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Coupled-cluster approaches with an approximate account of triexcitations and the optimized-inner-projection technique. III. Lower bounds to the ground-state correlation energy of cyclic-polyene model systems

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The optimized-inner-projection (OIP) method is implemented and applied to determine the lower bounds to the ground-state correlation energy for the Pariser-Parr-Pople and Hubbard models of cyclic polyenes C_NH_N, $N=4\nu+2$, $\nu=3$–5, in the whole range of the coupling constant. In actual calculations, the orthogonally spin-adapted form of the OIP equations is used, and full advantage is taken of the high symmetry of the cyclic polyene model, so that systems with $N\geq 14$ can be explored. Comparison is made with the results of both full and limited configuration-interaction calculations and with the correlation energies obtained with certain approximate coupled-cluster schemes. Contrary to the six- and ten-membered rings, the OIP lower bounds to the ground-state correlation energy of cyclic polyenes with larger number of sites are very poor and cannot serve as a meaningful source of information. Since the eigenvalues of the intermediate Hamiltonian, in terms of which the OIP technique is defined, are highly degenerate even in the weakly correlated region, and in view of the random behavior of the OIP bracketing function, the OIP method becomes computationally very demanding for $N\geq 14$ rings. Moreover, simple iterative schemes usually diverge and sophisticated root searching procedures have to be applied. The usefulness of the OIP technique for the determination of lower bounds to energy eigenvalues in larger systems is thus questioned.

I. INTRODUCTION

The determination of accurate lower bounds for energies of quantum-mechanical systems represents a very difficult and challenging problem to which much effort has been devoted in the past.[1–12] This is particularly the case for many-body systems, such as atoms and molecules. The early pioneering work of Weinstein on the intermediate problem method,[1] which was further developed by Aronszajn,[2] was first exploited in the quantum-mechanical context by Bazley[3] and Bazley and Fox.[4] These initial developments later culminated in Löwdin's formulation of the concept of the bracketing function[5,6] and inner-projection technique,[6–8] which in turn stimulated numerous studies and applications[9,10] (for additional references see the review, Ref. 8).

Löwdin's classical formulation of the inner-projection (IP) technique was recently slightly modified, resulting in the so-called optimized and/or renormalized inner-projection (OIP) method,[11] which was successfully applied to obtain very accurate lower-energy bounds for several one-dimensional quantum-mechanical problems.[11,12] More recently it was shown[13,14] that the same technique can also be applied to molecular electronic structure problems, at least when the semiempirical Pariser-Parr-Pople (PPP) Hamiltonian[15] description is employed. In this way, the lower-energy bounds were obtained for the PPP model of benzene,[13] and very recently for the cyclic polyene with ten sites,[14] representing the next member in the cyclic polyene homologous series[16] C_NH_N, $N=4\nu+2$.

Let us note at this point that these model systems have been widely studied (see, e.g. Refs. 17–23), because they are very challenging as far as the computation of correlation effects is concerned and because they provide valuable models for several interesting systems. Thus, the very first member of this homologous series represents an archetypal aromatic system, the benzene molecule, while large polyenes can be viewed as a simple model of a linear metal with Born–von Kármán boundary conditions. The latter aspect became of considerable interest with the synthesis of polyacetylene films,[24] whose fascinating electric, optic, and magnetic properties continue to be studied extensively.[25] A particularly convenient feature of these models is also the possibility of examining the correlation problem for a whole range of the coupling constant,[17,18,21] which can be modeled by the reciprocal value of the PPP resonance integral.[15] While negligible correlation effects are encountered in the uncorrelated limit ($\beta\sim-5$ to -10 eV), we face one of the most challenging correlation problems in the $\beta\rightarrow 0$ limit,[18,20,21] where a very high degree of degeneracy sets in. In view of this fact, many of the problems that occur for very large or extended systems can be examined on relatively small models characterized by a large coupling constant. In the same way, the limit of applicability of various theories and their relative merits can be assessed, particularly when a simpler Hubbard model is employed, in which case the exact solutions for any member of the cyclic polyene series are available.[23,26]

Although the OIP method provides less encouraging results for the $C_{10}H_{10}$ polyene[14] than for benzene (C_6H_6), as might be expected, we considered it worthwhile to explore this method for even larger systems in order to determine its characteristics, behavior, and limitations.

It should be recalled that since OIP is formulated in terms of perturbationlike expressions, the inherent computation problems are very similar to those appearing in certain coupled-cluster (CC) approximation schemes.[27–29] In particular, to account for triexcited clusters, one requires very similar expressions in both the OIP approach and coupled-cluster method with singly, doubly, and triply excited clusters using a first-order perturbative estimate for triples (CCSDT-1).[27–29] We have thus formulated the required formalism for these and other related CC methods in paper I (Ref. 28) of this series, exploiting the orthogonally spin-adapted version of the theory,[30,31] which in turn facilitates the exploitation of these methods for larger systems and makes the comparison with standard configuration-interaction (CI) results easier. Using, in addition, the available symmetries of these model systems,[17,21,29] we were able to proceed beyond the $C_{10}H_{10}$ system, which would hardly be possible with the technique of Ref. 14.

In Sec. II we briefly outline the OIP technique as it pertains to the PPP cyclic polyene models, and present the resulting lower bounds for the ground-state correlation energy of the 14-member cyclic polyene in Sec. III. The application to larger polyenes, namely $C_{18}H_{18}$ and $C_{22}H_{22}$, is then presented in Sec. IV, while the results are discussed in Sec. V. In all cases, both the PPP and Hubbard Hamiltonian models are examined.

II. OPTIMIZED INNER-PROJECTION TECHNIQUE FOR THE PPP MODEL OF CYCLIC POLYENES: AN OVERVIEW

Löwdin's inner-projection technique[7] as well as its optimized (OIP) version[11] are well documented in the literature.[6–14] Exploitation of the latter method for the PPP model of conjugated hydrocarbons,[15] particularly for cyclic polyenes,[16] is discussed in paper I of this series[28] and elsewhere.[13,14] We thus only briefly summarize the essential equations characterizing the OIP approach[13,14,28] as applied to the PPP cyclic polyene model.[16] For a detailed description of this model, we refer the reader to paper II of this series[29] and Refs. 17–21.

In order to apply the OIP technique, it must be possible to decompose a given Hamiltonian $\mathcal{H}$ into an unperturbed part $\mathcal{H}^{(0)}$ with known eigenfunctions $\phi_k^{(0)}$ and energies $\mathcal{E}_k^{(0)}$,

$$\mathcal{H}^{(0)}\phi_k^{(0)}=\mathcal{E}_k^{(0)}\phi_k^{(0)},\quad \mathcal{E}_0^{(0)}<\mathcal{E}_1^{(0)}\le\mathcal{E}_2^{(0)}\le\cdots\ , \tag{1}$$

and into the positive definite (not necessarily small) perturbation $\mathcal{V}$, so that

$$\mathcal{H}=\mathcal{H}^{(0)}+\mathcal{V}\ . \tag{2}$$

In the case of simple one-particle systems, such as anharmonic oscillator or hydrogen atom in a magnetic field, this can be achieved with the help of simple renormalization procedures.[11,12] However, when many-electron systems are considered at the *ab initio* level, decomposition of the Hamiltonian into $\mathcal{H}^{(0)}$ and a positive definite $\mathcal{V}$ may not be, in general, possible, since the positive definiteness of the perturbation is in this case affected by the presence of the effective one-electron part in the Hamiltonian. The problem is much easier at the semiempirical level: when the PPP model of neutral conjugated hydrocarbons is considered, the corresponding Hamiltonian naturally splits into an unperturbed Hückel part $\mathcal{H}^{(0)}$ and a positive definite perturbation $\mathcal{V}$, provided that the internuclear repulsion term is included in $\mathcal{V}$. For the cyclic polyenes C_NH_N ($N=2n=4\nu+2$, $\nu=1,2,\ldots$) we thus get[18,21,28,32]

$$\mathcal{H}^{(0)}=N\alpha+\beta\sum_{\mu}(E_{\mu,\mu+1}+E^{\dagger}_{\mu,\mu+1})\ , \tag{3}$$

$$\mathcal{V}=\tfrac{1}{2}\sum_{\mu,\nu}\gamma_{\mu\nu}(n_\mu-1)(n_\nu-1)\ , \tag{4}$$

where

$$E_{\mu\nu}=\sum_{\sigma=-1/2}^{1/2}X^{\dagger}_{\mu\sigma}X_{\nu\sigma} \tag{5}$$

are the orbital unitary group, U(N), generators,[32] and $X^{\dagger}_{\mu\sigma}$ ($X_{\mu\sigma}$) are the usual fermion creation (annihilation) operators of the second quantization formalism defined on a minimum basis set of symmetrically orthonormalized[33] $2p_z$ carbon atomic spin-orbitals $|\mu\sigma\rangle=|\mu\rangle|\sigma\rangle$, $\mu=0,1,\ldots,N-1$, $\sigma=\pm\frac{1}{2}$, localized on the vertices of the regular N-gon. Further, $n_\mu=E_{\mu\mu}$ is the μth site occupation number operator, parameter α, which can be set to zero to define the origin of the energy scale, is a so-called Coulomb integral, and $\beta=\beta_{\mu,\mu\pm1}$ is the resonance (or hopping) integral, whose reciprocal value can be interpreted as the coupling constant for our model. The physical value of β, as determined by the low-energy transitions in the electronic spectrum of benzene, is about -2.5 eV. It is, however, more instructive to consider β as a variable parameter defining the coupling constant and to examine the entire range of the correlation effects. Finally, for the two-electron Coulomb repulsion integrals $\gamma_{\mu\nu}$ we assume Mataga-Nishimoto[34] parametrization, with the one-center integrals $\gamma_{\mu\mu}=\gamma_{00}$ defined through the difference between the valence-state ionization potential and electron affinity (the so-called I-A approximation;[15] see Sec. II of paper II for more detail). We shall also consider the Hubbard model,[35] in which only the on-site interactions are allowed, so that

$$\gamma_{\mu\nu}=\gamma\delta_{\mu\nu}\ , \tag{6}$$

where $\gamma=5$ eV approximately equals the $\gamma_{00}-\gamma_{01}$ difference for the PPP Hamiltonian model.[36] The Hubbard model (and its variations) has been extensively exploited in theoretical solid-state physics. The principal attractiveness of this model lies undoubtedly in its simplicity, which makes it possible to obtain exact solutions of the ground-state eigenvalue problem for any finite[23] and even infinite[23,26] cyclic polyene. In spite of its simplicity, the Hubbard model possesses the main features of its more sophisticated PPP counterpart (see, e.g., Ref. 21).

The absence of other than one- and two-center Coulomb-type two-electron integrals in Eq. (4) is due to the assumption of zero differential overlap,[15] while the

Coulomb integral α, Eq. (3), arises from a so-called Goeppert-Mayer and Sklar approximation.[15] The resonance integral β, originating through the tight-binding approximation, characterizes the off-diagonal one-electron matrix elements of the electronic PPP Hamiltonian H, which is given by the formula[15]

$$H=\mathcal{H}-\sum_{\substack{\mu,\nu\\ \mu<\nu}}\gamma_{\mu\nu}\ . \tag{7}$$

A single resonance integral $\beta=\beta_{\mu,\mu\pm1}$, Eq. (3), suffices in view of the D_{Nh} or C_N symmetry of cyclic polyenes, which also drastically reduces the number of required two-electron integrals, since

$$\gamma_{\mu\nu}=\gamma_{\mu+\kappa,\nu+\kappa}=\gamma_{0,\mu-\nu}\ , \tag{8}$$

with all indices taken modulo N.

The positive definiteness (or, rather, semidefiniteness) of the operator $\mathcal{V}$, Eq. (4), results immediately from the fact that for any physically reasonable parametrization of the PPP model, $\gamma_{\mu\nu}>0$. Hence, the OIP method can be directly applied. We thus have to partition the solution space for the unperturbed Hamiltonian $\mathcal{H}^{(0)}$ into the manifold $\mathcal{M}_g^{(0)}$, spanned by $\phi_0^{(0)}$ together with chosen excited eigenstates of $\mathcal{H}^{(0)}$, and its orthogonal complement $\mathcal{M}_g^{(0)\perp}$. The Hamiltonian $\mathcal{H}^{(0)}$, Eq. (3), is the Hückel Hamiltonian. Consequently, its ground eigenstate $\phi_0^{(0)}$ is the Hückel solution for C_NH_N, $N=2n=4\nu+2$, $\nu=1,2,\ldots$, i.e., the independent-particle model single determinant Φ_0, built from the n lowest-lying doubly occupied Hückel orbitals. Excited eigenstates $\phi_k^{(0)}$ are then obtained by all single, double, triple, etc. excitations from the reference determinant Φ_0, while the corresponding eigenvalues $\mathcal{E}_k^{(0)}$ are the appropriate sums of the Hückel orbital energies. Clearly, only those excitations that interact with Φ_0 need to be considered, which automatically excludes all nonsinglet excitations as well as those that do not satisfy a zero quasimomentum rule and do not span the totally symmetric "minus" representation[37] A_{1g}^-, to which Φ_0 belongs.[38] In particular, no monoexcitations will intervene since they are invariably associated with a nonvanishing quasimomentum transfer and thus belong to a different symmetry species than Φ_0[18,21,38] (cf., Sec. II of paper II). However, among the doubly, triply, and higher-excited singlet configurations[18,38] we can always find some that satisfy the zero quasimomentum rule and interact with Φ_0. The most natural choice for $\mathcal{M}_g^{(0)}$ is thus a linear span

$$\mathcal{M}_g^{(0)}=\langle g_0,g_1,\ldots,g_M\rangle\ , \tag{9}$$

where

$$g_i=\Phi_i\quad(i=0,1,\ldots,M)\ , \tag{10}$$

and where Φ_i, $i=1,\ldots,M$, designate pertinent doubly excited configurations. We choose them as the orthogonally spin-adapted *pp-hh* (particle-particle–hole-hole) coupled biexcited singlet configurations[31]

$$\left|\begin{matrix} r & s\\ a & b\end{matrix}\right\rangle_{S_i}\ ,$$

where a,b designate orbitals occupied in Φ_0 (i.e., hole states), r,s the unoccupied ones (particle states), and the subscript S_i ($S_i=0,1$) the intermediate spin quantum number for the coupling of particle or holes. We use the *pp-hh* coupled configurations since they possess simple transformation properties with respect to interchanges of particle and/or hole orbital labels[30] so that the resulting formulation of the OIP method is computationally convenient.[14,28]

We could, of course, consider a larger manifold $\mathcal{M}_g^{(0)}$ that also includes triply and quadruply excited configurations, since the solution space for $\mathcal{H}^{(0)}$ can be partitioned into $\mathcal{M}_g^{(0)}$ and $\mathcal{M}_g^{(0)\perp}$ in an arbitrary manner. However, such an extension of the OIP technique is hardly feasible in view of a large number of triple and quadruple excitations, even at the orthogonally spin-adapted level. Thus, only one choice of the manifold $\mathcal{M}_g^{(0)}$, namely, the one defined by Eqs. (9) and (10), is considered in the present study.

Once the partitioning of the solution space for $\mathcal{H}^{(0)}$ into $\mathcal{M}_g^{(0)}$ and $\mathcal{M}_g^{(0)\perp}$ is defined, the OIP lower bounds to the exact eigenenergies $\mathcal{E}_k$ of the PPP Hamiltonian $\mathcal{H}$, Eqs. (2)–(5), are found by solving the equation[28]

$$f(\epsilon)=\epsilon\ , \tag{11}$$

where

$$f(\epsilon)=\sum_{i,j=0}^{M}\mathcal{V}_{0i}[\mathbf{A}(\epsilon)^{-1}]_{ij}\mathcal{V}_{j0}\ , \tag{12}$$

and $\mathbf{A}(\epsilon)$ is the $(M+1)\times(M+1)$ parameter-dependent matrix, whose entries are given by

$$A(\epsilon)_{ij}=\mathcal{V}_{ij}-[W_{ij}^{(2)}(\epsilon)+W_{ij}^{(3)}(\epsilon)+W_{ij}^{(4)}(\epsilon)]\ . \tag{13}$$

Here

$$\mathcal{V}_{ij}=\langle\Phi_i|\mathcal{V}|\Phi_j\rangle\ , \tag{14}$$

and $W_{ij}^{(k)}(\epsilon)$ ($k=2,3,4$) are the effective interaction matrix elements defined as follows:[28]

$$\begin{aligned}W_{ij}^{(k)}(\epsilon)&=\left\langle\Phi_i\left|\mathcal{V}\frac{Q^{(k)}}{\mathcal{E}-\mathcal{H}_N^{(0)}}\mathcal{V}\right|\Phi_j\right\rangle\\&=\left\langle\Phi_i\left|\mathcal{V}\frac{Q^{(k)}}{\epsilon-Z_N}\mathcal{V}\right|\Phi_j\right\rangle\ ,\end{aligned} \tag{15}$$

where $\mathcal{H}_N^{(0)}$ is a so-called normal product form of the Hückel Hamiltonian $\mathcal{H}^{(0)}$, Eq. (3), with respect to the reference state Φ_0[39,40], and Z_N is the normal product form of the one-electron part Z of the PPP Hamiltonian H, Eq. (7). Further, $Q^{(k)}$ designates a projector onto the subspace spanned by the k-times excited determinants relative to Φ_0.

As we pointed out in paper I (see also Ref. 14), both $\mathcal{V}_{ij}$ and $W_{ij}^{(2)}(\epsilon)$ can be simply evaluated using the two-body part of a standard doubly excited CI (D-CI) matrix. However, computation of $W_{ij}^{(k)}(\epsilon)$, $k=3,4$, requires the evaluation of perturbationlike expressions

$${}_{S_i}\left\langle\begin{matrix} r & s\\ a & b\end{matrix}\right|V_N\frac{Q^{(k)}}{\epsilon-Z_N}V_N\left|\begin{matrix}\bar r & \bar s\\ \bar a & \bar b\end{matrix}\right\rangle_{\bar S_i}\quad(k=3,4)\ ,$$

where V_N is the normal product form of the two-electron part of the Hamiltonian H, Eq. (7). In paper I we have shown that this can be most conveniently achieved by applying the diagrammatic approach[30] based on the graphical methods of spin algebras[41] and employing a Goldstone form for the two-electron interaction vertices.[39,40,42] Mathematical complexity of the resulting expressions is similar to the complexity of the second-order many-body perturbation theory (MBPT) formulas, although the number and variety of terms that we have to deal with is considerably larger.[28]

Solving Eq. (11) we find the OIP lower bounds to the eigenvalues of the operator $\mathcal{H}-\mathcal{E}_0^{(0)}$.[28] In order to find the lower bounds to the ground-state correlation energy of cyclic polyenes, we consider a new parameter

$$\Delta\mathcal{E}=\epsilon-\mathcal{V}_{00} . \tag{16}$$

It easily follows[28] that for every solution ϵ_k of Eq. (11), $\Delta\mathcal{E}_k$ given by Eq. (16) represents a lower bound to the corresponding eigenvalue of the electronic Hamiltonian H, Eq. (7), relative to the ground-state restricted Hartree-Fock (RHF) energy $E_0^{\rm RHF}$. We thus have

$$\Delta\mathcal{E}_k \equiv \epsilon_k-\mathcal{V}_{00} < \Delta E_k \equiv E_k - E_0^{\rm RHF} , \tag{17}$$

where $E_k=\mathcal{E}_k-\sum_{\mu,\nu(\mu<\nu)}\gamma_{\mu\nu}$ is the kth A_{1g}^- eigenenergy of H. In order to prove this fact one has to realize that Hückel molecular orbitals for cyclic polyenes are fully determined by the D_{Nh} or C_N symmetry, so that they simultaneously represent the RHF and Brueckner (maximum overlap) orbitals (cf., Sec. IV of paper I or Sec. II of paper II). Consequently, Φ_0 is identical with the RHF ground state and $E_0^{\rm RHF}=\langle\Phi_0|H|\Phi_0\rangle$. Inequality (17) thus implies that, subtracting $\mathcal{V}_{00}$ from the lowest root of Eq. (11), we obtain the OIP lower bound $\Delta E_0^{\rm OIP}$ to the correlation energy in the ground state of cyclic polyenes as described by the PPP model Hamiltonian $\mathcal{H}$, Eqs. (2)–(4), or its electronic counterpart H, Eq. (7).

To summarize, Eqs. (11)–(16) represent a set of working equations of the OIP approach. The main objective is to solve Eq. (11). This can be achieved by applying various numerical techniques for solving nonlinear equations. Simple iterative procedure, with the individual iterates oscillating about one of the roots ϵ_k, was suggested in Ref. 11. It employs the fact that $f(\epsilon)$, Eq. (12), is the bracketing function[5,6,8] for the Hamiltonian $\mathcal{H}'-\mathcal{E}_0^{(0)}$, where $\mathcal{H}'$ is the so-called intermediate Hamiltonian defined by

$$\mathcal{H}'=\mathcal{H}^{(0)}+\mathcal{V}' . \tag{18}$$

Here, $\mathcal{V}'$ is an inner projection[6,7] of the perturbation $\mathcal{V}$, Eq. (4), onto the manifold $\mathcal{M}_f^{(0)}=\mathcal{V}^{1/2}(\mathcal{M}_g^{(0)})$, where $\mathcal{V}^{1/2}$ denotes the positive square root of $\mathcal{V}$ (see paper I and references quoted therein for details). Thus, Hamiltonian (18) satisfies the inequality

$$\mathcal{H}'<\mathcal{H} , \tag{19}$$

and its eigenvalues $\mathcal{E}_k'$ can serve as lower bounds to the eigenvalues $\mathcal{E}_k$ of $\mathcal{H}$. The method of Ref. 11 is based on the iteration sequence $\epsilon_{k,m+1}=f(\epsilon_{k,m})$ $(m=0,1,\ldots)$, where the initial guess $\epsilon_{k,0}$ is the upper bound to ϵ_k. The sequence $\epsilon_{k,m}$ $(m=0,1,\ldots)$ converges to the lower bound ϵ_k, provided that

$$\left|\frac{df(\epsilon)}{d\epsilon}\right|<1$$

for every $\epsilon\in(\epsilon_k-\Delta\epsilon_k,\, \epsilon_k+\Delta\epsilon_k)$, where $\Delta\epsilon_k=|\epsilon_{k,0}-\epsilon_k|$. In view of the properties of the bracketing functions,[5,6,8] this implies that the initial guess $\epsilon_{k,0}$ lies on the same branch of $f(\epsilon)$ as does ϵ_k, and is sufficiently close to ϵ_k. We can take[11] $\epsilon_k^{\rm var}=\mathcal{E}_k^{\rm var}-\mathcal{E}_0^{(0)}$, where $\mathcal{E}_k^{\rm var}$ is the kth variational energy calculated in the basis $\{g_0,g_1,\ldots,g_M\}$, as an optimal choice for $\epsilon_{k,0}$, since this choice makes the whole procedure self-contained and transparent. In particular, $\epsilon_0^{\rm D\text{-}CI}\equiv\epsilon_0^{\rm var}=\Delta E_0^{\rm D\text{-}CI}+\mathcal{V}_{00}$, where $\Delta E_0^{\rm D\text{-}CI}$ is the D-CI ground-state correlation energy, is suggested to be chosen as initial guess $\epsilon_{0,0}$ in the calculation of the lowest root ϵ_0 of Eq. (11). We shall refer to this particular implementation of the OIP formalism as the D-OIP method. Unfortunately, the choice $\epsilon_{0,0}=\epsilon_0^{\rm D\text{-}CI}$ leads to serious convergence problems, particularly in the intermediately and strongly coupled regions. Thus, we must exploit higher-order procedures, specifically the Newton method, which is based on the iteration sequence

$$\epsilon_{k,m+1}=\epsilon_{k,m}-\left[\frac{df(\epsilon_{k,m})}{d\epsilon}\right]^{-1} f(\epsilon_{k,m}) , \tag{20}$$

as well as other, more powerful, root searching techniques, which are described in the next section.

Let us finally briefly mention the implications of the high symmetry of the studied models, already alluded to above. In addition to standard spin symmetry (implied by the spin independence of the PPP and Hubbard Hamiltonians), the cyclic polyene models possess relatively high spatial symmetry (D_{Nh}), so-called hole-particle (h-p) symmetry (implied by the use of the minimum basis set) and a very special alternancy symmetry, which is characteristic of the π-electron models of all alternant hydrocarbons.[15,36,38,43] In the implementation of the OIP method described in the next section, full advantage is taken of all these symmetries, which enables us to handle even fairly large cycles, such as $C_{22}H_{22}$. Indeed, this high symmetry significantly reduces the size of the matrix $\mathbf{A}(\epsilon)$, Eq. (13), which has to be constructed in order to evaluate the left-hand side of Eq. (11) [cf. Eq. (12)]. For example, the dimension of $\mathbf{A}(\epsilon)$ for $N=22$ reduces from 7382 (considering only spin symmetry) to 162 [for a more thorough discussion, see Sec. III of paper II and Ref. 21(a)]. However, this dimensional reduction is not the only benefit of the high symmetry of our models, since they also considerably simplify the OIP expressions themselves. Thus, the zero quasimomentum rule, which has to be satisfied by both the excited configurations and molecular integrals[21(a),29] as a consequence of the D_{Nh} or C_N symmetry, simplifies the explicit form of the expressions for the contributions $W_{ij}^{(3)}(\epsilon)$ and $W_{ij}^{(4)}(\epsilon)$, Eq. (15). According to the results of paper I,

$$W_{ij}^{(3)}(\epsilon)= \sum_{(x)=(a)}^{(h)} [R_{ij}^{(3)'}(x)+R_{ij}^{(3)''}(x)] \tag{21}$$

and

$$W_{ij}^{(4)}(\epsilon)= \sum_{(x)=(a)}^{(i)} R_{ij}^{(4)}(x) , \tag{22}$$

where $R_{ij}^{(k)}(x)$, $k=3,4$, are the algebraic expressions associated with Goldstone-Brandow orbital diagrams[30] given in Figs. 7–9 of paper I. Now, the zero quasi-momentum rule always eliminates one orbital summation in the expressions for $R_{ij}^{(k)}(x)$. In some cases, simplifications are even more drastic. As we have shown in Sec. III of paper II, $R_{ij}^{(3)''}(g)$ and $R_{ij}^{(3)''}(h)$ vanish altogether, while matrices $\mathbf{R}^{(3)'}(a)=\|R_{ij}^{(3)'}(a)\|_{1\le i,j\le M}$ and $\mathbf{R}^{(3)'}(b)=\|R_{ij}^{(3)'}(b)\|_{1\le i,j\le M}$ become diagonal. By applying the same reasoning, one can easily prove that the two other $\mathbf{A}(\epsilon)$-matrix contributions, namely, $\mathbf{R}^{(4)}(b) =\|R_{ij}^{(4)}(b)\|_{1\le i,j\le M}$ and $\mathbf{R}^{(4)}(c)=\|R_{ij}^{(4)}(c)\|_{1\le i,j\le M}$, become diagonal as well. We thus see that the high symmetry of cyclic polyene models greatly facilitates computations of the quantities ocurring in the OIP approach, similar to the cases of coupled cluster [cf. paper II and Ref. 21(a)], limited, and full CI[18,32,38] or MBPT[20] calculations.

III. LOWER BOUNDS TO THE GROUND-STATE CORRELATION ENERGY FOR $N=14$ CYCLIC POLYENE

In earlier papers[13,14] the OIP technique was applied to the first two members of the cyclic polyene homologous series. Results for the $N=6$ ring showed that OIP provides a very good lower bound to the ground-state correlation energy, not only for the spectroscopic value of β[13(a)], but over the entire range of the coupling constant.[13(b)] The maximum deviation of the OIP result from the exact one is only about 7% in this case, and in both weakly and fully correlated limits the OIP gives the exact result. However, for the $N=10$ cycle, the results are much less convincing.[14] Very good lower bounds are obtained only in the weakly correlated region and in the immediate vicinity of the $\beta=0$ limit. For the intermediate values of the coupling constant, including the region that corresponds to the spectroscopic parametrization, OIP provides rather poor results. Maximum error relative to the exact value of the correlation energy reaches almost 80% and is shifted towards larger negative β values in comparison with the $N=6$ case. In view of such a drastic difference between the $N=6$ and $N=10$ cases, it is difficult to draw a definite conclusion about the applicability of the OIP technique in general.

In this paper we consider the next three members of the cyclic polyene homologous series ranging from the medium sized $N=14$ cycle to the $N=22$ ring, whose general properties usually differ very little from an infinite $N\rightarrow\infty$ system.[23] We again investigate both PPP and Hubbard Hamiltonian models. In this section we shall concentrate on the results for the $N=14$ polyene, while $C_{18}H_{18}$ and $C_{22}H_{22}$ will be addressed in Sec. IV.

As usual [cf., Refs. 13(b), 14, 18, 20, 21, 23, and 29], we examine the entire range of correlation effects from the weakly correlated limit ($\beta\cong-5$ eV), where the independent-particle model provides quite an accurate description, to the fully correlated limit ($\beta=0$), where the interelectronic interactions completely govern the behavior of the system and we face a very demanding, highly degenerate situation, since the one-electron Hückel molecular orbital (HMO) levels, $\epsilon_m^{\mathrm{HMO}}$, as well as the exact ground state, become degenerate[21(a)] (for the Hubbard model, the RHF orbital levels become degenerate as well; for the PPP model, they become quasidegenerate, but the RHF highest-occupied–lowest-unoccupied molecular orbital (HOMO-LUMO) gap approaches zero with $N\rightarrow\infty$ as $(\ln N-1)/N$; cf., Refs. 29 and 44). In order to carry out the OIP calculations, we have written a special-purpose program exploiting all the available symmetries of the cyclic polyene model along the lines described in paper II and briefly outlined in Sec. II. Otherwise, examination of the $N\ge 14$ rings would be hardly feasible. For the same reason, we completely changed an earlier computational strategy that was used for the $N=6$ and 10 polyenes.[13,14] In the present scheme, matrix $\mathbf{A}(\epsilon)$, Eq. (13), is generated as in various coupled-cluster (CC) approaches involving triple excitations, e.g., CCDT-1,[28,45,46] perturbative estimate of triply excited contribution CCD+T(CCD),[46,47] and approximate coupled-pair theory with triple and quadruple excitations[28] (ACPTQ) (cf., paper II). In fact, we were able to use the existing codes for CCDT-1, CCD+T(CCD), and ACPTQ calculations on cyclic polyene systems[29] except for minor modifications.

The bracketing function $f(\epsilon)$, Eq. (12), which can also be written as

$$f(\epsilon)=\mathbf{v}^{T}\cdot[\mathbf{A}(\epsilon)]^{-1}\cdot\mathbf{v} , \tag{23}$$

where $\mathbf{v}$ is a one-column matrix with entries $\mathcal{V}_{j0}$, and its first derivative,

$$\begin{aligned}\frac{df(\epsilon)}{d\epsilon}&=\mathbf{v}^{T}\cdot\frac{d[\mathbf{A}(\epsilon)]^{-1}}{d\epsilon}\cdot\mathbf{v}\\ &=-\mathbf{v}^{T}\cdot[\mathbf{A}(\epsilon)]^{-1}\cdot\frac{d\,\mathbf{A}(\epsilon)}{d\epsilon}\cdot[\mathbf{A}(\epsilon)]^{-1}\cdot\mathbf{v} ,\end{aligned} \tag{24}$$

that is needed in Newton's scheme [see Eq. (20)] require a computation of the vector

$$\mathbf{y}(\epsilon)=[\mathbf{A}(\epsilon)]^{-1}\cdot\mathbf{v} . \tag{25}$$

In terms of this vector we have

$$f(\epsilon)=\mathbf{v}^{T}\cdot\mathbf{y}(\epsilon) , \tag{26}$$

$$\frac{df(\epsilon)}{d\epsilon}=-[\mathbf{y}(\epsilon)]^{T}\cdot\frac{d\,\mathbf{A}(\epsilon)}{d\epsilon}\cdot\mathbf{y}(\epsilon) . \tag{27}$$

We compute $\mathbf{y}(\epsilon)$ from the system $\mathbf{A}(\epsilon)\cdot\mathbf{y}(\epsilon)=\mathbf{v}$ by Gauss elimination. The derivative $d\,\mathbf{A}(\epsilon)/d\epsilon$ is then computed using an almost identical code as that used to evaluate the matrix $\mathbf{A}(\epsilon)$, except that the denominators must be squared. Indeed,

$$\frac{d[\mathbf{A}(\epsilon)]_{ij}}{d\epsilon}=W_{ij}^{(2)'}(\epsilon)+W_{ij}^{(3)'}(\epsilon)+W_{ij}^{(4)'}(\epsilon) , \tag{28}$$

where

TABLE I. Correlation energies (in eV) for the Hubbard Hamiltonian model of $C_{14}H_{14}$ for various values of the resonance integral β (in eV) ranging from the fully correlated ($\beta=0$) to the weakly correlated ($\beta=-5$ eV) limits. The correlation energies per electron are listed, in absolute value, as obtained with the following methods: optimized inner projection (OIP), configuration interaction limited to doubly excited configurations (D-CI), and the OIP iterative procedure,[11] in which the D-CI result is used as a starting guess (D-OIP). Exact correlation energies per electron, as obtained (Ref. 23) by solving the Lieb and Wu equations (Ref. 26), are given for a comparison. The percentage errors relative to, respectively, exact results (Ref. 23), correlation energies obtained with the approximate coupled pair many-electron theory corrected for the connected quadruply excited clusters (ACPQ) (Ref. 48) [see, Ref. 21(a)], and the results obtained with ACPQ method corrected for the connected triply excited clusters (ACPTQ) (Ref. 29), are given in parentheses. An asterisk indicates that for $\beta=0$ the ACPTQ result is not available (Ref. 29). NC designates that no convergence was obtained.

$-\beta$	Exact	OIP	D-OIP	D-CI
5.0	0.0853	0.0875	0.0875	0.0815
		(2.6;2.8;2.6)	(2.6;2.8;2.6)	(−4.5;−4.2;−4.5)
4.0	0.1071	0.2623	0.1119	0.0999
		(144.9;146.1;144.9)	(4.5;5.0;4.5)	(−6.7;−6.3;−6.7)
3.0	0.1442	0.5088	NC	0.1281
		(252.8;256.8;253.1)		(−11.2;−10.2;−11.1)
2.5	0.1747	0.6322	NC	0.1483
		(261.9;268.2;262.5)		(−15.1;−13.6;−15.0)
2.0	0.2220	0.7556	NC	0.1750
		(240.4;250.8;242.1)		(−21.2;−18.8;−20.8)
1.5	0.3032	0.8791	NC	0.2108
		(189.9;205.7;192.1)		(−30.5;−26.7;−30.0)
1.0	0.4555	1.0027	NC	0.2590
		(120.1;137.4;114.6)		(−43.1;−38.7;−44.6)
0.5	0.7424	1.1263	NC	0.3275
		(51.7;59.4;−7.1[a])		(−55.9;−53.7;−73.0[a])
0.0	1.25	1.25	NC	0.4217
		(0,0;0.0;*)		(−66.3;−66.3;*)

[a] The ACPTQ result for $\beta=-0.5$ eV is far from the exact value, so that the error relative to the ACPTQ is not meaningful.

TABLE II. Same as Table I for the PPP Hamiltonian model of $C_{14}H_{14}$. The exact correlation energies are not available except for $\beta=0$ (Ref. 18) and $\beta=-5$ eV (Ref. 52). Exact correlation energy per electron for $\beta=-5$ eV, as obtained with the full configuration interaction (F-CI) method, equals (Ref. 52) -0.1354 eV. The exact result for $\beta=0$ is (Ref. 18) -1.5149 eV. For -1.17 eV $<\beta<-0.07$ eV, ACPTQ results and consequently the corresponding percentage errors are not available (Ref. 29), as indicated by an asterisk.

$-\beta$	OIP	D-OIP	D-CI
5.0	0.2964	0.1331	0.1239
	(118.9;122.2;118.6)	(−1.7;−0.2;−1.8)	(−8.5;−7.1;−8.6)
4.0	0.5358	NC	0.1492
	(*;222.6;215.4)		(*;−10.2;−12.2)
3.0	0.7792	NC	0.1865
	(*;252.7;241.2)		(*;−15.6;−18.3)
2.5	0.9014	NC	0.2123
	(*;240.3;226.4)		(*;−19.9;−23.1)
2.0	1.0239	NC	0.2450
	(*;209.8;194.1)		(*;−25.9;−29.6)
1.5	1.1464	NC	0.2873
	(*;162.9;146.8)		(*;−34.1;−38.1)
1.0	1.2692	NC	0.3422
	(*;104.8;*)		(*;−44.8;*)
0.5	1.3920	NC	0.4142
	(*;45.3;*)		(*;−56.8;*)
0.0	1.5149	NC	0.5091
	(0.0;0.0;0.0)		(−66.4;−66.4;−66.4)

$$W_{ij}^{(k)'}(\epsilon)=\left\langle \Phi_i \left| \mathcal{V}\frac{Q^{(k)}}{(\epsilon-Z_N)^2}\mathcal{V} \right| \Phi_j \right\rangle . \quad (29)$$

The OIP results for the $N=14$ Hubbard Hamiltonian model are given in Table I, and for the more realistic PPP model in Table II. To facilitate the discussion, we include the percentage error relative to the exact correlation energy (in parentheses), wherever available, and relative to correlation energies obtained with approximate coupled-pair theory with connected quadruply excited clusters[48] (ACPQ) and ACPQ with connected triply excited clusters[28] (ACPTQ) schemes, whose performance was studied in detail in Ref. 21(a) and in paper II.[29] We recall that for $N \geq 14$ the exact energies over the whole range of the coupling constant were only determined[23] for the Hubbard Hamiltonian by solving the Lieb and Wu equations.[26] For the PPP Hamiltonian and $N \geq 14$, the exact correlation energies are only available for $\beta=0$ (Refs. 18 and 49) and for $\beta \rightarrow -\infty$, in which case the correlation energy approaches zero. Although the unitary group approach based algorithm of Zarrabian *et al.*,[50] as recently implemented for efficient operation on parallel vector computers,[51] allows us to carry out full CI (FCI) calculations for $N=14$ and, eventually, $N=18$, such calculations are computationally very demanding and, so far, have been carried out only for one value of $\beta=-5$ eV for the $N=14$ PPP model.[52] In contrast, ACPQ results are available for any $N \leq 34$ and any coupling constant for both PPP and Hubbard models.[21] This method provides an excellent remedy for the complete breakdown of standard coupled pairs theories, such as full CCD or its linear (L-CCD) version,[53] in the highly degenerate, strongly correlated region. The ACPTQ approximation, on the other hand, may suffer a singular behavior, as studied in detail in paper II of this series. However, the range of the applicability of the ACPTQ approach is sufficiently large and provides us with a meaningful source of information about the exact correlation energy values. Needless to say, whenever available, the ACPTQ results are closer to the exact data than the ACPQ ones,[29] even though the latter are already very good.[21]

In addition to the true OIP lower bounds corresponding to the lowest root of Eq. (11), we give results of the iterative D-OIP procedure,[11] in which the D-CI correlation energy (also listed) is used as a starting guess.

Results in Tables I and II indicate that simple D-OIP iterative procedure[11] is in most cases divergent. Even when it does converge (which happens only in the weakly coupled region), there is no guarantee that the resulting number is the lowest solution of Eq. (11). In fact, starting from the D-CI upper bound $\epsilon_0^{\text{D-CI}}$, we can converge to the OIP lower bound to one of the excited A_{1g}^- eigenvalues of the Hamiltonian $\mathcal{H}-\mathcal{E}_0^{(0)}$. Consequently, instead of the lower bound to the ground-state correlation energy, we can get the lower bound to one of the excited eigenenergies of the electronic Hamiltonian H, calculated relative to the ground-state RHF level E_0^{RHF}. This is indeed the case, e.g., for the PPP model of the $N=14$ ring with $\beta=-5$ eV. This lower bound may eventually become a lower bound to the ground-state correlation energy (cf., the Hubbard $N=14$ model for $\beta=-4$ eV), but this coincidence will only occur when Löwdin's "ordering theorem"[7(b)] is not satisfied and several eigenvalues of the intermediate Hamiltonian $\mathcal{H}'$, Eq. (18), are lower than the lowest eigenvalue of the Hamiltonian $\mathcal{H}$, Eqs. (2)-(4). For the Hubbard $N=14$ model with $\beta=-5$ eV this problem no longer arises (cf., Table I) and the D-OIP iterative procedure converges to the lowest root of Eq. (11), thus providing the true OIP lower bound to the ground-state correlation energy.

To overcome the convergence problems of the D-OIP iterative scheme, we have turned to Newton's method. Unfortunately, this technique is of little help, particularly when the initial guess $\epsilon_{0,0}=\epsilon_0^{\text{D-CI}}$ is employed. In some cases it only accelerates the convergence, without guaranteeing that we converge to the lowest solution of Eq. (11). We have also tested few higher-order versions of Newton's method, employing three or more terms of the Taylor-series expansion for $f(\epsilon)$, but none of these improvements proved useful.

Failure of the above schemes reflects a highly irregular behavior of the bracketing function $f(\epsilon)$. To illustrate this fact, we have plotted in Figs. 1(a)-1(c) the function

$$F(\epsilon)=f(\epsilon)-\epsilon , \quad (30)$$

whose zeros are the solutions of Eq. (11), for the PPP $N=14$ ring and two typical values of β ($\beta=-5$ and -2.5 eV). According to the properties of bracketing functions,[5,6,8] the function $F(\epsilon)$ consists of several continuous branches separated by vertical asymptotes, and every branch has a negative slope. In the $\epsilon \rightarrow -\infty$ limit, $F(\epsilon)$ varies as $-\epsilon$, since $\lim_{|\epsilon| \rightarrow \infty} f(\epsilon)$ is finite[5,6,8] [cf., Eqs. (12)-(15)]. Figures 1(a) and 1(b) show the behavior of $F(\epsilon)$ for $\epsilon \leq \epsilon_0^{\text{D-CI}}$. In view of a complicated nature of the function $F(\epsilon)$ for $\beta=-2.5$ eV [see Fig. 1(b)], the branches that are located in the neighborhood of the lowest root of Eq. (11) are shown in greater detail in Fig. 1(c).

The plots of Figs. 1(a)-1(c) clearly indicate that the number of singularities of the bracketing function $f(\epsilon)$ between the D-CI value of ϵ, $\epsilon_0^{\text{D-CI}}$, and the lowest solution of Eq. (11), ϵ_0, rapidly increases with decreasing $|\beta|$. This fact reflects an increasingly degenerate character of the spectrum of the intermediate Hamiltonian $\mathcal{H}'$ when we approach the strongly correlated region (cf. Sec. V). Thus, for the PPP $N=14$ ring and $\beta=-5$ eV, $f(\epsilon)$ has only two singularities when $\epsilon \leq \epsilon_0^{\text{D-CI}}$ [cf., Fig. 1(a)]. The D-CI value $\epsilon_0^{\text{D-CI}}$ is very close to ϵ_2 and lies on the same branch as ϵ_2, so that the D-OIP iterative procedure[11] converges and gives a lower bound to the energy of the second excited A_{1g}^- state. For $\beta=-4$ eV, however, there are already four singularities between ϵ_0 and $\epsilon_0^{\text{D-CI}}$, and more than 70 for the physical value of the coupling constant, $\beta=-2.5$ eV [cf., Fig. 1(b)]. For $|\beta| \leq 2$ eV, plots of $F(\epsilon)$ become so complex that it would be difficult to present them here. This dramatic increase in the number of singularities between ϵ_0 and $\epsilon_0^{\text{D-CI}}$ with decreasing $|\beta|$ must be associated with the monotonic increase in the distance between ϵ_0 and $\epsilon_0^{\text{D-CI}}$, which in turn results from the neglect of quadruply and higher excited configurations in the D-CI approach. Consequently,

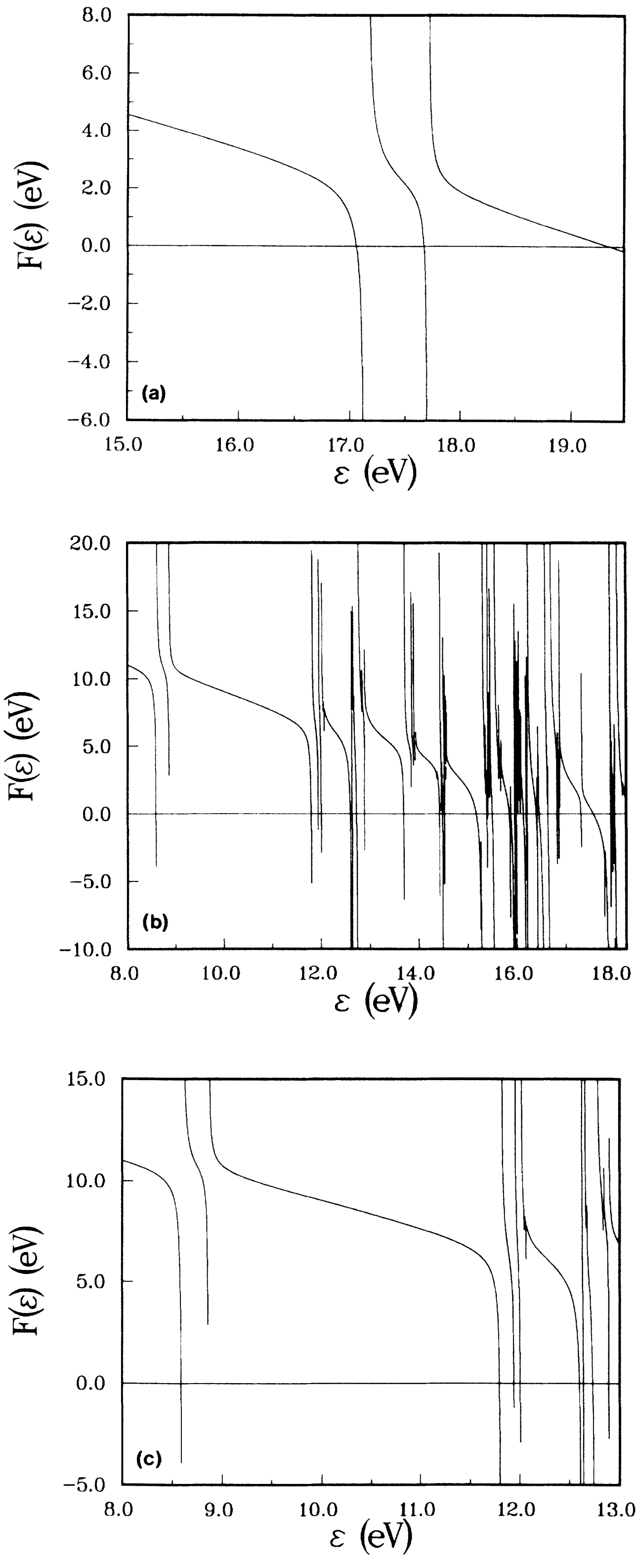

FIG. 1. Plot of the function $F(\epsilon)$, Eq. (30), for the PPP Hamiltonian model of $C_{14}H_{14}$ and two typical values of the resonance integral β, namely $\beta=-5$ eV (a) and $\beta=-2.5$ eV [(b) and (c)]. (a) and (b) show the function $F(\epsilon)$ for $\epsilon \leq \epsilon_0^{\text{D-CI}}$, where $\epsilon_0^{\text{D-CI}}$ is a D-CI value of the parameter ϵ calculated according to Eq. (16) (see text for details). The first few leftmost branches of the function $F(\epsilon)$ for $\beta=-2.5$ eV are presented in greater detail in (c).

D-CI is very ineffective in the strongly correlated region [e.g., for $N=14$, D-CI yields only 34% of the correlation energy in the fully correlated limit, and this fraction tends to zero with increasing N, cf., Refs. 21(a) and 29]. Indeed, Tables I and II indicate that the correlation-energy difference $|\Delta E_0^{\text{D-CI}}-\Delta E_0^{\text{OIP}}|$ monotonically increases when going from the weakly correlated region towards the fully correlated limit.

It is now clear why a straightforward application of both D-OIP and Newton's iterative methods encounters serious difficulties. The initial approximation $\epsilon_0^{\text{D-CI}}$ is simply too far away from the lowest OIP solution ϵ_0, so that the bracketing function $f(\epsilon)$ has numerous branches between ϵ_0 and $\epsilon_0^{\text{D-CI}}$. Obviously, these convergence problems may be overcome if we select a better initial guess $\epsilon_{0,0}$, which is in general not easy. We are faced, however, with another serious problem which must be overcome when using Newton's scheme, namely, we must prevent the possibility that the iterative procedure will jump from one branch of the bracketing function to another. To solve this problem, and thus to avoid the possibility of convergence to higher roots ϵ_k, we have developed and implemented an entirely different numerical procedure for solving Eq. (11). In this scheme, which is essentially a root-searching technique, we first check the local slope of the function $F(\epsilon)$, Eq. (30), in every iteration and decide whether to accept the result of the next Newton's iteration or to reject it. In the latter case, we intervene by taking an *a priori* selected step on the curve $F(\epsilon)$ towards smaller ϵ values. Although this semiautomatic procedure is, in principle, free from the basic shortcomings of D-OIP and Newton's methods, it still is not as fully reliable as one might hope. Due to the irregularity of shapes of different branches of the bracketing function [cf., Figs. 1(a)–1(c)], we found out that this procedure was often converging to higher solutions of Eq. (11) and that the risk of missing the lowest one was still present. For these reasons, we have finally decided to exploit the above described root-searching technique to proceed along the branches of $F(\epsilon)$ with sufficiently small (chosen *ad hoc*) steps in the lowering of ϵ. Only when we were absolutely certain that we had reached the leftmost branch and thus were in the immediate vicinity of the lowest solution of Eq. (11) did we activate Newton's method to find it. Clearly, this procedure has several disadvantages, be it its nonautomatic nature and the requirement to generate a large number (for $N=14$, hundreds) of points on the $F(\epsilon)$ curve. At the same time, special care must be exercised not to miss the lowest root ϵ_0, since for $\epsilon \leq \epsilon_0^{\text{D-CI}}$ many zeroes of $F(\epsilon)$ are nearly degenerate and in the neighborhood of ϵ_0, the function $F(\epsilon)$ is plagued with singularities, even for relatively large $|\beta|$ values corresponding to the intermediately coupled region [notice, for example, that the third leftmost branch of $F(\epsilon)$ has a very similar slope to the leftmost branch and that these two branches are separated by a branch which is very steep, so that one could misinterpret the third leftmost branch as the leftmost one and, consequently, confuse ϵ_2 with the lowest root ϵ_0; cf., Fig 1]. Unfortunately, this laborious procedure seems to be the only one which is fully reliable in the study of the $N=14$ polyene. We can, eventually, make is slightly less laborious (especially in the strongly correlated region) by proceeding along the curve $F(\epsilon)$ towards larger ϵ values, starting from the OIP lower bound for smaller value $|\beta|$, since (cf., Tables I and II)

$$\epsilon_0(\beta_1)<\epsilon_0(\beta_2) \quad \text{for } |\beta_1|<|\beta_2| \ . \qquad (31)$$

In addition, it can be proved that OIP provides exact correlation energy in the $\beta=0$ limit (see below), which is easily available[18,49] for both Hubbard and PPP models and any N. Nevertheless, proceeding towards larger ϵ values still requires generation of many points on the $F(\epsilon)$ curve, and we have to be extremely careful to make sure that the lower bound, which we have obtained, is the lowest solution of Eq. (11). Moreover, since we have to determine initially the OIP results for several smaller values of $|\beta|$, calculation of the OIP lower bounds for larger $|\beta|$ values is costly and time consuming. To eliminate the necessity of calculating first the OIP results for smaller $|\beta|$'s, we can use the fact that for any β, the inequality $\epsilon_0\geq 0$ holds, which is a consequence of the positive definiteness of $\mathcal{V}$ and the fact that ϵ_0 is the lowest eigenvalue[28] of $\mathcal{H}'-\mathcal{E}_0^{(0)}$ (for example, $\epsilon_0=0$ for $\beta=0$). However, except for very small values of $|\beta|$, ϵ_0 is a large positive number (cf., e.g., Fig. 1), so that again generation of numerous points on the curve $F(\epsilon)$ is required in order to obtain a single OIP value. Thus, using either method, the OIP technique is computationally intensive when applied to $N\geq 14$ polyenes. We emphasize that all the OIP lower bounds, given in Tables I and II, were obtained by the manual search for the lowest zero of the function $F(\epsilon)$.

Results shown in Tables I and II confirm very good performance of the OIP approach in the immediate vicinity of the fully correlated ($\beta=0$) limit, which was observed earlier for the $N=6$ and 10 cycles.[13(b),14] For $|\beta|\leq 0.5$ eV, OIP provides the lower bounds that are more accurate than the D-CI upper bounds (which are in fact rather poor). It is worth noting that the OIP formalism yields exact results for $\beta=0$. Explanation of this rather surprising phenomenon was given in Ref. 13(b). Unfortunately, the OIP lower bounds quickly deteriorate as we move towards larger $|\beta|$ values. In the weakly correlated limit ($|\beta|\rightarrow\infty$), where the correlation energy approaches zero, OIP results for the $N=14$ polyene are again very good. This is easy to understand, since the OIP procedure is correct up to the fourth order of perturbation theory.[14] Note, however, that already for $\beta=-4$ eV in the Hubbard case and for $\beta=-5$ eV in the PPP case, the error of the OIP correlation energies relative to the exact data exceeds 100%. The error further increases as we approach the intermediately correlated region, reaching its maximal value of about 260% around $\beta\cong -2.5$ eV for the Hubbard model and about 250% around $\beta\cong -3$ eV for the PPP model. Then, it gradually decreases as the strong coupling regime is approached. We must thus conclude that for $N=14$ polyene, OIP provides very poor estimates of the ground-state correlation energy for most of the resonance integral values considered. As Tables I and II indicate, they are usually much poorer than simple D-CI estimates.

Dependence of the percentage error of the OIP correlation energy on the resonance integral β for $N=14$, for both Hubbard and PPP models, is shown in Fig. 2. As already mentioned, exact (FCI) results are not available for the PPP model except for $\beta=-5$ eV (Ref. 52) and $\beta=0$.[18,49] We have thus used instead the ACPQ and ACPTQ correlation energies (the latter were interpolated across the interval -1.17 eV $<\beta<-0.07$ eV, where ACPTQ equations have no real solution). The comparison of the percentage errors relative to ACPQ, ACPTQ, and exact correlation energies for $N=14$ Hubbard model indicates (cf., Table I) that the ACPTQ results may be expected to be closer to the exact results than the ACPQ ones (cf., Ref. 29). In any case, both ACPQ and ACPTQ methods provide very good correlation energies, so that both error curves shown in Fig. 2 give good information about the real error curve for the PPP model of $C_{14}H_{14}$. This is also corroborated by the results for the Hubbard Hamiltonian model, since in this case the exact correlation energies are available for the entire range of the coupling constant.[23]

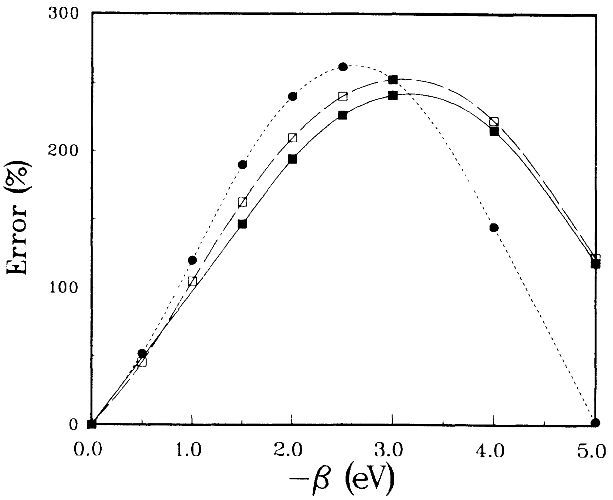

FIG. 2. Resonance-integral dependence of the percentage error of the OIP correlation energy for the Hubbard and PPP Hamiltonian models of $C_{14}H_{14}$. Solid circles (●) represent percentage errors of the OIP results for the Hubbard model, as calculated with respect to the exact correlation energies that were obtained (Ref. 23) by solving the Lieb and Wu equations (Ref. 26). Open and solid squares (□ and ■) represent percentage errors of the OIP results for the PPP model, as calculated relative to the ACPQ [Ref. 21(a)] and ACPTQ (Ref. 29) data, respectively. The corresponding short dashed, long dashed, and solid lines are a result of interpolation (see text for details).

We can thus conclude that the OIP approach encounters serious difficulties when employed for the medium-sized $N=14$ polyene. Problems encountered by the OIP method, when the extended ($N=18$ and 22) systems are examined, are briefly discussed in Sec. IV.

IV. APPLICATION OF THE OIP METHOD TO POLYENES $C_{18}H_{18}$ AND $C_{22}H_{22}$

Examination of the first three members of the cyclic polyene series, as reported in Refs. 13 ($N=6$) and 14

($N=10$), and in Sec. III ($N=14$), shows that difficulties encountered by the OIP approach dramatically increase with increasing N. Correspondingly, correlation energy estimates become poorer and poorer and the range of applicability of the OIP technique rapidly decreases with increasing N, so that already for $N=14$ polyene, reasonable correlation energy estimates can be obtained only for very large negative β values or in the immediate vicinity of the $\beta=0$ limit. Moreover, for $N=14$, the OIP technique becomes computationally very intensive, so that large computational effort is required just to obtain a single OIP result (especially to guarantee that the lowest root of Eq. (11) has been reached).

Our study of the $N=18$ and 22 cases only confirms these general trends. Although the core requirements are still rather small (thanks largely to the exploitation of all the available symmetries in our codes), calculations become very time consuming in view of a highly singular character of the bracketing function $f(\epsilon)$, even in the weakly correlated region. Again, hundreds of points on the $F(\epsilon)$ function curve have to be generated and it becomes increasingly difficult to ascertain that the lowest zero of $F(\epsilon)$ was reached. For these reasons, we present here only the results obtained with the D-OIP iterative scheme employing the D-CI upper bound ϵ value as a starting approximation. We use this approach, which we discussed above (Sec. III, also Refs. 13 and 14), in a kind of negative sense: clearly the convergence of the sequence $\epsilon_{0,m+1}=f(\epsilon_{0,m})$, $m=0,1,\ldots$; $\epsilon_{0,0}=\epsilon_0^{\text{D-CI}}$ does not guarantee that the lowest root of Eq. (11) has been reached, however, its divergence implies the highly singular character of the function $f(\epsilon)$ and, except for the immediate vicinity of $\beta=0$, it indicates that OIP will not provide a good estimate of the correlation energy.

A. Hubbard Hamiltonian model

For $\beta=-5$ eV and $N=18$, the D-OIP iterative method converges to -0.0868 eV for the correlation energy per electron. Exact and D-CI correlation energies per electron are in this case -0.0854 eV (Ref. 23) and -0.0804 eV,[21(a)] respectively. The D-OIP method is even convergent for $N=22$ at $\beta=-5$ eV. The resulting correlation energy per electron, designated as $\Delta E^{\text{D-OIP}}/N$, equals -0.0917 eV. For a comparison, exact and D-CI values are -0.0855 eV (Ref. 23) and -0.0794 eV,[21(a)] respectively. However, the convergence rate of the sequence $\epsilon_{0,m+1}=f(\epsilon_{0,m})$, $m=0,1,\ldots$; $\epsilon_{0,0}=\epsilon_0^{\text{D-CI}}$ is in this case very slow (60 iterations are required to achieve a seven-figure accuracy for the total correlation energy). This suggests that the absolute value of the derivative $df(\epsilon)/d\epsilon$ is close to 1 for $\epsilon\in(\epsilon^{\text{D-OIP}}-\Delta\epsilon^{\text{D-OIP}}, \epsilon^{\text{D-OIP}}+\Delta\epsilon^{\text{D-OIP}})$, where $\Delta\epsilon^{\text{D-OIP}}$ designates the distance between $\epsilon_0^{\text{D-CI}}$ and $\epsilon^{\text{D-OIP}}$, $\epsilon^{\text{D-OIP}}$ being the ϵ value corresponding to $\Delta E^{\text{D-OIP}}$ ($\epsilon^{\text{D-OIP}}=\Delta E^{\text{D-OIP}}+\mathcal{V}_{00}$), although it must be less than 1 to assure the convergence. This means that Newton's iterative method with the initial guess $\epsilon_{0,0}=\epsilon_0^{\text{D-CI}}$ should converge to $\epsilon^{\text{D-OIP}}$ very rapidly. Indeed, we have found that only four of Newton's iterations are needed to achieve the seven-figure accuracy.

Although for $\beta=-5$ eV and $N=18$ and 22, D-OIP iterative method provides correlation energies which are lower bounds to exact values, there is no guarantee that they are true OIP lower bounds corresponding to the lowest root of Eq. (11) (cf., e.g., the $N=14$ Hubbard model with $\beta=-4$ eV). Most likely, this is not the case. For example, the correlation energy, which we found for $\beta=-5$ eV and $N=18$ (-0.0868 eV per electron) seems to be too good in light of the OIP results for the same β value and $N=6-14$ [the percentage error of this result is 1.6% and must be compared with results for $N=6$ and 10 of Refs. 13(b) and 14, respectively, and those in Table I]. Indeed, we found that there exist at least three solutions of Eq. (11) which give lower values of the correlation energy per electron than $\Delta E^{\text{D-OIP}}/N=-0.0868$ eV (-0.1234, -0.1280, and -0.1286 eV) and, consequently, much larger percentage errors (44.5%, 49.9%, and 50.6%, respectively). For $\beta=-5$ eV and $N=22$, the situation is similar, which means that again $\Delta E_0^{\text{OIP}}<\Delta E^{\text{D-OIP}}$. In this case, however, even the better lower bound $\Delta E^{\text{D-OIP}}/N=-0.0917$ eV is less accurate than the upper bound provided by D-CI, so that the answer to the question of whether $\Delta E^{\text{D-OIP}}$ equals ΔE_0^{OIP} is not as relevant as it is for $N=18$.

For $\beta=-4$ eV, the D-OIP iterative procedure diverges for both $N=18$ and $N=22$ Hubbard models. Of course, the situation gets only worse as we move towards smaller $|\beta|$ values.

B. PPP Hamiltonian model

For both $N=18$ and 22 rings, the simple D-OIP iterative procedure employing $\epsilon_0^{\text{D-CI}}$ as a starting value does not converge in the whole range of the coupling constant considered in this paper, including the weakly correlated $\beta=-5$ eV limit. In view of the results for $N=6-14$ [cf., Tables I and II and Refs. 13(b) and 14] and $N=18$ and 22 Hubbard models (see Sec. IV A), the OIP estimates of the ground-state correlation energy are very poor for the PPP model of $N\geq 18$ polyenes, even for large $|\beta|$ values corresponding to the weakly coupled region. The fact that OIP provides exact correlation energies in the $\beta=0$ limit for any N is of little use here, since the OIP technique immediately deteriorates when we move away from $\beta=0$, as the results for $N=10$ (cf., Ref. 14) and $N=14$ (cf., Sec. III) rings convincingly demonstrate.

V. DISCUSSION

The study of lower bounds to energy eigenvalues is one of the most fundamental and challenging problems to have captured the attention of scientists since the early days of quantum theory (see, e.g., Refs. 1–12, in particular Ref. 10 and references therein; see also Ref. 54). Undeniably, the determination of lower bounds is much more difficult than the calculation of upper bounds that is based on a standard variation principle. Consequently, at the *ab initio* level, the attempts to determine accurate lower bounds were so far limited to at most two and three-electron systems.[10] A closer examination of simple model Hamiltonians is thus essential in order to achieve a better understanding of the difficulties arising in *ab initio* cases.

A study of cyclic polyenes C_NH_N, $N=2n=4\nu+2$, $\nu=1,2,\ldots$, as described by the PPP and Hubbard model Hamiltonians, provides us with a unique opportunity to find out precisely the limits of applicability of the lower-bound techniques, such as the OIP approach, to the many-electron correlation problem, and the type of difficulties one is going to face when larger systems, particularly those with quasidegenerate ground states, are considered. The attractiveness of the cyclic polyene model lies in its simplicity and high symmetry, in the availability of exact solutions, as well as in the possibility to vary continuously the magnitude of correlation effects and to achieve a transition from finite to extended systems. Another important feature of this model, which makes the application of the OIP technique possible, is that the corresponding PPP and Hubbard Hamiltonians automatically split into the exactly solvable unperturbed part and the positive definite electrostatic perturbation. Although similar decomposition of *ab initio* many-electron Hamiltonians may be in principle achieved by applying a sufficiently large constant shift, which would then be subtracted when the final results are obtained, such a shift would most likely loosen the OIP lower bounds beyond the acceptable level. Finally, the cyclic polyene model, like all metalliclike systems, represents one of the most demanding correlation problems. The explicit cluster analysis of the exact wave function[18] shows, for example, that higher-order excitations, especially even-number-of-times-excited higher than triply excited connected cluster components, such as the quadruply excited T_4 clusters, must be taken into account when the highly degenerate, strongly correlated region is approached. This must be done, at least in an approximate manner [as is done, e.g., in approximate CC schemes of the ACP type,[55] also referred to as the ACCD (Ref. 56) or ACPQ (Ref. 48) approaches], since the commonly used pair approximations, such as the full CCD approach, or its various versions accounting for the triples [CCDT-1, CCD+T(CCD)], in which T_4 clusters are neglected, completely break down in the strongly coupled region.[21,29,44] The importance of the highly excited configurations only increases with N, so that several other approaches, which are normally very successful for finite systems, like finite-order MBPT, limited CI, unrestricted Hartree-Fock (UHF) method, or (alternant molecular orbital (AMO) method[16(b)] are also plagued with fundamental difficulties when applied to the PPP and Hubbard cyclic polyene models [for a more thorough discussion and references, see Sec. VII of paper II and Ref. 21(a)]. Thus, application of the OIP technique to these models is a very severe test for the OIP formalism.

In this paper we focused our attention on large cyclic polyenes with $N=14$, 18, and 22 sites, thus complementing our earlier study of smaller $N=6$ and 10 rings,[13,14] which showed a definite promise of the OIP to provide satisfactory correlation-energy estimates over a broad range of the coupling constant. The results of this study clearly indicate, however, that the OIP technique, employing a linear span of Φ_0 and all the singly and doubly excited configurations as the manifold $\mathcal{M}_g^{(0)}$, is not capable of providing reasonable lower bounds to the ground-state correlation energy for extended $N\geq 14$ systems. Except for very small ($\beta\approx 0$) and very large ($\beta\rightarrow-\infty$) resonance-integral values, resulting lower bounds are too loose to serve as a meaningful source of information, in spite of the large computational effort that is required to obtain them. Indeed, the OIP estimates of the correlation energy for $N\geq 14$ are usually much worse than their simple D-CI counterparts, not to mention very good estimates provided by the approximate CC schemes, such as ACPQ (Ref. 21) or ACPTQ.[29]

Comparison of the results for $N\geq 14$ with those for $N=6$ and 10 (Refs. 13 and 14) indicates that the maximum error peak in the plot of the OIP correlation energies as a function of the coupling constant becomes broader and broader with increasing polyene size, so that the range of applicability of the OIP approach decreases with increasing N. The size of the maximal error also rapidly increases with N and moves towards larger $|\beta|$ values. Results for the $N=14$ ring also confirm our earlier observation[13,14] that the maximal error for the PPP model is slightly shifted towards the weakly coupled region relative to the Hubbard model.

The failure of the OIP method to provide good correlation-energy estimates for extended systems might be related with a possible lack of size extensivity of this procedure. This indeed would seem to be the case, in view of the fact that the OIP formalism is reminiscent of the Brillouin-Wigner rather than of the Rayleigh-Schrödinger perturbation theory. However, we are unable to make a definite conclusion concerning the size extensivity, or the lack of it, of the OIP method.

We must thus conclude that the applicability of the OIP technique for the determination of the lower bounds to the correlation energy is restricted to rather small (≤ 10 electron) systems. We must recall, however, that Löwdin's IP method[7] as well as its optimized version[11] were originally designed to provide the lower bounds to the eigenvalues of the total Hamiltonian [such as $\mathcal{H}$, Eqs. (2)–(4)], rather than to the correlation energy. Total-energy eigenvalues are, of course, much larger quantities than the correlation energies, so that lower bounds to the eigenenergies $\mathcal{E}_k$, as provided by the OIP technique, remain quite accurate even when the results for the correlation energies are relatively poor. Moreover, since there is no analog of the variation principle for the lower bounds, lower-bound to the ground-state correlation energy can be any real number belonging to an infinite range between $-\infty$ and the exact value. In the case of the OIP technique, we can eventually write

$$\mathcal{E}'_k \geq \mathcal{E}_k^{(0)} , \tag{32}$$

which for the ground state ($k=0$) gives $\epsilon_0\geq 0$ or [cf., Eq. (16)]

$$\Delta E_0^{\mathrm{OIP}} \equiv \Delta\mathcal{E}_0 \geq -\mathcal{V}_{00} , \tag{33}$$

but, as we have seen in Sec. III, this boundary condition is practically useless. Consequently, even very limited CI calculations can provide us with better correlation energies (i.e., closer to the exact result) than very sophisticated OIP considerations. We must not forget, however, that although the OIP produces poor correlation-energy estimates for medium-sized and extended systems, it has considerable potential to provide rather good lower bounds to the total-energy eigenvalues, as the calculations for simple one-particle systems, such as anharmonic oscillator or hydrogen atom in magnetic field, convincingly illustrate.[11,12]

We have seen in Sec. III (cf. Fig. 1), that the eigenvalues of the intermediate Hamiltonian $\mathcal{H}'$, Eq. (18), in terms of which the OIP technique is defined (cf., paper I), are highly degenerate, even in the region of weak correlation, where the eigenvalues of the Hamiltonian $\mathcal{H}$, Eqs. (2)–(4), are well separated. This is certainly the source of the problems for an application of the OIP method to cyclic polyenes, especially when $N \geq 14$. To overcome these problems and to obtain better estimates of the correlation energy, it would be necessary to enlarge the manifold $\mathcal{M}_g^{(0)}$, Eqs. (9) and (10), and to include higher excitations (mainly tetraexcitations) in $\mathcal{M}_g^{(0)}$ as well. Unfortunately, this is hardly feasible, at least in the near future, in view of a large number of triply and quadruply excited configurations for large N's, even at the orthogonally spin-adapted level. Thus, it seems that the most feasible method providing us with at least approximate lower bounds will have to rely on some kind of interpolation scheme. For the systems treated in this paper, the most convenient interpolation would be that by polynomial roots.[57] This method could be modified by replacing the exact values of the derivatives by their lower-bound estimates in both $\beta=0$ and $\beta \to -\infty$ limits. In this way we can hope to obtain reasonable lower bounds to the ground-state correlation energy even for intermediate values of the coupling constant.

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