Electronic correlation in cyclic polyenes. Behavior of approximate coupled-pair theories for large rings

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We investigate the cyclic polyenes (annulenes) C_MH_M, described by the Pariser-Parr-Pople (PPP) model, by means of the approximate coupled-pair theories (ACP, ACPQ). For the systems with the spectroscopic value of the PPP resonance integral $\beta = 2.5$ eV, the ACP method breaks down for $M \geq 446$ and the ACPQ method—for $M > 194$. In the ACPQ method, for $M > 170$, two close lying solutions have been observed that become quasi-degenerate for $M \geq 198$. The results indicate that the ACP and ACPQ methods cannot be applied to the one-dimensional metallic case.

INTRODUCTION

The problem of electronic correlation in the $\pi$-electron systems corresponding to small cyclic polyenes (annulenes) has been studied extensively within the Pariser-Parr-Pople (PPP) model by Paldus et al. [1, 2]. They have found that the coupled-cluster doubles method (CCD) [in annulenes equivalent to the coupled-cluster singles and doubles (CCSD) one] breaks down when the correlation effects become sufficiently strong. They devised the approximate coupled-pair method corrected for connected quadruple excited clusters (ACPQ) [3]. The ACPQ method, together with the similar ACP-D45 method (or ACP, in short) [3], was shown to perform very well for the small annulenes, being convergent and giving correlation energies close to the full configuration interaction (FCI) results.

Recently, small annulenes have been studied with the inclusion of the doubles (D), triples (T), and quadruples (Q) in the cluster operator [4]. It turned out that although the inclusion of quadruple excitations considerably improves the results in the weakly and moderately correlated regime (which correspond to large and moderate absolute values of the PPP resonance integral $\beta$, respectively), the CCDT, CCDQ, and CCDTQ methods break down in the strongly correlated regime. It was also found that in the strongly correlated system the $t_2$ amplitudes of the ACP and ACPQ methods differ considerably from the FCI $t_2$ amplitudes.

Even though the ACP and ACPQ methods are satisfactory for small annulenes, it has been unknown how the methods perform for large annulenes, where the quasi-degeneracy problems may be too strong. The strength of the correlation (and the level of quasi-degeneracy) can be adjusted by decreasing the absolute value of $\beta$ for small annulenes, but it has been unknown whether this procedure is equivalent to the increasing of the size of the ring and keeping the resonance integral constant. The behavior of the methods for large systems is important if one wants to extrapolate the results and study the limit of the one-dimensional metal. That motivated us to investigate the performance of the ACP and ACPQ methods for large annulenes.

THEORY

In this Letter, we provide only a brief description of the PPP model of annulenes; more details may be found in Ref. [4].

We shall consider annulenes of formula C_MH_M, where $M = 4m_0 + 2$, $m_0 = 1, 2, \ldots$ and the number of electrons $N = M$. The C atoms form a regular polygon, and the C-C bonds are assumed to be of the length $R^0 = 1.4$ Å. The Fock-space Hamiltonian $\hat{H}$, built according to the prescriptions of the PPP model, is given in Eq. (2) of Ref. [4]. The following semiempirical parameters are used: the Coulomb integral $\alpha = 0$, the resonance integral $\beta = -2.5$ eV (the so-called spectroscopic value), and the two-center two-electron integrals $\gamma_{mn}$ are parametrized with the Mataga–Nishimoto formula [13],

\[
\gamma(R) = e^2[R + e^2(\gamma^0)^{-1}]^{-1},
\]

where $e$ is the electron charge and $\gamma^0 = \gamma(0) = 10.84$ eV. Within the PPP computer code, the atomic units are used: 1 bohr = 0.529177 Å, 1 hartree = 27.2116 eV (the conversion factors are the same as employed in Refs. [14] and [15]).

The ACP and ACPQ methods are approximations to the CCD method. In this method we use exponential Ansatz and expand the ground-state wave function $\Psi$ by using the cluster operator $\hat{T}_2$,

\[
\Psi = \exp(\hat{T}_2)\Phi,
\]

where $\Phi$ is a single-determinant reference configuration, usually the RHF wave function. The $\hat{T}_2$ operator depends linearly on some parameters, the so-called $t_2$ amplitudes, that can be obtained by solving the set of nonlinear CCD equations given by

\[
\Phi^* \exp(-\hat{T}_2)\hat{H}\exp(\hat{T}_2)\Phi = 0,
\]

where $\Phi^*$ represent all the doubly excited configurations. The correlation energy for the ground state is completely determined by the $t_2$ amplitudes and can be calculated as

\[
E_{\text{corr}} = \langle \Phi | \hat{H} \hat{T}_2 \Phi \rangle - E_{\text{HF}}.
\]
FIG. 1: The Brandow diagrams representing the quadratic terms in the ACP method.

The cyclic symmetry of our PPP model imposes some extra conditions on the CC model. The \( t_1 \) amplitudes (singles) must vanish, and therefore \( \Phi \) is also the Brueckner determinantal function \[17, 18\]. Thus, the CCD method becomes equivalent to the CCSD one. In the presence of the cyclic symmetry, the amplitudes depend on 3 indices (instead of 4), and the number of amplitudes scales as \( M^3 \) (instead of \( M^4 \)). Moreover, the computational cost for the CCD iteration scales as \( M^4 \) instead of \( M^6 \). This makes enormous savings in the CPU time for large annulenes and makes them computationally accessible. The ACP and ACPQ methods violate the alternancy symmetry \[19\], and therefore we have not used this symmetry in the present calculations. The details of the implementation of the cyclic symmetry are given in Ref. 14.

The explicit form of the CCD equations is most conveniently presented in the form of diagrams (see, e.g., Ref. 20). The left hand side of Eq. 2 is then a sum of terms represented by these diagrams. In the ACP method, some of the quadratic terms of the CCD equations are omitted (these are the diagrams that do not factorize with respect to the hole lines). It was shown \[3\] that these terms are approximately canceled by the terms corresponding to the connected quadruple excitations. Thus, the omission of these terms may improve the results and was shown to be very effective for the annulenes in the strongly correlated regime \[3\]. The only quadratic terms that are present in the ACP method correspond to the diagrams in Fig. 1 (the labels below are the same as in Ref. 1 where the complete set of the diagrams may be found).

For closed-shell calculations, the CC equations may be put in a spin-adapted form. We use the nonorthogonally spin-adapted formalism \[21\], which for the CCD method and its variants is equivalent to the orthogonally spin-adapted formalism used by Paldus et al. \[3\]. With the latter formalism they devised an improvement to the ACP method called ACPQ. In this method the diagram (5) of Fig. 1 is multiplied by 9 in the triplet coupled equations of Ref. 2. The ACPQ method better approximates the quadruples and was shown to provide the exact solution in the limit of \( \beta \rightarrow 0 \) \[2\].

The ACPQ method can also be translated to the nonorthogonally spin-adapted formalism. Let \( g_{ij}^{ab} \) represent the nonorthogonally spin-adapted term corresponding to diagram (5) of Fig. 1 in the ACP method (\( i, j \) and \( a, b \) stand for the occupied and unoccupied orbitals, respectively). In the ACPQ method, the term should be modified in the following way:

\[
(ACP) \quad g_{ij}^{ab} \rightarrow 5g_{ij}^{ab} - 4g_{ji}^{ab} \quad (ACPQ)
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RESULTS

We performed the ACP and ACPQ calculations for the annulenes, \( C_MH_M \), for \( M \) up to 442. In Fig. 2, the ACP and ACPQ results for small annulenes are compared with the results of ACPQ+T(ACPQ) \[11\], FCI results \[22\], and the density matrix renormalization group (DMRG) calculations \[23\]. These are the methods that were shown to provide converged results for the small annulenes. It can be seen that the correlation energy corrected for the triples in the ACPQ+T(ACPQ) method is much better than in the ACPQ method. The method depends, however, on the \( t_2 \) amplitudes from the ACPQ method, and will work only if the latter method converges. For small annulenes the DMRG results are the most accurate and the deviation from the FCI is so small that it cannot be seen on the figure.
Since the ACP and ACPQ correlation energies do not change much with the increasing size of the ring around $M = 50$, it may suggest that the results are close to the saturation. However, it is not true for the larger annulenes, as shown in Fig. 3. Some numerical values are also shown in Table I. Surprisingly, the correlation energy is not monotonic with the increasing size of the ring and reaches a minimum. It means that the extrapolation of the results for smaller rings would lead to a completely wrong result.

We found that the ACP method is convergent up to $M = 442$. For $M > 270$, the use of the direct inversion in the iterative subspace method (DIIS) [24, 25] was necessary to provide converged results. The DIIS method was also very useful in accelerating the convergence for the smaller annulenes.

The results of the ACPQ method are even more complicated. For $M < 174$ there was one solution found, but between 174 and 194 we found two solutions. One set of solutions, later referred to as ACPQ1, is a continuation of the results for $M < 174$. It was found by using the ACP result for a given $M$ as a starting point for the iterative process with the DIIS method. The other set of solutions, of lower energy, was found by applying the DIIS iterative scheme to the MP2 starting point. For $M < 174$, both starting points resulted in the same solution (ACPQ1).

None of the ACPQ1 and ACPQ2 converged for $M \geq 198$. In Fig. 4, the results of the ACPQ method for $M$ from 150 to 198 are shown. It can be seen that the correlation energies of the two solutions approach each other. To test the similarity of the $t_2$ amplitudes of the two solutions, we calculated the parameters $\theta$ and $\eta$ defined in Eq. (22) of Ref. [14]. Here $\theta$ measures the angle between the vectors formed of the $t_2$ amplitudes, and $\eta$—the ratio of the vector lengths. For $M = 174$, we found $\theta = 2.69^\circ$ and $\eta = 0.9989$, while for $M = 194$, $\theta = 0.74^\circ$ and $\eta = 0.9999$. This shows that the $t_2$ amplitudes of the ACPQ1 and the ACPQ2 solutions are quite similar for $M = 174$, and are almost identical for $M = 194$.

The existence of multiple solutions of the CC equations has been observed previously for the H4 model [26, 27], and the complete set of solutions has been obtained with the homotopy method [28]. In those studies, one of the solutions was easily identified as the ground-state solution. In contrast, for the ACPQ method of our annulene, such identification is ambiguous. The ACPQ1 solution, which exists for small annulenes, and which may be considered as the standard solution, has the energy higher than the ACPQ2 solution. Some exotic solutions that have the energy lower than the ground state have been observed for the PPP model of benzene [29]. Our preliminary results for $C_{10}H_{10}$ also show the existence of such solutions [30].

**CONCLUSIONS**

The ACP and ACPQ methods, while performing satisfactorily for small annulenes, have convergence problems for large annulenes. The ACP and ACPQ correlation energies are not monotonic with the increasing size of the
TABLE I: The correlation energy per electron (in eV) for large annulenes; NC means no convergence of the DIIS iterations, NF means that the result was not found.

|      | 50   | 98   | 174  | 194  | 442  |
|------|------|------|------|------|------|
| ACP  | −0.278 470 | −0.278 859 | −0.278 466 | −0.278 392 | −0.278 028 |
| ACPQ1 | −0.284 306 | −0.285 034 | −0.284 838 | −0.284 898 | NC   |
| ACPQ2 | NF   | NF   | −0.285 599 | −0.285 096 | NC   |

ring. It shows that an extreme caution must be taken if one tries to extrapolate the results of the small annulenes to the infinite limit. In the case of the ACPQ method, two solutions are found for $174 \leq M \leq 194$, behaving as if they coalesce into a single solution between $M = 194$ and $M = 198$. However, no converged real solution of the ACPQ equations has been found beyond $M = 194$, which may indicate that the solutions become complex for $M \geq 198$. The above observations indicate that the ACP and ACPQ methods cannot be applied to the one-dimensional metallic case.

Among all the methods used in the calculations of the PPP annulenes, the DMRG method seems the most promising. However, it should be noted that the method was not tested in a broader range of the resonance integral $\beta$, especially in the strongly correlated regime of $\beta \approx 0$, where the various CC methods break down. It is also unclear whether the method can be applied to the large or infinite annulenes, since the method may not be size-extensive for the metallic case [3].

The existence of a method that can describe the large annulenes and the one-dimensional metal in the PPP model is still an open problem. It is unlikely that the method that cannot describe the strongly correlated regime of a small annulene would be able to describe the infinite case. It seems, however, that the proper behavior of a method in the strongly correlated regime of small annulenes still does not guarantee the correct description of the larger systems.

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[1] J. Paldus, M. Takahashi, and R. W. H. Cho, Phys. Rev. B 30, 4267 (1984).
[2] J. Paldus, J. Čížek, and M. Takahashi, Phys. Rev. A 30, 2193 (1984).
[3] J. Paldus and M. J. Boyle, Int. J. Quantum Chem. 22, 1281 (1982).
[4] M. Takahashi, J. Paldus, and J. Čížek, Int. J. Quantum Chem. 24, 707 (1983).
[5] J. Paldus, M. Takahashi, and R. W. H. Cho, Int. J. Quantum Chem. S18, 237 (1984).
[6] M. Takahashi and J. Paldus, Phys. Rev. B 31, 5121 (1985).
[7] P. Piecuch and J. Paldus, Theor. Chim. Acta. 78, 65 (1990).
[8] P. Piecuch, S. Zarrabian, J. Paldus, and J. Čížek, Phys. Rev. B 42, 3351 (1990).
[9] P. Piecuch, S. Zarrabian, J. Paldus, and J. Čížek, Phys. Rev. A 42, 5155 (1990).
[10] P. Piecuch and J. Paldus, Int. J. Quantum Chem. S25, 9 (1991).
[11] J. Paldus and P. Piecuch, Int. J. Quantum Chem. 42, 135 (1992).
[12] P. Piecuch, J. Čížek, and J. Paldus, Int. J. Quantum Chem. 42, 165 (1992).
[13] K. Jankowski and J. Paldus, Int. J. Quantum Chem. 18, 1243 (1980).
[14] R. Podeszwa, S. A. Kucharski, and L. Z. Stolarczyk, J. Chem. Phys 116, 480 (2002).
[15] N. Mataga and K. Nishimoto, Z. Phys. Chem. (Frankfurt am Main) 13, 140 (1957).
[16] L. Z. Stolarczyk, M. Jeziorska, and H. J. Monkhorst, Phys. Rev. B 37, 10646 (1988).
[17] J. Paldus, J. Čížek, and B. A. Keating, Phys. Rev. A 8, 640 (1973).
[18] L. Z. Stolarczyk and H. J. Monkhorst, Int. J. Quantum Chem. S18, 267 (1984).
[19] J. Koutecký, J. Paldus, and J. Čížek, J. Chem. Phys 83, 1722 (1985).
[20] S. Kucharski and R. J. Bartlett, Adv. Quantum Chem. 18, 281 (1986).
[21] J. Čížek, J. Chem. Phys. 45, 4256 (1966).
[22] G. L. Bendazzoli, S. Evangelisti, and L. Gagliardi, Int. J. Quantum Chem. 51, 13 (1994).
[23] G. Fano, F. Ortolani, and L. Ziosi, J. Chem. Phys. 108, 9246 (1998).
[24] P. Pulay, J. Comp. Chem. 3, 556 (1982).
[25] G. E. Scuseria, T. J. Lee, and H. F. Schaefer III, Chem. Phys. Lett. 130, 236 (1986).
[26] L. Meissner, A. Balková, and R. J. Bartlett, Chem. Phys. Lett. 212, 177 (1993).
[27] K. Jankowski and K. Kowalski, Int. J. Quantum Chem. 50, 353 (1994).
[28] K. Kowalski and K. Jankowski, Phys. Rev. Lett. 81, 1195 (1998).
[29] R. Podeszwa, L. Z. Stolarczyk, K. Jankowski, and K. Rubinie, physics/0207080, submitted to J. Chem. Phys.
[30] R. Podeszwa and L. Z. Stolarczyk, physics/0208077.
[31] G. K.-L. Chan and M. Head-Gordon, J. Chem. Phys. 116, 4462 (2002).