  and  $Q\tilde{H}Q$ . Assuming that we are interested in several eigenvalues only, we can restrict ourselves to diagonalizing  $P\tilde{H}P$ . In this way the eigenvalue problem corresponding to several eigenvalues can be extracted. It is easy to notice that  $P\tilde{H}P = PH(1 + X)P$  is identical with the ef-

fective Hamiltonian  $H_{\text{eff}}$ , Eq. (16). The equation for  $X$ , Eq. (20), is quadratic in  $X$  and has many solutions. For different solutions, all eigenvalues of  $H$  are differently divided into two subsets as those given by  $P\tilde{H}P$  and those given by  $Q\tilde{H}Q$ . The phenomenon is known as the multiple solution problem<sup>17,46-48</sup>. The problem of convergence of Eq. (20) to a desired solution<sup>49</sup> (corresponding to a set of eigenvalues of interest) is one of the aspects of the intruder state problem.

While within the similarity transformation formulation, the problem of all eigenvalues of  $H$  is well defined, the effective Hamiltonian approach based on the wave function formulation refers only to one of the two subproblems. In this way information of the remaining eigenvalues, which can be useful in some cases<sup>14,47</sup>, is lost. Note that diagonalization of  $Q\tilde{H}Q$  provides a subset of the eigenvalues of  $H$  without the necessity of determining the wave functions, which requires an additional calculation of the  $S$  operator from Eq. (23).

The next step comprises a suitable parameterization for  $X$ . Because of the success of the coupled-cluster method in its single-reference version, an exponential expansion for  $(1 + X)P$  seems preferable. Since cluster operators are defined as second-quantized operators they require selection of a Fermi vacuum. Two possible choices mentioned above lead to two multireference versions of the CC method. The first one assumes that  $(1 + X)P$  is defined as

$$(1 + X)P = \sum_{\alpha=1}^m (1 + X^{\alpha}) P^{\alpha} = \sum_{\alpha=1}^m e^{T^{\alpha}} P^{\alpha}, \quad (27)$$

and  $T^{\alpha}$  is a second-quantized excitation operator substituting spin orbitals occupied in  $\Phi^{\alpha}$  with unoccupied ones. The only restriction is that the excitation cannot generate another reference determinant so it must lead outside the model space  $M$ . The definition is very similar to that of  $T$  in the single-reference case; thus a significant part of the resulting CC equations resembles the SR-CC equations. The remaining part, the so-called renormalization term, has more complicated structure and couples sets of equations for different  $\alpha$  (see the second term in Eq. (15)).

The restriction that  $PT^{\alpha}P^{\alpha} = 0$ , in general, does not imply that  $PXP = 0$ . That holds for the complete model spaces. The definition of the complete model space is based on partitioning the orbital space into three classes: core orbitals which are occupied in all  $\Phi^{\alpha}$ , active orbitals which are occupied in some but not in all of them, and virtual orbitals which are unoccupied in the model space determinants. The complete model space is

spanned by determinants with all possible distributions of valence (active) particles among active spin orbitals. In such a case the so-called intermediate normalization holds, meaning that  $P \sum_{\alpha} e^{T^{\alpha}} P^{\alpha} = P$ . For the incomplete model spaces, the intermediate normalization must be abandoned to preserve connectivity of the CC equations and size-extensivity of the method. The approach is called the Hilbert-space (HS) or state-universal CC method.

Unlike the Hilbert-space CC method, the Fock-space or valence-universal CC formalism assumes a single Fermi vacuum for all reference functions. As a consequence, all reference determinants must be first generated from the vacuum. These generator operators are not, in general, particle-number conserving. The Fermi vacuum can be selected in many different ways and so many versions of the FS-CC method can be formulated; however, the basic assumption for all of them is to have a single determinant as a vacuum. Let us focus our attention on some specific version, namely, when the determinant built from the core spin orbitals serves as a vacuum. If  $N_c$  is the number of core spin orbitals, then to have a complete model space as described above,  $N_v = N - N_c$  valence particles must be created on active (valence) spin orbital levels. So functions spanning the complete model space can be generated by applying all possible sequences of  $N_v$  active spin orbital creation operators on the core determinant  $\Phi_c$

$$\Phi^{\alpha} = W^{\alpha} \Phi_c, \quad (28)$$

where  $W^{\alpha}$  contains a sequence of  $N_v$  creation operators ( $a^{\dagger}$ ) of active spin orbitals occupied in  $\Phi^{\alpha}$ . Excitation operators are defined through the normal-ordered product of particle-hole creation and particle-hole annihilation operators. Unlike the single-reference and Hilbert-space cases, where the cluster operators  $T$  and  $T^{\alpha}$  consist of particle-hole creation operators only, now the excitation operators can contain a sequence of particle-hole annihilation operators. We can distinguish simple excitations from  $\Phi^{\alpha}$  involving creation operators only, which generate a hole in the core and a particle on the unoccupied (valence or virtual) spin orbital level or several such particle-hole pairs. Valence particles appearing in  $\Phi^{\alpha}$  remain unchanged by the excitation and, of course, all functions from the orthogonal space cannot be reached in this way. Excitations from the core give only those determinants from the outer space that contain all valence spin orbitals occupied in  $\Phi^{\alpha}$ . Thus additional types of excitation operators are necessary to allow replacing valence spin orbitals appearing in  $\Phi^{\alpha}$  with

other, unoccupied in  $\Phi_c$ , spin orbitals. These operators must contain valence spin orbital annihilation operators. The second-quantized excitation operators from the reference determinants can be expressed as

$$M[(a_{a_1}^\dagger a_{i_1})(a_{a_2}^\dagger a_{i_2}) \dots (a_{a_k}^\dagger a_{i_k})(a_{a_{k+1}}^\dagger a_{A_1}) \dots (a_{a_{k+l}}^\dagger a_{A_l})], \quad (29)$$

where, in addition to the previously introduced notation ( $i, j, \dots$  – occupied,  $a, b, \dots$  – unoccupied in  $\Phi_c$ ); we use  $A, B, \dots$  for unoccupied active (valence) spin orbitals. The particle-hole annihilation operators are defined as

$$A_i = a_i^\dagger, \quad A_a = a_a. \quad (30)$$

$M[\dots]$  puts second-quantized operators in the normal order with respect to the core determinant  $\Phi_c$  which means that  $A^\dagger$  operators are followed by  $A$  operators in the product, so contractions between them are not possible. Index  $k$  runs from  $\delta_{0l}$  to the number of core spin orbitals  $N_c$ , while index  $l$  can be from 0 to the number of valence particles  $N_v$ . In case of  $k = 0$ , all spin orbital indices cannot be active since then the excitation leads to other reference function. One can classify the excitations (29) according to their particle rank  $k + l$  (number of pairs of creation and annihilation operators) and their valence rank  $l$ . To form the cluster operator  $S$  we have to associate cluster amplitudes with the excitation operators. Then  $S$  can be written in terms of the valence rank  $l$  and the particle rank  $k + l$  as

$$S = \sum_{l=0}^{N_v} S^{(l)} \quad (31)$$

$$S^{(l)} = \sum_{k=\delta_{0l}}^{N_c} S_{k+l}^{(l)}. \quad (32)$$

A redundancy problem can be noticed while analyzing the  $S$  definition, namely, the same excited determinant can be generated by several cluster operators  $S_{k+l}^{(l)}$  while acting on  $\Phi^\alpha$  like, for example,  $(a_a^\dagger a_i)$  and  $(a_a^\dagger a_i)(a_A^\dagger a_A)$  associated with  $S_1^{(0)}$  and  $S_2^{(1)}$ , respectively. Note that the problem is slightly different from that discussed in the context of the HS-CC method. Now the same excited determinant can be reached by applying several different cluster operators on the same reference function  $\Phi^\alpha$ . The other difference is

that the cluster operators can act on any  $\Phi^\alpha$  so there is no restriction similar to that in the HS-CC method and the cluster operator  $S$  can be called universal. This universality can be even extended if one, to resolve the redundancy problem, makes the cluster operators valence universal. However, to reach this point let us first use  $S$  in the exponential expansion. It can be seen immediately that due to the presence of particle-hole annihilation operators ( $a_A = A_A$ ) a simple form  $e^S$  admits contractions between  $S$ . To avoid this, it is convenient to use the normal-ordered form  $N[e^S]$  which, as can be shown, is general and can be obtained by performing all possible contractions in  $e^S$  according to generalized Wick's theorem and then through redefining the cluster operator by collecting all connected terms of the same particle rank<sup>4,5</sup>. The normal-ordered form prevents contractions between the cluster operators now. Moreover, since  $S^{(0)}$  does not contain any particle-hole annihilation operators and, hence, cannot be contracted with any other cluster operator, then

$$(1 + X)P = e^{S^{(0)}} N[e^{S'}]P \quad (33)$$

$$S' = S^{(1)} + S^{(2)} + \dots \quad (34)$$

Using this form in Eqs (16) and (20) but premultiplying the equations from the left by  $e^{-S^{(0)}}$  before projecting them on  $M$  and  $M_\perp$ , we have

$$Q\tilde{H}P = Q(\bar{H}N[e^{S'}] - N[e^{S'}]P\bar{H}N[e^{S'}])P = 0 \quad (35)$$

$$H_{\text{eff}} = \tilde{H}P = P\bar{H}N[e^{S'}]P \quad (36)$$

$$\bar{H} = e^{-S^{(0)}} H e^{S^{(0)}} \quad (37)$$

It is convenient at this point to introduce a diagrammatic representation for the second-quantized operators in the normal form. A second-quantized operator in the normal form is represented graphically by a vertex consisting of a horizontal line and attached pairs of oriented lines. Each pair of



lines is associated with a pair containing a creation operator and an annihilation operator ( $a_m^\dagger a_n$ ). The outgoing line denotes the creation operator  $a_m^\dagger$  while the incoming line is designated for the annihilation operator  $a_n$ . The horizontal line, characteristic of a particular operator, represents matrix elements of the second-quantized operator with indices of incoming and outgoing lines. Lines directed upwards are particle lines while those directed downwards are designated for holes. Thus the particle-hole creation operators ( $a_a^\dagger, a_i$ ) are given by lines lying above the vertex while the particle-hole annihilation operators ( $a_a, a_i^\dagger$ ) are associated with those below the vertex. According to generalized Wick's theorem, a product of two operators in the normal form can be expressed as a sum of normal products of the operators without contraction, with all possible single contractions, with all possible double contractions and so on, between annihilation operators  $A$  from the first operator and creation operators  $A^\dagger$  from the second one. Diagrammatically, all contributions to the sum are obtained by drawing diagrams of both operators to form a disconnected diagram (no contractions), then by drawing diagram of the first operator on the top of the diagram of the second one to create diagrams with single contractions (by performing all possible single connections between lines at the bottom of the first diagram with those at the top of the second one), double contractions and so on. For more details on the diagrammatic representation of the second-quantized operators, we refer to other papers<sup>50</sup>. Figure 1 shows examples of  $S$  diagrams (wavy line is used for matrix elements of  $S$ ) representing  $S^{(0)}$ ,  $S^{(1)}$  and  $S^{(2)}$ . Double arrows are used to indicate lines which can have active (valence) indices only. Diagrams shown explicitly are those corresponding to the one- and two-particle part of  $S$

$$S_1 = S_1^{(0)} + S_1^{(1)} \quad (38)$$

$$S_2 = S_2^{(0)} + S_2^{(1)} + S_2^{(2)}. \quad (39)$$

One can notice that within approximation  $S \approx S_1 + S_2$  (FS-CCSD), in principle, only systems with two valence particles can be described. Assuming this basic approximation for  $S$  and restricting ourselves to  $N_v = 2$ , the cluster expansion can be written as

$$M[e^{S'}]P^{(2)} = (1 + S_1^{(1)} + S_2^{(1)} + S_2^{(2)} + M_{\frac{1}{2}}S_1^{(1)^2} + S_1^{(1)}S_2^{(1)} + \frac{1}{2}S_2^{(1)^2})P^{(2)}, \quad (40)$$

where the fact that  $S^{(0)}$  is included in  $\bar{H}$  is used, so it does not have to be explicitly considered.  $P^{(2)}$  is introduced to emphasize that systems with two valence electrons are under consideration at this level of approximation. Figure 1D presents diagrammatic representation of the expansion.

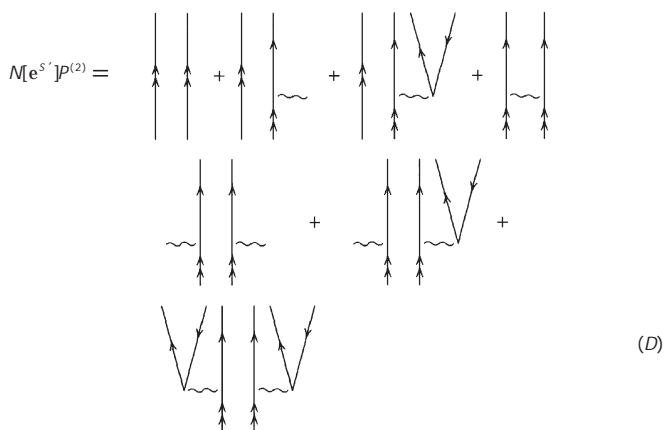


FIG. 1

Diagrams representing components of the  $S$  operator:  $S^{(0)}$  (A),  $S^{(1)}$  (B) and  $S^{(2)}$  (C). Part (D) shows diagrammatic representation of the cluster expansion in the two-valence sector with  $S' \approx S_1^{(1)} + S_2^{(1)} + S_2^{(2)}$

Let us now consider diagrammatic representation of the FS-CC equations Eqs (35), (36) and return to the redundancy problem. In a general case, all orthogonal space determinants can be generated from any reference determinant  $\Phi^\alpha$  by the action of excitation operators associated with  $S^{(2)}$ ; so the number of the FS-CC equations is equal to the number of the  $S^{(2)}$  cluster amplitudes. However, we have additional  $S^{(0)}$  and  $S^{(1)}$  amplitudes to determine which can produce redundant excitations while acting on the reference functions  $\Phi^\alpha$ . The  $S^{(0)}$  and  $S^{(1)}$  operators are important if we want to truncate  $S^{(2)}$  at some relatively low particle-rank level and then higher-level excitations are approximated by  $S^{(0)}$ ,  $S^{(1)}$ , and their products. Within the FS-CCSD approximation  $S^{(2)} \approx S_2^{(2)}$  and the projection subspace of the orthogonal space is spanned by determinants with occupied core spin orbitals and two other particles occupying spin orbitals from which at least one is virtual (inactive). Using diagrams for representing operators appearing in the FS-CCSD equations and using diagrammatic techniques based on the graphical interpretation of Wick's theorem, one can construct diagrammatic representation of the FS-CCSD equations. The resulting diagrams must have two particle lines at the top, which are not simultaneously active and two active particle lines at the bottom. They represent determinants from  $M_\perp$  and  $M$ . It is convenient to divide diagrams into open, which have at least one external line inactive, and closed, which have no external lines at all or have all of them active. Diagrams having parts which are not connected *via* interaction or oriented lines are called disconnected. If the disconnected part is closed, then the diagram is called unlinked. While constructing diagrams representing the left-hand side of Eq. (35), it is easy to see that all unlinked diagrams which can be constructed for the second (renormalization) term are identical with all those unlinked diagrams that can be generated from the first (principal) term in the equation. Diagrams representing Eq. (35), after cancellation of unlinked contributions, are shown in Fig. 2A–2E in a schematic way. Matrix elements of the non-Hermitian operator  $\bar{H}$  are denoted by double horizontal line. The linked but disconnected contribution in A containing open part D is irreducible. However, if we look closer at diagrams D, it can be seen that they represent diagrammatic representation of a subset of the FS-CC equations for a problem with one valence particle (one-valence problem). If the one-valence problem is solved, then D is equal to zero. That leads to disappearance of disconnected contribution in A and provides additional equations for the redundant cluster amplitudes. The remaining equations for the one-valence problem are shown in Fig. 2F and 2G. Again, we have an irreducible linked but disconnected part which disappears if the zero-valence problem shown

$$\begin{array}{c} \uparrow \uparrow \\ \square \\ \uparrow \uparrow \end{array} + \left( \begin{array}{c} | \\ | \\ | \end{array} + \begin{array}{c} | \\ | \\ | \sim \end{array} \right) \times \begin{array}{c} \uparrow \\ \square \\ \uparrow \end{array} = 0 \quad (A)$$

$$\begin{array}{c} \uparrow \uparrow \\ \square \\ \uparrow \uparrow \end{array} = \begin{array}{c} | \\ | \\ | \sim \end{array} + \begin{array}{c} | \\ | \sim \\ | \end{array} + \begin{array}{c} | \\ | \sim \\ | \end{array} + \begin{array}{c} | \\ | \\ | \sim \end{array} \\
 + \begin{array}{c} | \\ | \sim \\ | \end{array} + \begin{array}{c} | \\ | \sim \\ | \end{array} + \begin{array}{c} | \\ | \sim \\ | \end{array} + \begin{array}{c} | \\ | \sim \\ | \end{array} \\
 + \begin{array}{c} | \\ | \sim \\ | \end{array} + \begin{array}{c} | \\ | \sim \\ | \end{array} + \begin{array}{c} | \\ | \sim \\ | \end{array} \\
 - \begin{array}{c} \sim \\ \uparrow \uparrow \\ \square \\ \uparrow \uparrow \end{array} - \begin{array}{c} \sim \sim \\ \uparrow \uparrow \\ \square \\ \uparrow \uparrow \end{array} - \begin{array}{c} \sim \\ \uparrow \uparrow \\ \square \\ \uparrow \uparrow \end{array} - \begin{array}{c} \sim \\ \uparrow \uparrow \\ \square \\ \uparrow \uparrow \end{array} \quad (B)$$

FIG. 2  
Effective Hamiltonian FS-CCSD equations in diagrammatic form

$$\begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} = \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \dots + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} \quad (C)$$

$$\begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} = \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} - \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} \quad (D)$$

$$\begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} = \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \dots + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} \quad (E)$$

$$\begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \left( \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} \right) \times \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} = 0 \quad (F)$$

$$\begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} = \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} + \dots + \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} - \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} \quad (G)$$

$$\begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} = 0 \quad \begin{array}{c} \text{Diagram} \\ \text{Diagram} \\ \text{Diagram} \end{array} = 0 \quad (H)$$

FIG. 2 (Continued)

in Fig. 2H is solved. The zero-valence problem represents the SR-CCSD calculation for the core. Now the number of equations is equal to the number of unknown cluster amplitudes and the redundancy problem is removed. We can say now that the cluster expansion is valence-universal, *i.e.*, allows us to solve a hierarchy of problems with the increasing number of valence particles. Note that these problems must be solved in a hierarchical way starting with the zero-valence problem which involves only the  $S^{(0)}$  operators. Having  $S^{(0)}$ , the one-valence problem can be solved and  $S^{(1)}$  can be determined.  $S^{(0)}$  amplitudes play a role of parameters in the one-valence calculations. The two-valence problem requires determining  $S^{(2)}$ , all other cluster operators ( $S^{(0)}$  and  $S^{(1)}$ ) appearing in the equations are known from the lower-valence-rank calculations. Contributions to the effective Hamiltonian are provided by closed diagrams.

Let us point out several characteristic features of the FS-CC method. First of all, the excitation operators associated with the cluster operator  $S$  cannot be, in general, classified as those of single, double, *etc.*, replacements in the reference determinants, they are classified as one-, two-, *etc.*, body operators. Because of that the  $M_{\perp}$  space generated by them is identical for all reference determinants. Thus, the situation is different from that in the Hilbert-space CC case. Second, due to valence universality, at each valence level beyond the zero one, the cluster expansion is linear in the unknown cluster amplitudes. The set of FS-CCSD equations discussed above requires solving the eigenvalue problem in two steps, first the cluster amplitudes must be determined from Eq. (35) and then the energies are obtained by diagonalization of the effective Hamiltonian. This type of approach couples eigenvalue problems for several states and requires considering all of them at a time. However, the linearity of the expansion suggests the possibility of significant simplifications and decoupling of the eigenvalue problem into separate subproblems. The specific features of the FS-CC method emphasized above allow us to obtain a very simple intermediate Hamiltonian version of the FS-CC method.

#### INTERMEDIATE HAMILTONIAN FORMULATION OF THE FOCK-SPACE COUPLED-CLUSTER METHOD

The idea underlying the intermediate Hamiltonian formalism is to change the way some contributions from the outer space  $M_{\perp}$  are calculated<sup>21,23</sup>. In many practical situations, some contributions from  $M_{\perp}$  to the wave functions under consideration can be large causing perturbation expansions to diverge if a perturbation expansion is used for  $X$ , or causing convergence

problems within nonperturbative schemes like MR-CC methods. The problem can be related to the occurrence of intruder states, the states which are not well energetically separated from the model space states<sup>22,49,51-53</sup>. The basic formulations of the MR-CC methods assume completeness of the model space, which makes the intruder state problem difficult to deal with. The completeness of the model space is essential for connectivity of the CC equations if the intermediate normalization is imposed. However, if the intermediate normalization is abandoned and the normalization condition is implicitly introduced through the definition of the cluster operators, then size-extensive incomplete-model-space CC methods can be formulated<sup>54,55</sup>. The use of incomplete model spaces allows us to deal more efficiently with the intruder state problem. The intermediate Hamiltonian technique offers another way of making multireference schemes more reliable. Within the effective Hamiltonian formulation, only contributions from the model space to the wave functions are calculated "exactly", *i.e.*, by diagonalization of  $H_{\text{eff}}$ . The fact whether the diagonalization gives approximate or exact energies depends on  $X$  but not on the way contributions from the model space are determined. The intermediate Hamiltonian formalism assumes that also some contributions from the outer space, which can cause problems when the effective Hamiltonian formulation is used, are determined by diagonalization. To do this, a subspace of  $M_{\perp}$  is extracted and called the intermediate space  $M_1$  while the original model space  $M$  is now called the main model space. Both subspaces,  $M_1$  and  $M$ , of the new model space  $M_0$  play different roles. While  $M$  is designated to the determination of  $m = \dim M$  eigenvalues,  $M_1$  is used to provide contributions to these eigenvalues in a safe way. Both goals are achieved by diagonalization of the intermediate Hamiltonian which acts in the extended model space  $M_0$ . Obviously, the diagonalization gives more than  $m$  eigenvalues, but only  $m$  of them have, in general, a well defined physical meaning. The remaining eigenvalues can be considered spurious.

There are many ways the intermediate Hamiltonians can be constructed<sup>21,23</sup>, some of them can be quite complicated. However, here we concentrate on the simplest one, which can be easily implemented. But first let us emphasize the reasons for which the Fock-space CC method is particularly convenient for the intermediate Hamiltonian reformulation. Due to the universal character of the cluster operators, the orthogonal space is uniquely defined for all reference determinants; so the intermediate space can be easily defined through excitation operators of a given particle rank acting on the main model space. For example, excitation

operators associated with  $S_2^{(2)}$  acting on any of the reference functions  $\Phi^\alpha$  generate the same set of excited functions. These are determinants built from core spin orbitals and two unoccupied (in  $\Phi_c$ ) spin orbitals from which at least one is inactive. However, the most important is that, in spite of generally nonlinear character of the cluster expansion, the expansion is linear in the unknown cluster amplitudes at each valence level beyond the zero one. This is, of course, because of the valence-universal strategy of solving the FS-CC equations. The main-model and the intermediate space functions are generated by the linear expansion; this suggests that both contributions to a particular eigenvalue can be calculated in a single-root calculation. As we will see, that does not guarantee determination of the cluster amplitudes.

The simplest intermediate Hamiltonian scheme can be introduced by dividing the  $X$  operator introduced in the effective Hamiltonian formulation into two parts<sup>21</sup>

$$X = Y + Z \quad (41)$$

$$Z = P_I X P, \quad Y = X - Z, \quad (42)$$

where  $P_I$  is the projection on the intermediate space  $M_I$ . Thus  $Z$  represents excitations to the intermediate space while  $Y$  generates excitations to the reduced orthogonal space  $M_\perp$ .

It can be seen immediately that

$$(1 + X) = (1 + Y)(1 + Z). \quad (43)$$

The intermediate space we select at all levels beyond the zero one is that generated by the cluster operators, which have to be determined at a particular  $i$ -valence level, namely by the  $S^{(i)}$  operators. Note that the intermediate space becomes identical with the projection space used in the FS-CC equations; so excitations from the main model space to the orthogonal space  $M_\perp$  can be given by cluster operators from the lower-valence sectors or by their products only. Due to the valence-universal strategy of solving the equations, they are known. Hence, the unknown  $S$  operators are contained in  $Z$  while  $Y$  is exclusively constructed from the known  $S$  operators. Taking



into account our FS-CCSD scheme with the assumption that the zero-valence amplitudes are already included in  $\bar{H}$ , we have

$$\begin{aligned} Z^{(1)} &= P_1^{(1)} M[e^{S^{(1)+S^{(2)}}}] P^{(1)} = (S_1^{(1)} + S_2^{(1)}) P^{(1)}, \\ Y^{(1)} &= 0 \end{aligned} \quad (44)$$

$$Z^{(2)} = P_1^{(2)} M[e^{S^{(1)+S^{(2)}}}] P^{(2)} = (S_1^{(1)} + \frac{1}{2} M[S_1^{(1)^2}] + S_2^{(2)}) P^{(2)}, \quad (45)$$

$$Y^{(2)} = (S_2^{(1)} + M[S_1^{(1)} S_2^{(1)}] + \frac{1}{2} M[S_2^{(1)^2}]) P^{(2)}. \quad (46)$$

The similarity-transformed Hamiltonian can be expressed as

$$\tilde{H}^{(i)} = (1 - Z^{(i)})(1 - Y^{(i)})\bar{H}(1 + Y^{(i)})(1 + Z^{(i)}), \quad (47)$$

and if the FS-CCSD equations are satisfied,

$$P_1^{(i)}(1 - Z^{(i)})(1 - Y^{(i)})\bar{H}(1 + Y^{(i)})(1 + Z^{(i)})P^{(i)} = 0, \quad (48)$$

then the matrix representation of  $\tilde{H}^{(i)}$  in the model space  $M_0^{(i)}(P_0^{(i)})$  has a structure characteristic of the effective Hamiltonian approach with one off-diagonal block ( $P_1$ - $P$ ) equal to zero. If so, then the  $P$ - $P$  block represents the effective Hamiltonian and its diagonalization gives  $m^{(i)} = \dim M^{(i)}$  eigenvalues. Obviously, because of Eq. (48), these eigenvalues are among those obtained from diagonalization of the transformed Hamiltonian (47) within the entire model space  $M_0^{(i)}$ . Let us recall here that in such a case all eigenvalues of  $P_0^{(i)}\tilde{H}^{(i)}P_0^{(i)}$  can be obtained by separate diagonalizations of  $P^{(i)}\tilde{H}^{(i)}P^{(i)}$  and  $P_1^{(i)}\tilde{H}^{(i)}P_1^{(i)}$ . If we compare now  $P_0^{(i)}\tilde{H}^{(i)}P_0^{(i)}$  with

$$P_0^{(i)}(1 - Y^{(i)})\bar{H}(1 + Y^{(i)})P_0^{(i)}, \quad (49)$$

we can see that both of them have the same eigenvalues. The reason is that they are related through similarity transformation within the model space  $M_0^{(i)}$ , which does not change the eigenvalues. The operator (49) can be

called the intermediate Hamiltonian since a subset of its eigenvalues is identical with eigenvalues given by the effective Hamiltonian. The difference is in obtaining contributions from the intermediate space which are now generated during diagonalization of the intermediate Hamiltonian. Taking into account that  $Y^{(i)}$  excites out of the model space  $M_0^{(i)}$  the final form of the intermediate Hamiltonian can be written as

$$H_{\text{int}}^{(i)} = P_0^{(i)} \bar{H} (1 + Y^{(i)}) P_0^{(i)}. \quad (50)$$

$H_{\text{int}}^{(i)}$  does not depend on the unknown cluster amplitudes  $S^{(i)}$  and so it is not necessary to determine them to obtain eigenvalues of interest. Having a single-root diagonalization procedure, one can concentrate on obtaining a single eigenvalue or can obtain them one by one without the necessity of considering all of them at a time. Thus, the method is state-specific in a sense. It is easy to understand why the method is not completely state-specific if we notice that to construct  $H_{\text{int}}^{(i)}$ , we need cluster amplitudes from all lower valence-rank sectors since they are contained in  $Y^{(i)}$ . Thus, in the final sector like, for example, in the two-valence sector within the FS-CCSD scheme, we can focus on obtaining only eigenvalues of interest while in the lower-valence sectors, all eigenvalues and eigenvectors of the intermediate Hamiltonian corresponding to the main model spaces must be determined since only the complete set of eigenvectors allows us to determine the cluster amplitudes. However, it must be stressed that, due to the decoupling of the eigenvalue problems, they can be obtained one by one.

The structure of the intermediate Hamiltonian in the one- and two-valence sectors is very simple compared with the standard FS-CCSD equations. Indeed, at the one-valence level, because of Eq. (44), the intermediate Hamiltonian is represented by nothing else but the matrix representation of  $\bar{H}$  in the model space  $M_0^{(1)}$

$$H_{\text{int}}^{(1)} = P_0^{(1)} \bar{H} P_0^{(1)}. \quad (51)$$

It should be noted here that the one-valence sector energies do not depend on the model space, *i.e.*, on the choice of active orbital levels. Again, this can be easily understood if we recall that the zero-valence level calculation is the standard single-reference CCSD calculation for the core for which the selection of active orbitals is irrelevant. Thus, the information about active

orbital levels is not transferred to  $H_{\text{int}}^{(1)}$ . Contrary to the energies, the one-valence cluster amplitudes do depend on active spin orbital indices and, to obtain them, a set of  $m^{(1)} = \dim M^{(1)}$  ( $m^{(1)}$  is the number of active spin orbitals) eigenvectors of  $H_{\text{int}}^{(1)}$  must be determined. Let the matrix of  $m^{(1)}$  eigenvectors of  $H_{\text{int}}^{(1)}$  consists of the  $m^{(1)} \times m^{(1)}$  submatrix  $V_0^{(1)}$  containing the main-model-space coefficients and the remaining submatrix  $V^{(1)}$  containing the intermediate-space coefficients. With this notation, the matrix representation of  $Z^{(1)}$  which is built from cluster amplitudes of  $S_1^{(1)}$  and  $S_2^{(1)}$ , Eq. (44), is given by

$$Z^{(1)} = V^{(1)}V_0^{(1)-1}. \quad (52)$$

One can easily realize that since the choice of  $m^{(1)}$  eigenvalues and corresponding eigenvectors can be done in many different ways, we can obtain many solutions of the FS-CCSD equations. The phenomenon is known from the standard FS-CC applications as the multiple solution effect<sup>48</sup>. Here, along with the so-called principal solution for which a selected model space is the best possible choice, also alternative solutions are obtained in more or less systematic manner. Within the intermediate Hamiltonian formulation, the phenomenon of multiple solutions finds its simple interpretation<sup>47</sup>. The standard FS-CC equations (48) are quadratic in the unknown cluster amplitudes and so, depending on the starting vectors, they can be converged to different solutions. These different solutions correspond to a different partitioning of eigenvalues between two diagonal blocks of the transformed Hamiltonian  $\tilde{H}$ . While generation of alternative solutions within the standard approach requires multiple iterative solutions of the FS-CC equations, each of them providing a set of  $m$  eigenvalues and corresponding cluster amplitudes, the intermediate Hamiltonian approach allows us their *a posteriori* construction from the available eigenvalues and eigenvectors of  $H_{\text{int}}$ . Moreover, the intermediate Hamiltonian formulation shows that, if no additional approximation is introduced in the standard FS-CC equations, the energy provided by  $H_{\text{eff}}$  corresponding to a given state should be the same in all possible solutions<sup>47</sup>. That has not been observed in the standard FS-CC calculations because of such additional approximations involved<sup>48</sup>. The above, of course, concerns not only one- but also higher-valence rank sectors.

The structure of  $H_{\text{int}}^{(2)}$  is again simple; however, it is not so simple as that of  $H_{\text{int}}^{(1)}$ . From Eqs (50) and (46), we have

$$H_{\text{int}}^{(2)} = P_0^{(2)} \overline{H} P_0^{(2)} + P_0^{(2)} \overline{H} Y^{(2)} P^{(2)}. \quad (53)$$

The principal part is again the matrix representation of  $\overline{H}$ . The second term modifies its  $m^{(2)}$  columns corresponding to the main-model-space functions. It can be seen that also disconnected diagrams contribute to  $H_{\text{int}}^{(2)}$  and that they are generated by the second term in Eq. (53). This does not mean, however, that the approach is not size-extensive. One can even say that the disconnected part is essential for extensivity since it cancels out disconnected terms generated by the diagonalization. Thus, unlike the standard approach which takes advantage of the Connected Diagram Theorem, the intermediate Hamiltonian assumes numerical cancellation of disconnected terms and that is one of its essential features. The reason is that terms generated by the diagonalization cannot be explicitly considered. The presence of disconnected diagrams does not complicate diagrammatic representation of  $H_{\text{int}}^{(2)}$ , which is shown in Fig. 3. One can see a substantial reduction in the number of diagrams which have to be considered compared with the standard approach. There is no renormalization term which can be troublesome, especially if more efficient iterative schemes, like Newton–Raphson, are used<sup>56</sup>. One can also notice disappearance of many other types of diagrammatic contributions. The only additional diagrams are disconnected ones but these are very easy to implement<sup>57–59</sup>.

However, the most important advantage of the intermediate Hamiltonian FS-CC formulation is the way the CC equations are solved. This is, of course, an exemplification of the basic idea underlying the intermediate Hamiltonian strategy. The intermediate Hamiltonian offers diagonalization as a way the main-model space and the intermediate space contributions to the eigenvalues are calculated. The assumption that the intermediate space contributions should be small becomes less relevant in such a case in view of the existence of many efficient diagonalization procedures for non-symmetric matrices. Not only the principal solutions can be reached without problems but also alternative ones are easily accessible. The traditional Jacobi or modified Jacobi iterative schemes used within the standard formulation in many cases cause tremendous convergence problems. For example, it was not possible to converge the FS-CCSD equations in calculations for Be for a very long time<sup>51–53</sup>. The Newton–Raphson scheme is effective but it requires relatively reliable starting vectors and is numerically demanding<sup>56,60</sup>. Thus, the intermediate Hamiltonian FS-CC seems a good

remedy for convergence problems caused by the intruder state problem and our calculations for Be has proved this<sup>58</sup>.

Let us finally mention the methods that also take advantage of some specific features of the FS-CC scheme. The pioneering works on the energy-independent partitioning technique by the Mukherjee group must be cited here<sup>25</sup> as well as the recently developed Similarity Transformed Equation of Motion CC (STEOM-CC) method by Nooijen<sup>61</sup>. Although the STEOM-CC method is formulated without any direct reference to the FS-CC scheme, both methods are closely related<sup>62</sup>. That becomes especially visible when the intermediate Hamiltonian version of the FS-CC method is used for comparison<sup>57</sup>.

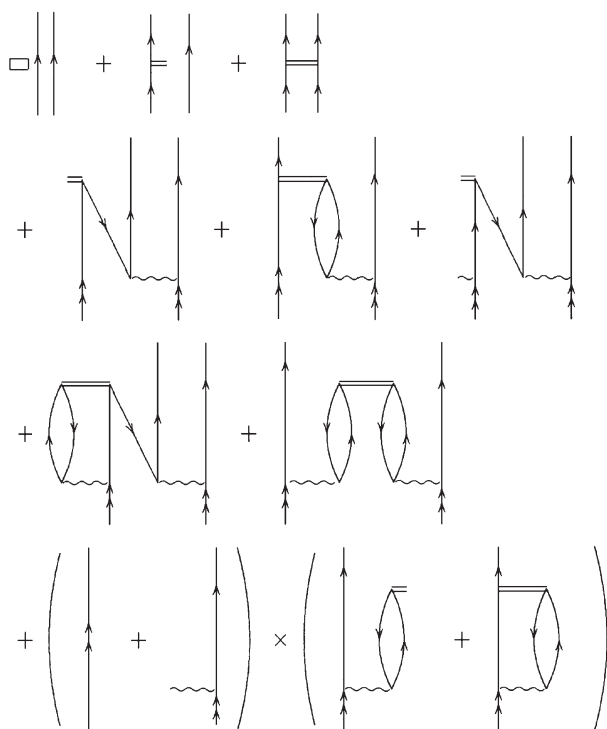


FIG. 3

Diagrammatic representation of the intermediate Hamiltonian FS-CCSD in the two-valence sector

## CONCLUDING REMARKS

In spite of substantial effort that has been put in extending applicability of single-reference methods to cases when some, even significant, degree of quasi-degeneracy is present, development of methods using a linear combination of several determinants as a reference and attempts to combine multireference and single-reference approaches to come out with approximate schemes that are simple yet effective, it seems that further development of genuine multireference schemes, in particular those based on the exponential *Ansatz*, is highly desirable. In this paper we have reported the progress that has been recently made within the Fock-space CC method. Starting with a brief description of the single-reference approaches we have tried to show fundamental problems occurring when one wants to generalize them to multireference cases. These problems are caused by a different treatment of nondynamic and dynamic correlation required by multireference methods. The effective Hamiltonian formalism which provides such a treatment of both kinds of correlation leads to quite complicated formulations and assumes solving eigenvalue problems for several states at a time. Moreover, in practical applications, methods based on the effective Hamiltonian formulations seem very vulnerable to intruder states. If both types of correlation effects are treated in the same manner, which takes place in the MR-CI approach, then the effective Hamiltonian formalism is not necessary and the method preserves its formal and computational simplicity. Keeping this in mind and taking advantage of some specific features of the FS-CC method, we have taken the opportunity given by the intermediate Hamiltonian technique to remove the effective Hamiltonian from the Fock-space CC formulation. This is possible due to the fact that the intermediate Hamiltonian permits the same treatment of nondynamic and a large portion of dynamic correlation. As a consequence, the resulting method in some aspects resembles MR-CI, the basic difference being that MR-CI assumes diagonalization of  $H$ , while in the intermediate Hamiltonian FS-CC method the similarity-transformed Hamiltonian  $(1 - Y)\bar{H}(1 + Y)$  is diagonalized. The Equation of Motion (EOM) CC method<sup>63</sup> is even more closely related to the intermediate Hamiltonian FS-CC scheme. The EOM-CC method relies on diagonalization of  $\bar{H}$  in a selected space, thus for the one-valence sector both methods are identical. The difference is visible in the two-valence sector where, in addition to  $\bar{H}$ , the Fock-space CC scheme makes use of the one-valence results contained in  $Y$  to perform a subsequent similarity transformation of slightly different character.

The intermediate Hamiltonian FS-CC method is equivalent to the standard FS-CC formulation in all basic versions. As mentioned, due to a different treatment of the disconnected contributions, some versions of the standard FS-CC method may not be easy to reproduce within the intermediate Hamiltonian formulation. That mainly concerns those versions in which the wave function is not well defined due to removing some terms from the FS-CC equations, like, for example, restricting them to be at most quadratic in cluster amplitudes<sup>48</sup>.

Although our considerations have been focused on one specific version of the FS-CC method, namely that in which the core serves as a vacuum, also for all other variants of the FS-CC method, similar intermediate Hamiltonian formulations are easy to obtain<sup>47</sup>. In particular, a version with the HF determinant as a vacuum having selected active hole and active particle levels is very useful in the direct excitation energy calculations<sup>57</sup>. These both kinds of the FS-CC method have been implemented and results of preliminary calculations have been obtained<sup>57-59</sup>. In the case of our atomically oriented FS-CCSD/R method with the core as a vacuum, designated to description of quasi-degenerate ground states and low-lying excited states of atomic systems, the intermediate Hamiltonian reformulation is not completely straightforward<sup>58</sup>. If the spherical symmetry of atomic systems is explicitly taken into account and the angular part is separated from the CC equations, the equations are for the radial part only. Due to the specific definition of the radial cluster operators<sup>6</sup>, the intermediate space as generated by the cluster excitation operators appears not uniquely defined. To overcome the problem, a single-reference function is chosen to generate all main-model and intermediate space functions. The method is invariant with respect to this choice in the sense that the energy values are not affected by the selection, only the number of states that can be described differs. Our numerical experience with both versions of the FS-CC method confirms the efficiency of the intermediate Hamiltonian formulation. We are currently working on more efficient codes enabling us to perform large-scale calculations. Another direction of developing the method is an *a posteriori* correction evaluating the effect of the three-body cluster operators.

Let us now summarize with pointing out main advantages of the FS-CC intermediate Hamiltonian formulation which, in our opinion, can help the FS-CC implementations reaching the so-called black-box status. They are: (i) formal simplicity compared with the standard effective Hamiltonian formulation; (ii) replacing the two-step procedure of obtaining cluster amplitudes first and then the energies by diagonalization of the effective

Hamiltonian with the one-step procedure of solving the eigenvalue problem of the intermediate Hamiltonian or, if the determination of cluster amplitudes is required, with the two-step procedure in which the eigenvalues are obtained first and then the cluster amplitudes by imposing the intermediate normalization on the eigenvectors; (iii) elimination of the effective Hamiltonian from the equations which leads to decoupling of the eigenvalue problems for individual states; (iv) effective way of solving the equations enabling us to deal more efficiently with the intruder state problem. We believe that the above features can make the FS-CC calculations routine.

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