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Intermediate Hamiltonian formulation of the valence-universal coupled-cluster method for atoms

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A formulation of the valence-universal coupled-cluster (VU-CC) method for atoms is presented. The method is based on Lindgren's normal-ordered exponential expansion, in which the cluster operator is restricted to its one- and two-body components represented in terms of radial amplitudes defined by the configurational excitations. The approach employs an intermediate Hamiltonian technique which replaces the effective Hamiltonian formalism used in the standard VU-CC formulation. The modified version introduces many simplifications in comparison with the standard one and, in particular, offers an efficient way of solving coupled-cluster equations. The advantages of the approach are illustrated in a calculation for the Be atom, representing one of the basic yet very challenging applications for VU-CC methods.

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I. INTRODUCTION

In recent years, single-reference coupled-cluster (CC) methods [1] have been demonstrated to be among the most promising tools for the treatment of electron correlation effects [2,3]. The success of the single-reference CC (SR-CC) methods in describing closed-shell systems has inspired intensive research activity towards a generalization of the CC scheme to multireference cases which would enable an application of CC methods to open-shell or quasidegenerate states. These states are characterized by a large component of nondynamical correlation that is usually difficult or even impossible to handle by the SR-CC approaches. The idea the multireference CC (MR-CC) theories are based on is to introduce different types of descriptions for dynamical and nondynamical electron correlation effects. The zero-order picture provided by independent-particle models can be used to divide the functional space into the reference (model) space and its orthogonal complement. The reference space is spanned by zero-order functions (determinants) which dominate in the target state eigenvectors, whereas excitation operators in the so-called wave operator generate contributions from outer space while acting on the reference functions. Hence the wave operator is assumed to give us information about dynamical correlation, whereas the reference space is associated with nondynamical correlation effects. The wave operator must be determined in a self-consistent manner imposed by the iterative character of the equations, and is then used to construct an effective Hamiltonian whose action is restricted to the reference space [4–6]. Its diagonalization within this space gives the final contribution of nondynamical correlation to the target state functions.

The distinction between descriptions of dynamical and nondynamical correlations, made by the effective Hamiltonian approach, may be seen as an efficient and safe way of providing information about dominant and less important components of the wave functions. For the latter, different approximate schemes can be considered as truncated perturbation [6,7] or CC [8–13] expansion. However, both types of correlation effects are coupled together through the equations, and the success of this kind of formulation to a large extent depends on their clear separation meaning, that the model space should be properly selected to ensure that the wave operator is truly responsible for generating the dynamical part of the correlation only. In practice this may be difficult to achieve. First, the effective Hamiltonian formalism assumes a description of several states at a time [4–6], and the requirement should be fulfilled for all of them. Second, in early formulations of multireference CC theories only complete reference spaces were admitted, which seriously limited their applicability [14]. The incomplete reference space versions formulated later [15–17] increased flexibility with respect to the reference space choice while still preserving the size extensivity of the methods. The possibility of having a general model space allows multireference CC schemes to deal efficiently with more demanding systems reducing the intruder state [18] or convergence problems [14]. The latter may, however, also depend on the iterative procedures employed [19].

In order to define cluster operators in a second-quantized form, one has to make a suitable choice of a Fermi vacuum. All operators can then be expressed in a normal product form with respect to the selected vacuum, and many-body techniques based on the generalized Wick's theorem can be used [20]. For SR-CC methods the reference function (mostly the Hartree-Fock determinant) is usually considered as a natural choice for the vacuum. In the case of multireference formulations there is no such obvious choice, because we have several reference functions which span the model space. Basically two strategies can be followed in the MR case. The first one is to have one Fermi vacuum for all operators entering MR-CC equations independently of the reference function they can be associated with. The next possibility is to introduce several different vacuua. Here, for each CC equation corresponding to a particular reference function, this function is used as a vacuum. The first strategy, which has its origin in Brandow's MR perturbation expansion [6], leads to the so-called valence-universal (or Fock-space) CC theories (VU-CC or FS-CC) [8–10,16]. The second one follows the idea introduced in Hose-Kaldor perturbation theory [7] and it is used in the state-universal (or Hilbert-space) CC methods (SU-CC or HS-CC) [11–13]. In the following we concentrate on the VU-CC methods, which, due to the fact of having one vacuum, are more suitable for space and spin symmetry adaptations, and thus for the specific case of atomic calculations.

The use of one Fermi vacuum, that is assumed in VU-CC methods, does not mean that there is one preferable choice of vacuum. In fact, several possibilities can be considered depending on the system and property we want to describe. Two basic options are the core for describing the ground state and low-lying excited states in the presence of quasidegeneracy [8,9,21]; and the Slater determinant for the neutral system for a direct calculation of excitation energies from the closed-shell ground state to quasidegenerate excited states [22–27]. In this paper we will focus on the first version of the VU-CC method. The cluster operator is defined as a second-quantized normal-ordered excitation operator from the reference functions to the outer space. Because we have one Fermi vacuum, the excitation operators can contain not only particle-hole creation operators but also particle-hole annihilation operators [8–10,21]. The reason for this is that the reference functions are generated from the vacuum through the action of a sequence of particle creation operators, and then particle-hole annihilation operators are necessary in the excitation operators to create orthogonal space functions. There are two important consequences of this. The first one is that contractions between cluster operators in the exponential expansion are possible. Second, the same outer space function can be obtained from a particular reference by several different excitation operators, which leads to the so-called VU-CC redundancy problem. The first problem has been resolved by defining a normal-ordered cluster expansion in which the normal form of the wave operator prevents contractions between cluster operators [9,10]. The redundancy can be removed by introducing a valence-universal strategy which assumes that cluster operators have to satisfy the CC equations with zero, one, etc. up to the final number of valence electrons [8,9,28,29]. This provides additional equations for cluster amplitudes, and additional information about the system under consideration. The equations have to be solved hierarchically, starting with the zero-valence problem. Valence-universal strategy gives the method a Fock-space character [16,29].

Because of their formal complexity, and problems that the use of an effective Hamiltonian technique brings, MR-CC methods have not been very widely used in routine calculations. This has been the reason for turning back to single-reference CC formulations to make them more applicable to quasidegenerate [30–33] and open-shell systems [34]. Some attempts along this line introduced two-step approaches in which the main part of the nondynamical correlation was determined within a conceptually simple and numerically stable MR configuration interaction (CI), scheme while a subsequent single-reference CC calculation provided us with a more adequate description of dynamical correlation effects [32,33]. One may also replace the CC calculation by a noniterative correction to the MR-CI energy [35]. However, it seems that these approaches have their limitations, so a further development of MR-CC schemes is highly desirable. One possible way of making the MR-CC methods more attractive is to reformulate them by employing intermediate Hamiltonian techniques [36,5]. Such attempts have been made within both VU-CC [37–40] and SU-CC approaches [41–43]. The idea underlying the intermediate Hamiltonian approach is to divide the functional space into three subspaces instead of two [36,5]. The additional intermediate space plays the role of a buffer between the model space and the remaining external space. The contribution from the intermediate space, which is generated by the wave operator in the effective Hamiltonian formulation, is now given in a process of diagonalization of the intermediate Hamiltonian [36,5]. That provides more effective computational schemes. VU-CC approaches are especially suitable for the intermediate Hamiltonian reformulation [38]. While general considerations of possible implementations of the intermediate Hamiltonian technique within VU-CC schemes can be found in Ref. [38], and preliminary results of the intermediate Hamiltonian VU-CCSD method designated for calculation of excitation energies in Ref. [39], in this paper we present an intermediate Hamiltonian VU-CC scheme especially designed for a specific case of atomic calculations. In spite of the fact that most of the existing general purpose methods can also be applied to atoms, their accuracy is relatively low from the point of view of the requirements of atomic physics. To fully exploit the power of CC methods one should take the advantage of the simplifications afforded by the spherical symmetry of the problem. Whereas the single-reference CC formulation for atoms was put forward by Adams and Paldus [44], the multi reference CC formalism was proposed by the Göteborg group [21]. Here the cluster amplitudes are represented in terms of products of radial, angular, and spin factors, allowing us to obtain a set of equations for the radial part only [21]. While the Göteborg group's approach is based on the use of numerical one- and two-electron radial-function contributions to the wave function, an algebraic analog of this method was proposed by Jankowski and Malinowski [45–48,19]. The latter is the basis for the intermediate Hamiltonian reformulation we would like to propose. In Sec. II we present a brief description the VU-CC expansion, and details of the effective and intermediate Hamiltonian formulations employing this kind of representation for the wave operator.

II. METHOD

A. Effective Hamiltonian formulation

While considering the Schrödinger equation describing a many-electron system,

$$H\Psi = E\Psi, \tag{1}$$

we assume that we have to deal with a quasidegenerate situation in which more than one determinant is necessary to obtain a reliable zero-order description of the state. Let us define the reference (model) space M as spanned by several determinants (reference functions) which dominate in the Ψ-function expansion. The orbitals can then be divided into three classes: core (C) orbitals which are doubly occupied in all reference determinants, valence (V) or active orbitals which are occupied in some determinants but not in all of them, and excited (E) orbitals which are unoccupied in the reference functions. The spin orbitals will be labeled according to the conventions $a,b,c \in C, i,j,k \in V, r,s,t \in E, \alpha,\beta,\gamma \in C \cup V, \rho,\sigma,\tau \in V \cup E$, and $\lambda,\kappa,\mu \in C \cup V \cup E$. In the following we assume that the model space is complete, which means that all possible distributions of valence electrons among valence spin orbitals are included in the reference space functions. However, an incomplete model space version can also be considered if necessary. The Fermi vacuum Φ is defined as a determinant constructed from the core spin orbitals. Hence the core spin orbitals will be referred to as holes, and all other spin orbitals as particles. The reference functions Φ_n can then be expressed using creation operators ($X^\dagger$) as

$$\Phi_n = X^\dagger_{i_1}, \ldots, X^\dagger_{i_L}\Phi \quad (i_1 < \cdots < i_L), \tag{2}$$

where L is the number of valence electrons. Second-quantized normal-ordered excitation operators acting on the reference functions can be classified into operators leading to the model space (internal) and operators leading to its orthogonal complement (external). A general form of the excitation operators can written as

$$N[e^{\rho}_{\alpha}], N[e^{\rho\sigma}_{\alpha\beta}], \ldots, \tag{3}$$

where

$$e^{\lambda\kappa\cdots}_{\mu\nu\cdots} = X^\dagger_\lambda X^\dagger_\kappa \cdots X_\nu X_\mu, \tag{4}$$

and $N[\cdots]$ means the normal product form with respect to Φ. The internal excitations are those having exclusively valence spin orbital labels, whereas all others constitute external excitations.

Internal excitations are responsible for a description of nondynamical electron correlation, whereas external ones are associated with the dynamical correlation. One possible way of describing the dynamical part is a coupled-cluster-type expansion, which has proven so successful in the single reference case. Truncation of the cluster operator allows not only an effective approximation of higher-level excitations via products of lower excitation rank operators, but also guarantees the size extensivity of the method, which is nowadays considered a very important feature. However, the nondynamical effects should be treated exactly, meaning that coefficients associated with the internal excitations are determined by diagonalization. These different treatments of both types of correlation can be realized within the effective Hamiltonian scheme [4]. The concept of the effective Hamiltonian can be introduced by considering simple similarity transformations [5]. Let us denote the projection operator on the reference space M by P, and that on its orthogonal complement $M_\perp$ by Q. Introducing the operator

$$X = QXP, \tag{5}$$

we can consider the following similarity transformation:

$$\tilde{H} = e^{-X}He^{X} = (1-X)H(1+X). \tag{6}$$

Requiring the transformed Hamiltonian $\tilde{H}$ to satisfy

$$Q\tilde{H}P = 0, \tag{7}$$

we can divide the eigenvalue problem of H into two subproblems. Now all eigenvalues of H can be obtained by separate diagonalizations of $P\tilde{H}P$ and $Q\tilde{H}Q$. Since usually we are not interested in all eigenvalues but only in a small subset of them, diagonalization of $P\tilde{H}P$ in a relatively low-dimensional model space is the final goal. One can view this procedure as a way of extracting a subproblem corresponding to $m = \dim M$ eigenvalues from the complete eigenvalue problem. Contributions from orthogonal and model spaces to those eigenvalues are given by X and a diagonalization of $P\tilde{H}P$, respectively. There are many X operators satisfying Eq. (7) [5], but we assume that by using a suitable starting point in an iterative procedure for X based on Eq. (7) we would be able to converge at the desired solution i.e., that $P\tilde{H}P$ gives eigenvalues of interest. A proper selection of the model space can be a key factor here, since the effectiveness of the scheme may depend to a large extent on a clear separation of dynamical and nondynamical correlation effects. It is usually assumed that the dominant part of the eigenfunctions of all m states under consideration should be included in the model space. Then X can be viewed as relatively small, and easy to determine in a self-consistent manner. The solution that satisfies the condition is called the principal (or standard) one, whereas all others are considered as alternative (or nonstandard) [48]. The $P\tilde{H}P$ part of the transformed Hamiltonian can be called the effective Hamiltonian:

$$H_{eff} = P\tilde{H}P = PH(1+X)P. \tag{8}$$

Using this notation, Eq. (7) can be expressed in a more standard way [4,6] as

$$QH(1+X)P - XH_{eff} = 0. \tag{9}$$

In order to introduce the exponential expansion for $(1+X)$, a suitable definition of the cluster operator must be introduced. In our case the cluster operator S is defined by associating cluster amplitudes with the external part of excitation operators (3). In the following we restrict our consideration to the case of systems having two valence electrons ($L=2$) and S approximated by one- and two-body components

$$S \approx S_1 + S_2, \tag{10}$$

where

$$S_1 = S^a_\rho N[e^\rho_a] + S^i_r N[e^r_i], \tag{11}$$

$$S_2 = \frac{1}{4}S^{ab}_{\rho\sigma}N[e^{\rho\sigma}_{ab}] + \frac{1}{2}S^{ia}_{\rho\sigma}N[e^{\rho\sigma}_{ia}] + \frac{1}{4}S^{ij}_{\rho\sigma}N[e^{\rho\sigma}_{ij}]. \tag{12}$$

The Einstein summation convention is used here, and cluster amplitudes having exclusively valence spin orbital labels are excluded so only external excitations are permitted in the cluster operator. The cluster amplitudes are antisymmetric in their lower and upper indices, except for $S^{ia}_{\rho\sigma}$, which is antisymmetric in its lower indices only. Due to Eqs. (11) and (12) the S_1 and S_2 operators can be additionally classified according to the number of active labels of the annihilation operators:

$$S_1=S_1^{(0)}+S_1^{(1)},\quad S_2=S_2^{(0)}+S_2^{(1)}+S_2^{(2)}. \tag{13}$$

Due to Lindgren [10], the cluster expansion can be introduced in the normal-ordered forms

$$N[e^S]=e^{S^{(0)}}N[e^{S^{(1)}+S^{(2)}}], \tag{14}$$

$$S^{(0)}=S_1^{(0)}+S_2^{(0)},\quad S^{(1)}=S_1^{(1)}+S_2^{(1)},\quad S^{(2)}=S_2^{(2)}. \tag{15}$$

The normal-ordered form prevents contractions between cluster operators in the expansion which are, in general, possible since the cluster operators can contain particle-hole annihilation operators. The exception is $S^{(0)}$, which is expressed by particle-hole creation operators only. Hence $S^{(0)}$ cannot be contracted with the remaining S operators, and its exponential expansion is already in normal-ordered form. We have taken advantage of this in Eq. (14). Because of specific form of the cluster expansion (14), we can replace transformation (6) with a double transformation satisfying

$$\overline{P}^{(2)}(1-X^{(2)})\overline{H}(1+X^{(2)})P^{(2)}=0, \tag{16}$$

$$\overline{H}=e^{-S^{(0)}}He^{S^{(0)}}, \tag{17}$$

$$X^{(2)}=Q^{(2)}N[e^{S^{(1)}+S^{(2)}}]P^{(2)}, \tag{18}$$

where the first transformation has a many-body character. The superscript (2) indicates that we are concerned with a two-valence-electron problem. $\overline{P}^{(2)}$ denotes a projection onto a subspace of $M_\perp^{(2)}$ that is reached by excitations generated by $S^{(2)}$ while acting on $M^{(2)}$, so the number of equations equals the number of the $S^{(2)}$ amplitudes. The remaining amplitudes associated with $S^{(0)}$ and $S^{(1)}$ must be obtained from separate calculations. This is a consequence of the cluster operator definitions (11) and (12), which allows several operators to generate the same orthogonal space determinant while acting on the reference functions. The additional equations for $S^{(0)}$ and $S^{(1)}$ are provided by the valence-universal strategy of solving the CC equations [9,28,16,29]. The strategy assumes a hierarchical way of solving problems with an increasing number of valence particles, starting with the zero-valence-particle problem, so that the number of equations becomes equal to the number cluster amplitudes. Now the notation introduced in Eq. (15) is consistent with that of Eqs. (16)–(18), as $S^{(i)}$ can be really associated with the i valence problem. It must be mentioned that while solving problems with a lower number of valence particles, we obtain an additional information of the system.

For the zero- and one-valence sectors which must be considered in our VU-CCSD scheme, we have

$$X^{(0)}=Q^{(0)}N[e^{S^{(1)}+S^{(2)}}]P^{(0)}=0, \tag{19}$$

$$X^{(1)}=Q^{(1)}N[e^{S^{(1)}+S^{(2)}}]P^{(1)}=S^{(1)}P^{(1)}. \tag{20}$$

The explicit form of the CC equations can be obtained by employing diagrammatic techniques which allow us to represent basic second-quantized normal-ordered operators by diagrams. Then a graphical representation of the CC equations can be constructed using simple rules of operating with diagrams based on the generalized Wick's theorem. An additional simplification is introduced by the linked diagram theorem (LDT) that can be proven for the VU-CC method [10,16]. This states it that disconnected terms are canceled out in the equations, so that only connected diagrams have to be considered. Also, the linked diagram theorem guarantees the size extensivity of the method. Using Eqs. (19) and (20), and taking advantage of the LDT, the hierarchy of the VU-CCSD equations can be expressed in the forms

$$\overline{P}^{(0)}\overline{H}_N P^{(0)}=0,$$

$$\langle\Phi|H^{(0)}_{eff}|\Phi\rangle=E_{core}=\langle\Phi|\overline{H}|\Phi\rangle, \tag{21}$$

$$\overline{P}^{(1)}\{\overline{H}_N(1+S^{(1)})-S^{(1)}H^{(1)}_{eff}\}_c P^{(1)}=0,$$

$$H^{(1)}_{eff}=P^{(1)}\overline{H}_N(1+S^{(1)})P^{(1)}, \tag{22}$$

$$\overline{P}^{(2)}\left\{\overline{H}_N N\left[1+S^{(1)}+\frac{1}{2}S^{(1)2}+S^{(2)}\right]\right.$$

$$\left.-N\left[S^{(1)}+\frac{1}{2}S^{(1)2}+S^{(2)}\right]H^{(2)}_{eff}\right\}_{c,2}P^{(2)}=0,$$

$$H^{(2)}_{eff}=P^{(2)}\overline{H}_N N\left[1+S^{(1)}+\frac{1}{2}S^{(1)2}+S^{(2)}\right]P^{(2)}, \tag{23}$$

where subscripts c and 2 mean connected and two-body diagrams, respectively, and

$$\overline{H}_N=\overline{H}-\langle\Phi|\overline{H}|\Phi\rangle. \tag{24}$$

The use of $\overline{H}_N$ instead of $\overline{H}$ means that the effective Hamiltonians $H^{(1)}_{eff}$ and $H^{(2)}_{eff}$ are redefined to give energies relative to the core energy E_{core}. $\overline{P}^{(0)}$ and $\overline{P}^{(1)}$ are defined in a way analogous to $\overline{P}^{(2)}$. It is worth noting that the hierarchical strategy is indeed possible because of separation of valence problems, meaning that the CC equations in a particular valence sector do not depend on the higher sector cluster amplitudes. As mentioned, the VU-CCSD equations are expressed through connected terms, however, only in the cases where disconnected contributions can be constructed has the necessity of eliminating them been explicitly indicated.

The cluster operator definition [Eqs. (11) and (12)] can be used to obtain a general purpose version of the VU-CCSD method; however, to take advantage of the high symmetry of atomic systems, one should follow a strategy similar to that described by Lindgren and Morrison [21] for separating out the angular and spin dependences from the diagrams. We assume that the one- and two-electron cluster amplitudes are expressed as

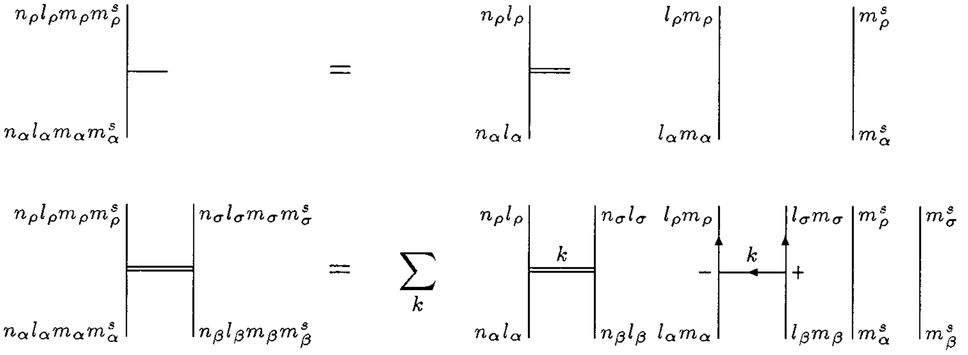

FIG. 1. Graphical representation of the radial-angular-spin separation of the one- and two-particle cluster amplitudes.

$$S^{n_\alpha l_\alpha m_\alpha m^s_\alpha}_{n_\rho l_\rho m_\rho m^s_\rho} = R^{n_\alpha l_\alpha}_{n_\rho l_\rho} G_1(\alpha;\rho), \tag{25}$$

$$S^{n_\alpha l_\alpha m_\alpha m^s_\alpha, n_\beta l_\beta m_\beta m^s_\beta}_{n_\rho l_\rho m_\rho m^s_\rho, n_\sigma l_\sigma m_\sigma m^s_\sigma} = \sum_k R^{n_\alpha l_\alpha, n_\beta l_\beta}_{n_\rho l_\rho, n_\sigma l_\sigma}(k) G^{(k)}_2(\alpha\beta;\rho\sigma), \tag{26}$$

with

$$G_1(\alpha;\rho) = \delta(l_\alpha, l_\rho)\,\delta(m_\alpha, m_\rho)\,\delta(m^s_\alpha, m^s_\rho) \tag{27}$$

$$\begin{aligned} &G^{(k)}_2(\alpha\beta;\rho\sigma) \\ &= \sum_q (-1)^{l_\rho - m_\rho + l_\sigma - m_\sigma + k - q} \begin{pmatrix} l_\rho & k & l_\alpha \\ -m_\rho & q & m_\alpha \end{pmatrix} \\ &\quad \times \begin{pmatrix} l_\sigma & k & l_\beta \\ -m_\sigma & -q & m_\beta \end{pmatrix} \delta(m^s_\alpha, m^s_\rho)\,\delta(m^s_\beta, m^s_\sigma), \end{aligned} \tag{28}$$

where $(\cdots)$ denotes the 3-j Wigner coefficient, and R stands for radial one- and two-particle cluster amplitudes. The spin orbital indices are used as orbital ones. The structure of $G^{(k)}_2(\alpha\beta;\rho\sigma)$ restricts the possible k values to those simultaneously satisfying the triangular conditions for (l_α, k, l_ρ) and (l_β, k, l_σ). The radial-angular-spin ansatz of the cluster amplitudes defined by Eqs. (25) and (26) can be represented graphically in the form shown in Fig. 1. On the right-hand side of the graphical representation, the horizontal double-line vertices denote the radial cluster amplitudes, and the remaining ones stand for the angular-momentum graphs $(G_1(\alpha;\rho)$ and $G^{(k)}_2(\alpha\beta;\rho\sigma))$ [21]. Let us note that to apply the separation one has to label the spin-orbital amplitudes explicitly in terms of all orbital and spin indices, and that the indices of the R amplitudes are labeled by atomic-shell indices only. One of the great advantages of the separation is the enormous reduction of the number of unknown cluster amplitudes [21,46].

The VU-CCSD method for atoms has been referred to as VU-CCSD/R, where R stands for indicating the reduction to radial-type equations. An explicit diagrammatic form of the VU-CCSD/R equations, in which an additional restriction to quadratic terms in S has been imposed, can be found elsewhere [46,48], and we refer to these papers for the derivation and a more complete discussion.

B. Intermediate Hamiltonian formulation

There are several characteristic features of the effective Hamiltonian VU-CC formulation which one can consider as important drawbacks of the method. First of all, this is a two-step approach. In the first step cluster amplitudes are calculated, allowing us to construct the effective Hamiltonian and its diagonalization in the second step. Second, several eigenvalue problems are coupled together through the equations, so that we have to consider all of them at a time. Moreover, numerical experience shows that effective iterative schemes are required to solve the equations for cluster amplitudes [19,47]. In this section we will show how the intermediate Hamiltonian formulation can change the situation introducing many simplifications and offering an efficient way of solving the VU-CC equations.

The intermediate Hamiltonian technique was introduced and primarily used in the context of multireference perturbation theory [36]. The idea was to divide the functional space into three subspaces instead of two. The additional intermediate space plays the role of a buffer between the model space and the remaining external space [36]. Its contribution to the eigenvalues given by the effective Hamiltonian in the standard formulation is not provided via perturbation expansion but by diagonalization. In this way small denominators in the expansion can be avoided in cases of the occurrence of intruder states. Very soon nonperturbative schemes also started using this kind of technique [37–43]. However, it seems that application of the intermediate Hamiltonian scheme is especially advantageous with respect to the VU-CC method [37–40]. This follows from the fact that, in spite of its generally nonlinear character, the VU-CC expansion is linear in the unknown cluster amplitudes in each valence sector beyond the zero sector [see Eqs. (22) and (23)]. All nonlinear terms in S in the expansion are products of cluster operators from the lower valence sectors, which, due to valence-universal strategy, are *a priori* determined. As a consequence the eigenvalue problem can be solved via diagonalization of some operator which depends only on the lower sector cluster amplitudes. The operator can be easily identified as an intermediate Hamiltonian.

As mentioned, our intermediate Hamiltonian formulation of the VU-CCSD method concerns valence sectors of a rank higher than zero. The zero-valence sector represents the standard single-reference CCSD method for the core. For higher sectors the intermediate space is extracted from the orthogonal complement of the model space $M^{(i)}$ ($i=1$ and 2), and can be defined in a simple way as that associated with the projection operator $\overline{P^{(i)}}$. For the projection on the remaining part of the $M_{\perp}^{(i)}$ space we use $\overline{Q}^{(i)}$. Hence

$$Q^{(i)}=\overline{P}^{(i)}+\overline{Q}^{(i)}. \tag{29}$$

The starting point in our derivation is again a similarity transformed Hamiltonian for one- and two-valence sectors satisfying equations analogous to Eq. (16):

$$\overline{P^{(i)}}(1-X^{(i)})\overline{H}_N(1+X^{(i)})P^{(i)}=0, \tag{30}$$

$$X^{(i)}=Q^{(i)}N[e^{S^{(1)}+S^{(2)}}]P^{(i)} \quad (i=1,2). \tag{31}$$

Let us now introduce the operators

$$\begin{gathered} Y^{(i)}=\overline{Q}^{(i)}X^{(i)}, \quad Z^{(i)}=\overline{P}^{(i)}X^{(i)}, \\ X^{(i)}=Z^{(i)}+Y^{(i)}. \end{gathered} \tag{32}$$

With this notation Eq. (30) can be written as

$$\overline{P}^{(i)}(1-Z^{(i)})(1-Y^{(i)})\overline{H}_N(1+Y^{(i)})(1+Z^{(i)})P^{(i)}=0, \tag{33}$$

since

$$1+X^{(i)}=(1+Y^{(i)})(1+Z^{(i)}). \tag{34}$$

Condition (33) leads to separation of a problem corresponding to several eigenvalues which are now provided by diagonalization of the $P^{(i)}$-$P^{(i)}$ part of the transformed Hamiltonian (the effective Hamiltonian). However, the same eigenvalues can be obtained as a subset of eigenvalues of the operator

$$P_0^{(i)}(1-Z^{(i)})(1-Y^{(i)})\overline{H}_N(1+Y^{(i)})(1+Z^{(i)})P_0^{(i)}, \tag{35}$$

where

$$P_0^{(i)}=P^{(i)}+\overline{P}^{(i)} \tag{36}$$

is a projection operator on the model and intermediate space. Since operator (35) and the operator

$$P_0^{(i)}(1-Y^{(i)})\overline{H}_N(1+Y^{(i)})P_0^{(i)} \tag{37}$$

are related by similarity transformation, they have the same eigenvalues. So the eigenvalues obtained within the effective Hamiltonian formulation are among those given by diagonalization of operator (37). Operator (37) can be recognized as an intermediate Hamiltonian. To obtain its more explicit form let us first note that, due to definition (32), we have

$$\begin{aligned} H_{int}^{(i)}&=P_0^{(i)}(1-Y^{(i)})\overline{H}_N(1+Y^{(i)})P_0^{(i)} \\ &=P_0^{(i)}\overline{H}_N(1+Y^{(i)})P_0^{(i)}. \end{aligned} \tag{38}$$

It is also easy to see that for the one- and two-valence sectors we have

$$Y^{(1)}=0, \quad Y^{(2)}=N\left[S_2^{(1)}+S_1^{(1)}S_2^{(1)}+\frac{1}{2}S_2^{(1)2}\right]P^{(2)}, \tag{39}$$

and the intermediate Hamiltonians for these sectors can be written as

$$H_{int}^{(1)}=P_0^{(1)}\overline{H}_N P_0^{(1)}, \tag{40}$$

$$H_{int}^{(2)}=P_0^{(2)}\overline{H}_N P_0^{(2)}+P_0^{(2)}\overline{H}_N N\left[S_2^{(1)}+S_1^{(1)}S_2^{(1)}+\frac{1}{2}S_2^{(1)2}\right]P^{(2)}. \tag{41}$$

Let us now discuss the advantages of dealing with the intermediate Hamiltonian approach instead of the effective Hamiltonian one. First of all the two-step effective Hamiltonian formalism is replaced with a one-step procedure which is a diagonalization of the intermediate Hamiltonian. The diagonalization provides eigenvalues and eigenstates at the same time. The intermediate Hamiltonians (40) and (41) are constructed from cluster operators from the lower sectors which are known due to the hierarchical strategy of solving the equations. Hence there is no dependence of the intermediate Hamiltonian matrix on its eigenvector or eigenvalue, which is frequently the case in many other implementations of the intermediate Hamiltonian technique. Moreover, since the coupling term between different eigenstate problems disappears, then the eigenvalues can be obtained one by one with a properly selected diagonalization procedure. It must be stressed, however, that a set of cluster amplitudes can be determined when all eigenvectors of H_{int} corresponding to the model space under consideration are at our disposal. Since the cluster amplitudes are only necessary to construct the higher-valence-sector intermediate Hamiltonians, they are not required in the final sector. In our case the two-valence sector is the final one so, for example, if we are interested only in the ground-state energy we can concentrate on obtaining this single eigenvalue without the necessity of considering the others. On the other hand, the complete set of eigenvalues of H_{int} also contains energies which are given by the so-called alternative solutions of the effective Hamiltonian approach. The important feature of these eigenvalues is that they have to be the same in all solutions they appear in. This is not so obvious when the effective Hamiltonian formulation is discussed, and it has not been detected in the numerical studies made so far because of the additional approximations imposed on the VU-CCSD equations [49]. Let us finally state that the intermediate Hamiltonian technique, applied to the VU-CCSD method, offers a very dependable way of solving the equations because of the existence of efficient diagonalization procedures. Perturbation-expansion-based iterative techniques that have been mostly used to solve the standard VU-CCSD equations can be seen to be much less effective and fail to reach convergence in some cases, even in those instances for which the intruder state problem does not seem to be too severe [14,19]. The Newton-Raphson scheme, just recently introduced, and successfully employed in VU-CCSD calculations, is numerically demanding, and depends much on quality of the starting vector. Therefore, its applicability is rather limited to relatively small systems.

Structure of the intermediate Hamiltonians (40) and (41) is very simple comparing to the equations of the effective Hamiltonian approach [Eqs. (22) and (23)]. For the one-valence sector this is a matrix representation of $\overline{H}_N$ in the space spanned by $\{X_\rho^\dagger\Phi, X_\rho^\dagger X_\sigma^\dagger X_a\Phi\}$. Since ρ and σ are indices of unoccupied spin orbitals in Φ, and a represents occupied ones, then the eigenvalue problem of $H_{int}^{(1)}$ does not depend on the selection made for valence orbitals. Hence it follows immediately that the effective Hamiltonian approach for the one-valence sector is also invariant with respect to the choice of valence orbitals as far as eigenvalues are concerned. However, for cluster amplitudes this is not the case. The cluster amplitudes must be obtained from $m^{(1)}$ (the number of valence spin orbitals, and the dimension of the $M^{(1)}$ model space) eigenvectors of $H_{int}^{(1)}$ corresponding to selected eigenvalues of interest. Let us denote by $\mathbf{V}_0$ an $m^{(1)}\times m^{(1)}$ matrix consisting of coefficients of the reference functions in these $m^{(1)}$ eigenvectors, and by $\mathbf{V}$ a matrix containing coefficients of the excited determinants in the eigenvectors. According to Eq. (32) we have

$$Z^{(1)}=\overline{P}^{(1)}N[e^{S^{(1)}}]P^{(1)}=S^{(1)}P^{(1)}, \tag{42}$$

which means that matrix representation of the Z operator contains $S^{(1)}$ amplitudes. Matrix $\mathbf{Z}$ can be easily obtained by imposing the intermediate normalization on selected $m^{(1)}$ eigenvectors of $H_{int}^{(1)}$,

$$\begin{bmatrix}\mathbf{I}\\ \mathbf{Z}\end{bmatrix}=\begin{bmatrix}\mathbf{V}_0\\ \mathbf{V}\end{bmatrix}[\mathbf{V}_0]^{-1}, \tag{43}$$

where $\mathbf{I}$ is an $m^{(1)}\times m^{(1)}$ unit matrix. We assume that $\mathbf{V}_0$ is invertible (nonsingular). The cluster amplitudes are then given by the matrix

$$\mathbf{Z}=\mathbf{V}\mathbf{V_0}^{-1}, \tag{44}$$

and the number of them as well as their values depend on the choice of the active orbital levels. The structure of $H_{int}^{(2)}$ [Eq. (41)], is more complicated. In addition to the $P_0^{(2)}\overline{H}_N P_0^{(2)}$ part, that is analogous to the expression for $H_{int}^{(1)}$, it contains a second term that is constructed from $\overline{H}_N$ and $S^{(1)}$ operators obtained in the previous one-valence sector. The $S^{(1)}$ operators transfer the information about active orbital levels to the two-valence sector, so the $H_{int}^{(2)}$ eigenvalues are not independent of the active orbital selection. As in the one-valence sector, a matrix representation of $Z^{(2)}$ can be obtained from $m^{(2)}=\dim M^{(2)}$ eigenvectors of $H_{int}^{(2)}$ by imposing the intermediate normalization. However, unlike the one-valence sector, cluster amplitudes are not given directly but must be calculated, if necessary, according to Eqs. (31) and (32):

$$S^{(2)}P^{(2)}=Z^{(2)}-N\left[S_1^{(1)}+\frac{1}{2}S_1^{(1)2}\right]P^{(2)}. \tag{45}$$

It can be seen that, contrary to the effective Hamiltonian VU-CCSD equations, a graphical representation of $H_{int}^{(2)}$ can contain disconnected diagrams. This is because of the intermediate Hamiltonian specific formulation, which does not allow us to eliminate the disconnected part. This does not mean that the method generates disconnected contributions and, hence, is not size extensive. The approach is fully size extensive; however, cancellation of the disconnected terms is purely numerical, and takes place during diagonalization of $H_{int}^{(2)}$. One may say that the disconnected part is essential for size extensivity, since it cancels out all disconnected terms generated by the diagonalization. The disconnected terms which must be included are simple, and do not make the explicit expression for $H_{int}^{(2)}$ more complicated. However, one has to be very careful when introducing approximations other than those imposed on the S operator. In such cases cancellation of the disconnected terms in $H_{int}^{(2)}$, and those generated by the diagonalization, may not be complete, leading to a size-extensivity error. The simple structure of the intermediate Hamiltonians enables us to base construction of their matrix elements on diagrams appearing in the effective Hamiltonian approach. Many of them are not required in the formulation, including some quite troublesome ones likes those arising from the renormalization term. As mentioned above only a few disconnected simple diagrams must be added.

In order to describe specific features of the atomic version of the VU-CCSD method, let us note that it is essential for the intermediate Hamiltonian formulation to have the model and intermediate space uniquely defined by internal excitations and external excitations associated with the cluster operator in a given sector. This means that the same space should be generated by the excitation operators independently of the particular reference function they act on. In the spin-orbital version this is the case, because the intermediate space functions can be associated with spin-orbital indices of particle-hole creation operators in the excitation operators. The reference functions can be related to all possible distributions of valence electrons among valence orbitals. That makes the labeling of matrix elements of the intermediate Hamiltonian well defined. In case of the VU-CCSD/R method, where cluster operators are represented in terms of radial amplitudes, the problem is more complicated. This is because of the angular-momentum coupling present in the S_2 definition [Eq. (26)], which can involve active orbital indices of the annihilation operators. The coupling makes two-particle radial amplitude labeling dependent on a particular occupation of valence orbitals in the model space. Therefore, a direct use of radial amplitude labels for matrix elements of the intermediate Hamiltonian is not possible. The problem can be overcome by specifying one of the possible occupan-

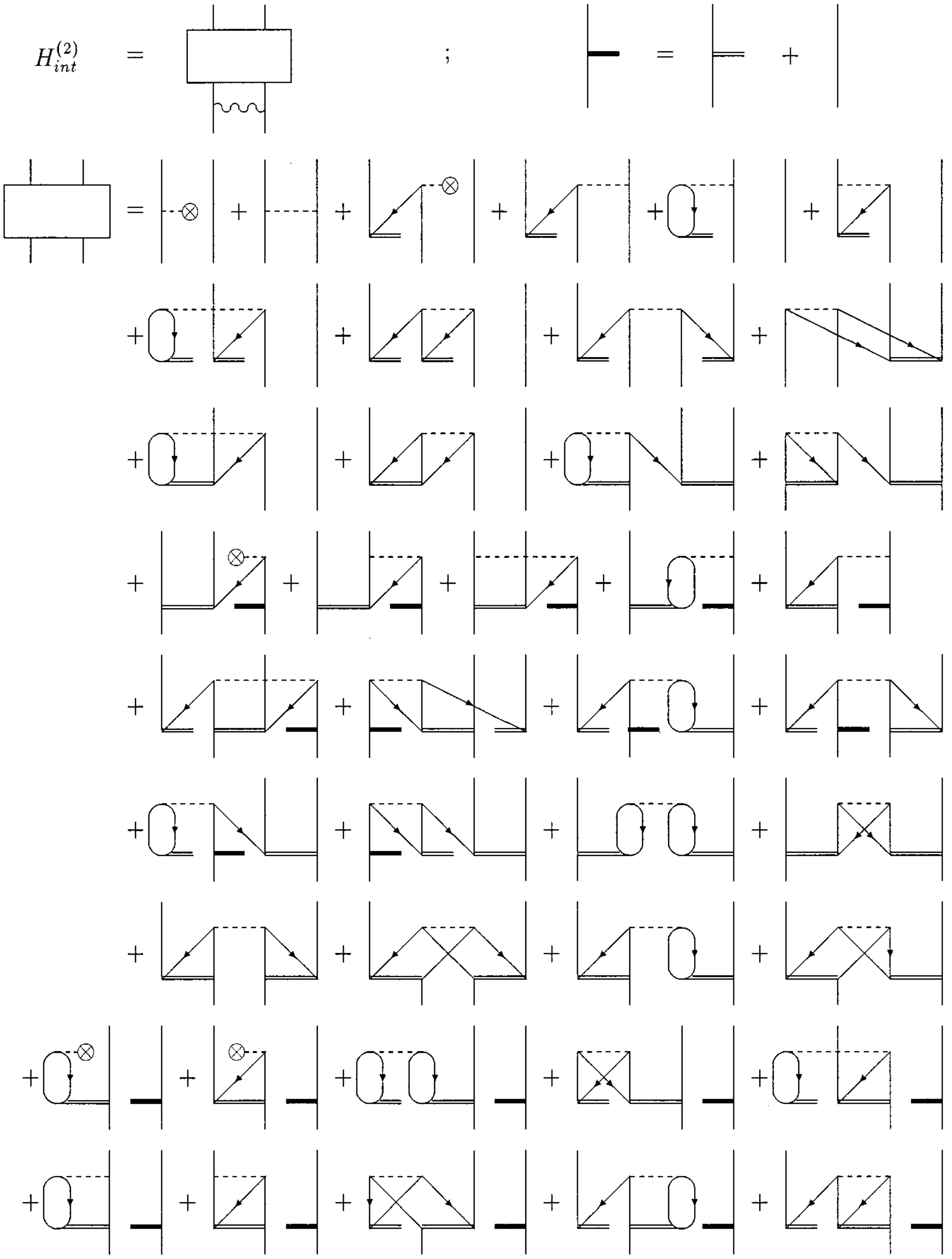

FIG. 2. Graphical representation of $H^{(2)}_{int}$.

cies of valence orbitals in the model space as a basic one, and then defining all internal and external radial amplitudes with respect to that choice.

For the one-valence sector the possibility of making different choices for the basic occupancy does not lead to any ambiguity, since symmetry blocks are entirely defined by the symmetry of occupied valence orbital, thus $H^{(1)}_{int}$ can be individually constructed for each active orbital symmetry and then diagonalized. However, in case of the two-valence sector we do not have this property. Here the intermediate Hamiltonian matrix representation does depend on the selected occupancy for valence electrons, and the number of radial amplitudes associated with one occupancy can, in general, be different from that corresponding to another one. Therefore, while constructing matrix representation of $H^{(2)}_{int}$ we should be aware of the fact that a description of certain states may not be provided for some selections. A diagrammatic representation of $H^{(2)}_{int}$ is shown in Fig. 2. The dashed and double lines are designated for one- and two-particle vertices of H and R, respectively [46]. The rectangle contains basic graphs of $H^{(2)}_{int}$ which must be contracted with the angular-momentum $G^{(k)}_2(m,n;\rho,\sigma)$ diagram for which the wavy line is used. One may compare the diagrammatic representation of $H^{(2)}_{int}$ with that of the standard VU-CCSD equations shown in Ref. [46]. In Sec. III we present a more detailed discussion of the intermediate Hamiltonian VU-CCSD/R method, as well as results of our preliminary calculation for the beryllium atom.

III. COMPUTATIONAL DETAILS AND RESULTS

While applying the VU-CC theory, various researchers encountered serious solvability problems. The first documented and best known example of such a problem is due to Salomonson *et al.* [50], who studied the $2s^{2\,1}S$ and $2p^{2\,1}S$ states in the beryllium atom. These authors were also the first to explain the failure in reaching a convergence of their iterative procedure of solving equations in the presence of intruder states. The intruder state problem of VU-CC methods was related by many authors to the requirement of completeness of the model space present in the early formulations of the theory [14,51]. A formulation of the incomplete model space version of the VU-CC method [15,16,22–25] was then considered the best remedy to the problem [14]. However, in spite of the indisputable progress that has been made in solving the intruder state problem by introducing incomplete model spaces into the calculation, one cannot be sure that the problem has been truly overcome. As been shown by Jankowski and Malinowski [19], the solvability problem of the VU-CC equations can also be related to the efficiency of various iterative schemes used for solving the equations. It was demonstrated that use of the Newton-Raphson (NR) method, which belongs to a category very effective quadratically convergent procedures enables one to reach convergence in several iterations in cases when the standard Jacobi method or most commonly used reduced linear equation [52] methods either do not converge, diverge, or are at most very slowly convergent [19]. Moreover, it has been emphasized that the power of a method used for solving the equations can also be illustrated by showing its ability to provide along with a standard solution, so-called nonstandard solutions in which the role of the model space determinants in not so dominant [49,19]. Again the NR scheme has proven its effectiveness in attaining many physically meaningful nonstandard solutions while employing different starting vectors [49,53].

The Jankowski-Malinowski results indicated the importance of the effectiveness of iterative schemes used for solving the equations. Unfortunately, the NR method, that proved so efficient, is not feasible for larger systems (at least in its most straightforward form) because of large core demands. The use of the scheme in realistic non model calculations was basically possible within the VU-CCSD/R method because of the significant reduction of the dimension of the problem caused by the use of configurational cluster amplitudes. In this context the intermediate Hamiltonian formulation of the VU-CC method offers not only a dependable and numerically stable way of solving the equations, but it can also be easily applied in large-scale calculations; this is not to mention many other advantages of the approach, discussed in Sec. II B.

Motivated by the special importance of the Be atom in the history of VU-CC applications, we will illustrate the advantages of the intermediate Hamiltonian formulation on this system. The intermediate Hamiltonian version of the VU-CCSD/R program can be easily obtained from the NR VU-CCSD/R code. The zero-valence sector calculation remains unchanged, representing the standard SR-CCSD approach to the core. For higher sectors let us note that the NR scheme requires the construction of matrices of coefficients of linear and nonlinear terms. The general structure of the cluster amplitude equations looks like [46]

$$a_i+\sum_i b_{ij}t_j+\sum_{j\leqslant k} c_{ijk}t_jt_k=0, \tag{46}$$

where indices *i*, *j*, and *k* run over all cluster amplitudes which must be determined in a given sector. For the one-valence sector the $\mathbf{B}(=[b_{ij}])$ matrix contains a matrix representation of $\overline{P}^{(1)}\overline{H}_N\overline{P}^{(1)}$ [see Eq. (22)]. Now it is sufficient to extend the set of amplitudes by admitting internal excitations when constructing this contribution to $\mathbf{B}$ to obtain, according to Eq. (40), the $H_{int}^{(1)}$ matrix. After selecting one of several possible occupancies of valence orbitals of a given symmetry $(s,p,d,\ldots)$ and generating internal and external radial amplitude labels corresponding to this symmetry, an $H_{int}^{(1)}$ matrix can be constructed for each symmetry block $({}^2S,{}^2P,{}^2D,\ldots)$ separately.

After renormalization of chosen eigenvectors of $H_{int}^{(1)}$ corresponding to selected valence orbitals [Eq. (43)], one can obtain $R^{(1)}$-cluster amplitudes from the $Z^{(1)}$ matrix,

$$Z_r^j[{}^{j}_{i}]=R_r^i, \tag{47}$$

$$Z_{\rho\sigma}^{j\,a}(k)[{}^{j}_{i}]=R_{\rho\sigma}^{i\,a}(k) \quad (i=1,\ldots,L), \tag{48}$$

where $Z_r^j[{}^{j}_{i}]$ $(Z_{\rho\sigma}^{j\,a}(k)[{}^{j}_{i}])$ should be understood as a matrix element of $\mathbf{Z}^{(1)}$ taken from a row numbered by the external amplitude label $[{}^{j}_{r}]$ $([{}^{j\,a}_{\rho\sigma}(k)])$, and a column numbered by the internal amplitude label $[{}^{j}_{i}]$. Index *j* is related to the basic occupancy selected for a given symmetry block.

In the two-valence sector the situation is a bit more complicated. Unlike the one-valence sector, the dimension of the $H_{int}^{(2)}$ matrix, whose rows and columns are labeled by internal and external radial amplitude indices, is different for different occupations of valence orbitals. For example, if in the Be calculation one selects $2s$ and $2p$ orbitals as active in the ground-state calculation, then, due to the definition of the cluster amplitudes [Eq. (26)], we have two internal radial labels when $2s$ is doubly occupied $([{}^{2s\,2s}_{2s\,2s}(0)]$ and $[{}^{2s\,2s}_{2p\,2p}(1)])$, and four of them for double occupation for $2p$ $([{}^{2p\,2p}_{2s\,2s}(1)]$ and $[{}^{2p\,2p}_{2p\,2p}(k)]$ $(k=0,1,2))$. Similarly, the number of external amplitudes differs in both cases. Hence the dimension of $H_{int}^{(2)}$ and the number of its eigenvalues can be different depending on the selected basic occupancy. However the eigenvalues are not affected by the choice, and a description of the same state is always identical in all cases while some eigenvalues may not be given by all $H_{int}^{(2)}$. Assuming that the selection is made and internal and external amplitudes are defined by that choice, a matrix representation of the principal part of $H_{int}^{(2)}$, meaning the first term in Eq. (41), can be obtained from the two-valence $\mathbf{B}$ matrix as in the one-valence sector. Construction of a matrix representation of the second term is less straightforward, but again diagrams used to build the $\mathbf{A}(=[a_i])$ matrix in the NR VU-CCSD version [Eq. (46)] can be utilized. In fact we need only some of them, i.e., those which do not represent the renormalization term and involve at least one two-body $S^{(1)}$ diagram [see Eq. (41)]. Since only connected diagrams can be obtained from the standard version, we have to supplement them with disconnected diagrams which must be included in the intermediate Hamiltonian formulation. In addition, all the diagrams must be connected with the $G^{(2)}(k)(m,n;\rho,\sigma)$ diagram, as shown in Fig. 2. For the principal part of the intermediate Hamiltonian the ρ and σ indices run over all unoccupied orbital labels, whereas for the second term in Eq. (41) they are restricted to valence labels because the second operator acts on the model space.

The numerical cancellation of disconnected contributions taking place in the intermediate Hamiltonian formulation basically requires the inclusion of all terms in the equations that approximation (10) leads to. Any additional simplifications may generate irreducible disconnected components. The reason for this is that diagonalization of the intermediate Hamiltonian gives disconnected contributions, and they must have their counterparts in the matrix elements of H_{int} to cancel them out. Moreover, any approximation made in the one-valence sector can affect the cancellation of disconnected terms in the two-valence sector. Thus the best way to guarantee a complete cancellation of disconnected contributions is to utilize the fact that without additional simplifications both schemes give the same result. Let us recall here that in the NR implementation of the VU-CCSD/R method [45–48,53], such additional simplifications have been introduced. That is terms only up to and including quadratic terms in S have been taken into account in the equations for cluster amplitudes and in the expression for the effective Hamiltonian at each level of valence rank. It must be emphasized the distinction between this and the general form of the VU-CCSD equations (46) which are quadratic in the unknown cluster amplitudes $S^{(i)}$ at each i-valence level beyond the zero level. For the reasons given above, reproduction of the quadratic version within the intermediate Hamiltonian formulation is not simple. So we have supplemented the NR VU-CCSD/R equations with the remaining terms (higher than quadratic) that should be present in the full VU-CCSD/R scheme at the one- and two-valence level, leaving the zero-valence sector unchanged. Having the new NR VU-CCSD/R version implemented, we could use a more complete set of diagrams to build the intermediate Hamiltonians in addition, we were able to check the code, since results provided by both schemes should be the same.

Although there is no need to construct two-valence cluster amplitudes (the two-valence sector is the final one) we give a prescription of how to obtain them from the $Z^{(2)}$ matrix. Since the $Z^{(2)}$ radial amplitudes are defined with respect to some selected valence orbital occupancy, one has to consider the angular coupling between different occupancies while trying to calculate cluster radial amplitudes. As a consequence the relation between the $R^{(2)}$ cluster amplitudes and matrix elements of $\mathbf{Z}^{(2)}$ is more complicated, and can be written in the form

$$\sum_{\kappa} Z^{mn}_{\rho\sigma}(k)\left[{}^{mn}_{i\,j}(\kappa)\right]=[k]\sum_{\kappa,k_1}\begin{Bmatrix}\kappa & k_1 & k\\ l_\rho & l_m & l_i\end{Bmatrix}\begin{Bmatrix}\kappa & k_1 & k\\ l_\sigma & l_n & l_j\end{Bmatrix}\times\left[R^{i\,j}_{\rho\sigma}(k_1)+\delta(k_1,0)[l_i,l_j]^{1/2}R^{i}_{\rho}R^{j}_{\sigma}\right], \tag{49}$$

where $\{\cdots\}$ denotes the 6-j coefficients, $[l_i,l_j]=(2l_i+1)(2l_j+1)$, and m and n are indices of valence orbitals selected for the basic occupancy in the reference space. The relation holds for a given pair of i and j valence indices. Generally, relation (49) is a small system of linear equations which does not always gives $R^{(2)}$ radial amplitudes as they are defined by Eq. (26). This depends on the pair of i and j indices, and the choice made for m and n. When excitations from $1s^2 2s^2$ are considered (i.e., when one is interested only in ^{1}S states), only $R^{2s\,2s}_{nl\,n'l}(l)$ and $R^{2p\,2p}_{ns\,n's}(1)$ cluster amplitudes can be obtained via relation (49). That is,

$$Z^{2s\,2s}_{nl\,n'l}(l)\left[{}^{2s\,2s}_{2s\,2s}(0)\right]=R^{2s\,2s}_{nl\,n'l}(l)+R^{2s}_{nl}R^{2s}_{n'l}, \tag{50}$$

$$Z^{2s\,2s}_{ns\,n's}(0)\left[{}^{2s\,2s}_{2p\,2p}(1)\right]=R^{2p\,2p}_{ns\,n's}(1). \tag{51}$$

The $R^{2p\,2p}_{nl\,n'l'}(k_1)$ amplitudes (l or $l'>0$) cannot be determined this way because there are no $Z^{2s\,2s}_{nl\,n'l'}(k)$ (for $l\neq l'$) and not enough equations of type (49) which link $Z^{2s\,2s}_{nl\,n'l}(l)$ and $R^{2p\,2p}_{nl\,n'l}(k_1)$ (for $l=l'$), namely,

$$Z^{2s\,2s}_{nl\,n'l}(l)\left[{}^{2s\,2s}_{2p\,2p}(1)\right]=\frac{1}{3}\sum_{k_1=|l-1|}^{l+1}R^{2p\,2p}_{nl\,n'l}(k_1)+\delta(l,1)R^{2p}_{nl}R^{2p}_{n'l}. \tag{52}$$

If one is interested in even-parity states of ^3P and ^1D symmetry, in addition to those of ^1S symmetry, then amplitudes which describe excitations from $1s^2 2p^2$ must be used. This time all $R^{(2)}$ radial cluster amplitudes can be determined from $Z^{2p\,2p}_{nl\,n'l'}(k)\left[{}^{2p\,2p}_{2s\,2s}(1)\right]$ and $Z^{2p\,2p}_{nl\,n'l'}(k)\left[{}^{2p\,2p}_{2p\,2p}(\kappa)\right]$ matrix elements.

In the present calculations $1s^2$ defines the Fermi vacuum and $2s$ and $2p$ orbitals are used as valence ones. This determines the complete model space $(2s,2p)$ both at one- and two-valence levels because the knowledge of the active orbital set specifies the relevant complete model spaces considered at both valence levels. We have employed the $9s\,9p\,7d\,7f\,5g$ Slater-type basis set introduced in our previous calculations [48] (which was denoted there as the A_d basis set). The computations were performed when using our program package to solve the system of nonlinear equations at the zero-valence level (by means of the effective Newton-Raphson iterative procedure), and the eigenvalue problem of the intermediate Hamiltonian at one- and two-valences levels (by diagonalization of non-Hermitian $H^{(n)}_{int}$ matrices).

For symmetry reasons the eigenvalue problem of H_{int} at the one-valence level can be separated into two subproblems corresponding to two possible occupancies in the $(2s,2p)$ model space: $1s^2 2s$ and $1s^2 2p$. At the two-valence level the problem can be split into a subproblem associated with double occupancy of $2s$ and $2p$ ($1s^2 2s^2$ and $1s^2 2p^2$) and a subproblem corresponding to $1s^2 2s 2p$. Therefore, different types of radial amplitudes can be obtained within each subproblem. For the one-valence sector those will be Z^{2s}_{r} and $Z^{1s\,2s}_{\rho\sigma}(k)$ for $2s$ and Z^{2p}_{r} and $Z^{1s\,2p}_{\rho\sigma}(k)$ for $2p$. In Table I we collect the numbers of one- and two-particle radial Z amplitudes to be considered. As written in Sec. II, the eigenvalues of $H^{(1)}_{\mathrm{int}}$ do not depend on the choice of valence orbitals.

TABLE I. Number of one- and two-electron Z amplitudes of the VU-CCSD/R method for the $9s9p7d7f5g$ basis set.

Model space	one-valence					two-valence		
	Z^{i}_{ρ}		$Z^{a\,i}_{\rho\sigma}(k)$			$Z^{i\,j}_{\rho\sigma}(k)$		
	i		a	i		i	j	
$(2s,2p)$	$2s$	7 (+1)[a]	$1s$	$2s$	268	$2s$	$2s$	150 (+2)[a]
	$2p$	8 (+1)[a]	$1s$	$2p$	438	$2p$	$2p$	534 (+4)[a]
						$2s$	$2p$	436 (+2)[a]

[a] The number in parentheses denotes the number of internal amplitudes.

Therefore, it is sufficient to construct $H^{(1)}_{int}$ using a radial amplitude labeling which corresponds to excitations from any symmetry-representative of valence orbitals. Increasing the number of valence orbitals of the same symmetry does not change $H^{(1)}_{int}$, whereas in the case of an effective Hamiltonian approach the size of the set of nonlinear equations to be solved increases according to the growing number of one-valence cluster amplitudes.

At the two-valence level one can consider two possible occupancies in the $(2s,2p)$ model space for even-parity states. In order to calculate energies of ${}^1S$ states it is sufficient to take into account only excitations from $1s^2 2s^2$, i.e., to consider only 152 radial amplitudes (whereas in the effective Hamiltonian formulation one has to use 684 R-type amplitudes). If one is also interested in the other even-parity states (of ${}^1D$ and ${}^3P$ symmetry) which come from the $(2s,2p)$ model space, then it is necessary to consider 538 radial amplitudes corresponding to excitations from $2s^2 2p^2$. The degree of the reduction depends on the angular structure and the size of the model space used, and is especially significant when more valence orbitals of the same symmetry are included in the model space.

Values of the energies of the lowest states of even- and odd-parity are collected in Tables II and III. The states are

TABLE III. Energies of odd-parity states for Be calculated with the VU-CCSD/R method based on the intermediate Hamiltonian formulation (in hartree).

No	State	Present work	Previous work	Other work
1’	$2s2p\,{}^3P$	−14.567 133	−14.567 146[a]	−14.533 624[b]
2’	$2s2p\,{}^1P$	−14.471 649	−14.471 686[a]	−14.438 003[b]
3’	$2s3p\,{}^3P$	−14.346 542		
4’	$2s3p\,{}^1P$	−14.340 974		
5’	$3s2p\,{}^3P$	−14.240 547	−14.245 493[a,c]	
6’	$3s2p\,{}^1P$	−14.216 832	−14.221 221[a,c]	

[a] Malinowski and Jankowski, CC equations limited to quadratic terms [48].

[b] Kaldor, CCSD method with *spd* Gaussian-type orbital basis set [14].

[c] Within the $(2s,3s,2p)$ model space.

TABLE II. Energies of even-parity states for Be calculated with the VU-CCSD/R method based on the intermediate Hamiltonian formulation (in hartree).

No	State	Present work	Previous work		Other work	
1	$2s^2\,{}^1S$	−14.667 098	−14.667 109[a,b] −14.667 111[a,c]	−14.667 133[a,c] −14.667 033[a,c]	−14.667 328[d] −14.667 373[f]	−14.633 618[e] −14.667 2[g]
2	$2p^2\,{}^1D$	−14.402 151	−14.402 179[a,b]		−14.373 619[e]	
3	$2p^2\,{}^3P$	−14.395 297	−14.395 306[a,b]		−14.361 565[e]	
4	$2s3s\,{}^1S$	−14.375 318	−14.376 036[a,c] −14.372 909[a,c]	−14.372 991[a,c]	−14.385 011[e,h]	−14.417 8[g,i]
5	$2p^2\,{}^1S$	−14.316 673	−14.316 671[a,b] −14.316 592[a,c]	−14.319 313[a,c]	−14.283 768[e,h]	−14.319 9[g,j]
6	$2s3d\,{}^1D$	−14.270 227				
7	$2p3p\,{}^3P$	−14.182 709				
8	$2p3p\,{}^1D$	−14.175 995				
9	$2p3p\,{}^1S$	−14.121 836	−14.126 188[a,c] −14.121 685[a,c]	−14.121 815[a,c]		
10	$3s^2\,{}^1S$	−14.040 489	−14.038 628[a,c]			

[a] Malinowski and Jankowski, CC equations limited to quadratic terms [48].

[b] Jankowski and Malinowski, standard solution in $(2s,2p)$ model space [53].

[c] Jankowski and Malinowski, nonstandard solution in $(2s,2p)$ model space [53].

[d] Bunge, CI method [54].

[e] Kaldor, CCSD method with *spd* Gaussian-type orbital basis set [14].

[f] Lindroth *et al.*, extensive multiconfiguration Hartree-Fock calculations [55].

[g] Lindroth and Måartensson-Pendrill, CCSD calculations with a special choice of potential [56].

[h] With the $2s3s$ configuration added to the model space.

[i] Within the $(2s,3s,2p)$ model space.

[j] The method of complex rotation used to describe the autoionizing property of this state.

TABLE IV. Magnitudes of the most significant two-valence radial amplitudes $R^{ij}_{\rho\sigma}(k)$ for nonstandard solutions corresponding to even-parity states.

		$R^{ij}_{\rho\sigma}(k)$ Indices					
Replacement	Solution	i	j	ρ	σ	k	Value
1→4	2-3-4-5	$2s$	$2s$	$2s$	$3s$	0	−3.521
		$2s$	$2s$	$2p$	$3p$	1	1.936
		$2p$	$2p$	$2s$	$3s$	1	−1.934
5→4	1-2-3-4	$2p$	$2p$	$2s$	$3s$	1	−8.175
		$2p$	$2p$	$2p$	$3p$	2	1.856
		$2p$	$2p$	$2s$	$4s$	1	1.664
1→9	2-3-5-9	$2s$	$2s$	$2p$	$3p$	1	−71.856
		$2s$	$2s$	$2p$	$4p$	1	−23.894
		$2p$	$2p$	$2p$	$3p$	2	−22.533
5→9	1-2-3-9	$2p$	$2p$	$2p$	$3p$	2	2.264
		$2p$	$2p$	$2p$	$3d$	1	−1.453
		$2p$	$2p$	$2p$	$3p$	1	1.407
1→10	2-3-5-10	$2s$	$2s$	$3s$	$3s$	0	−55.866
		$2s$	$2s$	$3p$	$3p$	1	−41.682
		$2p$	$2p$	$3s$	$3s$	1	−30.890
5→10	1-2-3-10	$2p$	$2p$	$3s$	$3s$	1	40.804
		$2p$	$2p$	$3p$	$3p$	2	16.870
		$2p$	$2p$	$3p$	$3p$	1	10.123
2→6	1-3-5-6	$2p$	$2p$	$2s$	$3d$	1	6.029
		$2p$	$2p$	$2s$	$4d$	1	1.173
		$2p$	$2p$	$2p$	$4f$	2	−1.114
3→7	1-2-5-7	$2p$	$2p$	$2p$	$3p$	2	−6.417
		$2p$	$2p$	$2p$	$3p$	1	3.519
		$2p$	$2p$	$3p$	$3p$	0	1.633
2→8	1-3-5-8	$2p$	$2p$	$2p$	$3p$	1	−5.845
		$2p$	$2p$	$2p$	$3p$	0	2.995
		$2p$	$2p$	$2p$	$3p$	2	1.585

TABLE V. Magnitudes of the most significant two-valence radial amplitudes $R^{ij}_{\rho\sigma}(k)$ for nonstandard solutions corresponding to odd-parity states.

		$R^{ij}_{\rho\sigma}(k)$ Indices					
Replacement	Solution	i	j	ρ	σ	k	Value
1’→3’	2’-3’	$2s$	$2p$	$3p$	$2s$	1	−8.171
		$2p$	$2p$	$2p$	$3p$	0	3.916
		$2p$	$2p$	$4p$	$2p$	1	−1.632
2’→ 4’	1’-4’	$2s$	$2p$	$3p$	$2s$	1	4.340
		$2s$	$2p$	$2s$	$3p$	0	2.152
		$2s$	$2p$	$2p$	$3s$	1	1.867
1’→5’	2’-5’	$2s$	$2p$	$2p$	$3s$	1	16.343
		$2s$	$2p$	$3s$	$2p$	0	−9.201
		$2s$	$2p$	$2p$	$4s$	1	−2.554
2’→6’	1’-6’	$2s$	$2p$	$2p$	$3s$	1	−6.022
		$2s$	$2p$	$3s$	$2p$	0	−3.256
		$2s$	$2p$	$3p$	$2s$	1	2.245

numbered 1,2,3, . . . (for even-parity states, see Table II) and $1',2',3'$, . . . (for odd-parity states, see Table III) according to increasing value of the energy. As emphasized, a set of cluster amplitudes cannot by associated with a single eigenvalue but with a subset of eigenvalues and corresponding eigenvectors. These subsets are labeled by i-j-k-l or i'-j' where $i, \ldots, i', \ldots$ are the state numbers. For example, the standard solution for the two-valence R amplitudes will be denoted by 1-2-3-5 and $1'$-$2'$ within the two subproblems of the complete $(2s,2p)$ model space problem. Comparing results of the present work with previous results of the effective Hamiltonian approach, where coupled-cluster equations (22) and (23) were limited to quadratic terms [48], one can see that for the standard solution the omission of higher nonlinear terms has a minor influence on the final results of energies (as it should be expected). Inclusion of these terms into equations usually slightly raises energies (from 9 μhartree for the $2p^{2\,3}P$ state to 37 μhartree for the $2s2p\,^1P$ state). The only exception is the $2p^{2\,1}S$ state, where higher nonlinear terms lower the energy by 2 μhartree. However, the omission of higher than quadratic terms causes significant differences of energies obtained for a given state in different solutions. As can be seen from the entries of Table II, the energies for $2s^{2\,1}S$, $2s3s\,^1S$, $2p^{2\,1}S$, and $2p3p\,^1S$ states are within the range of 100, 3127, 2721, and 4503 μhartree, respectively. Of course, the complete version of the VU-CCSD/R effective Hamiltonian method yields the same energies. The trouble is that there is no simple prescription as to how to obtain nonstandard solutions within the effective Hamiltonian approach. This depends on the starting vector of R cluster amplitudes, which must be guessed in some way. The problem can be resolved by employing the intermediate Hamiltonian scheme presented in this paper, which gives the possibility of calculating R amplitudes corresponding to any selected set of the eigenvalues via relation (49). Using these as a starting point in the effective Hamiltonian iterative procedure we have obtained all multiple solutions presented in Tables IV and V, each time obtained the same energy for a given state (Tables II and III). This is a numerical confirmation of our previous theoretical considerations [38]. Tables IV and V give values of the leading R cluster amplitudes for some nonstandard solutions. The solutions correspond to set of eigenvalues which can be obtained from the standard solution sets 1-2-3-5 and 1’-2’ by changing one of the eigenvalues. The first column in the tables specifies the substitution. One can note that in such cases cluster amplitudes can be significantly larger than 1.

IV. CONCLUSIONS

We have presented an intermediate Hamiltonian formulation of the VU-CCSD method for atoms. The method uses the core as a vacuum, and is designated for a description of the ground and low-lying excited states. The formalism takes advantage of the simplifications afforded by the spherical symmetry of atomic systems representing cluster operators in terms of radial amplitudes defined by configurational excitations. The necessity of using radial amplitude labels makes the intermediate Hamiltonian reformulation of the VU-CCSD/R method not completely straightforward. In order to obtain a matrix representation of the intermediate Hamiltonian we specify one of the possible occupancies of valence electrons in the model space as a basic one, and define all internal and external radial amplitudes with respect to that choice. The rows and columns of the intermediate Hamiltonian matrix are numbered by these radial amplitude labels. The method is not uniquely defined in this way because the number of radial amplitudes, and thus the dimension of the intermediate Hamiltonian and the number of its eigenvalues, can be different for the different valence orbital occupancies. The energy values are not affected by this, however, a description of certain states may not be available in some cases.

The most important advantages of the intermediate Hamiltonian formulation in comparison with the effective Hamiltonian one are: (i) the relatively simple structure of the intermediate Hamiltonian matrix; (ii) the one-step procedure for solving the equations instead of a two-step procedures (iii) the decoupling of the eigenvalue problems; (iv) the simple and effective way of solving the equations via diagonalization; and (v) easily obtainable alternative solutions. We have shown the simplicity and effectiveness of the approach in a calculation for the Be atom, where all the above features of the intermediate Hamiltonian approach have been discussed.

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