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Complete set of solutions of multireference coupled-cluster equations: The state-universal formalism

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The homotopy method is used to obtain a complete set of solutions of multireference coupled-cluster equations within the framework of the state-universal coupled-cluster (SUCC) formalism. The solutions are obtained for an *ab initio* four-electron model system consisting of four hydrogen atoms in rectangular arrangement. Essential information about the structure of solutions of nonlinear SUCC equations is provided and analyzed, both numerically and analytically, in the form of two theorems. The existence of multiple solutions of SUCC equations provides new insights into the nature of convergence problems often encountered in SUCC calculations. The evidence for the possible association of some solutions of the SUCC equations with the intruder-state problem is presented and briefly discussed.

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I. INTRODUCTION

A common feature shared by many approaches to electron correlation in atoms and molecules is their nonlinearity. One of the best known examples of nonlinear many-electron theory is the single-reference coupled-cluster (CC) method [1–4] and its multireference extensions [4–7] designed to describe quasidegenerate and electronically excited states in size-extensive manner.

The nonlinearity of genuine multireference CC approaches, which are classified as the *Hilbert-space* or *state-universal* methods [4,5,8–17] and the *Fock-space* or *valence-universal* methods [4,6,7,18,19], is largely a consequence of the nonlinear nature of the generalized Bloch equation [20]. Exponential parametrization of the wave operator increases the nonlinearity of multireference CC approaches even further, and this leads to problems with the interpretation of multiple solutions and numerical attainability of a desired solution [8,19]. It is not clear how many solutions of nonlinear multireference CC equations are physically meaningful and whether we can use them to describe highly excited electronic states. In addition, as demonstrated in Refs. [8,14,15,19], the multireference CC approaches are often plagued by intruder states, which cause divergent behavior of the multireference many-body perturbation theory (MBPT) [21–25]. The intruder-state problem plaguing the multireference MBPT and multireference CC approaches is related to energy-level crossing between the perturbed energies anywhere in the unit circle of the complex perturbation parameter [21,23]. The existence of intruder states, singular [8,14,15,19], and multiple solutions in multireference CC calculations are the main reasons why these theories are not routinely used in electronic structure calculations. It is usually very difficult to obtain the desired physical solution of multireference CC equations, due to serious convergence problems caused by the intruder states and the presence of close-lying multiple solutions.

It is essential to improve our understanding of convergence and other problems plaguing the multireference CC approaches, so that better theories can be formulated in the future. In this paper, we analyze all solutions of nonlinear multireference CC equations, obtained for the *state-universal* formulation of the multireference CC theory [4,5,8–17] with the homotopy method [26]. We use the homotopy method to generate a complete set of solutions of the state-universal CC (SUCC) equations for an *ab initio* four-electron system, referred to as the P4 model [27]. The homotopy approach has recently been used to study multiple solutions of single-reference CC equations [28].

This study provides an insight into the structure of solutions of nonlinear SUCC equations. In particular, we explain (using numerical and analytic arguments) why there may exist several solutions of truncated SUCC equations that provide nearly exact eigenvalues of the electronic Hamiltonian, in spite of the fact that eigenstates are represented very poorly. The results of the analysis presented in this paper provide a nonperturbative explanation of the origin of convergence problems encountered in multireference CC calculations of the SUCC type. The need for a nonperturbative explanation of convergence problems plaguing multireference CC theory stems from the fact that these problems do not have to be related to the divergent nature of the multireference MBPT expansion. As demonstrated in Ref. [19] in the context of valence-universal multireference CC studies, it may happen that the multireference CC solutions are very difficult to obtain, in spite of the fact that the standard multireference MBPT series converges. On the other hand, as amply documented in the literature, CC methods can provide physically meaningful solutions, despite the divergent nature of the MBPT series.

II. THEORY

A. The state-universal coupled-cluster theory

In all multireference theories, we assume that there exists a multidimensional *model* or *reference space* $\mathcal{M}_0$, spanned by a suitably chosen set of configuration state functions $\{|\Phi_q\rangle\}_{q=1}^{M}$, which gives a reasonable zero-order description of a *target space* $\mathcal{M}$ spanned by M exact electronic wave functions $|\Psi_\mu\rangle$, $\mu=1,\dots,M$. The wave operator $U:\mathcal{M}_0$

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$\rightarrow \mathcal{M}$ is defined as a one-to-one mapping between $\mathcal{M}_0$ and $\mathcal{M}$, which satisfies the relations $PU=P$, $UP=U$, and $UQ=0$, where $P=\Sigma_{q=1}^{M}|\Phi_q\rangle\langle\Phi_q|$ is a projection operator onto $\mathcal{M}_0$ and $Q=1-P$. The wave functions $|\Psi_\mu\rangle$ are calculated using the formula

$$|\Psi_\mu\rangle = U\left(\sum_{q=1}^{M} c_{q,\mu}|\Phi_q\rangle\right) = \sum_{q=1}^{M} c_{q,\mu}U|\Phi_q\rangle, \quad \mu=1,\ldots,M, \tag{1}$$

where the coefficient vectors $\mathbf{c}_\mu=(c_{1,\mu},\ldots,c_{M,\mu})$ and the energies E_μ of states $|\Psi_\mu\rangle$ are obtained by diagonalizing the effective Hamiltonian

$$H^{\mathrm{eff}} \equiv H^{\mathrm{eff}}(U)=PHU, \tag{2}$$

where H is the N-electron Hamiltonian. The operator U is obtained by solving the generalized Bloch equation [20],

$$HU=UHU. \tag{3}$$

Since H^{eff} is not Hermitian, we distinguish between the right and left eigenvectors of H^{eff}.

In the SUCC formalism, considered in this paper, the wave operator U is defined as follows [5]:

$$U=\sum_{q=1}^{M} e^{T^{(q)}}|\Phi_q\rangle\langle\Phi_q|. \tag{4}$$

Each cluster operator $T^{(q)}$ is written as $T^{(q)}=\Sigma_I{}^{(q)}t_I{}^{(q)}G_I$, where ${}^{(q)}G_I$ are the operators generating the excited configurations with respect to $|\Phi_q\rangle$ and ${}^{(q)}t_I$ are the corresponding cluster amplitudes. For a *complete model space* [5], the cluster operators $T^{(q)}$ involve only excitations from $\mathcal{M}_0$ to $\mathcal{M}_0^{\perp}$.

Inserting ansatz (4) into the generalized Bloch equation (3) and projecting the resulting equation from the left onto all configurations ${}^{(p)}G_I|\Phi_p\rangle\in\mathcal{M}_0^{\perp}$ that correspond to excitations included in $T^{(p)}$ and from the right onto $|\Phi_p\rangle$, we obtain a system of highly nonlinear equations for ${}^{(p)}t_I$,

$$Q^{(p)}HU|\Phi_p\rangle=\sum_{q=1}^{M} Q^{(p)}U|\Phi_q\rangle H^{\mathrm{eff}}_{qp}(U), \quad p=1,\ldots,M, \tag{5}$$

where U is given by Eq. (4) and $Q^{(p)}$ is a projection operator onto the subspace $\mathcal{M}_0^{(p)}=Q^{(p)}\mathcal{M}_0^{\perp}\subseteq\mathcal{M}_0^{\perp}$ spanned by configurations ${}^{(p)}G_I|\Phi_p\rangle$. In the exact SUCC theory, in which all excitations up to the N-fold ones are included in each $T^{(p)}$, we have $\mathcal{M}_0^{(p)}=\mathcal{M}_0^{\perp}$, for every p. In approximate SUCC methods, the many-body expansion of each $T^{(p)}$ is truncated and $\mathcal{M}_0^{(p)}\subset\mathcal{M}_0^{\perp}$.

The SUCC method works best in quasidegenerate situations, where each eigenstate $|\Psi_\mu\rangle$, $\mu=1,\ldots,M$, has a large $\mathcal{M}_0$ component [8,10,12–15]. However, the nonlinear Eq. (5) possesses multiple solutions. Some solutions of Eq. (5) provide excellent values of energies of highly excited electronic states that are poorly approximated by $\mathcal{M}_0$ [8,14]. The nature of these solutions is investigated here.

B. The homotopy method

The basic idea of the homotopy approach, when applied to a system of nonlinear algebraic equations $\mathbf{F}(\mathbf{x})=\mathbf{0}$, is consideration of a family of equations,

$$\mathbf{H}(\mathbf{x},\lambda)=(1-\lambda)\mathbf{G}(\mathbf{x})+\lambda\mathbf{F}(\mathbf{x})=\mathbf{0}, \tag{6}$$

where $\mathbf{G}(\mathbf{x})$ is such that all solutions of $\mathbf{G}(\mathbf{x})=\mathbf{0}$ are known and λ is the continuation parameter. For $\lambda=0$, Eq. (6) reduces to $\mathbf{G}(\mathbf{x})=\mathbf{0}$. For $\lambda=1$, it reduces to $\mathbf{F}(\mathbf{x})=\mathbf{0}$. If $\mathbf{G}(\mathbf{x})$ is defined as $G_i(\mathbf{x})=x_i^{d_i}-b_i$, where $d_i\geqslant \deg F_i$ (deg is the total degree of the polynomial), and if parameters b_i are chosen randomly, then the transversality theorem [26,29] guarantees that all solutions of $\mathbf{H}(\mathbf{x},1)=\mathbf{0}$ can be obtained by continuation of all solutions of $\mathbf{H}(\mathbf{x},0)=\mathbf{0}$. For solving the system of nonlinear SUCC equations, Eq. (5), with the homotopy method, we used a suite of programs HOMPACK [30].

III. COMPUTATIONAL DETAILS AND MODEL DESCRIPTION

In order to study the solutions of SUCC equations, we applied the orthogonally spin-adapted SUCCD method (the SUCC method with double excitations) [9–13], in which each cluster operator $T^{(q)}$ is approximated by two-body terms, to an *ab initio* minimum basis set P4 model system consisting of four hydrogen atoms in rectangular arrangement [27]. The geometry of the P4 model is determined by parameter α, which is defined as a distance between two stretched H_2 molecules ($r_{\text{H-H}}=2.0a_0$). The complete model space consists, in this case, of two configurations, $|\Phi_1\rangle=|(\phi_1)^2(\phi_2)^2|$ and $|\Phi_2\rangle=|(\phi_1)^2(\phi_3)^2|$, where $\{\phi_i\}_{i=1}^4$ are the ground-state restricted Hartree-Fock orbitals arranged according to increasing orbital energies. For geometries near the square one ($\alpha\simeq2.0a_0$), $|\Phi_1\rangle$ and $|\Phi_2\rangle$ are the dominant configurations in the full configuration interaction (full CI) expansions of the lowest two ${}^1A_g$ states (the dimension of the full CI ${}^1A_g$ subproblem is 8). For example, for $\alpha=2.1a_0$, the coefficients at $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in the full CI expansion of the ground ($1{}^1A_g$) state equal 0.827 and -0.514, respectively. For the first-excited $2{}^1A_g$ state, these coefficients are 0.501 and 0.813, respectively. For larger α values, only the ground state has a large $\mathcal{M}_0$ component. For example, for $\alpha=6.0a_0$, the coefficients at $|\Phi_1\rangle$ and $|\Phi_2\rangle$ in the full CI expansion of the ground state are 0.968 and -0.090, respectively. For the $2{}^1A_g$ state, they are 0.001 and 0.468, respectively. Thus, by varying α, we can study quasidegenerate ($\alpha\simeq2.0a_0$) and nondegenerate ($\alpha\rightarrow\infty$) situations. The orthogonally spin-adapted two-reference SUCCD equations for the minimum basis set P4 model form a system of ten nonlinear algebraic equations for ten biexcited cluster amplitudes, containing, at most, quartic terms.

IV. RESULTS

Our homotopy calculations indicate that the SUCCD equations have 133 solutions (including the complex ones). This is a very large number, compared to 28 solutions for the wave operator U given by the exact two-reference SUCC

TABLE I. The energies $\Delta E_\mu^{\rm SUCCD}=E_\mu^{\rm SUCCD}-\langle\Phi_1|H|\Phi_1\rangle$ (in mhartree), the proximities d between the subspaces $\mathcal{M}_0$ and $\mathcal{M}^{\rm SUCCD}$, as defined by Eq. (7), and the contributions $S_{Q_C}^{(\mu),\rm SUCCD}$ from the subspace $\mathcal{M}_C$ to the SUCCD wave functions $|\Psi_\mu^{\rm SUCCD}\rangle,(\mu=1,2)$, as defined by Eq. (9), corresponding to all real solutions of the SUCCD equations for the minimum basis set P4 model with $\alpha=2.1$ and $6.0a_0$. A pair of indices (κ,λ) at a given solution of the SUCCD equations indicates that out of all possible pairs of full CI states, the pair $\{|\Psi_\kappa^{\rm FCI}\rangle,|\Psi_\lambda^{\rm FCI}\rangle\}$ gives the largest proximity Δ with the corresponding SUCCD target space $\mathcal{M}^{\rm SUCCD}=\text{span}\{|\Psi_\mu^{\rm SUCCD}\rangle\}_{\mu=1}^2$ [cf. Eq. (10) for the definition of Δ]. Solution (1,2) represents the physical solution of the SUCCD equations.

		$\alpha=2.1a_0$						$\alpha=6.0a_0$			
Solution number	$\Delta E_1^{\rm SUCCD}$	$\Delta E_2^{\rm SUCCD}$	d	$S_{Q_C}^{(1),\rm SUCCD}$	$S_{Q_C}^{(2),\rm SUCCD}$	Solution number	$\Delta E_1^{\rm SUCCD}$	$\Delta E_2^{\rm SUCCD}$	d	$S_{Q_C}^{(1),\rm SUCCD}$	$S_{Q_C}^{(2),\rm SUCCD}$
1	−1648.99	−31.517	0.003	0.042	0.072	1	−655.325	1011.93	0.027	0.446	0.430
2	−476.513	929.900	0.032	0.615	0.273	2	−570.130	993.338	0.033	0.486	0.470
3	−446.818	944.213	0.017	0.833	0.603	3	−140.070	1009.49	0.048	0.819	0.715
4	−221.611	1636.81	0.169	0.566	0.169	4	−130.502	995.166	0.053	0.837	0.744
5(1,2)	−95.806	27.956	1.860	0.042	0.093	5(1,2)	−59.596	398.386	1.037	0.098	0.476
6	−33.839	937.633	0.004	0.987	0.941	6(1,5)	−54.045	1009.93	1.182	0.047	0.544
7	−32.502	944.119	0.004	0.993	0.962	7(1,4)	−54.003	993.908	1.166	0.050	0.529
8	−31.195	2199.05	0.077	0.412	0.042	8	−29.230	2397.41	0.843	0.121	0.233
9(1,5)	−18.848	940.801	0.250	0.678	0.680	9(2,4)	462.043	995.785	0.409	0.526	0.700
10(1,4)	−17.909	943.783	0.183	0.766	0.745	10(2,5)	466.052	1008.06	0.412	0.534	0.720
11	−7.659	1943.46	0.570	0.016	0.068	11	910.008	1009.84	0.512	0.528	0.562
12	28.990	2239.76	0.062	0.366	0.034	12	916.177	994.205	0.455	0.529	0.560
13(2,5)	31.170	941.747	0.123	0.801	0.645	13	993.337	2909.30	0.022	0.474	0.128
14(2,4)	32.210	943.151	0.143	0.768	0.612	14	993.895	1932.20	0.297	0.512	0.096
15	41.958	940.251	0.004	0.999	0.995	15	993.962	1938.63	0.261	0.529	0.038
16	58.445	942.867	0.001	0.999	0.999	16	995.216	1400.05	0.305	0.560	0.110
17	65.319	1936.73	0.478	0.015	0.068	17	996.803	1063.57	0.089	0.504	0.551
18	116.783	942.663	0.011	0.963	0.920	18	997.780	1930.36	0.257	0.829	0.624
19	166.963	941.562	0.034	0.793	0.739	19	1000.07	1505.20	0.068	0.856	0.217
20	347.173	2008.30	0.073	0.125	0.062	20	1001.30	1083.76	0.019	0.948	0.850
21	376.413	2035.33	0.054	0.159	0.054	21	1007.94	1085.57	0.048	0.442	0.545
22	560.929	942.032	0.075	0.584	0.806	22	1008.82	1401.63	0.303	0.573	0.108
23	562.445	943.218	0.083	0.583	0.794	23	1009.83	1938.16	0.261	0.548	0.038
24	886.697	1965.96	0.067	0.020	0.087	24	1009.88	1932.78	0.293	0.534	0.095
25	937.151	6577.44	0.011	0.425	0.007	25	1011.92	3053.97	0.018	0.433	0.107
26	938.727	1944.40	0.055	0.266	0.097						
27	942.500	1221.55	0.017	0.956	0.845						
28	942.991	1217.68	0.016	0.950	0.873						
29	943.212	1957.33	0.050	0.356	0.083						
30	943.612	5715.18	0.007	0.733	0.017						
31	944.249	6047.79	0.006	0.724	0.017						

theory [in general, the exact SUCC theory gives $\binom{N_C}{M}$ solutions, where N_C is the dimension of the corresponding full CI problem]. Although the number of solutions of SUCCD equations remains the same for all geometries (we confirmed this by solving the SUCCD equations for several geometries), the numbers of real and complex solutions vary with α.

The energies $E_\mu^{\rm SUCCD}$, $\mu=1,2$, corresponding to all real solutions of SUCCD equations for two representative values of α, are given in Table I. Each solution is characterized by the parameter

$$d=\text{tr}(\mathbf{V}^\dagger\mathbf{V}), \tag{7}$$

where

$$V_{q\mu}=\langle\Phi_q|\Psi_\mu^{\rm SUCCD}\rangle, \quad q,\mu=1,2, \tag{8}$$

which provides us with a measure of the proximity between $\mathcal{M}_0$ and the corresponding target space $\mathcal{M}^{\rm SUCCD}=\text{span}\{|\Psi_\mu^{\rm SUCCD}\rangle\}_{\mu=1}^2$ $(0\leqslant d\leqslant 2)$ (Ref. [31]). We also introduce useful quantities

$$S_Y^{(\mu),X}=\||Y|\Psi_\mu^X\rangle\|^2, \quad X=\text{SUCCD, FCI}, \quad Y=P,Q_C,Q_R, \tag{9}$$

where Q_C is a projector onto the subspace $\mathcal{M}_C=\bigcap_{q=1}^M\mathcal{M}_0^{(q)}$ and $Q_R=Q-Q_C$, which describe the importance of $\mathcal{M}_0$, $\mathcal{M}_C$, and $\mathcal{M}_R\equiv\mathcal{M}_0^\perp-\mathcal{M}_C$ configurations in

TABLE II. The energies $\Delta E_{\mu}^{\mathrm{FCI}}=E_{\mu}^{\mathrm{FCI}}-\langle\Phi_1|H|\Phi_1\rangle$ (in mhartree) and the parameters $S_Y^{(\mu),\mathrm{FCI}}, Y=P, Q_C, Q_R$, Eq. (9), characterizing the full CI states $\mu^1A_g\equiv|\Psi_{\mu}^{\mathrm{FCI}}\rangle$ of the minimum basis set P4 model system with $\alpha=2.1$ and $6.0a_0$.

Geometry		1^1A_g	2^1A_g	3^1A_g	4^1A_g	5^1A_g	6^1A_g	7^1A_g	8^1A_g
$\alpha=2.1$	$S_P^{(\mu),\mathrm{FCI}}$	0.94860	0.91116	0.07224	0.00017	0.05072	0.01118	0.00128	0.00464
	$S_{Q_C}^{(\mu),\mathrm{FCI}}$	0.04722	0.08850	0.90261	0.99982	0.78415	0.91436	0.17359	0.08975
	$S_{Q_R}^{(\mu),\mathrm{FCI}}$	0.00418	0.00035	0.02514	0.00001	0.16513	0.07445	0.82513	0.90561
	$\Delta E_{\mu}^{\mathrm{FCI}}$	−95.815	27.951	644.678	942.456	1110.90	1237.28	1760.55	1839.35
$\alpha=6.0$	$S_P^{(\mu),\mathrm{FCI}}$	0.94531	0.21871	0.23397	0.36093	0.10493	0.01480	0.00655	0.11479
	$S_{Q_C}^{(\mu),\mathrm{FCI}}$	0.04695	0.62156	0.63357	0.23818	0.79848	0.86272	0.04974	0.74880
	$S_{Q_R}^{(\mu),\mathrm{FCI}}$	0.00774	0.15974	0.13246	0.40089	0.09659	0.12248	0.94371	0.13640
	$\Delta E_{\mu}^{\mathrm{FCI}}$	−54.840	468.891	801.027	985.964	1006.28	1076.04	1665.16	1937.30

CI expansions of the SUCCD and exact (full CI) wave functions, $|\Psi_{\mu}^{\mathrm{SUCCD}}\rangle$ and $|\Psi_{\mu}^{\mathrm{FCI}}\rangle$, respectively (see Tables I and II).

Some solutions of the SUCCD equations can be identified by pairs of indices (κ,λ), referring to these particular full CI states $|\Psi_{\kappa}^{\mathrm{FCI}}\rangle$ and $|\Psi_{\lambda}^{\mathrm{FCI}}\rangle$, which give the largest overlap with the SUCCD states $|\Psi_1^{\mathrm{SUCCD}}\rangle$ and $|\Psi_2^{\mathrm{SUCCD}}\rangle$ or the largest proximity Δ between the SUCCD and full CI target spaces, $\mathcal{M}^{\mathrm{SUCCD}}$ and $\mathcal{M}_{\kappa,\lambda}^{\mathrm{FCI}}=\mathrm{span}\{|\Psi_{\kappa}^{\mathrm{FCI}}\rangle,|\Psi_{\lambda}^{\mathrm{FCI}}\rangle\}$, respectively, at $\alpha=6.0a_0$. In general, the proximity Δ between the SUCCD and full CI target spaces, $\mathcal{M}^{\mathrm{SUCCD}}$ and $\mathcal{M}_{\kappa,\lambda}^{\mathrm{FCI}}$, is defined in a very similar way as the proximity d, i.e., [cf. Eqs. (7) and (8)]

$$\Delta=\mathrm{tr}(\mathbf{Z}^{\dagger}\mathbf{Z}), \tag{10}$$

where

$$\mathbf{Z}=\begin{pmatrix}\langle\Psi_1^{\mathrm{SUCCD}}|\Psi_{\kappa}^{\mathrm{FCI}}\rangle & \langle\Psi_1^{\mathrm{SUCCD}}|\Psi_{\lambda}^{\mathrm{FCI}}\rangle\\ \langle\Psi_2^{\mathrm{SUCCD}}|\Psi_{\kappa}^{\mathrm{FCI}}\rangle & \langle\Psi_2^{\mathrm{SUCCD}}|\Psi_{\lambda}^{\mathrm{FCI}}\rangle\end{pmatrix}. \tag{11}$$

For example, the target space $\mathcal{M}^{\mathrm{SUCCD}}$ corresponding to the SUCCD solution labeled as (1,2) has the largest overlap Δ, Eq. (10), at $\alpha=6.0a_0$, with the full CI target space $\mathcal{M}_{1,2}^{\mathrm{FCI}}$ spanned by the first and second full CI states of the ^1A_g symmetry, $|\Psi_1^{\mathrm{FCI}}\rangle=1^1A_g$ and $|\Psi_2^{\mathrm{FCI}}\rangle=2^1A_g$, respectively. Solution (1,2) is referred to as the physical solution. On the other hand, the target space $\mathcal{M}^{\mathrm{SUCCD}}$ characterizing the solution labeled as (2,4) has the largest overlap Δ, Eq. (10), at $\alpha=6.0a_0$, with the full CI target space $\mathcal{M}_{2,4}^{\mathrm{FCI}}=\mathrm{span}\{|\Psi_2^{\mathrm{FCI}}\rangle,|\Psi_4^{\mathrm{FCI}}\rangle\}$.

For $\alpha=2.1a_0$, the only solution that has large proximity with the model space $\mathcal{M}_0$, or large value of d, Eq. (7), is a physical solution (1,2) (in this case, $d=1.860$). For $\alpha=6.0a_0$, the proximity d characterizing solution (1,2) drops down to ~ 1.0. This is related to a poor description of the 2^1A_g state by $\mathcal{M}_0$ and has consequences in the poor description of this state by the SUCCD method (cf. Tables I and II).

The results in Table I indicate that, for $\alpha=2.1a_0$, there are many solutions of the SUCCD equations [e.g., (1,4) and (2,4)], which very accurately approximate the energy of the 4^1A_g state, in spite of the fact that $|\Psi_4^{\mathrm{FCI}}\rangle$ is practically orthogonal to $\mathcal{M}_0$ (belongs to $\mathcal{M}_C$). This surprising observation is a consequence of the following theorems.

Theorem I. If $|\Psi_{\mu}\rangle$ is an exact solution of the Schrödinger equation and E_{μ} is its energy and if, for a given solution U of the Bloch equation (3), not all components of the vector $\mathbf{x}_{\mu}=(x_{\mu,1},\ldots,x_{\mu,M})$, $x_{\mu,p}=\langle\Psi_{\mu}|U\Phi_p\rangle$, equal zero, then E_{μ} is an eigenvalue and $\mathbf{x}_{\mu}$ is the left eigenvector of the effective Hamiltonian $H^{\mathrm{eff}}(U)$.

Theorem II. If $|\Psi_{\mu}\rangle$ is an exact solution of the Schrödinger equation and E_{μ} is its energy and, in addition, $Q_C|\Psi_{\mu}\rangle=|\Psi_{\mu}\rangle$, and if, for a given solution U of the projected Bloch equation (5), not all components of the vector $\mathbf{x}_{\mu}=(x_{\mu,1},\ldots,x_{\mu,M})$, $x_{\mu,p}=\langle\Psi_{\mu}|U\Phi_p\rangle$, equal zero, then E_{μ} is an eigenvalue and $\mathbf{x}_{\mu}$ is the left eigenvector of the effective Hamiltonian $H^{\mathrm{eff}}(U)$.

In order to prove Theorem I, we project Eq. (3) from the left onto $|\Psi_{\mu}\rangle$ and from the right onto $|\Phi_p\rangle$, use the fact that $\langle\Psi_{\mu}|H=E_{\mu}\langle\Psi_{\mu}|$ and that $UP=U$, and use the definition of $H^{\mathrm{eff}}(U)$, Eq. (2). The proof of Theorem II is almost identical. The only difference is that we use Eq. (5) instead of Eq. (3) and employ the relationship $\langle\Psi_{\mu}|Q^{(p)}=\langle\Psi_{\mu}|$, which is true for every p if $Q_C|\Psi_{\mu}\rangle=|\Psi_{\mu}\rangle$.

In principle, Theorem I assumes that U is exact [since U satisfies the Bloch equation (3)], in which case the SUCC theory [each of the $\binom{N_C}{M}$ solutions of the exact SUCC equations] yields M exact eigenstates of H. However, on the basis of Theorem I, we can expect that, if U is one of numerous approximate solutions of the Bloch equation, obtained, for example, by solving the SUCCD equations, the diagonalization of the corresponding effective Hamiltonian may produce a nearly exact eigenvalue E_{μ} of H, in spite of the fact that none of the wave functions provided by this U approximates the exact eigenstate $|\Psi_{\mu}\rangle$. The only condition that needs to be satisfied, for this situation to occur, is that not all components of $\mathbf{x}_{\mu}$ vanish for this particular U and $|\Psi_{\mu}\rangle$. Although these conditions are satisfied by the physical solution describing M lowest eigenstates of H, such as solution (1,2) obtained here (in this case, the left eigenvectors $\mathbf{x}_{\mu}$ and the right eigenvectors $\mathbf{c}_{\mu}$, $\mu=1,\ldots,M$, should form biorthogonal sets; departure from biorthogonality of $\{\mathbf{x}_{\mu}\}_{\mu=1}^{M}$ and $\{\mathbf{c}_{\mu}\}_{\mu=1}^{M}$ may be viewed as yet another measure of accuracy of truncated SUCC theory), they may also be satisfied by

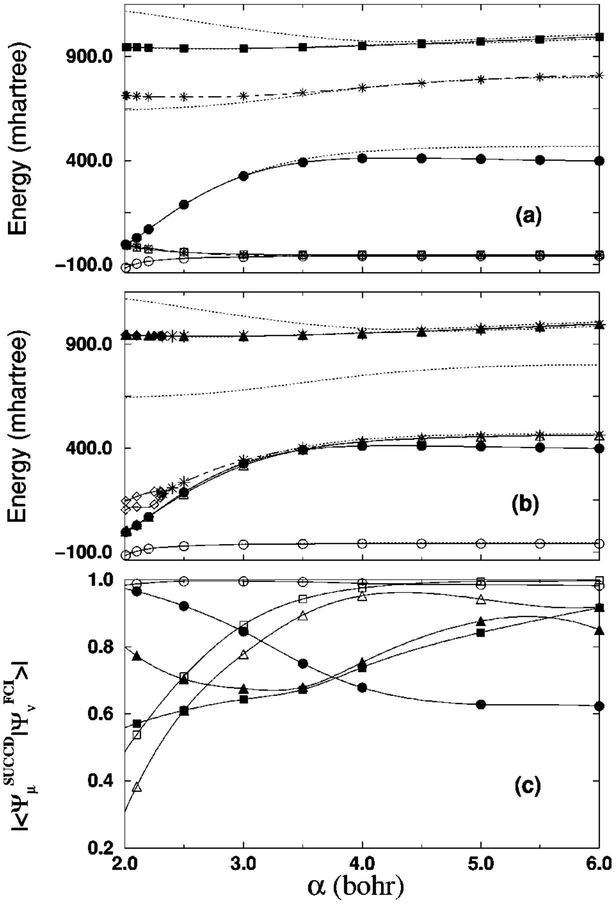

FIG. 1. Dependence of SUCCD energies $\Delta E_\mu^{\rm SUCCD} = E_\mu^{\rm SUCCD} - \langle\Phi_1|H|\Phi_1\rangle$ [(a) and (b)] and overlaps between the SUCCD states $|\Phi_\mu^{\rm SUCCD}\rangle$, $\mu = 1,2$, and the relevant full CI states ν^1A_g (c) for selected solutions of the SUCCD equations. The real solutions (1,2) [shown in (a) and (b)], (1,4) [shown in (a)], and (2,4) [shown in (b)] are marked by (○,●), (□,■), and (△,▲), respectively. The asterisks (*) represent complex solutions [(1,3) in (a) and (2,4) in (b)]. The complex solution (2,4) shown in (b) bifurcates into a pair of real solutions (marked by ◇) at $\alpha = 2.32a_0$. Solid and dashed-dotted lines correspond to real and complex solutions, respectively. Dotted lines represent full CI states of ^1A_g symmetry.

many other solutions of truncated SUCC equations, which do not describe the eigenstates of H, while providing at least one nearly exact eigenvalue E_μ. Theorem II implies that some solutions of truncated SUCC equations may lead to effective Hamiltonians, whose diagonalization gives nearly exact energies of states that are orthogonal to $\mathcal{M}_0$. The real solutions (1,4) and (2,4) [shown in Figs. 1(a) and 1(b) and Table I] belong to this category. For $\alpha \approx 2.0a_0$, they give virtually exact energies of the 4^1A_g state, which practically belongs to $\mathcal{M}_C$ (cf. Table II), although none of the SUCCD wave functions corresponding to solutions (1,4) and (2,4) describes the 4^1A_g state [cf. Fig. 1(c)].

We claim that solutions of this type, which yield one or more energies of states that have small overlaps with $\mathcal{M}_0$ in the quasidegenerate region, are responsible for the emergence of problems with converging the desired physical solution [(1,2) in our case] in the nondegenerate region. It is, therefore, likely that at least some solutions that have small overlaps with $\mathcal{M}_0$ in the quasidegenerate region can be associated with intruder states that plague multireference CC and multireference MBPT calculations for the P4 model for larger α values [8,23].

Indeed, let us consider real solutions (1,4) and (2,4). Solution (2,4) provides virtually exact energies of the 2^1A_g and 4^1A_g states for the whole range of α values, but it describes the corresponding wave functions only for large values of α [see Fig. 1(c)]. A similar observation holds for solution (1,4), although, in this case, description of the ground-state energy is good only for $\alpha \gtrsim 3.5a_0$ (description of the energy of the 4^1A_g state remains excellent for all α's). The overlaps between the SUCCD states $|\Psi_\mu^{\rm SUCCD}\rangle$, $\mu = 1,2$, corresponding to solution (2,4), and the full CI states 2^1A_g and 4^1A_g, i.e., the quantities [cf. Eq. (11)] $\langle\Psi_1^{\rm SUCCD}|\Psi_2^{\rm FCI}\rangle$ and $\langle\Psi_2^{\rm SUCCD}|\Psi_4^{\rm FCI}\rangle$, increase from 0.383 and 0.773, respectively, at $\alpha = 2.1a_0$ to 0.919 and 0.850, respectively, at $\alpha = 6.0a_0$. The overlaps between the SUCCD states corresponding to solution (1,4) and the full CI states 1^1A_g and 4^1A_g, i.e., $\langle\Psi_1^{\rm SUCCD}|\Psi_1^{\rm FCI}\rangle$ and $\langle\Psi_2^{\rm SUCCD}|\Psi_4^{\rm FCI}\rangle$, increase from 0.537 and 0.572, respectively, at $\alpha = 2.1a_0$ to 0.998 and 0.916, respectively, at $\alpha = 6.0a_0$. Thus, at $\alpha = 6.0a_0$, solution (1,4) provides a better description of the ground state than the physical solution (1,2). The latter solution gives 0.982 for the corresponding overlap of SUCCD and full CI wave functions. Description of the 2^1A_g state by solution (2,4) is a lot better than description of this state provided by solution (1,2), which gives only 0.623 for the corresponding overlap of SUCCD and full CI states. This is why, for large values of α, we experience problems with converging the physical solution (1,2) with standard numerical algorithms, such as the Newton-Raphson or reduced linear equation procedures [8]. In this region, solutions (1,4) and (2,4) provide a better description of the lowest two states than solution (1,2). The existence of solutions (1,4) and (2,4) does not cause any problems in obtaining the physical solution (1,2) for $\alpha \approx 2.0a_0$, since, in this region, solutions (1,4) and (2,4) no longer describe the eigenstates of H, and the proximity d, Eq. (7), between $\mathcal{M}_0$ and $\mathcal{M}^{\rm SUCCD}$ characterizing solutions (1,4) and (2,4) drops almost to zero as α approaches $2.0a_0$.

A similar analysis applies to some other real solutions, such as (1,5) and (2,5) (cf. Table I), and to several complex solutions, including (1,3) and (2,4) (see Fig. 1). Each of these additional solutions is characterized by very small proximity with $\mathcal{M}_0$ (small d) in the quasidegenerate region and larger d values for larger α's.

It is interesting to note (see Fig. 2) that the proximity D (defined below) between the physical solution (1,2) and solutions (1,3) (complex), (1,4) (real), and (1,5) (real) increases significantly in the region where the intruder-state problem appears in the multireference MBPT calculations ($\alpha \approx 3.0a_0$ [23]). In complete analogy to the proximity between the SUCCD and full CI target spaces, we define the proximity between solutions A and B as the proximity between the corresponding SUCCD target spaces, $\mathcal{M}^{\rm SUCCD}({\rm A}) = {\rm span}\{|\Psi_\mu^{\rm SUCCD}({\rm A})\rangle\}_{\mu=1}^2$ and $\mathcal{M}^{\rm SUCCD}({\rm B}) = {\rm span}\{|\Psi_\mu^{\rm SUCCD}({\rm B})\rangle\}_{\mu=1}^2$, respectively, i.e.,

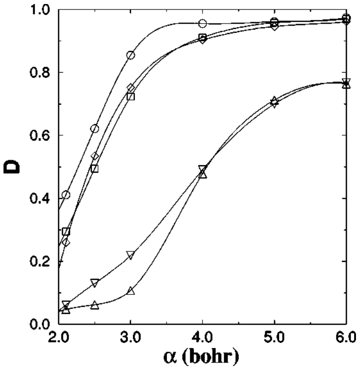

FIG. 2. The proximities D, Eq. (12), between the physical solution (1,2) and selected other solutions of the SUCCD equations for the minimum basis set P4 model as functions of the parameter α (in a_0) (cf. text for details). The complex solution (1,3) is marked by ○. The real solutions (1,4), (1,5), (2,4), and (2,5) are marked by □, ◇, ▽, and △, respectively.

$$D = \mathrm{tr}(\mathbf{W}^{\dagger}\mathbf{W}), \tag{12}$$

where

$$W_{\mu\nu} = \langle \Psi_{\mu}^{\mathrm{SUCCD}}(\mathrm{A}) | \Psi_{\nu}^{\mathrm{SUCCD}}(\mathrm{B}) \rangle, \quad \mu,\nu = 1,2. \tag{13}$$

Although we cannot, at this point, provide a rigorous proof, it seems to us that solution (1,3) and the intruder state studied for the minimum basis set P4 model in Ref. [23] (also, reported earlier in Refs. [8,25]) are related. The intruder state causing the divergent behavior of the multireference MBPT expansion at $\alpha \simeq 3.0a_0$ is related to energy-level crossing of perturbed energies corresponding to states 2^1A_g and 3^1A_g inside the unit circle of the complex perturbation parameter [23]. At the same time, the $\alpha \simeq 3.0a_0$ region is precisely the region, where the proximity D, Eq. (12), between solutions (1,2) and (1,3) sharply increases from small values for $\alpha < 3.0a_0$ to a large value of 0.85 at $\alpha = 3.0a_0$ (the maximum value of the proximity between solutions (1,2) and (1,3) for $\alpha \rightarrow \infty$ is 0.97; cf. Fig. 2).

Although the relationship between multiple solutions of the SUCC equations and intruder states observed in the multireference MBPT calculations needs to be examined further, convergence problems encountered in the SUCC calculations employing standard numerical procedures [8,14,15] can be even more severe than one might expect just by analyzing the crossings of perturbed energy levels. The SUCCD equations for the minimum basis set P4 model have many other solutions, such as the real solutions (1,4), (1,5), (2,4), and (2,5) shown in Figs. 1 and 2 and Table I, and several complex solutions that are characterized by the large overlap [large proximity D, Eq. (12)] with the physical solution (1,2) for large α and the small proximity D with solution (1,2) in the quasidegenerate region (cf. Fig. 2). All these additional solutions contribute to convergence problems encountered in the SUCCD calculations in the nondegenerate region (large α), in spite of the fact that there may not always be a clear relationship between the intruder states of multireference MBPT approach and multiple solutions of the SUCC equations. One might even propose a new term, *the intruder-solution problem* or *intruder solutions*, to describe all these solutions of truncated SUCC equations that are characterized by small proximities with $\mathcal{M}_0$ and small proximities with the standard physical solution in the quasidegenerate region and large proximities with $\mathcal{M}_0$ and the physical solution in other regions. The intruder solutions may cause problems with converging the physical solution of SUCC equations with standard numerical procedures in the same way the intruder states cause divergent behavior of the multireference MBPT expansions. Other solutions of the SUCC equations, which have relatively small proximities with $\mathcal{M}_0$ over the entire region of nuclear geometries, do not have large overlaps with the physical solution. For the minimum basis set P4 model, we verified this statement by calculating the proximity D, Eq. (12), between the physical solution (1,2) and all other solutions of the SUCCD system of equations.

V. SUMMARY AND CONCLUDING REMARKS

In this paper, we used the homotopy method to obtain a complete set of solutions of the SUCCD equations for the four-electron *ab initio* model system, referred to as the minimum basis set P4 model. We demonstrated that the number of solutions of the SUCCD equations (133) exceeds, by far, the number of the exact solutions of the Bloch equation (28). The existence of multiple solutions of the SUCC equations is related to (i) the nonlinearity of the Bloch equation and (ii) the nonlinear parametrization of the wave operator in the Jeziorski-Monkhorst formalism.

We demonstrated that there exist many solutions of the SUCCD equations, whose proximities with the model space and with the standard solution (1,2) are small in the quasidegenerate region of the P4 model system and large in the nondegenerate region. These solutions contribute to serious problems with converging the physical solution in the nondegenerate region with standard numerical procedures.

It is possible that some solutions of the SUCC equations that cause convergence problems in the SUCC calculations are related to intruder states of the multireference MBPT method. On the other hand, the number of multiple solutions identified in this paper as causing convergence problems in the SUCC calculations seems larger than the number of perturbed energy-level crossings causing divergence of the multireference MBPT series. We believe that the complicated nonlinear nature of the SUCC formalism (including the nonlinear nature of the Bloch equation itself) and the complicated structure of solutions of the SUCC equations reported in this work are the primary reasons of problems plaguing this theory. Although the SUCC and multireference MBPT methods are strongly related, the nature of solutions of the SUCC equations can be a lot more complicated than the standard perturbative analysis (cf. Ref. [5]) suggests. As demonstrated in the past, problems with multiple solutions in the alternative class of genuine multireference CC formalisms, referred to as the valence-universal CC theories [4,6,7,18,19], can be substantially more severe than those encountered in the SUCC calculations [19].

We believe that findings reported in this work apply to SUCC calculations of electronic potential energy surfaces for larger molecular systems employing larger basis sets. Solutions of truncated SUCC equations that have small proximities with $\mathcal{M}_0$ in one region of nuclear geometries may evolve into solutions that strongly interact with $\mathcal{M}_0$ in another region, causing difficulties in obtaining a desired physical solution with standard numerical procedures and the emergence of intruder states. Although the homotopy calculations for larger many-electron systems and larger basis sets are not possible at this point, the main observations obtained for a small model, such as P4, are usually transferable to large-scale calculations, as we and others demonstrated many times in the past.

The results of the present analysis indicate that, in order to eliminate convergence problems from SUCC calculations (and, perhaps, the intruder-state problem), we should modify the SUCC equations (including the form of the wave operator), so that the solutions that strongly interact with $\mathcal{M}_0$ and with the physical solution disappear or become, at the very least, clearly separated from the physical solution. We have already started to explore one such modified SUCC procedure, in which the number of cluster amplitudes is significantly reduced by assuming that the core-virtual amplitudes are no longer labeled with the reference label p (so that a single set of these amplitudes is used). Our preliminary homotopy calculations, which we plan to report elsewhere, show that at least some solutions causing problems in the SUCCD calculations for the minimum basis set P4 model, such as the real solutions (2,4) and (2,5), are significantly shifted to a complex plane and that they are so significantly deformed that their interaction with the physical solution (1,2) is smaller. At the same time, the accuracy of the SUCCD results for the lowest two, totally symmetric, singlet eigenstates of the Hamiltonian practically does not change in both quasidegenerate and nondegenerate regions. This indicates that changing the algebraic structure of solutions of multireference CC equations by, for example, eliminating certain classes of cluster amplitudes from the formalism and modifying the equations accordingly might lead to better genuine multireference CC theories, which will be free from drawbacks of the existing formalisms. This issue requires, however, further and detailed studies.

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