Multiple solutions of coupled-cluster equations for PPP model of [10]annulene

Rafał Podeszwa and Leszek Z. Stolarczyk
Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland

Multiple (real) solutions of the CC equations (corresponding to the CCD, ACP and ACPQ methods) are studied for the PPP model of [10]annulene, C_{10}H_{10}. The long-range electrostatic interactions are represented either by the Mataga–Nishimoto potential, or Pople’s R^{-2} potential. The multiple solutions are obtained in a quasi-random manner, by generating a pool of starting amplitudes and applying a standard CC iterative procedure combined with Pulay’s DIIS method. Several unexpected features of these solutions are uncovered, including the switching between two CCD solutions when moving between the weakly and strongly correlated regime of the PPP model with Pople’s potential.

I. INTRODUCTION

The coupled-cluster (CC) method is one of the basic tools for studying the electronic-correlation effects in many-electron systems. Due to their nonlinearity, the CC equations may have multiple solutions; this problem was first analyzed by Živković and Monkkorst [2]. Recently, Kowalski and Jankowski [3] applied to the CC equations a new powerful mathematical tool—the homotopy (continuation) method [4]. By using this tool they were able to find the complete sets of solutions for the CCD and the CCSD equations corresponding to some four-electron four-orbital systems, known as the H4 and P4 models. Very recently, Podeszwa et al. [5] used the homotopy method in a study of multiple solutions to the CCD equations for the Pariser-Parr-Pople (PPP) model [6, 7] of benzene (6 electrons, 6 orbitals). The available data on the CC multiple-solution problem is still very limited. The purpose of this paper is to get some insight into the multiple solutions of the CCD equations (as well as the equations of some modified CCD methods) for the PPP model of [10]annulene (10 electrons, 10 orbitals), a system which is already too big to be treated by the homotopy method.

Benzene and [10]annulene are the first two members of the family of cyclic polyenes (annulenes) C_MH_M, where M = 4m_0 + 2, m_0 = 1, 2, ..., and the assumed point-symmetry group is D_{M_M}. The problem of electronic correlations in annulenes, which may serve as prototypes of one-dimensional metal, have been thoroughly studied within the PPP model by Paldus and co-workers [8, 9, 10]. Due to the high symmetry of annulenes, the contributions from the single excitations are absent in the PPP model, and the CCSD method reduces to the CCD one. Paldus et al. discovered and documented the breakdown of the CCD method for these systems. They also showed that this breakdown may be attributed to the neglect in the CCD method the terms providing the coupling between the D and Q excitations. Paldus et al. devised an approximate coupled-pair method, called ACPQ [11], in which these coupling terms (approximately) canceled certain quadratic terms in the CCD equations. Unlike the CCD method, the ACPQ method, and a related ACP-D45 method (ACP in short) introduced earlier [12], were shown to perform well for the annulenes, being convergent and giving the correlation energies close to the full configuration-interaction (FCI) results. However, a recent CC study [13] of annulenes, taking into account the double (D), triple (T), and quadruple (Q) excitations in the CC operator, showed that even the CCD-TQ method breaks down for these systems when the correlation effects become sufficiently strong. Moreover, the ACP and ACPQ methods were shown to fail for very large annulenes [14]. Thus, the annulenes remain a challenging problem for the many-electron theories.

II. FINDING MULTIPLE SOLUTIONS OF CCD, ACP, AND ACPQ EQUATIONS FOR [10]ANNULENE

In the CCD method, the CC operator corresponding to the double excitations depends on some linear parameters, hereafter referred to as the t_2 amplitudes. The CCD equations comprise a set of quadratic equations for the unknown t_2 amplitudes. In the nonorthogonally spin-adapted formalism (see, e.g., Ref. [4]), the number of t_2 amplitudes is equal to K = n_o n_u (n_o n_u + 1)/2, where n_o and n_u are the number of occupied and unoccupied orbitals, respectively (no symmetry other than the spin one is assumed). According to the Bézout theorem, such a set of quadratic equations may have up to 2^K solutions, a truly astronomical number in most applications. Therefore, finding the complete set of CCD solutions may be attempted only when the number of t_2 amplitudes is very small (e.g., due to the spatial symmetry of the many-electron system). In the homotopy study of the H4 model [3] (corresponding to 6 spin- and spatial-symmetry–adapted t_2 amplitudes), the complete set of CCD solutions numbered 12, which is distinctly smaller than the Bézout limit (64). On the other hand, the application of the homotopy method to the PPP model of benzene [5] (having 8 t_2 amplitudes adapted to spin, spatial, and time-reversal symmetry) has brought in some quite disturbing findings: not only the total number of solutions (230) approached the theoretical limit (256), but some solutions led to the correlation energies much
more negative than that of the “standard” CCD solution (which approximate the ground-state FCI solution); in addition all the “nonstandard” solutions were hardly similar to the FCI ones.

In the PPP model of [10]annulene, the CCD equations adapted to spin, spatial, and time-reversal symmetry correspond to 29 \( t_2 \) amplitudes. The ACP and ACPQ equations are obtained by neglecting (ACP and ACPQ) and modifying (ACPQ) some of the quadratic terms in the CCD equations, see, e.g., Ref. 13. In the present paper we use the PPP model of annulenes described in Ref. 12 and follow the notation used there: \( \beta \leq 0 \) eV is the resonance integral of the PPP model, and \( \gamma(R) \) is a potential describing the long-range electrostatic interactions. We shall report the results obtained for two variants of the PPP model: the PPP-MN model, employing the Mataga-Nishimoto potential \( \gamma(R) = e^2[R + e^2(\gamma_0)^{-1}]^{-2} \), with \( \gamma_0 = 10.84 \) eV, and the PPP-P model, using Pople’s potential \( \gamma(R) = e^2/R \) for \( R \neq 0 \), with \( \gamma_0 = 14.25878 \) eV (\( e \) is the elementary charge).

If the CCD results for benzene \([8]\) may be extrapolated, the CCD (and ACP and ACPQ) equations for [10]annulene may have more than \( 10^8 \) solutions; that makes the application of the homotopy method hopeless in this case. On the other hand, it was found in Ref. \( 8 \) that some of the real CCD solutions for benzene were stable within their close neighborhoods: such a solution (subject to the numerical rounding errors) led to a convergent iteration process when the direct-inversion-of-the-iterative-subspace (DIIS) method \([14]\) was used. Thus, one may expect that the DIIS method is able to trace various solutions, if only the starting points are suitably chosen.

A standard method of solving the CCD equations is based on the iterative procedure represented in Eq. (14) of Ref. \( 8 \). By starting from the \( t_2 \) amplitudes equal to zero, one recovers in the first iteration the \( t_2^{(1)} \) amplitudes corresponding to the first order of the Möller-Plesset (MP) perturbation theory; in the subsequent iterations higher-order MP contributions are added. Such an iteration procedure, if convergent, furnishes the standard CCD solution corresponding (as it is often \( a \ priori \) assumed) to the ground state of the system. The CCD electronic-correlation energy is then calculated as a certain linear function of the converged \( t_2 \) amplitudes (the \( t_2^{(1)} \) amplitudes correspond to the second-order MP correlation energy and will be, after Ref. \( 13 \) referred to as the MP2 amplitudes). The above treatment applies also to the ACP and ACPQ equations. In annulenes one may also use a kind of analytical-continuation procedure to find the standard solution for those values of parameter \( \beta \) for which the standard procedure (starting from the MP2 amplitudes) does not converge: one uses as the starting point the converged \( t_2 \) amplitudes found for the sufficiently close \( \beta \) value.

The multiple solutions of the CCD, ACP, and ACPQ equations presented in this paper were found in a quasi-random manner, by generating a pool of the initial \( t_2 \) amplitudes and then applying the DIIS procedure. The starting pool included the results of several hundred converged CCD, ACP, and ACPQ calculations obtained for different \( \beta \) values and for different forms of function \( \gamma(R) \) (these sets of \( t_2 \) amplitudes indeed looked random). Most of the calculations starting from this quasi-random amplitudes either diverge, or converge to the standard solution, but in some cases a new solution is obtained. Certainly, this is not a very efficient method of finding the multiple solutions, but since a single CCD calculation for [10]annulene usually takes only several seconds, a lot of data may be generated that way. We have found that the strongly correlated regime (\( \beta > -1.5 \) eV) is rich in multiple solutions, while in the weakly correlated regime (\( \beta < -3.0 \) eV) practically only the standard solution could be reached that way. Therefore, we performed calculations for several values of \( \beta \) from interval \((-1.0, 0, 0)\). These results were then extended as far as possible by a careful application of our analytical-continuation procedure. The obtained results are not supposed to provide the complete set of real solutions for [10]annulene. Nevertheless, they provide a rather intriguing glimpse at the “tip of the iceberg” of the multiple solution problem for this system. Let us note that the multiple solutions of the ACP and ACPQ equations have never been studied before.

### III. RESULTS

In Figs. \( 1, 2 \) we present the electronic-correlation energies corresponding to the multiple solutions of the CCD, ACP, and ACPQ equations, respectively. These results are obtained within the PPP-MN model for \(-5.0 \leq \beta < 0 \) eV, each solution is represented by a continuous line. The line endpoints (not touching the graph’s boundaries) indicate the limiting \( \beta \) values corresponding to our analytical-continuation procedure. It is seen that some of the new solutions exist for a very broad range of \( \beta \), while some can be continued only within a very narrow interval. The ground-state FCI correlation energies, shown as the broken line, are provided for a reference. The solution line that approaches the FCI line in the weakly correlated regime corresponds to the standard solution discussed in the previous papers \( 8, 22 \).

The CCD results in Fig. \( 1, 2 \) are rather simple: The standard-solution line is the only extending for all the \( \beta \) values. (When the standard iteration procedure is combined with the DIIS technique, the standard CCD solution for [10]annulene can be obtained for all negative values of \( \beta \), as shown previously by Paldus et al. \( 8 \) by using the Newton-Raphson method.) In the strongly correlated regime (\( \beta > -1.5 \) eV), the standard CCD solution provides a rather poor approximation to the ground state, and the corresponding correlation energy falls well below the FCI line. Other solutions have the energies higher than the FCI result, some of them may represent excited states. Most of them can be found only in the
proximity of $\beta = 0$, where the quasidegeneracy effects are the strongest.

The ACP and ACPQ results (Figs. 2 and 3 respectively) display a different and more complicated behavior. Unlike the CCD standard solution, the ACP and ACPQ standard solutions stay close to the FCI line also in the strongly correlated regime (although the corresponding $t_2$ amplitudes show increasing deviations from the FCI $t_2$ amplitudes as $\beta \to 0$ [12]). The ACP and ACPQ standard solutions can be found for $\beta < 0$ by applying the standard iteration procedure starting from the MP2 amplitudes [12]. Quite a few nonstandard solutions have been found, some of them extending for the whole range of $\beta$. Quite unusual is the presence of the solution lines lying below the standard-solution
TABLE I: PPP-P model of [10]annulene, CCD equations. Correlation energies for two solutions, CCD1 and CCD2; ground-state MP2 and FCI results shown for comparison (all energies in eV). $\theta$ (in deg) and $\eta$ gauge the similarity of a given solution to the FCI solution (see text).

| $\beta$ (eV) | $E_{\text{corr}}$ | $\theta$ | $\eta$ | $E_{\text{corr}}$ | $\theta$ | $\eta$ | $E_{\text{corr}}$ | $\theta$ | $\eta$ |
|-------------|-----------------|---------|--------|-----------------|---------|--------|-----------------|---------|--------|
| -2.500      | -2.825          | 5.1    | 0.92   | -4.937          | 19.0    | 1.30   | -36.539         | 46.4    | 8.05   |
| -1.175      | -16.896         | 91.3   | 15.00  | -4.937          | 88.2    | 1.14   | -6.856          | 50.9    | 0.53   |
| -0.500      | -1.933          | 23.1   | 0.66   | -2.388          | 42.9    | 0.41   | -2.714          | 57.3    | 0.20   |
| FCI         | -3.045          | 0.00   | 1.00   | -4.908          | 0.00    | 1.00   | -7.769          | 0.00    | 1.00   |

Such exotic solutions have been observed in the study of benzene \cite{1}; however, they were unstable in the DIIS iterative procedure (could be found only by the homotopy method). The “underground” solutions obviously have no physical meaning, and it is a little disturbing that they may appear while iteratively solving the ACP or ACPQ equations. One of the ACPQ “underground-solution” lines is especially peculiar: it starts with the lowest energy for $\beta = 0$ and rises quite steeply with the decreasing $\beta$, crossing several solution lines, including the standard-solution line (apparently there is no “non-crossing rule” for different solution lines).

Quite intriguing are the solutions of the CCD equations corresponding to the PPP-P model, displayed in Fig. \ref{fig:cc} together with the ground-state FCI results. We were able to find only two solutions, hereafter referred to as CCD1 (the standard solution) and CCD2 (the nonstandard one). Despite the use of the extensive quasi-random search, the CCD iterations invariably led to CCD1 or CCD2 (these solutions were so strong attractors that the iterations rarely diverged). In contrast to the CCD results for the PPP-MN model, the iterations starting directly from the MP2 amplitudes converge to the CCD1 solution in the weakly correlated regime, while in the strongly correlated regime the CCD2 solution is obtained. In Fig. \ref{fig:cc} we mark by the squares the endpoints of the respective direct-convergence domains. One may thus obtain the CCD1 and CCD2 solutions in a deterministic way, by starting the calculations within these regions. Moreover, by applying our algorithmic-continuation procedure, we are able to extend a given solution line outside its domain of (direct) convergence.

The CCD1-solution line resembles closely the line corresponding to the standard solution CCD1 for the PPP-MN model, see Fig. \ref{fig:ppp-mn}, while the CCD2 line has no counterpart in that figure. The CCD1 and CCD2 lines cross for $\beta = -1.17479$ eV, in the vicinity of the FCI-solution line. In Table \ref{table:ppp-mn} we present the CCD1, CCD2, MP2 and FCI correlation energies calculated for three representative $\beta$ values, including the intersection coordinate. In addition, we show there the values of parameters $\theta$ and $\eta$ which provide a measure of similarity between the vector of $t_2$ amplitudes corresponding to a given solution and the vector of $t_2$ amplitudes extracted from the linear coefficients of the ground-state FCI wavefunction: $\theta$ is the angle between the vectors, and $\eta$ is the ratio of the vector lengths (for details, see Ref. \cite{2}).

From Fig. \ref{fig:cc} and Table \ref{table:ppp-mn} a consistent picture emerges: The CCD1 solution provides an acceptable approximation to the ground-state FCI solution up to the vicinity of the CCD1/CCD2 crossing; then, in the strongly-correlated region, it deteriorates and hardly deserves the name of the standard solution. The CCD2 solution, on the other hand, starts as the “underground” in the weak correlation regime (bearing no resemblance to the FCI solution), but it improves in the strongly-correlated regime, and, finally, becomes a slightly better (but still poor) approximation to the FCI solution (the CCD2 correlation energies are surprisingly similar to the FCI ones in the strongly correlated regime). Thus, it looks as CCD1 and CCD2 swap their roles as the standard and “underground” solutions. The behavior of the MP2 results agrees with the observed convergence pattern for iterations starting from the MP2 amplitudes. Interestingly, if one performed a CCD study of the PPP-P model of [10]annulene by applying a standard iteration procedure (starting with the MP2 amplitudes) at some representative $\beta$ values (say, $-5.0$, $-2.5$, $-1.5$, and $-0.5$ eV), the conspicuous switch between the CCD1 and CCD2 solutions would have been passed unnoticed. By looking at the CCD correlation energies alone, one would then proclaimed a very good performance of the CCD method up to very small $\beta$ values, contrary to the results found by Paldus et al. \cite{3} for the PPP-MN model.

The study of the ACP and ACPQ equations in the PPP-P model brings in some additional unexpected findings: the standard ACP solution cannot be found for $\beta$ between $-0.80$ and $-0.4$ eV, while the standard ACPQ solution encounters problems already for $\beta > -2.53$ eV. Apparently, in the strongly correlated regime of the PPP-P model both methods become unstable.

Our search of the multiple real solutions of the CCD, ACP, and ACPQ equations has brought several unexpected findings: (i) while solving the CC equations by iterations, one may arrive at an “underground” solution, (ii) in the PPP model, the character of multiple solutions is sensitive to the form of the long-range potential (the $\gamma$ function), (iii) different solutions may play the role of the standard solution when the strength of the electronic-
correlation effects is varied (this may apply to the changes in molecular geometry, e.g., to the bond breaking). In conclusion: it seems that the problem of multiple solutions of the CC equations deserves still more attention. Some variants of our random-search approach may be tried also on larger many-electron systems.

This work was supported in part by the Committee for Scientific Research (KBN) through grant No. 7 T09A 019 20.

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