Theor Chem Acc (2000) 104:426–438
DOI 10.1007/s002140000169

Theoretical
Chemistry Accounts

Regular article

Dressed coupled-electron-pair-approximation methods for periodic systems

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Received: 28 August 1999 / Accepted: 5 March 2000 / Published online: 21 June 2000

Abstract. The techniques of matrix dressing for configuration-interaction (CI)-type or coupled-electron-pair-approximation (CEPA)-type correlation treatments are reviewed with respect to the application to periodic systems. All methods ranging from canonical second-order Møller–Plesset perturbation theory over CI of single and double excitation, CEPA-0 or the averaged-coupled-pair-functional to self-consistent size-consistent CI can be formulated completely equivalently as an eigenvalue problem or as a solution to a system of linear equations. The size consistency of each method is obtained in a natural way, and invariance under orbital rotations is clearly assessible. A remark on the size consistency of the Davidson correction is presented. Additionally, the direct generation of localized Hartree–Fock orbitals as basic ingredients for the correlation calculations are addressed, as well as selected results on ring molecules, polymers, and 3D cubic beryllium as a model crystal.

Key words: Periodic systems – Correlation – Dressing – Size consistency

1 Introduction

Quantum chemistry has been able to deal with the electron correlation problem for a long time, overcoming the limitations given by a single Hartree–Fock reference wave function towards a description of the true many-body system. At least when addressing small molecules, a vast arsenal of methods is available, implemented in standard program packages. The situation is much different in the case of infinite periodic systems, where solid-state physics relies on density functional theory or the use of model Hamiltonians, such as the spin models (Heisenberg or Ising Hamiltonian) or the Hubbard model. Only recently has serious effort been made to introduce the known quantum chemical methods for periodic systems – polymers, surfaces, and crystals – to go beyond the one-electron picture. Hartree–Fock theory within periodic boundary conditions, together with the commonly employed linear algebra, was formulated long ago [1, 2], and powerful implementations, such as CRYSTAL [3], are available to obtain a Hartree–Fock wave function expanded in Gaussian basis functions, in complete analogy to basic quantum chemical codes for studies on molecules. Electron correlation may be accounted for by means of density functionals [4] or by calculating correlation contributions of small increments, obtained from adequate molecular setups [5, 6]. The incremental approach rests strongly on the hypothesis that the electron correlation is in general of short-range nature.

The same hypothesis can be taken as a basis for a correlation treatment entirely within the periodic-system approach. Furnished with a set of sufficiently localized orbitals, the individual contribution in the incremental expansion can be looked for and summed up in a straightforward manner. Additionally, quantum chemical correlation schemes can be applied directly when respecting two basic aspects: the summation of contributions may be truncated somewhere in space and the correlation energy per unit cell is calculated directly, not the correlation energy for a large setup, which will be divided in a later step by the number of unit cells involved in the actual calculation. As can be deduced from the literature, the modern linear-scaling methods for molecules [7] should also be able to furnish a correlation energy per unit cell with manageable effort.

The purpose of this article is to present a language and some aspects of up-to-date single-reference correlation methods when adapting them to periodic boundary conditions. The construction of localized orbitals is recalled briefly in the next section, then configuration interaction of single and double excitations (CISD) and the coupled-electron-pair-approximation (CEPA) in its simplest form (CEPA-0) are introduced as basic schemes for the electron correlation problem

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beyond perturbation theory. The articles by Kutzelnigg [8], for the discussion of the correspondence of these two methods Paldus et al. [9], and the more recently published work of Meissner and Szalay and coworkers [10], may serve as references. As a slightly different access to the methods, dressing of the Hamiltonian matrix involved permits access to all kinds of methodological variations up to coupled-cluster theory of single and double excitations (CCSD) [11]. That the individual methods are applicable to solids has been shown in the literature [12, 13] as well; however, the present formulation within dressing techniques may shed some new light on the situation and existing implementations.

Canonical second-order Møller–Plesset perturbation theory (MP2) is introduced as a small modification of the procedure and the result on the behavior of Davidson's correction to the CISD correlation energy is discussed. Some results on model ring systems, polymers and a 3D crystal are shown as applications of the working scheme and conclude the article.

2 Generating localized Hartree–Fock orbitals

In order to employ a quantum chemical correlation scheme for a fragment of a molecule or the unit cell of a periodic system, one of the basis ingredients is a set of localized Hartree–Fock orbitals. It should, however, be mentioned that the work of Sun and Bartlett [14] opens an alternative way to the correlation problem in periodic systems, relying entirely on the set of canonical Hartree–Fock orbitals, i.e. the Bloch picture of the one-electron theory.

Furthermore, two branches of development can be distinguished. On one hand, local correlation methods may invoke the full set of Hartree–Fock orbitals, the occupied space and the virtual space. This is the strategy followed as a basis for the present work. Large saving can be achieved, on the other hand, by restricting the virtual space either to well-adapted virtual orbitals, for instance, the so-called pair natural orbitals [12, 15], or by using simply the set of (nonorthogonal) atomic orbitals. The basis of the latter has to be reduced for the presence of the occupied molecular orbitals, but their degree of localization may be a good counterweight of the more complex algebra involved [16]. Thus, in these schemes Hartree–Fock orbitals are used only to represent the occupied space, as is also the intention of the recently proposed localization scheme of Marzari and Vanderbilt [17] or the construction scheme of Shukla and co workers [18].

In the approach employed for the construction of localized orbitals in the present case, the virtual space is indispensable, for the following reason: the procedure starts from highly localized guess orbitals and relies on a self-consistency loop with three steps orthogonalization, construction of a Fock matrix and diagonalization of a simplified CI matrix, built from singly excited determinants. Convergence is achieved when Brillouin's theorem is fulfilled, i.e. the interaction of the reference wave function with mono-excited wave functions vanishes:

$$\langle \Phi_0 | \mathbf{H} | \Phi_i^a \rangle = 0 \ . \tag{1}$$

For the description of a monoexcitation, a notion is needed of what a virtual orbital may be. This can be either the (reduced) set of nonorthogonal atomic basis functions, which leads to the quite complex nonorthogonal CI algebra [19, 20], or it may be a set of orthogonalized guess orbitals. The orthogonalization step, in the iteration scheme employed, is, therefore, organized in a hierarchical manner, in orthogonalizing first the occupied molecular orbitals among themselves, then projecting out the occupied space from the orbitals designed to be virtuals and, last, orthogonalizing the virtual orbitals among themselves. For the first and third step, the symmetric Löwdin orthogonalization with $\mathbf{S}^{-1/2}$ is used, since this preserves the individual functions as much as possible.

This procedure has been presented in the literature several times already [21–23], and some more details of an implementation for ring systems can be found in Ref. [24]. One of the major drawbacks lies in the difficulties of orthogonalizing the virtual orbitals among themselves, in particular when studying infinite periodic systems, where orthogonalization tails may become rather long-ranged. For the present study, where some aspects of the correlation problem address near-metallic systems, most of the work is carried out on ring systems, where the orthogonalization can be performed exactly within nontruncated and still finite matrices.

3 Electron correlation schemes

The simplest correlation schemes, also applicable to periodic systems, are given by perturbation theory. The partition of the full Hamiltonian into its contributions from the Fock matrix and a perturbation (Møller–Plesset) or into the diagonal part of the full Hamiltonian $|\Phi_I\rangle\langle\Phi_I|\mathbf{H}|\Phi_I\rangle\langle\Phi_I|$ and a perturbation (Epstein–Nesbet) has been discussed elsewhere [25]. In the present work, schemes beyond perturbation theory are addressed, coming, on one hand, from the variational CI approach and, on the other hand from the a priori size-consistent coupled-cluster ansatz. In the literature, the connections between the two extreme points of view have been the subject of numerous publications [8–10] and can be used in the present context as the general view on the different methods is completely independent of whether the type of system studied is molecular or periodic. Therefore, the general statements of this section are useful for both types of systems. The notation employed is that for a ring system, made of N equal unit cells; thus, a molecule will be the special case of a one-cell ring and a polymer will be the limit towards an infinite number of cells. Note, that going to infinite 3D systems will not alter the logic, only the connectivity of the unit cells and, especially, the number of neighboring cells changes. Since in any dimension cell indices can be enumerated linearily, one still can speak of a cell $i+1$ when regarding a cell i. Cell $i+1$, however, is not necessarily a neighboring cell of cell i.

Atomic orbitals, $\chi_\alpha^{\vec{g}}(\vec{r})$, centered in respective cells, $\vec{g}$, serve as basis functions. Molecular orbitals are indexed

with roman letters and are also centered in cells – as in the Wannier picture of one-electron orbitals:

$$\phi_i^{\vec{g}}(\vec{r}) = \sum_{\alpha,\vec{h}} c_{\alpha i}^{\vec{h}} \chi_\alpha^{\vec{g}+\vec{h}}(\vec{r}) = \sum_{\alpha,\vec{h}} c_{\alpha i}^{\vec{h}-\vec{g}} \chi_\alpha^{\vec{h}}(\vec{r}) \quad . \tag{2}$$

Matrix elements of totally symmetric operators, **A**, will be translationally invariant in atomic orbitals or molecular orbitals:

$$\langle \chi_\alpha^{\vec{g}} | \mathbf{A} | \chi_\beta^{\vec{h}} \rangle = \langle \chi_\alpha^{\vec{0}} | \mathbf{A} | \chi_\beta^{\vec{h}-\vec{g}} \rangle = \mathrm{A}_{\alpha\beta}^{\vec{h}-\vec{g}}$$
$$\langle \phi_i^{\vec{g}} | \mathbf{A} | \phi_j^{\vec{h}} \rangle = \langle \phi_i^{\vec{0}} | \mathbf{A} | \phi_j^{\vec{h}-\vec{g}} \rangle = \mathrm{A}_{ij}^{\vec{h}-\vec{g}}$$

Finally, the Hartree–Fock reference determinant is Φ_0, and excited determinants are labelled as

$$\Phi_i^{\mathrm{a}},\ \Phi_{ij}^{\mathrm{ab}}, \ldots \quad \text{or} \quad \Phi_{\vec{i}^{\vec{i}}}^{a^{\vec{a}}},\ \Phi_{\vec{i}^{\vec{i}}\,\vec{j}^{\vec{j}}}^{a^{\vec{a}}b^{\vec{b}}}, \ldots \quad , \tag{3}$$

where a double index $\vec{i}^{\vec{i}}$ means orbital i located in cell $\vec{i}$ and lower and higher indices stand for occupied and virtual molecular (spin) orbitals, respectively.

Introducing electron correlation means, in the quantum chemical sense, finding a linear combination of Hartree–Fock reference and excited determinants,

$$\Psi = \Phi_0 + \sum_{(\vec{i}\vec{i})(a\vec{a})} c_{\vec{i}^{\vec{i}}}^{a^{\vec{a}}} \Phi_{\vec{i}^{\vec{i}}}^{a^{\vec{a}}} + \sum_{(\vec{i}\vec{i})(\vec{j}\vec{j})(a\vec{a})(b\vec{b})} c_{\vec{i}^{\vec{i}}\,\vec{j}^{\vec{j}}}^{a^{\vec{a}}b^{\vec{b}}} \Phi_{\vec{i}^{\vec{i}}\,\vec{j}^{\vec{j}}}^{a^{\vec{a}}b^{\vec{b}}} \quad , \tag{4}$$

which minimizes the total energy, in this expansion within the space of maximally doubly excited determinants. This leads to the CI method and a matrix eigenvalue problem to determine the expansion coefficients, c_I. Matrix elements are the elements of the Hamilton matrix, **H**, taken in the basis of the determinants, i.e. $H_{IJ} = \langle \Phi_I | \mathbf{H} | \Phi_J \rangle$. Taking into account the periodic structure of the underlying system the number of unique determinants can be reduced, since it should not matter whether an excitation starts in cell $\vec{g}$ and ends in cell $\vec{g}+\vec{h}$ or if it starts in the reference cell and ends in cell $\vec{h}$; the first index of each coefficient can be held in the reference cell, the other being taken as relative to the reference unit cell. Therefore the matrix elements are reducible in the sense that, for instance,

$$\langle \Phi_0 | \mathbf{H} | \Phi_{\vec{i}^{\vec{i}}}^{a^{\vec{a}}} \rangle = \langle \Phi_0 | \mathbf{H} | \Phi_{\vec{i}^{\vec{0}}}^{a^{\vec{a}-\vec{i}}} \rangle = H_{0(ia\vec{a}-\vec{i})} \tag{5}$$

and

$$\langle \Phi_{\vec{i}^{\vec{i}}}^{a^{\vec{a}}} | \mathbf{H} | \Phi_{\vec{j}^{\vec{j}}}^{b^{\vec{b}}} \rangle = \langle \Phi_{\vec{i}^{\vec{0}}}^{a^{\vec{a}-\vec{i}}} | \mathbf{H} | \Phi_{\vec{j}^{\vec{j}-\vec{i}}}^{b^{\vec{b}-\vec{i}}} \rangle = H_{(ia\vec{a}-\vec{i}),(jb\vec{b}-\vec{j})}^{\vec{j}-\vec{i}} \quad . \tag{6}$$

The same simultaneous shift of all determinantal indices in matrix elements applies, of course, to higher excited determinants.

Writing in a shorthand notation 0 for the reference and 1 for lower index for the ensemble of excited determinants, the general eigenvalue problem for a finite system

$$\begin{pmatrix} 0 & H_{01} \\ H_{01}^\dagger & H_{11} \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = E_{\mathrm{Corr}} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} \tag{7}$$

can be written for the periodic system with cell indices and the use of the translational invariance as

$$\begin{pmatrix} 0 & H_{01} & H_{01} & H_{01} & \cdots \\ H_{01}^\dagger & H_{11}^0 & H_{11}^1 & H_{11}^2 & \cdots \\ H_{01}^\dagger & H_{11}^{(-1)} & H_{11}^0 & H_{11}^1 & \cdots \\ H_{01}^\dagger & \vdots & \vdots & H_{11}^0 & \\ \vdots & \vdots & \vdots & & \ddots \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ c_1 \\ c_1 \\ \vdots \end{pmatrix} = E_{\mathrm{Corr}} \begin{pmatrix} c_0 \\ c_1 \\ c_1 \\ c_1 \\ \vdots \end{pmatrix} . \tag{8}$$

The same eigenvalue problem can be recast in a smaller one, by introducing the number of cells – in the underlying ring problem – and by arranging for a still hermitean matrix through the introduction of $\sqrt{N}$:

$$\begin{pmatrix} 0 & \sqrt{N} H_{01} \\ \sqrt{N} H_{01}^\dagger & H_{11}^0 + H_{11}^1 + \cdots \end{pmatrix} \begin{pmatrix} c_0 \\ \sqrt{N} c_1 \end{pmatrix} = E_{\mathrm{Corr}} \begin{pmatrix} c_0 \\ \sqrt{N} c_1 \end{pmatrix} . \tag{9}$$

From this it is directly clear that the truncated CI approach can never be size-consistent. It should be remarked that the factor $\sqrt{N}$ only enters the first row and the first column of the matrix, and thus, the interaction of the reference determinant with excited determinants and the coefficients of the excited determinants. The part of the matrix concerning excited determinants only is not affected by the system size beyond the range of the summation of the contributions. This point will become essential when going to dressing techniques and the CEPA-derived methods.

3.1 CEPA-0 as a basic alternative to CI

Besides perturbation theory and the variational CI approach, the coupled-cluster ansatz is one of the basic approaches to the correlation problem. The wavefunction is written as an exponential excitation operator acting on the Hartree–Fock reference determinant:

$$\Psi = \mathrm{e}^S \Phi_0 \quad , \tag{10}$$

with S commonly being the combination of single and double excitations

$$S = \sum_{(\vec{i}\vec{i})(a\vec{a})} t_{\vec{i}^{\vec{i}}}^{a^{\vec{a}}} a_{(i,\vec{i})} a_{(a,\vec{a})}^\dagger + \sum_{(\vec{i}\vec{i})(\vec{j}\vec{j})(a\vec{a})(b\vec{b})} t_{\vec{i}^{\vec{i}}\,\vec{j}^{\vec{j}}}^{a^{\vec{a}}b^{\vec{b}}} a_{(i,\vec{i})} a_{(j,\vec{j})} a_{(a,\vec{a})}^\dagger a_{(b,\vec{b})}^\dagger \quad . \tag{11}$$

Projection of the Schrödinger equation, $\mathbf{H}\Psi = E\Psi$, against the reference determinant yields one equation for the correlation energy, and the projection against the set of excited determinants leaves a system of nonlinear equations in the amplitudes, t. t can be related to the coefficients, c_1, of the expansion of the wavefunction in

the common determinantal expansion (Eq. 4). Since for the correlation energy only the coefficients of the double excitations are of interest, it is sufficient to determine these from the coupled-cluster equations. Disregarding now all the nonlinear terms, one arrives at the linearized coupled-cluster method (LCCD), which can be equivalently derived from perturbation theory in double excitations or the interaction of electron pairs with reduced interpair coupling (CEPA-0). For the interested reader the details of the different derivations can be found in the literature [26, 27].

The essential difference of the CI and the CEPA approaches lies in the fact that for CEPA-0 an eigenvalue problem is not obtained, but a system of linear equations has to be solved. This reads in the notation for the ring system, with the wavefunction in intermediate normalization ($c_0 = 1$),

$$H_{01}c_1 = \frac{E_{\mathrm{Corr}}}{N}$$
$$H_{01}^{\dagger} + \left(H_{11}^{0} + H_{11}^{1} + \cdots\right)c_1 = 0 \ . \tag{12}$$

Reintroducing the coefficient c_0 as a variable, multiplying the first equation by N, and subtracting from the diagonal of the matrix block $H_{11}^{0} + H_{11}^{1} + \cdots$ the full correlation energy, E_{Corr}, the CISD equations (Eq. 9) are exactly reproduced as an eigenvalue problem. This procedure of manipulating the diagonal of the Hamiltonian matrix is commonly called "dressing", and is normally applied to the CI problem. In the following a dressing, Δ, will always denote a diagonal dressing ($I \neq J : \langle\Phi_I|H|\Phi_I\rangle, \langle\Phi_I|H|\Phi_J\rangle \rightarrow \langle\Phi_I|H + \Delta_I|\Phi_I\rangle, \langle\Phi_I|H|\Phi_J\rangle$):

$$H_{01}c_1 = \frac{E_{\mathrm{Corr}}}{N}$$
$$H_{01}^{\dagger} + \left(H_{11}^{0} + H_{11}^{1} + \cdots + \Delta_1\right)c_1 = 0 \ , \tag{13}$$

which is completely equivalent to the self-consistently dressed "eigenvalue" problem

$$\begin{pmatrix} 0 & \sqrt{N}H_{01} \\ \sqrt{N}H_{01}^{\dagger} & H_{11}^{0} + H_{11}^{1} + \cdots + (E_{\mathrm{Corr}} + \Delta_1) \end{pmatrix} \begin{pmatrix} c_0 \\ \sqrt{N}c_1 \end{pmatrix} = E_{\mathrm{Corr}} \begin{pmatrix} c_0 \\ \sqrt{N}c_1 \end{pmatrix} \ . \tag{14}$$

The dressing to be introduced is only that for the first matrix block, H_{11}^{0}, in Eq. (8); thus, if it does not contain the number of cells, N, in an explicit manner, any dressing, Δ, which can be written in the above form, either as pure Δ in CEPA-0 equations or as $E_{\mathrm{Corr}} + \Delta$ from the CI eigenvalue problem, should result in a size-consistent correlation method. It has to be stressed, although, that the only variational method is given by the CISD procedure.

The different CEPA methods compared and discussed in the literature, a meeting point, the "full CEPA", from the CEPA side, or self-consistent size-consistent CI [$(SC)^2$CI] from the CI side, of Daudey et al. [28] may serve as a model. To restore the size consistency of the CI eigenvalue problem, unlinked diagrams of double excitations are suppressed through inclusion of diagrams involving appropriate quadriexcited determinants. The dressing involved (of the CI matrix in Ref. [28]) can be written as the full correlation energy minus the forbidden quadriexcitations – the exclusion principle violating (EPV) diagrams for example, indices i, j, a and b:

$$E_{\mathrm{Corr}} + \Delta_{ij}^{ab} = E_{\mathrm{Corr}} - \frac{\underbrace{\sum_{klcd \in \mathrm{EPV}(i,j,a,b)} \langle\Phi_{ij}^{ab}|\mathbf{H}|\Phi_{ijkl}^{abcd}\rangle c_{kl}^{cd}}}{\sum_{klcd \in \mathrm{EPV}(i,j,a,b)} \langle\Phi_0|\mathbf{H}|\Phi_{kl}^{cd}\rangle c_{kl}^{cd}} \tag{15}$$

EPV means here that at least one of the indices k, l, c, d is equal to i, j, a, b. As shown in detail in Ref. [28] all other CEPA variants can be obtained by including specific subsets of the EPVs in the summations – CEPA-2 takes further into account only determinants with the same holes as the original determinant to be dressed and CEPA-3 leaves the additional freedom of a third hole index. As the to the $(SC)^2$CI opposed extreme of the CEPA methods figures CEPA-0, by not correcting at all for EPV diagrams. It may be stressed that the inclusion of EPV diagrams corrects the size-consistency error for the CI procedures, whereas CEPA methods themselves are from the start size-consistent. The dressings for the methods discussed so far are collected in Table 1. As orbital indices, and in particular limited sets of orbital indices, enter explicitly in the dressing formulae, CEPA methods beyond CEPA-0 can never be invariant under internal orbital rotations, such as localization procedures.

Another class of correlation methods is accessible from the CI eigenvalue problem. Gdanitz and Ahlrichs [30] corrected the size-consistency problem by introducing a functional acting on the norm of the CI wave function. This results in a correction by a factor $(1 - \frac{2}{n}E_{\mathrm{Corr}})$, with n being the number of electrons in the system [10, 30]. The deeper origin of this so-called averaged-coupled-pair functional (ACPF) lies in the accounting for possible pair excitations, leading to an

Table 1. Different dressings, Δ_{ij}^{ab}, to address the variety of coupled-electron-pair-approximation (*CEPA*) methods within the same algebra. For CEPA-2 the quadriexcited exclusion-principle-violating (*EPV*) determinants are written explicitly and reference is made to the "*e*" tables introduced in Ref. [29]

CEPA-0	0
CEPA-2	$-\sum_{cd}\langle\Phi_{ij}^{ab}\|\mathbf{H}\|\Phi_{ijij}^{abcd}\rangle c_{ij}^{cd} \approx -\sum_{cd}\langle\Phi_0\|\mathbf{H}\|\Phi_{ij}^{cd}\rangle c_{ij}^{cd} = -e(i,j)$
CEPA-3	$-\sum_{kcd}\langle\Phi_0\|\mathbf{H}\|\Phi_{ik}^{cd}\rangle c_{ik}^{cd} - \sum_{kcd}\langle\Phi_0\|\mathbf{H}\|\Phi_{kj}^{cd}\rangle c_{kj}^{cd} + \sum_{cd}\langle\Phi_0\|\mathbf{H}\|\Phi_{ij}^{cd}\rangle c_{ij}^{cd} = -e(i) - e(j) + e(i,j)$
$(SC)^2$CI	$-\sum_{\mathrm{EPV}(i,j,a,b)}\langle\Phi_0\|\mathbf{H}\|\Phi_{kl}^{cd}\rangle c_{kl}^{cd}$

exact result if the electron pairs do not interact between themselves. In the present, CEPA-adapted, writing of the CI approach, the dressing is still diagonal and, furthermore, all excited determinants are dressed equally. This makes it evident that ACPF will be, as CI and CEPA-0 are, invariant with respect to orbital rotations within the Hartree–Fock wave function. By partitioning the total number of electrons of the system into the number of electrons per unit cell, n, and the number of cells, N, the dressing, Δ, consists of two quantities which are directly accessible, even for an infinite periodic system:

$$\Delta = -\frac{2}{n}\left(\frac{E_{\mathrm{Corr}}}{N}\right) \ . \tag{16}$$

The ACPF has been considered in more detail by Szalay and Bartlett, leading to the averaged-quadratic-coupled-cluster (AQCC) approximation [10], which, despite its name, is an extension of the ACPF in that corrections to the CISD for the two-electron system should be avoided and interacting pair excitations are also impossible for three electrons. Unlike ACPF, however, AQCC is not exact for noninteracting electron pairs [31].

When including the possibilities and restrictions of pair formation in virtual space, the method has been termed AQCC-v [32]. As the AQCC methods have their origin in the ACPF, the expressions are quite similar to the ACPF dressing in the periodic system context, namely in that the number of electrons can be partitioned into electrons per cell and the number of cells equally for the number of virtual orbitals in the total system. In the limit of large systems, the AQCC yields exactly twice the ACPF dressing and AQCC-v includes the ration of the number of occupied and virtual orbital per cell. These more CI-oriented methods are presented in Table 2 in the same notation as in Table 1. In molecular quantum chemistry, one interesting feature of CI, ACPF, and AQCC lies in the easy generalization to multireference cases, an aspect which has been developed by the original authors. This will, however, not be followed here, where a connection to the CEPA and coupled-cluster-derived methods is the main issue.

Quite recently, the dressing techniques for CI methods have been extended to the CCSD level of theory [11, 33]. The commonly employed iterative algorithm to solve the nonlinear CCSD equations is given by a Newton–Raphson scheme, but the equations can be rearranged to be solved with linear algebra methods. The equivalent of the solution of the simplest quadratic equation

$$x^2 + bx + c = 0$$

would be the iteration prescription

$$x_i = -\frac{c + x_{i-1}^2}{b}$$

with the same solutions, if convergent. The CCD equations (without single excitations), read, as given in Ref. [11],

$$\langle \Phi_I | \mathbf{H}\left(1 + \frac{1}{2}T_2^2\right)|\Phi_0\rangle + \sum_J \langle \Phi_I|\mathbf{H}|\Phi_J\rangle c_J - E_{\mathrm{Corr}} c_I = 0 \ , \tag{17}$$

where the analogy with the simple quadratic equation may be obtained within a few manipulations.

To stabilize the algorithm for solving the CCSD equations by means of a CI-like eigenvalue problem, the authors of Ref. [11] proposed not a diagonal dressing of the CI matrix, but rather a dressing of the first column of the Hamiltonian matrix. In order to remain within the diagonalization of a hermition matrix, a dressing of the first row and, to counterbalance this dressing, a dressing even of the Hartree–Fock energy, $\langle \Phi_0|\mathbf{H}|\Phi_0\rangle$, was necessary. Within the present CEPA dressing this redressing of the reference becomes obsolete and the non-linear CCSD equations are already reduced (by Eq. 17) to the solution of a system of self-consistently dressed linear equations.

By including monoexcitations, i.e. CCSD instead of CCD, the nonlinear terms will comprise combinations of T_1 and T_2, at most fourth order in T_1 due to the bielectronic nature of $\mathbf{H}$. Looking at the matrix element $\langle \Phi_I|\frac{1}{2}\mathbf{H}T_2^2|\Phi_0\rangle$, this can be partitioned into

$$\langle \Phi_I|\tfrac{1}{2}\mathbf{H}T_2^2|\Phi_0\rangle = \underbrace{\left(\sum_{J, D_J\Phi_I \neq 0} \langle \Phi_0|\mathbf{H}|\Phi_J\rangle c_J\right)}_{\text{in (SC)}^2\text{DCI as } E_{\mathrm{Corr}} - \sum \text{EPV}} c_I + \underbrace{\sum_{J<K, J,K\neq I} \langle \Phi_I|\mathbf{H}|\Phi_{J+K}\rangle \ c_J \ c_K}_{\text{true quadriexcitations}} \ , \tag{18}$$

with diexcitations I, J, and K. $D_J\Phi_I \neq 0$ stands here for diexcitations, J, acting on Φ_I, which lead to possible, non-EPV, quadriexcitations. One may recognize that the first term serves as in (SC)^{2}CI for the suppression of unlinked diagrams introduced via the CI, but leading to the noninvariance within orbital rotations and that the second term adds higher excitations and additionally restores the invariance with respect to orbital rotations. It might be added that for the derivation of the LCCD equations from the CCD equations the suppression of the nonlinear terms $(1/2\mathbf{H}T_2^2)$ is the second step after accounting for the correlation energy, E_{C} [34]; therefore,

Table 2. Different dressings, Δ_{ij}^{ab}, for more configuration-interaction (*CI*)-based correlation methods. The dressing applies as previously to the CEPA-0 derived systems of linear equations. N_{e} and N_{v} are the total number of electrons and virtual orbitals, respectively, and n and n_{v} are the same quantities per unit cell. N denotes the number of cells in the system

CISD	$-E_{\mathrm{Corr}}$
ACPF	$-\frac{2}{n}(E_{\mathrm{Corr}}/N)$
AQCC	$-E_{\mathrm{Corr}}\left(1 - \frac{(N_{\mathrm{e}}-2)(N_{\mathrm{e}}-3)}{N_{\mathrm{e}}(N_{\mathrm{e}}-1)}\right) \rightarrow -\frac{4}{n}(E_{\mathrm{Corr}}/N)$
AQCC-v	$-E_{\mathrm{Corr}}\left(1 - \frac{(N_{\mathrm{e}}-2)(N_{\mathrm{e}}-3)}{N_{\mathrm{e}}(N_{\mathrm{e}}-1)}\frac{(N_{\mathrm{v}}-2)(N_{\mathrm{v}}-3)}{N_{\mathrm{v}}(N_{\mathrm{v}}-1)}\right) \rightarrow -\frac{4}{n}(E_{\mathrm{Corr}}/N)\left(1 + \frac{n}{2n_{\mathrm{v}}}\right)$
	N_{e}, n: electrons; N_{v}, n_{v}: orbitals

both properties, invariance with respect to orbital rotations and size consistency, are present in CEPA-0.

A last point can be made about the invariant formulation of MP2 as given by Pulay and Sæbϕ [35] and Förner [13]. The invariance with respect to orbital rotations is achieved by summing to infinity all diagrams containing off-diagonal Fock-matrix elements as additional pertubation series. Remembering that the Fock operator is a pure one-electron operator and that summing to infinity the series of double excitations leads to the CEPA-0 equations, the equivalent will now be not to solve the CEPA-0 equations with the matrix formed by elements of the Hamiltonian ($\langle\Phi_I|\mathbf{H}|\Phi_J\rangle$) but rather the equations formed by elements $\langle\Phi_I|\mathbf{F}|\Phi_J\rangle$ of the Fock operator instead. The resulting system of equations is exactly the same as that given by Pulay and Sæbϕ or Förner and, not surprisingly, size consistency and invariance are present.

3.2 Aspects of possible implementations

For the solution of the CI eigenvalue problem a standard procedure has become the iterative Davidson diagonalization [36] with the direct construction of the action of $\mathbf{H}$ on Ψ, without explicit storage of the Hamiltonian matrix. A self-consistent dressing can be easily introduced into the Davidson iterations so that dressing and solution of the (dressed) eigenvalue problem are managed in a single set of iteration cycles. Things are slightly different when trying to solve iteratively the system of linear equations. The commonly employed conjugate-gradient procedure [9, 37, 38] builds a sequence of optimal directions towards the minimum of a quadratic form. This sequence of directions is more difficult to modify for a self-consistent dressing of the matrix than the effective Hamiltonian in the Davidson procedure. Thus, in the case of solving a system of linear equations, a solution is iteratively attempted at a low precision, the dressing is calculated and applied, and the new system of linear equations is solved at a higher precision. This is repeated until the loop of dressing and solution converges to a given maximum precision. Note that for all the dressings presented, with the exception of coupled-cluster theory, only matrix elements of the Hamiltonian matrix enter which have already been computed as interactions of the reference determinant with excited determinants. The dressing, as long as it is applied to the diagonal only, is therefore of negligible computational demand with respect to the actual solution of the linear algebra problem and the contruction of the action of $\mathbf{H}$ on Ψ.

The calculations reported in the next section were performed with different working codes: for ring systems the necessary integrals over atomic orbitals are generated with a standard tool, for example, MOLCAS [39] or DALTON [40], and preparation of the integrals, the self-consistent-field (SCF) cycles, the four-index transformation, and the correlation calculations are treated by several specific routines. For the infinite systems the Fock matrix was obtained from the periodic SCF code CRYSTAL92 [41], and generation of the localized orbitals, the four-index transformation, as well as the calculation of the correlation energy in the various schemes is performed within routines similar to those of the ring systems – cell indices are cut at a reasonable distance from the reference cell. Thus, the information, whether an infinite system or a finite ring system is dealt with, is only apparent in the construction of the Fock matrix. Once these matrix elements are present, the further steps can be executed without knowing the real size of the system, on the condition that the system is periodic and that all information necessary can be obtained from a region around the reference cell.

4 Selected results

4.1 Hydrogen rings

As in previous work [25, 42] hydrogen rings are considered in a minimal basis: in a molecular setup, having interatomic spacings r and $2r$ and as a metal-like system with equal interatomic spacings with the same r of 0.74747Å.[1] With this model system one can gain an overview of the performance of the different methods with respect to increasing system sizes: with a realization of weakly interacting electron pairs and with completely delocalized electrons, facing problems such as symmetry breaking and a slow decrease of individual contributions to a total correlation energy (per H_2 unit). For the smallest hydrogen rings, even full CI results can be obtained with reasonable effort[2].

First, the molecular case is studied.[3] The implemented correlation methods of Tables 1 and 2, except for the non-size-consistent CISD, and the full CI in comparison to the "pairs" CCSD/$(SC)^2$CI and CCSD(T)/ACPF are shown in Fig. 1. The close coincidence of the CCSD and the $(SC)^2$CI results can be explained by the electron pairing on individual sites: linked diagrams involving quadriexcitations (as in Fig. 2) are of only minor importance when localized orbitals are used, because either an EPV is produced or orbital indices are located in different unit cells. In canonical, completely delocalized orbitals electron pairs on the individual unit cells are no longer represented by a single molecular orbital; thus, the diagrams not included in $(SC)^2$ of the above type should be larger in magnitude and one expects that the $(SC)^2$ gives smaller correlation energies in canonical orbitals. CCSD is invariant under orbital rotations.

In this model system, ACPF and CCSD(T) are closest to the full-CI curve. Not too astonishingly, AQCC and AQCC-v lie in this case far off from the ensemble of

[1] In order to study the metal-like systems, ring molecules of the size H_{4n+2} should be chosen to avoid multireference cases with degenerate canonical frontier orbitals

[2] Full CI results were obtained by *S. Evangelisti*, Bologna (Italy) and Toulouse (France)

[3] CCSD and CCSD(T) energies were calculated with the MOLCAS program package [40]

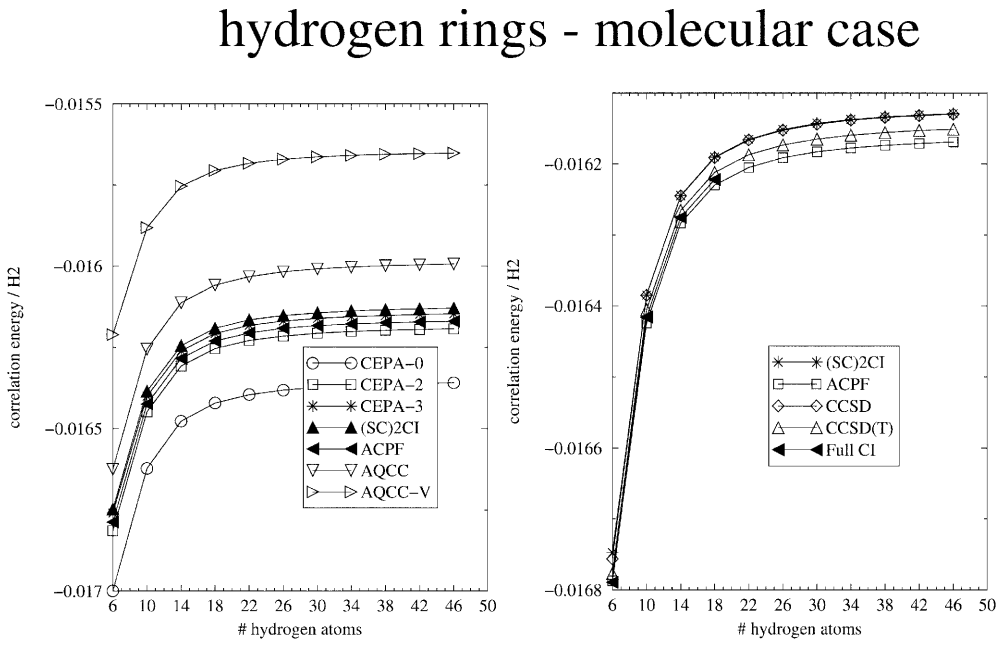

Fig. 1. Correlation energy per H_2 molecule. *Left*, the different correlated-electron-pair-approximation (*CEPA*) methods as well as the averaged-coupled-pair functional (*ACPF*), the averaged-quadratic coupled cluster (*AQCC*), and the AQCC with inclusion of the possibilities and restrictions of pair formation in virtual space (*AQCC-v*). *Right*, comparison of self-consistent size-consistent configuration interaction [$(SC)^2CI$] and ACPF to coupled-cluster single and double excitations (*CCSD*), CCSD with perturbative triple excitations [*CCSD*(*T*)], and full CI

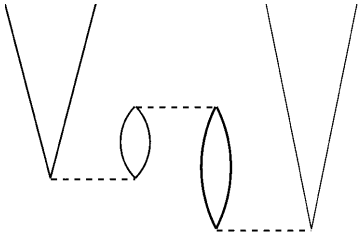

Fig. 2. The simplest of the linked diagrams passing through a quadriexcitation. Diagrams of this type are included in CCSD, but are absent in $(SC)^2CI$

CEPA methods, because they seriously underestimate the correlation energy. This reflects the incorrect treatment of the only essentially weakly interacting electron pairs in AQCC, as stated in the previous section.

A slightly different picture emerges when going to the metal-like case. From the closing of the gap – the smallest difference of the orbital energies of occupied and virtual orbitals in canonical orbitals – when increasing the ring size, one expects that perturbation theory in canonical orbitals will result in an increasing correlation energy, since diagrams involving orbitals around the gap will become overproportionally more and more important due to small energy denominators. Methods invariant to orbital rotations should follow this trend, as was show in a previous article [25].

Quadriexctitations are more important now, and thus CCSD and $(SC)^2CI$ coincide less than for the molecular case. The importance of triples manifests itself in the rather important difference of CCSD and CCSD(T), the latter still being close to the much less expensive ACPF. CCSD(T), ACPF, and the full CI are well comparable. AQCC-v, however, again underestimates the correlation energy significantly, but not as seriously as in the molecular case, and is now in close coincidence with $(SC)^2CI$ and CCSD. CEPA-2, with the inclusion of EPV corrections acting on the holes of the excited determinants, improves the CEPA-0 overestimation of the correlation energy by only a very small amount, whereas CEPA-3, which introduces a third hole in the matrix element, lies very close to AQCC, but is still far from $(SC)^2CI$.

4.1.1 Orbital rotations and $(SC)^2CI$

The CEPA methods beyond CEPA-0 are not invariant under orbital rotations, as the explicit use of orbital indices already indicates. In Ref. [28] the authors state that $(SC)^2CI$ will be size-consistent and lead to separable wave functions, at least when localized orbitals are used. In this subsection dealing with the calculations on (small) hydrogen rings, the question of the importance of orbital rotations will be followed. For $(H_2)_{4n+2}$ in a minimal basis, perturbation theory is invariant to localization beyond the creation of Wannier functions, i.e. one occupied and one virtual orbital per H_2 molecule. This is due to the structure of the formulae, which demand evaluation of bielectronic integrals and in this case a single energy denominator. For CEPA methods with the (self-consistent) solution of a system of linear equations, orbital rotations beyond the Wannier-function definition may become of importance. To investigate this, three different sets of orbitals are used and the results are compared to CCSD and SDCI. Two sets of localized orbitals are obtained by starting the SCF procedure either with orbitals centered on the atoms, an ionic starting vector, or with orbitals centered on the bonds, i.e. the σ and σ^* orbital of the hydrogen molecule in the reference unit cell. In the case of the metal-like rings this leads without correction to the two symmetry-broken solutions, described as the atom-centered charge density wave or the bond-centered charge density wave as alternative solutions to the Hartree–Fock equations [42] with their own density matrix. By forcing the density matrix to maintain a

structure according to the symmetry-adapted Hartree–Fock solution, orbital rotations may still lead to atom- or bond-centered molecular orbitals. The third set of molecular orbitals for the rings are the canonical ones, the equivalent to Bloch orbitals. In principle, by defining unit cells with more than one H_2 molecule, a whole series of localizations or orbital mixtures may be possible, filling the space between the highest localization of the smallest possible unit cell and the complete delocalization of the Bloch functions.

The curves for the $(SC)^2CI$ results for the three sets of orbitals together with the ACPF and CCSD results are displayed in Fig. 4. In the molecular case the dependence on orbital localization on the $(SC)^2CI$ results is much stronger than the splitting between CCSD and ACPF, leading in canonical orbitals to an underestimation of the correlation energy comparable to that of AQCC-v (Fig. 1). For both the atom-centered and the bond-centered Hartree–Fock orbitals localization gives very small contributions of quadriexcitations; thus, the difference to CCSD remains small – the optimum being the symmetric, bond-centered orbital set. In the metal-like case, on the other hand, where quadriexcitations become quite important due to the inherent delocalization of

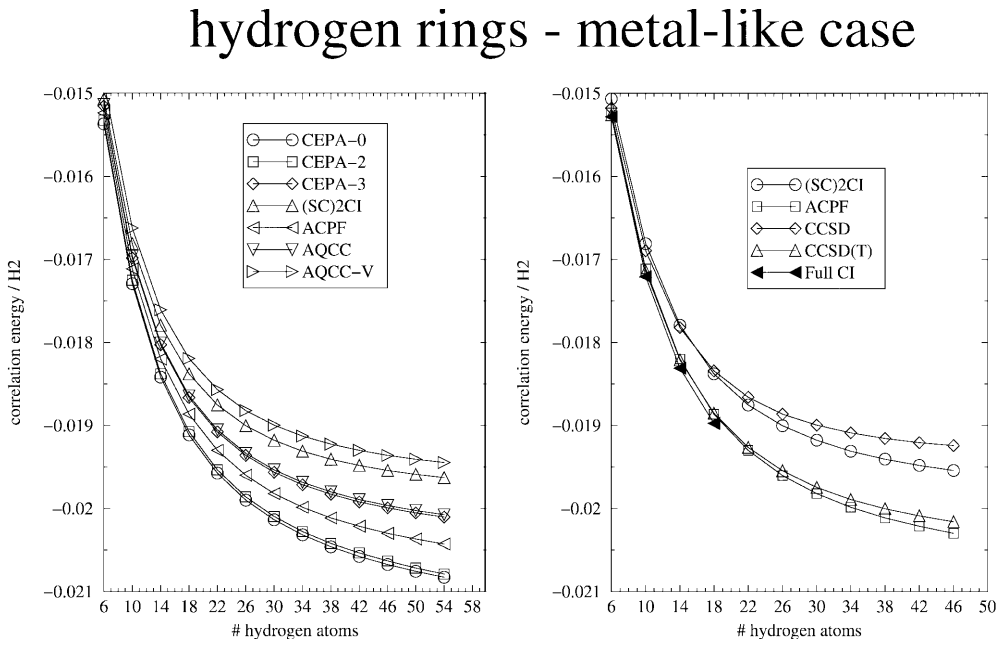

Fig. 3. Correlation energy per H_2 molecule. *Left*, the different CEPA methods, ACPF, AQCC, and AQCC-v. *Right*, comparison to CCSD and CCSD(T)

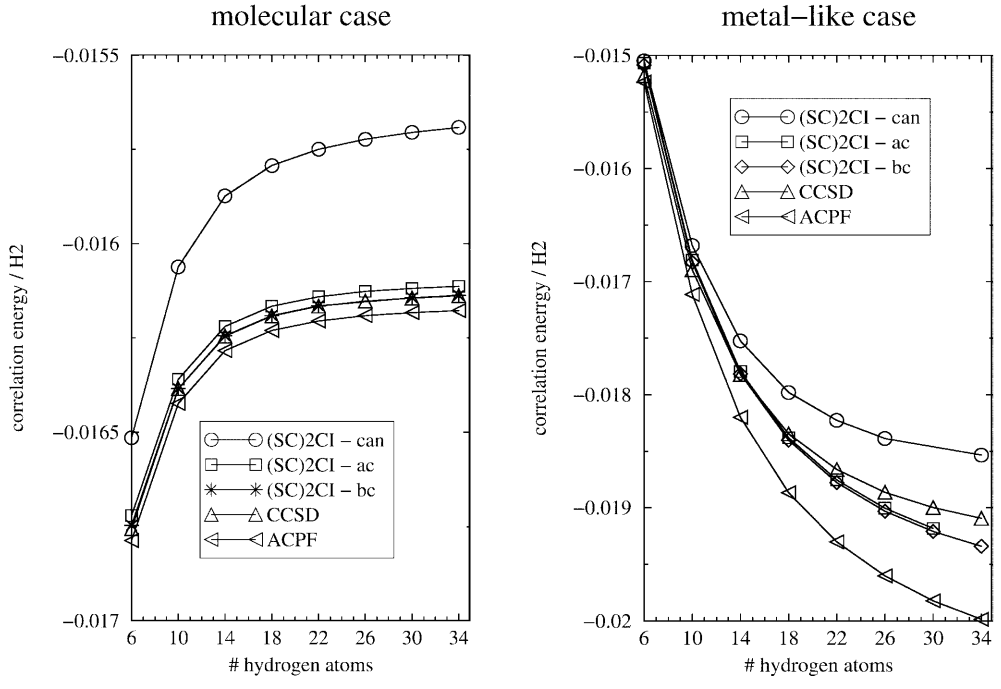

Fig. 4. Results of $(SC)^2CI$ for different sets of molecular orbitals, together with the invariant ACPF and CCSD curves. The density matrix of all cases, thus the reference wave function, is the same for all localizations

molecular orbitals, the deviation of $(SC)^2CI$ from CCSD or ACPF is less dramatic and also the difference between the two sets of localized orbitals becomes negligible. The spread of the different $(SC)^2CI$ curves now has the same magnitude as the difference between ACPF and CCSD.

4.1.2 Size consistency of the Davidson correction

For the ring systems, a widely used formula for correcting the size-consistency error of the CISD correlation energy in the form of the so-called Davidson correction may be employed. The particular usefulness of the Davidson correction lies in the fact that only the coefficient of the reference determinant, c_0, has to be considered, without changing the wave function. The original version of Davidson [43] as $1 - c_0^2$ was renormalized by Siegbahn [44] to $(1 - c_0^2)/c_0^2$. Davidson and Silver [45] proposed a more elaborate form, based on higher-order perturbation expansions: $(1 - c_0^2)/(2c_0^2 - 1)$.

Both corrections, Siegbahn's and Davidson and Silver's, have been applied to the two series of hydrogen rings and are displayed together with the CISD and CEPA-0 results on these systems (Fig. 5). Clearly, the CISD curve did not scale correctly with the system size, and Siegbahn's proposition of restoring size consistency fails to maintain a stable value for the correlation energy per hydrogen molecule even for moderately sized rings. The correction of Davidson and Silver, on the other hand, coincides in the molecular case with the overestimation of the correlation energy by CEPA-0 and fails as in the metal-like case to restore the size consistency.

One may wonder why the corrected CI energy lies so close to the CEPA-0 curve in the case of molecular hydrogen. From the model CI problem of N noninteracting electron pairs

$$\begin{pmatrix} 0 & \sqrt{N}H_{01} \\ \sqrt{N}H_{01}^{\dagger} & H_{11} \end{pmatrix} \begin{pmatrix} c_0 \\ \sqrt{N}c_1 \end{pmatrix} = E_{\mathrm{Corr}} \begin{pmatrix} c_0 \\ \sqrt{N}c_1 \end{pmatrix} \quad (19)$$

one arrives at the eigenvalues

$$E = \frac{H_{11}}{2} \pm \sqrt{\left(\frac{H_{11}}{2}\right)^2 + NH_{01}^2} \rightarrow \sqrt{N}H_{01} \quad \text{for large } N$$

and an expression for c_0:

$$\frac{H_{11}}{\sqrt{N}H_{01}} = \frac{1 - 2c_0^2}{c_0\sqrt{1 - c_0^2}} \ . \quad (20)$$

On substituting c_0 by $\cos\varphi$ and using the trigonometrical formulae one has

$$\varphi = -\frac{1}{2}\,\mathrm{arc\ cot}\,\frac{H_{11}}{2\sqrt{N}H_{01}} \ , \quad (21)$$

which can be expanded around $\varphi = \pi/4$ by help of $\cos(a + b) = \cos a \cos b - \sin a \sin b$, leading to

$$c_0 = \frac{1}{2}\sqrt{2} + \frac{1}{2}\sqrt{2}\,\frac{H_{11}}{4\sqrt{N}H_{01}} \ . \quad (22)$$

On inserting this expression into the formula of Davidson and Silver, one corrects the CISD energy exactly towards the CEPA-0 result

$$E = -N\frac{H_{01}^2}{H_{11}} \ ,$$

at least in the limit of large N.

In the case of metal-like hydrogen rings, where not only local electron pairs dominate the scenario, the Davidson formula remains a first approximation and one should apply instead the full correlation methods.

4.2 The LiH polymer

For the hydrogen systems results were obtained entirely in the framework of rings. In this section an infinite polymer is studied, with the same methods, in close comparison to similar rings. One could deduce polymer

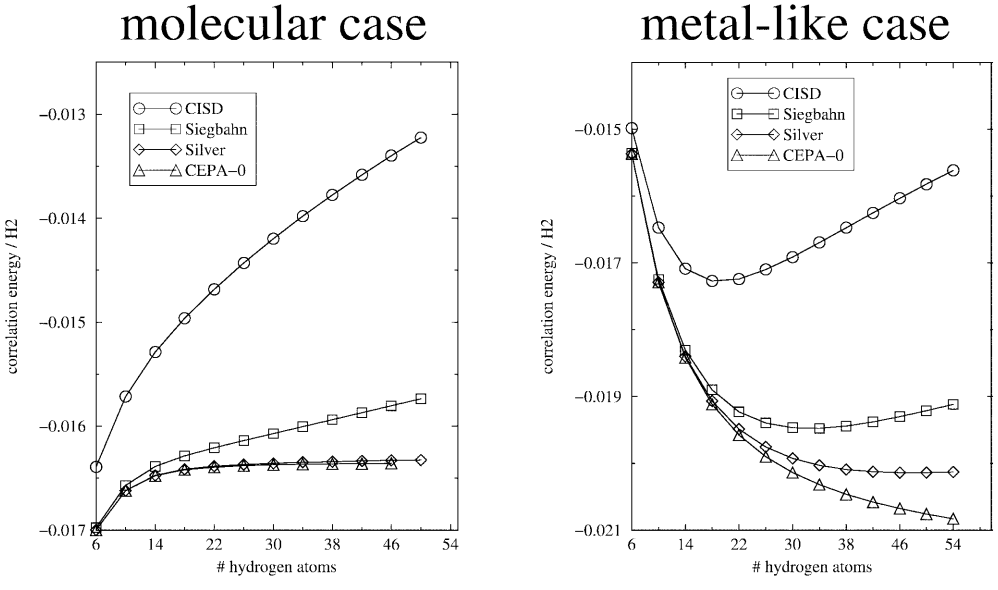

Fig. 5. The two variants of the Davidson correction, applied to the model hydrogen systems

properties in the spirit of the incremental scheme from smaller sections of the polymer, these then being treated as molecules. Convergence of the difference of a section of $N+1$ cells and a section of N cells may be rather rapid, as has been shown for polyacetylene [6]. With the ring approach convergence towards polymer properties is much slower due do the varying curvature with the system size and, therefore, the constantly varying bond geometries. In the incremental scheme, however, several calculations on larger systems have to be performed and differences are to be calculated.

When treating larger molecules or ring systems and, certainly, when studying infinite periodic systems, summations and molecular orbitals have to be truncated somewhere in space and orbital indices in the determinantal expansion must be restricted to some surroundings of the reference unit cell. In the SCF iterations on the ring systems, all cells are taken into account. In the polymer case, for which the converged Fock matrix of a periodic Hartree–Fock calculation employing CRYSTAL [41] was used to construct the localized orbitals within a minimal basis composed of s-type basis functions only, molecular orbitals were allowed to extend over 77 unit cells, but coefficients of basis functions lower than 10^{-8} were neglected. Four basis functions are defined per unit cell, of which two were assigned to be occupied and two to represent virtual molecular orbitals in the starting vector. The four-index transformation was carried out for a set of molecular orbitals located in up to 13 cells in total, thus six to each side of the reference cell. The indices of the determinants involved run, apart from one index in the reference cell, over all these included molecular orbitals. For the CEPA-based correlation step on the ring systems, the same truncation was employed after the four-index transformation, since as in the ring cases the number of determinants grows very rapidly with the overall system size. Additionally, of course, CCSD and CCSD(T) calculations in canonical orbitals become prohibitive.

Two results will be looked at in this section: the comparison of results on ring systems with results on the polymer and the convergence of the correlation energy for the various correlation methods with respect to the number of cells included in the four-index transformation and in the correlation schemes, now for the infinite polymer.

The SCF energy and the correlation energies obtained with the different methods presented in the previous sections are given for three ring systems and a polymer in Table 3.

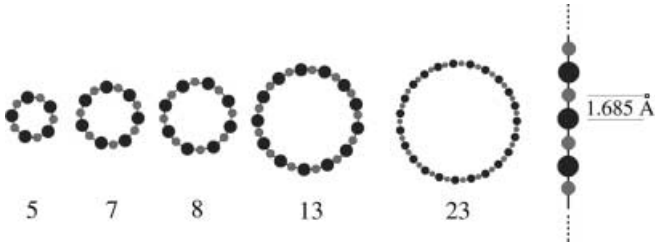

Fig. 6. LiH rings and a polymer. The Li—H distance was chosen to be 1.685 Å

Table 3. LiH, 2ζ, s functions. All energies are in atomic units per LiH. CISD + DAV stands here for the Davidson correction of Davidson and Silver [46]

	Li_7H_7	$Li_{13}H_{13}$	$Li_{23}H_{23}$	Polymer (7 cells)
SCF	−8.0316123	−8.0335019	−8.034020	−8.0342660
CMP2	−0.0166306	−0.0166354	−0.016637	−0.0166378
CISD	−0.0213675	−0.0202962	−0.018928	–
CISD + DAV	−0.0230031	−0.0223003	−0.022721	–
CEPA-0	−0.0230020	−0.0230165	−0.023021	−0.0230229
$(SC)^2CI$	−0.0228865	−0.0229004	−0.022904[a]	−0.0229067
CCSD	−0.0228825	−0.0228967	–	–
ACPF	−0.0229133	−0.0229271	−0.022931[a]	−0.0229332
CCSD(T)	−0.0228945	−0.0229084	–	–
AQCC	−0.0227798	−0.0227909	−0.022793[a]	−0.0227941
AQCC-V	−0.0225092	−0.0225219	−0.022525[a]	−0.0225275

[a] Correlation contributions within seven of the 23 cells only

First of all it can be noted that the correlation energy stays fairly constant with the ring size, at least for the systems shown in the table. This may show the very localized nature of the correlation energy in this highly ionic system with Mulliken charges of ±1.015 and the main correlation contribution being assignable to the H^- ion. The Davidson correction again suffers from the approximate CEPA-0 treatment and, as in the molecular hydrogen case, AQCC and AQCC-v yield results which are outside the ensemble given by all other methods beyond MP2, again due to the presence of well-localized and effectively well separated electron pairs. The results on the polymer, as available, fit nicely in the extrapolation of the ring data. These data on the ring systems, as displayed in more detail in Fig. 7, show the strong dependence on the bond angle, with a maximum at four LiH units or an H—Li—H angle of 135°, leading thereafter to a smooth dependence on the ring size.

Whether the correlation contributions have to be collected within a larger or smaller range, may be shown by the dependence of the results on the cut-off radius in the CEPA scheme. For the given polymer in the minimal basis, 13 cells were sufficient to describe the tails of the two occupied and the two virtual orbitals when restricting the coefficients to be larger than 10^{-7} in the molecular orbitals. Into the four-index transformation 13 cells were included as well, which presents the maximum number of cells in which the correlation energy may be evaluated. Taking all possible determinants into account, one ends up with 73179 spin determinants with one index in the reference cell, and 878136 spin determinants when performing the simultaneous rotations of all indices of excited determinants. As shown in Fig. 8, the inclusion of five cells with 4027 primary and 16104 secondary determinants is sufficient to arrive at a fairly converged result for the polymer correlation energy.

4.3 Cubic Be as a model 3D system

The last model example is an artificial 3D crystal, made from beryllium. The crystal structure of beryllium is

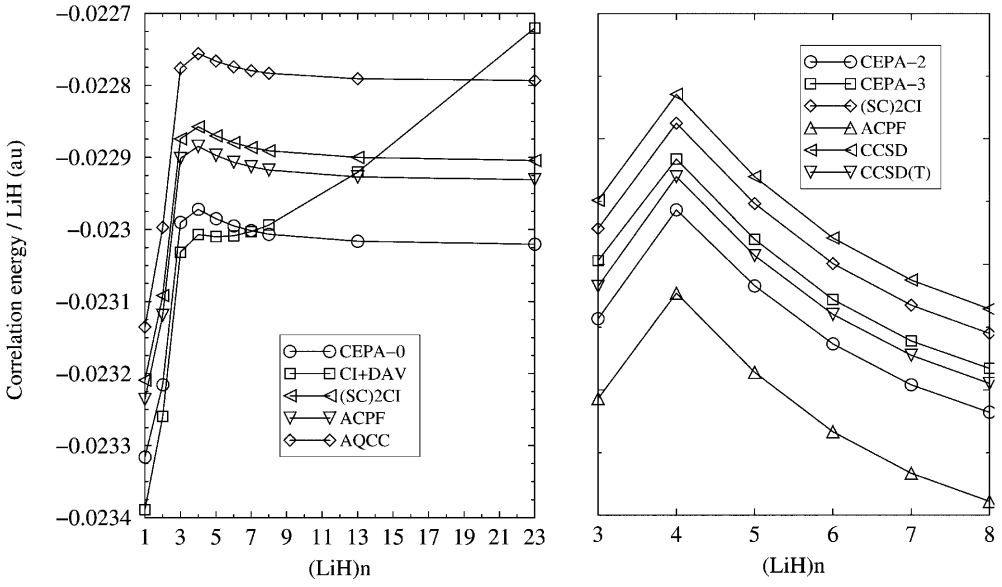

Fig. 7. Correlation energy per LiH unit for various ring sizes. *Left*, CI + DAV stands for the Davidson correction after Davidson and Silver [45]. *Right*, CEPA-2, CEPA-3, CCSD, and CCSD(T) are displayed in more detail together with $(SC)^2CI$ and ACPF from the *left panel*

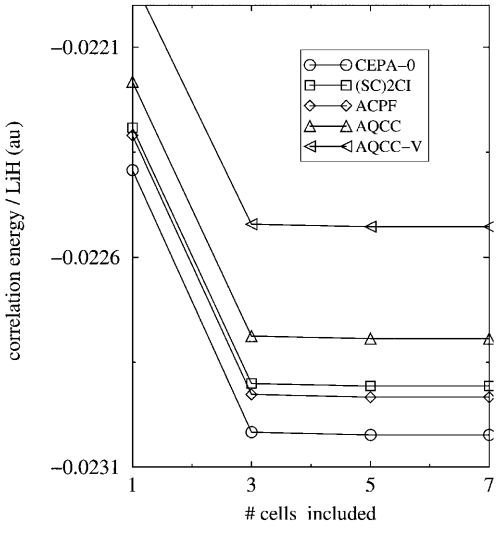

Fig. 8. Correlation energy in the LiH polymer, with respect to the number of cells included for describing excited determinants

normally a hexagonally close-packed (hcp) one with lattice parameters $a = 2.29$ Å and $c = 3.59$ Å, i.e. a Be–Be next-neighbour distance of 2.23 Å. For the present case a simple cubic structure is used, with a rather long lattice constant of 3.0 Å. The cubic structure was chosen since possibly large saving factors due to the high symmetry of the hcp crystal – a Bravais lattice with a two-atom basis – are not exploited explicitly, neither in the construction of the localized orbitals, nor in the correlation treatment. If one would like to introduce symmetry operations into the algorithms, two different symmetry-adapted representations may be used, one reflecting the point symmetry of the unit cell for the representation of molecular orbitals centered in the unit cell and one for the calculation of bielectronic integrals over basis functions, within a finite cluster region, for the four-index transformation. This has not yet been taken into account in the actual implementation, but it certainly presents a field of further development.

In the model cubic crystal a rather limited basis is again employed, consisting of three s-type basis functions (Huzinaga 8s basis, contracted as 5111, without the most diffuse exponent of 0.05936678). Per Be there are thus two occupied molecular orbitals and a single virtual orbital, with a total SCF energy for the atom of -14.47730 au, to be compared to the Hartree–Fock limit of -14.57303 au. With this basis, molecular, or crystalline, localized orbitals – constructed in the same way as for the LiH polymer – were allowed to extend over 485 centers in the SCF iterations and were cut to 57 cells or five coordination stars (with 6, 12, 8, 6, and 24 members, respectively) around the reference unit cell. The coefficients of the molecular orbitals dropped to less than 10^{-4} in the outer coordination sphere, and the overlap integrals between molecular orbitals of different cells were smaller than 10^{-6} for this case. The Fock matrix in localized orbitals was diagonalized within the reference cell in order to arrive at diagonal matrix elements, F^0_{ii}, which are close to the canonical orbital energies of the free atom.

Essentially, the crystalline, localized orbitals remain the orbitals of the free atom, with small tails being attached due to orthogonalization and interatom interaction. In order to obtain the correlation energy within a limited number of neighboring cells from these crystal orbitals, for instance, within 19 cells, i.e. the reference and the next two coordination spheres, a cluster of 195 Be atoms has to be cut from the bulk as the superposition of the the localized molecular orbitals within the 57-cell expansion around each of the 19 cells to be used in the correlation calculation and atomic bielectronic integrals are to be calculated for this cluster.

From the large variety of correlation energies, applying the different methods presented in the previous sections, only perturbation theory, CEPA-0, $(SC)^2CI$, and ACPF are displayed in Table 4 as being characteristic in their behavior. As the case is still atomic-like, the

Table 4. Results of the correlation calculations on the single Be atom and the 3D crystal. Localized molecular orbitals extend over 57 cells and the atomic orbital → molecular orbital transformation was carried out for a cluster of 19 unit cells, where molecular orbitals were attached. Determinants were allowed to have indices in the reference cell, up to seven cells, and up to 19 cells, respectively

	Be atom	Ref. cell	7 cells	19 cells
No. of primary determinants	9	9	3507	70575
No. of secondary determinants	0	0	21036	1270332
LMP2	−0.0102859	−0.0102666	−0.0102787	−0.0102788
CMP2	−0.0102859	−0.0102666	−0.0102822	−0.0102830
CEPA-0	−0.0116997	−0.0116730	−0.0116924	−0.0116925
$(SC)^2CI$	−0.0117011	−0.0116755	−0.0116902	−0.0116940
ACPF	−0.0117053	−0.0116760	−0.0116980	−0.0116981

results do not differ very much between the crystal and the atom case, with differences lying in the microhartree region. The largest difference between atom and solid arises when looking at the most restricted correlation treatment in the solid by calculating the contributions of the reference cell only. When including more and more unit cells in the determinantal expansion, the closer the results become with respect to the free atom, as if the correlation energy per atom were a fixed quantity, but in the case of the solid dispersed over a larger region than in the single atom. By including more than the first coordination sphere of the reference cell, i.e. going from seven to 19 cells, however, the overall results change little.

5 Conclusions

It has been shown how the dressing techniques known from the CISD approach can be transferred to CEPA methods. The terms CI and CEPA stand here not for the underlying derivation or physical aspects, but signify rather the practical aspect in that for the solution of the eigenvalue problem (CI) another numerical strategy is followed than for the iterative solution of the system of linear equations emerging from the CEPA theories. The advantage of the latter strategy is the simple applicability to infinite periodic systems, since the (infinite) quantity E_{Corr} in the CI problem is used as the desired and limited quantity E_{Corr}/N. Applied to ring systems as finite, but still periodic systems, the results of both approaches are exactly the same.

Despite its completeness, the full CEPA or $(SC)^2CI$ still suffers from noninvariance with respect to different molecular orbital sets. Averaging methods, such as ACPF or AQCC, and the basic CI and CEPA-0, being accessible via the same matrix-dressing techniques, have the advantage of resulting in invariant correlation energies whatever the orbitals are in which the wave function is expressed. In perturbation theory (MP2) the same invariance is achieved in a CEPA-0-like solution of a system of linear equations, by replacing the full Hamiltonian, **H**, by the Fock matrix, **F**.

Concerning practical results it has been shown that the commonly employed Davidson correction, in two of its published variants, has to be carefully regarded for large systems. For ring systems and 1D systems, polymers, the number of determinants included in a correlation treatment remains a quantity which can be handled with standard computational resources. When going to 3D periodic systems, however, the numerical effort grows very rapidly with the necessarily present delocalization of molecular orbitals. The beryllium cubic crystal shows that even the very limited interatomic interaction and the limited basis set tails of the orthogonal localized orbitals demand a quite large region of the solid to be exploited, for example, the decay of the orbitals is about a factor of 10^{-4} when going from the reference cell to the outer cells of the first five coordination spheres. Therefore it should be of predominant interest to include explicitly symmetry considerations in the working scheme – the road is already being prepared [47] by the development of the practical implementation of CRYSTAL from the original concept of solving the Hartree–Fock equations for periodic systems.

Acknowledgements. This work resulted from a post-doctoral collaboration with J.-P. Malrieu in Toulouse, including discussions with J.-L. Heully, D. Maynau, N. BenAmor, and J.-P. Daudey. Helpful remarks of M. Dolg, Dresden, are gratefully acknowledged. The work was supported by the Max Planck Society in the framework of the visitors program of the Dresden insitute, and calculations were performed at the institute on DEC workstations, except the full CI results. For these I am indebted to S. Evangelisti (Bologna, Toulouse). Finally, the warm hospitality of P. Fulde, Dresden, should not be left unmentioned.

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