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Size consistent properties from size-consistent self-consistent configuration interaction coefficients

Abstract The size-consistent self-consistent configuration interaction method, $(SC)^2$-CI, is a procedure based on the matrix dressing formulation of the intermediate hamiltonian theory, which aims to correct the size-extensivity problem in truncated or selected configuration interaction (CI) calculations. Corrected energies and CI-like functions are obtained. In the present paper, a procedure is proposed to get size consistent mean values of properties from the $(SC)^2$-SR-SDCI vectors. It can be easily extended, though in a less rigorous way, to $(SC)^2$-MR-SDCI functions. Calculations have been performed in 13 trial systems to test the size consistency behaviour of mean value one-electron properties obtained from $(SC)^2$ vectors and the accuracy limits of the procedure. Properties for ground and excited states have been tested in the SR-SDCI, $(SC)^2$-SR-SDCI, MR-SDCI, and $(SC)^2$-MR-SDCI approximations. The dipole and quadrupole moments of several small molecules have been calculated with the corrected $(SC)^2$-SR-SDCI method. The values are compared to experimental and theoretical reference values.

Keywords Size-consistent properties · Matrix dressing · Size consistency · Configuration interaction · One-electron properties · Quadrupole moments

1 Introduction

It is commonly recognized that configuration interaction (CI) is the most straightforward, general and flexible approach for dealing with the electron correlation problem [1,2]. The CI method maintains a very long and solid tradition in the application of quantum mechanics to atomic and molecular spec-

troscopy and potential energy surfaces calculations [1]. As a consequence, CI has provided chemists and molecular physicists with well-established concepts, terms and language shortcuts for describing complicated electronic structures, notably in those cases where the single reference approach is inappropriate [3].

The conceptual simplicity and the variational nature of the CI method are, perhaps, its greater merits. On the other hand, the lack of size-extensivity (i.e., adequate scaling with the number of particles) of truncated CI, its lack of size-consistency (adequate separability, e.g. adequate scaling with the number of identical independent subsystems), and the explosive dimensional increase of CI matrices at full CI level are its more important weaknesses. Hence, it is not surprising that efforts have been devoted to developing corrections for these deficiencies while preserving the language and conceptual framework of the CI approach. We can mention, as an example, the simplest routinely applied correction, namely, the 'quadruples correction' that provides 'a posteriori' corrected CISD energies [4–6] without correcting the wave function. The conceptual framework for these and more involved corrections is provided by the many body perturbation theory [7] in terms of the high order perturbation diagrams that remain uncancelled after the diagonalization of any truncated CI matrix. Some series of perturbative effects are summed up to infinite order while other effects, required to satisfy the linked cluster theorem [7–11], are not even taken into account.

If one is interested in molecular properties that are calculated from the CI wave function, correction procedures that modify the CI coefficients must be considered. This, of course, implies modifying the CI procedure itself. The resulting approaches can no longer behave as linear variation methods.

Among the CI correction methods, those that most noticeably preserve the CI framework and know-how are based on the matrix dressing technique [12]. These methods are based on the formalism of the intermediate Hamiltonian theory (IHT). Intermediate Hamiltonians were introduced by Malrieu and co-workers in the eighties [13,14] as a

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generalization of the effective Hamiltonians theory (EHT) [13,15,16] in order to set up a general strategy to deal with the intruder states problem in EHT [17]. The term 'matrix dressing' refers to perturb-then-diagonalize methods in which convenient shifts are added to the elements of a truncated CI matrix. In some cases where these shifts or 'dressing elements' are dependent on the CI expansion coefficients, iterative 'dress-then-diagonalize' self-consistent procedures are required, but the formal structure of the truncated CI matrix is preserved and the resulting CI-like expansion looks formally as a conventional truncated CI normalized wave function. Many electron correlation methods commonly practiced in, e.g. quantum chemistry or solid state physics, can be formally thought of and analysed in the matrix dressing formalism as has been discussed in detail for single-reference correlation methods elsewhere [18]. In particular, the coupled electron pair functions (CEPA) approach [19,20] can be given a CI-like matrix dressing formulation that allows for a complete inclusion of the exclusion principle violating (EPV) diagram effects which have been taken into account at increasing levels in the successive CEPA approaches (CEPA-0, 1, 2...) [19,20] so that the method, applied to a CISD matrix, can be considered as a complete or full single reference CEPA approach. Such a method was introduced by Daudey et al. [14] who named it in a descriptive way as size-consistent self-consistent configuration interaction, $(SC)^2$-CI. It has a distinctive property that can be applied to any truncated or selected CI matrix even if it is built from a previously chosen multi-reference such as in the MR-SDCI or CAS-SDCI cases. The method was introduced for closed shell ground states, but its application has been extended to single reference open shell ground states [21] and to the calculation of excited state energies. The $(SC)^2$-CI method has also been applied to molecular magnetism problems [17] and to periodic systems [22]. All applications to date have focussed on the calculation of correct energy differences or bond dissociation curves.

The $(SC)^2$ approach can also be analysed from the point of view of the CC ansatz, and, when applied to a MRCI matrix, can serve as starting point for multi-reference CEPA approaches. Such a point of view has been explored in the past by Malrieu and co-workers [23], and recently by Mukherjee and co-workers [24,25] who have developed one approach to their state specific multireference coupled cluster (SS-MRCC) approach that is called state specific multireference coupled electron-pair approximation (SS-MRCEPA). The application of the so called SS-MRCEPA(D) approach, where D stands for diagonal dressing, to the calculation of properties from the linear-response approach has been very recently explored by Chattopadhyay [26]. The SS-MRCEPA(D) method is conceptually very close to the diagonal matrix dressing techniques. The relationship between the $(SC)^2$-CI approach and the coupled pair functional (CPF) formulation has recently been discussed by Meller et al. [27]. These authors have shown how a multireference full coupled pair functional, MR-FCPF, can be introduced as the functional counterpart of the $(SC)^2$-CI method.

In the $(SC)^2$-CI matrix dressing method, size-extensive energies and CI-like expansions are calculated. In the present work, a general procedure is introduced to calculate size-consistent first order monoelectronic properties as mean values from these CI-like vectors. A note of caution is convenient here. It can be argued that the $(SC)^2$ dressing procedure does not yield a true wave function as one cannot define an a priori $(SC)^2$ hamiltonian. Only an effective hamiltonian can be defined after the self-consistent convergence has been achieved. However, as has been discussed in a recent paper [27], one can properly define an $(SC)^2$ energy functional by assuming that once the iterative process has converged to self consistency in the coefficients and to an energy value, the coefficient ratios used to calculate the dressing shifts remain fixed, or conveniently averaged, for small perturbations. In the conventional formulation that we have used in the present work, the $(SC)^2$ energy is obtained as the numerical eigenvalue of a real symmetric matrix. A uniquely defined vector of self-consistent coefficients $\{\tilde{c}_i\}$ is obtained for each state, also on the basis of the Slater determinants $\{\phi_i\}$.

2 Size-consistent mean value property values from $(SC)^2$ dressed CI vectors

2.1 The single-reference SDCI case

The single-reference $(SC)^2$ dressing procedure assumes that a particular dressing reference state (DRS), which is dominated by a single determinant, can be selected for the molecular system at the geometry of interest. In the present work we are considering such a class of DRS states (e.g., common closed shell ground states). As mentioned above, the $(SC)^2$ dressing is an application of the state specific IHT. In the single-reference dressing, one tries to calculate for the DRS both the exact correlation energy and a projection of the exact wave function on a model space (constituted, e.g., by the dominant determinant-commonly the Hartree–Fock ϕ_0 one- and all the single and double hole-particle replacements on it).

Now, let R represent the property in which we are interested and $\hat{R}$ its associated one-particle operator. For the FCI wave function $|\Psi\rangle$ of the DRS in the same one-electron basis set, one can write

$$R = R_{00} + \Delta R, \tag{1}$$

where $R = \langle\Psi|\ \hat{R}\ |\Psi\rangle \big/ \langle\Psi|\ \Psi\rangle$, $R_{00} = \langle\phi_0|\ \hat{R}\ |\phi_0\rangle$, and

$$\Delta R = \frac{\langle\Psi|\ \hat{R} - R_{00}\ |\Psi\rangle}{\langle\Psi\ |\ \Psi\rangle}. \tag{2}$$

In IHT, the FCI space is partitioned into the main or principal space (PS), $\{\phi_I\}$, the intermediate space (IS), $\{\phi_i\}$, and the outer space (OS), $\{\phi_\alpha\}$. In the cases where the non-dynamical correlation effects are irrelevant and a single determinant can

describe the system, the PS just comprises the HF determinant, ϕ_0. The reunion of the PS and the IS is referred to as the model space (MS). If the PS is ϕ_0, the MS consists of the conventional space of singles and doubles of ϕ_0. A note of caution is required here because the MS in IHT should not be confused with the model space as defined, e.g., in CC or MBPT theories. The authors follow in the present work the notation that was introduced by Malrieu and co-workers in the development of IHT and the $(SC)^2$-CI method.

It is clear that one can take the FCI function $|\Psi\rangle$ as normalized so that the denominator in Eq. (2) is unity, and following the partitioning notation described above, one can write

$$|\Psi\rangle = c_0\phi_0 + \sum_i c_i\phi_i + \sum_\alpha c_\alpha\phi_\alpha \tag{3}$$

and

$$1 = c_0^2 + \sum_i c_i^2 + \sum_\alpha c_\alpha^2. \tag{4}$$

so that Eq. (2) can be written as

$$\Delta R = \left\langle c_0\phi_0 + \sum_i c_i\phi_i \right. \\ \left. + \sum_\alpha c_\alpha\phi_\alpha \right| \hat{R} - R_{00} \left| c_0\phi_0 + \sum_i ... \right\rangle. \tag{5}$$

Of course, the FCI value of R is size-consistent and size-extensive. Let us suppose now that the $(SC)^2$ method succeeds in getting the projection of the exact FCI wave function $|\Psi\rangle$ onto the model space. We will denote $\left|\tilde{\Psi}\right\rangle$ the $(SC)^2$ vector that is obtained by means of an eigenvalue-like diagonalization. Consequently, it is normalised in a truncated space, namely, the MS (PS+IS). One could be tempted to write, similar to Eq. (2),

$$\Delta\tilde{R} = \left\langle \tilde{c}_0\phi_0 + \sum_i \tilde{c}_i\phi_i \right| \hat{R} - R_{00} \left| \tilde{c}_0\phi_0 + \sum_j \tilde{c}_j\phi_j \right\rangle, \tag{6}$$

where

$$1 = \tilde{c}_0^2 + \sum_i \tilde{c}_i^2. \tag{7}$$

By comparing Eqs. (4) and (7) it is immediately clear that it is impossible to satisfy both conditions, namely, to have exact projected coefficients and to fulfill the normalisation conditions in both the FCI space and the truncated one. Hence, the denominator in the calculation of $\Delta\tilde{R}$ by means of Eq. (6) along with the $(SC)^2$ expansion must differ from unity, i.e., $\left|\tilde{\Psi}\right\rangle$ must be somehow unnormalised. We shall

denote the unnormalised $(SC)^2$ function as $\left|\tilde{\Psi}'\right\rangle$. One can get some idea how to proceed by looking closer at the actual nature of the $(SC)^2$ coefficients $\{\tilde{c}_0, \tilde{c}_i\}$. The $\tilde{c}_i$ coefficients of the singles and the doubles that belong to the IS incorporate partially the effects of triply and quadruply excited determinants that belong to the OS $\{\phi_\alpha\}$. More precisely, the effects that have been incorporated by the $(SC)^2$ procedure to the coefficients correspond to those that lead to unlinked diagrams in the MBPT expansion of the energy. These diagrams are required to cancel the renormalization terms occurring in the third and higher orders [7,11].

The simplest way for having a denominator smaller than 1 in Eq. (6) is to take it as $\tilde{c}_0^2$, which is equivalent to ignoring the summation in Eq. (7). It can be argued that this is a suitable choice. Let r and s be indexes that run in the model space PS+IS (in this way, the $\tilde{c}_0\phi_0$ term is accounted for in the summations). Now, Eq. (6) can be written as

$$\Delta\tilde{R} = \frac{\left\langle \sum_r \tilde{c}_r\phi_r \right| \hat{R} - R_{00} \left| \sum_s \tilde{c}_s\phi_s \right\rangle}{\tilde{c}_0^2 + \sum_i \tilde{c}_i^2} \\ = \frac{\sum_{r,s} \tilde{c}_r\tilde{c}_s \langle\phi_r| \hat{R} - R_{00} |\phi_s\rangle}{\tilde{c}_0^2(1 + \sum_i \tilde{c}_i'^2)}, \tag{8}$$

where the prime in the coefficients $\tilde{c}_i'$ denotes that they correspond to the denormalised $\left|\tilde{\Psi}'\right\rangle$ expansion. By cutting off the series expansion of $1/(1 + \sum_i \tilde{c}_i'^2)$ after the second term, Eq. (8) can be written as

$$\Delta\tilde{R} \approx \frac{\sum_{r,s} \tilde{c}_r\tilde{c}_s \langle\phi_r| \hat{R} - R_{00} |\phi_s\rangle}{\tilde{c}_0^2}(1 - \sum_i \tilde{c}_i'^2). \tag{9}$$

It is clear in this way that neglecting the $\sum_i \tilde{c}_i'^2$ (and subsequent) terms in the denominator of $\Delta\tilde{R}$ avoids the subtraction of fifth (and higher) order perturbation effects that should in fact be required to cancel terms between determinants of the OS that cannot be present because $\left|\tilde{\Psi}\right\rangle$ expands only on the MS. This argument is formally related to those applied to the energy in the well-known Davidson's "quadruples correction", commonly denoted as SDCI+Q, which was mentioned in the introduction.

The procedure proposed to obtain size-consistent mean value properties from an energy converged $(SC)^2$-SR-SDCI expansion, can then be written as follows

$$\tilde{R} = R_{00} + \Delta\tilde{R} = R_{00} + \frac{\left\langle \tilde{\Psi} \right| \hat{R} - R_{00} \left| \tilde{\Psi} \right\rangle}{\tilde{c}_0^2}, \tag{10}$$

where $\left\langle \tilde{\Psi} \mid \tilde{\Psi} \right\rangle = 1$ as it is obtained from the $(SC)^2$ dress-then-diagonalize iterative algorithm. One should note that in Eq. (10), $\Delta\tilde{R}$ is calculated with the denormalised coefficient ratios $\tilde{c}_i/\tilde{c}_0$. While one can hardly expect that the actual

single-reference $(SC)^2$ coefficients are close to the exact ones (they are certainly closer to them than the conventional SDCI ones anyway) [21], the ratios $\tilde{c}_i/\tilde{c}_0$ should be much closer to the exact ratios than the coefficients themselves are [27]. This is so because the main purpose of the dressing can be seen as an attempt to improve these ratios. A simple way to understand this is by realizing that the correlation energy,

$$E_{corr} = \sum_i \frac{c_i}{c_0} \langle \phi_0 | H | \phi_i \rangle, \tag{11}$$

(for i running on the space of doubles excitations of ϕ_0), is closer to the FCI correlation energy if one uses the converged $(SC)^2$ coefficients $\{\tilde{c}_i\}$ instead of the SDCI ones. In general, the $(SC)^2$ correlation energy lies near the CCSD one.

2.2 The multi-reference SDCI case

The one-state specific $(SC)^2$ dressing procedure can be applied in a straightforward way to any selected or general multi-reference configuration interaction space (MR-CI) irrespective of whether the multireference is a CAS, a suitable subset of a CAS or a selected reference [14,28]. Multi-state specific $(SC)^2$ dressing procedures, denoted as MR-$(SC)^2$ methods by Malrieu et al. [23], have been also proposed, but they have been hardly used [24,25]. For applying these methods, a convenient principal space (PS) should be the one formed by a number of thoroughly selected determinants $\{\phi_I\}$ needed for descriving, e.g., either a given multiconfigurational situation or several states of the same system. The IS should be that of the (non-redundant) single and double replacements that can be performed on the determinants of the PS. A MR-$(SC)^2$ procedure should provide better coefficients for the MRCI expansions than any SR-$(SC)^2$ approach, in the same way as MRCC methods are better than single-reference CC approaches, because they can deal simultaneously in a more balanced way with dynamical and non-dynamical correlation effects. However, to remain in an SR-$(SC)^2$ dressing approach but applying it to a MR-CI space is straightforward, and the only practical difficulty relies in the efficient managing of the redundancies. Contrarily to the MR-$(SC)^2$ theories, the SR-$(SC)^2$ theory does not face the problem of the concurrence of replacement operators (and consequently, of the associated amplitudes) leading to the same determinant in the IS from different determinants in the reference space of the DRS. Moreover, it has been proved that the roots and vectors corresponding to the excited states are physical, show size-extensive behaviour and generally provide better approaches to FCI than the corresponding non-dressed MR-CI. In this section we propose a generalisation of the procedure for getting the size-consistent property values described in the previous section, so that they can be applied to the SR-$(SC)^2$ dressing of MR-SDCI matrices.

In order to generalise the procedure proposed above, we write Eq. (10) in the following way:

$$\tilde{R} = \tilde{R}^{CI} \left(\frac{1}{\tilde{c}_0^2} \right) + R_{00}^{SCF} \left(1 - \frac{1}{\tilde{c}_0^2} \right), \tag{12}$$

where $\tilde{R}^{CI}$ stands for $\langle \tilde{\Psi} | \hat{R} | \tilde{\Psi} \rangle$. The CI superscript helps to make explicit that $\tilde{R}^{CI}$ is calculated with a (truncated) CI-like expansion normalised to unity. The SCF redundant superscript has been added to R_{00}^{SCF} in order to accord the notation with that used below in this section. Note now that $(1/\tilde{c}_0^2)$ is the quotient of the norms of $\left| \tilde{\Psi} \right\rangle$ and its denormalised counterpart $\left| \tilde{\Psi}' \right\rangle$. If we denote as a_0 this norms quotient

$$a_0 = \frac{\left\| \tilde{\Psi}' \right\|}{\left\| \tilde{\Psi} \right\|} = \frac{1}{\tilde{c}_0^2} \tag{13}$$

then Eq. (12) can be written as:

$$\tilde{R} = \tilde{R}^{CI} a_0 + R_{00}^{SCF} (1 - a_0). \tag{14}$$

Written in this way, Eq. (14) looks similar to the expression derived by Ahlrichs et al. [29] for the first order density matrix corresponding to the CPF. In the CPF case, the factor a_0 can be rigorously defined and corresponds to a quotient of the traces of appropriately defined one-particle density matrices.

Suppose now that we are dealing with a state m that would be properly represented by an MR main space, in the MR-$(SC)^2$ approach. In the corresponding model space (PS+IS), we would have

$$\left| \tilde{\Psi}^m \right\rangle = \sum_{I \in MR_m} \tilde{C}_I^m \phi_I + \sum_i \tilde{c}_i^m \phi_i. \tag{15}$$

If $\left| \tilde{\Psi}^m \right\rangle$ would have been calculated by means of a true MR-$(SC)^2$ method, it would look rather simple to generalise Eq. (14) since one could write

$$a_0 \approx \frac{1}{\sum_{I \in MR_m} \left(\tilde{C}_I^m \right)^2} \tag{16}$$

and replace R_{00}^{SCF} by R_{mm}^{MR} in Eq. (14), obtaining the following expression:

$$\tilde{R}_m = \tilde{R}_m^{CI} a_0 + R_{mm}^{MR} (1 - a_0), \tag{17}$$

where $\tilde{R}_m^{CI} = \left\langle \tilde{\Psi}^m \right| \hat{R} \left| \tilde{\Psi}^m \right\rangle$ and $R_{mm}^{MR} = \left\langle \Psi_m^{MR} \right| \hat{R} \left| \Psi_m^{MR} \right\rangle$. The last quantity requires a small independent calculation in the MR space of determinants as practiced in the generalised Davidson correction of MR-CI energies.

As indicated above, we have not used an MR-$(SC)^2$ method. We use instead the simpler approach that combines the one-state SR-$(SC)^2$ dressing with MR-SDCI spaces of determinants that adds flexibility to the description of the electronic situations. We will assume that Eqs. (16) and (17) can be used at this level of approximation. In the present work, some test calculations have been performed to evaluate this assumption. We have derived here the Eq. (17) as a simple generalization of Eq. (14). However, it shows a formal structure that is similar to that derived by Gdanitz and Ahlrichs [30] for the density matrix for the MR-ACPF functional, which, in turn, can be generalised to other related functionals such as the MR-AQCC one [31].

In the next section, we propose simple test calculations to verify that the procedures described above yield size-consistent values accurate enough for practical purposes. The size-consistent behaviour of the $(SC)^2$ calculations is tested by calculating some property values for separated systems (systems 1 and 2) and, after adding them, comparing the results to those obtained by a single calculation in the corresponding super-molecule (system 3). Properties calculated for a system with a size-consistent method should not be affected by the presence of other systems that are far enough apart. We intend to verify to what extent the mean value property calculations from the SR-$(SC)^2$-CI expansions satisfies this separability condition.

The next section is organized in three main parts. In the first one some tests are reported concerning the reference dressing state (RDS) itself and using single reference SDCI functions to calculate ground state properties. In a second part, tests of the generalised size-consistent correction applied to multireference SDCI based functions for ground state properties are reported. Finally, the test calculations in the third part involve MR-SDCI functions for either ground state or excited state properties.

In Sect. 4 a number of ground state calculated dipole and quadrupole moments are reported and compared to theoretical and experimental values in order to show the improvement of the corrected dressing results in relation to the undressed SDCI ones.

3 Results and discussion; size-consistency tests

3.1 Simple reference ground state calculation tests

3.1.1 Computational details

The molecular electric quadrupole moment of C_2H_2 (System 1) was calculated in the presence of two Beryllium atoms separated by 600 a.u. (System 2) so that the supermolecule (System 3) has a Be atom at each side of the C_2H_2. All the atoms were placed on the same axis and the Systems 1 and 2 are centred in the same point. The electric quadrupole is the first non-vanishing electric moment for these systems. The basis set is of ANO type [32,33] $3s2p1d/2s1p$ and

the experimental geometry [34] was used for C_2H_2($R_{(C-C)}$ 2.27351 a.u.; $R_{(C-H)}$ 2.00719 a.u.).

As a second test example, the dipole and quadrupole moment of SiO were calculated with the d-aug-cc-pVTZ basis set [35]. The Si–O distance was 1.509739 Å [36]. In this case, two helium atoms at ca. 756 a.u. (400.00 Å) compose the System 2. Systems 1, 2, and 3 had all their atoms placed on the same axis and the centre of mass of all of them was located at the same point.

Unless otherwise indicated the quadrupole moments are reported in the θ traceless form described by Buckingham [37]. In linear systems placed along the z axis, the three components of quadrupole moment are related by $\theta_{zz} = -2\theta_{xx} = -2\theta_{yy}$ so that only the zz component needs to be reported. The calculated properties are given relative to the centre of mass in all cases.

In the above mentioned examples, the properties of the System 2 are zero for symmetry reasons. This would make computations simpler. However, we have explicitly calculated the null property components in order to test that the computer codes were working properly and that round off errors due to long distances in the actual calculation of supermolecule system 3, did not occur. These "zero-calculation" tests can be significant. Note, e.g., that the result must be a null quadrupole moment of two Be atoms lying 600 a.u. apart consequent upon an adequate cancellation of both the electronic and the nuclear point charge contributions, both being large due to large distances from the common origin.

3.1.2 Results

The values of the calculated properties for the two examples described above are shown in Table 1. The results are detailed for the sum of the individual systems 1 and 2 and for the supermolecule System 3. The last column in Table 1 reports the size consistency errors calculated as the absolute value of the difference between the values in the two previous columns.

As indicated above, the traceless quadrupole moments and the dipole moments of System 2 are null in the examples of this section. Consequently, the calculated property values with a size-consistent method should be the same for Systems 1 and 3, irrespective of whether the System 2 is present or not.

We can see from Table 1 that the mean value properties obtained using Eqs. (1) and (2) with the SR-SDCI and the $(SC)^2$-SR-SDCI ground state vectors are not size-consistent because the moments of System 3 are different from those of System 1 plus System 2 in all cases. In order to test the arguments that lead to Eq. (10), this equation has been applied also with the SR-SDCI and $(SC)^2$-SR-SDCI vectors. The corresponding values are reported as corresponding to *corrected* methods, and clearly show that only the corrected $(SC)^2$-SR-SDCI values achieve the size consistency. Of course, the application of the correction algorithm to the SR-SDCI method is not justified and this is clearly reflected in the results. It was performed just as an independent

Table 1 Ground state size-consistency tests. Property values and size-consistency errors for SR calculations

Tests and methods	System 1 + system 2	System 3	S-C error (Abs value)
Be–C_2H_2–Be, θ_{zz}			
SR-SDCI	5.1622	5.2295	0.0673
$(SC)^2$-SR-SDCI	5.0072	5.0952	0.0880
Corrected SR-SDCI	5.1104	5.1563	0.0459
Corrected $(SC)^2$ -SR-SDCI	4.9260	4.9261	0.0001
He–SiO–He, μ_z			
SR-SDCI	1.3110	1.3197	0.0087
$(SC)^2$-SR-SDCI	1.1585	1.1608	0.0023
Corrected SR-SDCI	1.2953	1.3043	0.0090
Corrected $(SC)^2$-SR-SDCI	1.1124	1.1124	0.0000
He–SiO–He, θ_{zz}			
SR-SDCI	−3.4610	−3.4857	0.0246
$(SC)^2$-SR-SDCI	−3.0027	−3.0094	0.0067
Corrected SR-SDCI	−3.4168	−3.4423	0.0255
Corrected $(SC)^2$-SR-SDCI	−2.8686	−2.8687	0.0001

All values in atomic units. See text for details and a complete description of Systems 1–3 for each test

control. Note that the behaviour of the *corrected* SDCI is even worse than that of the non-corrected SDCI. On the other hand, the corrected $(SC)^2$-SR-SDCI properties are size consistent in all the tests, showing a maximum size-consistency error of 0.0001 a.u. This result is satisfactory because the energies were converged usually at 10^{-6}–10^{-8} a.u., so that the property errors lie in the order of the calculated precision for the expansion coefficients.

As the first example reveals, using Eq. (2) with $(SC)^2$-SR-SDCI function can lead to greater size-consistency errors than those from conventional SDCI. Moreover, the size-consistent errors concerning the quadrupole moment are not negligible. In the same molecular system (acetylene, two Be atoms, DZP ANO basis set) the size-consistency error for the energy amounts to 0.03 a.u. for SR-SDCI while that of $(SC)^2$ is smaller than 10^{-6} a.u. The examples in Table 1 show that the calculation of $(SC)^2$ mean value properties can make sense only when the correction by Eq. (10) is applied.

3.2 Multireference ground state calculation test

3.2.1 Computational details

Three example systems have been used to test ground state wave functions in the form of MR-CI expansions. In the first example, System 1 is the chlorine molecule (Cl_2). Its quadrupole moment components were calculated at the experimental equilibrium geometry [38] ($R = 3.75639$ a.u.) with the d-aug-cc-pVTZ basis set. A small multireference space was used involving two MOs, two electrons and two determinants ($|0\rangle$ and $(HOMO)^{-2} \rightarrow (LUMO)^{+2}$). System 2 consists of two Helium atoms separated by ca. 189 a.u. (100.00 Å). Their properties, just for test purposes, have been calculated with a small ANO $2s$ basis set. In this way it was easy to have MOs essentially localized for the supermolecule System 3 and to choose an MR space for System 3 equivalent to that of System 1. System 3 had all its atoms placed on the same axis and Systems 1, 2, and 3 were centred at the same point.

In the second example, Systems 1 and 2 were identical: a chlorine molecule at the experimental equilibrium geometry. The quadrupole moment was calculated using a basis set $4s3p2d1f$ of ANO type [32,33]. System 3 is formed in this example by the two chlorine molecules with all the atoms placed on the same axis at a distance of ca. 756 a.u. (400.00 Å) between their centres of mass. The multireference space for each Cl_2 was the same as that for the previous example, but that of System 3 comprised the four MOs, four electrons and three determinants that resulted from the combination of the active spaces of Systems 1 and 2. The core electrons were kept frozen in the post-SCF calculations.

Finally, the third example system is the SiO plus two He model described in Sect. 3.1.1. Both the dipole and quadrupole moments were calculated in this case. The active space for Systems 1 and 3 included four electrons in four MOs, and five determinants ($|0\rangle$ and the two single excitations that describe the first excited singlet state of SiO, as well as their spin partners)

Computational rounding errors occur in the Cl_2 + Cl_2 system due to the huge value of the nuclear contribution to the quadrupole moment. Hence, the property reported in the Cl_2 + Cl_2 test system is the traced quadrupole moment Q_{xx} for which the nuclear component is zero and has not been calculated. The traceless quadrupole moments are reported in the other two examples.

3.2.2 Results

The results obtained for ground state properties with MR-CI expansions are shown in Table 2. The size-consistency errors reported in the last column show that, in spite of the approximated nature of Eq. (17) used along with Eq. (16), the corrected $(SC)^2$-MR-SDCI values behave much better than the others. The size-consistency correction is relevant in all cases where it is clearly needed. The correction slightly improves the values for the first example. In this case the size-consistency errors are close to the precision limit of the calculations

Table 2 Ground state size-consistency tests. Property values and size-consistency errors for MR calculations

Tests and methods	System 1 + system 2	System 3	S-C error (Abs value)
He–Cl_2–He, θ_{zz}			
MR-SDCI	2.2500	2.2495	0.0005
$(SC)^2$-MR-SDCI	2.2713	2.2709	0.0005
Corrected MR-SDCI	2.2530	2.2526	0.0005
Corrected $(SC)^2$-MR-SDCI	2.2789	2.2788	0.0002
Cl_2–Cl_2, Q_{xx}			
MR-SDCI	−38.5508	−38.4954	0.0553
$(SC)^2$-MR-SDCI	−38.6106	−38.5804	0.0303
Corrected MR-SDCI	−38.5684	−38.5144	0.0540
Corrected $(SC)^2$-MR-SDCI	−38.6425	−38.6390	0.0035
He–SiO–He, μ_z			
MR-SDCI	1.2861	1.2931	0.0069
$(SC)^2$-MR-SDCI	1.2103	1.2125	0.0022
Corrected MR-SDCI	1.2674	1.2744	0.0070
Corrected $(SC)^2$-MR-SDCI	1.1727	1.1731	0.0004
He–SiO–He, θ_z			
MR-SDCI	−3.3606	−3.3857	0.0251
$(SC)^2$-MR-SDCI	−3.0060	−3.0138	0.0078
Corrected MR-SDCI	−3.3048	−3.3305	0.0257
Corrected $(SC)^2$-MR-SDCI	−2.8748	−2.8762	0.0014

All values in atomic units. See text for more details and a complete description of Systems 1–3 for each test

and this example is of small relevance just for this reason. On the other hand it can be seen once more that applying the proposed correction to undressed MR-SDCI wave functions makes no sense. The uncorrected $(SC)^2$-MR-SDCI values reveal important size-consistency errors, even if they are distinctly smaller than those of the undressed calculations.

The Cl_2–Cl_2 test shows the greatest size-consistency error reported in the present work for a corrected $(SC)^2$ calculation. However, this is a case where the $(SC)^2$ energy itself is not strictly size-consistent [1838.8202 a.u. (system 1 + system 2) versus 1838.8175 a.u. (System 3)]. In spite of this, the size-consistency error in the $(SC)^2$ energy (2.7 mhartree) is much smaller than that of the equivalent conventional undressed MR-SDCI calculation that amounts to 74 mhartree. Nevertheless, it is not strictly null. This fact is related to the delocalized nature of the MOs, because the $(SC)^2$ energies are size-extensive but they are strictly size-consistent only if the whole set of MOs, including virtuals, are localized in the separated fragments. The calculation of the $Cl_2 + Cl_2$ system has been performed in the C_{2v} symmetry group. If the same calculation is performed in the D_{2h} symmetry group, inversion symmetry favours delocalization of the MOs even at very large distances and the size-consistency error in the $(SC)^2$ energy rises to 7 mhartree. The size-consistency of property values calculated with the corrected $(SC)^2$ approach can then be affected by the extent of the size-consistency condition in the energy at each particular case.

3.3 Multireference Excited States calculation tests

3.3.1 Computational details

Two example systems are included in this section. In the first one, System 1 is the CH^+ cation in the calculation conditions

(geometry and basis set) of the FCI study by Olsen et al. [39]. System 2 is composed of two Helium atoms at 100 a.u. and the ANO type $2s1p$ basis set [32,33] has been used for them. Systems 1 and 2 were placed on two perpendicular axes to form the supermolecule System 3: the centre of mass of System 2 was located in the CH axis at 0.1025 a.u. of the C atom (i.e., at 0.26808 a.u. from the centre of mass of CH group). The selected MR space for systems 1 and 3 included six MOs, two electrons, and nine determinants (|0>, two diexcitations and three single excitations that are needed for an appropriate description of the first four A_1 states of CH^+). Both the dipole and the quadrupole moments were calculated for the ground state and the first two excited states of A_1 symmetry. The calculation was performed in the C_{2v} symmetry group.

Due to the geometry of System 3, its centre of mass is not the same as that for System 1. In this case, the quadrupole moment is not the first non-null electric moment so that it depends on the origin. In order to report quadrupole data relative to the same origin, the quadrupole moments of both systems were calculated relative to the centre of mass of CH^+ that occurs at (0.16558134, 0.0, 0.0) a.u. if the origin is placed at the C atom.

In the second example, system 1 was the C_2H_2 molecule as described in Sect. 3.1.1. The same $3s2p1d$ basis set was used for System 2, which was made of two Ne atoms separated by 100 a.u. In the supermolecule System 3, all the atoms were placed in the same axis, and Systems 1 and 2 were centred at the same point. The selected MR space included four MOs, four electrons, and five determinants. The quadrupole moments of the ground state and the first A_g state were calculated. The calculation was carried out in the D_{2h} symmetry group. All the quadrupole moments for these examples are reported in the traceless form and the θ_{zz} component is shown.

Table 3 Ground and excited states size-consistency tests. Property values and size-consistency errors for MR calculations

Tests and methods	System 1 + system 2	System 3	S-C error (Abs value)
He–CH$^+$–He, μ_z			
(SC)^2-MR-SDCI G.S.	0.8045	0.8055	0.0010
(SC)^2-MR-SDCI 1^1 A$_1$	0.6055	0.6045	0.0011
(SC)^2-MR-SDCI 2^1 A$_1$	0.7176	0.7162	0.0015
Corrected (SC)^2-MR-SDCI G.S.	0.7986	0.7987	0.0001
Corrected (SC)^2-MR-SDCI 1^1 A$_1$	0.6308	0.6313	0.0005
Corrected (SC)^2-MR-SDCI 2^1 A$_1$	0.7547	0.7553	0.0006
He–CH$^+$–He, θ_{zz}			
(SC)^2-MR-SDCI G.S.	−0.2356	−0.2357	0.0000
(SC)^2-MR-SDCI 1^1 A$_1$	3.7498	3.7538	0.0041
(SC)^2-MR-SDCI 2^1 A$_1$	3.8166	3.8195	0.0029
Corrected (SC)^2-MR-SDCI G.S.	−0.2374	−0.2377	0.0003
Corrected (SC)^2-MR-SDCI 1^1 A$_1$	3.6637	3.6627	0.0010
Corrected (SC)^2-MR-SDCI 2^1 A$_1$	4.2673	4.2673	0.0000
Ne–C$_2$H$_2$–Ne, θ_{zz}			
(SC)^2-MR-SDCI G.S.	5.1052	5.1354	0.0302
(SC)^2-MR-SDCI 1^1 A$_g$	9.0107	8.9992	0.0115
Corrected (SC)^2-MR-SDCI G.S.	5.0370	5.0403	0.0033
Corrected (SC)^2-MR-SDCI 1^1 A$_g$	9.0379	9.0367	0.0013

All values in atomic units. See text for more details and a complete description of Systems 1–3 for each test

3.3.2 Results

The calculated values of dipole and quadrupole moments of these example systems are reported in Table 3. The uncorrected and corrected (SC)^2-MR-SDCI results are shown. The size-consistency errors show that the correction works to similar accuracy for both ground and excited states. The accuracy is similar also for dipole or quadrupole moments. The corrections lead to an important decrease of the size-consistent error, which is placed in some cases in the limits of the numerical convergence accuracy. As was found in previous examples, the uncorrected values can lead to small errors, even to unexpected size-consistent behaviour (see, e.g., the θ_{zz} values for the GS of CH$^+$·He$_2$), but in some cases, as it happens in the θ_{zz} values of the C$_2$H$_2$·Ne$_2$ example, the error is not completely eliminated.

4 Size-consistent calculations of properties: Further examples

We have shown in the previous sections that the procedure to calculate size-consistent mean value (SC)^2 properties seems to be well founded, specially for the SR-SDCI case, and it works also for the SR-(SC)^2 approach applied to MR-CI expansions. In the present section, we report a number of calculations of dipole and quadrupole moments to be compared either to accurate theoretical values or to experimental ones. All the results reported in the present section have been obtained in the simplest approach, the (SC)^2-SR-SDCI one. The authors have shown in a previous paper [40] that this method, even in the uncorrected approach, can lead to suitable values of molecular quadrupole moments, provided that basis sets of at least augmented triple zeta quality are

used. Corrected values calculated according to Eq. (10) are reported in Tables 4 and 5 that show the results and allow them to be compared to theoretical and experimental values. The values from conventional SR-SDCI are also reported.

The quadrupole moments reported in Tables 4 and 5 are called effective quadrupole moments ($\theta_{eff} = 2/3 \, [\theta_{xx}^2 + \theta_{yy}^2 + \theta_{zz}^2 \,]^{1/2}$). This θ_{eff} is the value that can be directly compared with experimental measurements and it matches the θ_{zz} component in those molecules where symmetry considerations enforces the condition $\theta_{zz} = -2\theta_{xx} = -2\theta_{yy}$. All the properties were calculated relative to the centre of mass. In the case of polar molecules, if the experimental quadrupole moment was determined from electric field gradient induced birefringence (EFGB) measurements, the experimental property is referred to the effective quadrupole centre (EQC). Otherwise, the experimental values may differ considerably. However, the quadrupole moment value referred to the centre of mass can be calculated from the EQC one only if the dipole moment of the system is known, while other measurement techniques do not present this problem. All the experimental values of quadrupole moment for polar molecules that are quoted in Table 5 refer to the centre of mass and experimental values that could not satisfy this condition have been excluded.

The basis sets used in the calculations are indicated in the tables. In Table 4, the geometry and basis sets were those of the reference calculations unless indicated otherwise. Experimental geometries were used in the calculations reported in Table 5. No ro-vibrational or relativistic effect corrections have been included in the present calculations. The molecular electric properties can exhibit a significant rovibrational dependence that should be taken into account in order to compare properly to experimental values. Moreover, the measurements are usually performed at normal temperatures (ca. 298 K). However, in the case of the quadrupole moments,

Table 4 Dipole and quadrupole moment of different molecules compared to reference theoretical values (Atomic units)

System	Basis set	$\mu_{SR-SDCI}$	$\mu_{(SC)2-SR-SDCI}$	$\mu_{reference}$	Reference
HF	aug-cc-pVDZ	0.7087	0.6945	0.7025	FCI
BH	d-aug-cc-pVQZ	0.5818	0.5537	0.5456	FCI
H_2O	d-aug-cc-pVTZ	0.7408	0.7227	0.7231	CCSD(T)
HCl	d-aug-cc-pVTZ	0.4410	0.4255	0.4209	CCSD(T)
SiS	aug-cc-pVTZ	0.7740	0.5665	0.6099	CCSD(T)
SiO	aug-cc-pVTZ	1.3089	1.1131	1.1870	CCSD(T)
System	Basis Set	$\theta_{SR-SDCI}$	$\theta_{(SC)2-SR-SDCI}$	$\theta_{reference}$	Reference
HF	aug-cc-pVDZ	1.7000	1.6967	1.6959	FCI
BH	d-aug-cc-pVQZ	-2.3590	-2.2852	-2.3213	FCI
Be_3	ANOs 3s2p1d	-2.1620	-2.3412	-2.6461	FCI
N_2	d-aug-cc-pVQZ	-1.0625	-1.1376	-1.1170	CCSD(T)
CO	d-aug-cc-pVQZ	-1.5075	-1.4690	-1.4625	CCSD(T)
CO_2	d-aug-cc-pVQZ	-3.4246	-3.0062	-3.1689	CCSD(T)
C_2H_2	d-aug-cc-pVTZ	5.1019	4.8295	4.8348	CCSD(T)
Cl_2	d-aug-cc-pVTZ	2.2619	2.2886	2.2813	CCSD(T)

Reference FCI values have been taken from references [42] for HF and BH molecules and from reference [45] for Be_3. CCSD(T) values come from references [43] and [44] for H_2O and HCl, reference [36] for SiS and SiO, and references [46–48,34], and [49] for N_2, CO, CO_2, C_2H_2, and Cl_2, respectively

Table 5 Dipole and quadrupole moments of different molecules compared to experimental values (Atomic units)

System	Basis set	$\mu_{SR-SDCI}$	$\mu_{(SC)2-SR-SDCI}$	$\mu_{experimental}^{a}$
BH	d-aug-cc-pVQZ	0.5818	0.5537	0.5335
HCl	d-aug-cc-pVTZ	0.4410	0.4255	0.4301
H_2O	d-aug-cc-pVTZ	0.7408	0.7227	0.7268
NH_3	d-aug-cc-pVTZ	0.6124	0.5976	0.603
System	Basis set	$\theta_{SR-SDCI}$	$\theta_{(SC)2-SR-SDCI}$	$\theta_{experimental}^{b}$
NH_3	d-aug-cc-pVTZ	-2.1664	-2.1988	-2.45 ± 0.3
PH_3	d-aug-cc-pVTZ	-1.6335	-1.5764	-1.56 ± 0.7
H_2O	d-aug-cc-pVTZ	2.1433	2.1612	2.20
HCl	d-aug-cc-pVTZ	2.7022	2.6670	2.62 ± 0.14
SO_2	aug-cc-pVTZ	-4.3258	-3.7010	-3.84
CS_2	aug-cc-pVTZ	2.4221	2.5337	2.56 ± 0.11

[a] Experimental dipole moment reference values have been taken from references [38,44,50] and [51] for BH, HCl, H_2O, NH_3, respectively
[b] Experimental quadrupole moment reference values have been taken from references [52–58] for NH_3, PH_3, H_2O, HCl, SO_2, and CS_2, respectively

this dependence is expected to be small, especially for rigid molecules. Particularly, the rovibrational corrections for the ground rovibrational state contribute no more than a small percentage to the quadrupole moment value [41]. This feature can contribute to the fact that the calculated values of quadrupole moments, even in the absence of rovibrational corrections, generally show good agreement with experimental values. Now, the ammonia molecule is a well known case of a non-rigid system in which the vibrational contributions are quite important (see, e.g., ref [41] and references therein). This could be the root cause of the difference between the calculated and the experimental value for this system. The PH_3 system could also be in a similar case, but the experimental value for PH_3 is affected by a large error. There is a noticeable agreement between the calculated and the experimental values in this molecule but these values could be less representative than those for other systems.

Our experience indicates that the vibrational corrections are expected to be of similar amount for both dressed and undressed SDCI calculations so that comparing the respective values to experimental ones is relevant even in the absence of ro-vibrational corrections. As a general trend, the $(SC)^2$-

SR-SDCI property values are in better agreement with both theoretical values and experimental reference values than the undressed SR-SDCI ones. Only for the dipole moment of HF, the SR-SDCI result compares slightly better to the reference calculated value than the $(SC)^2$-SR-SDCI one. This can be explained in terms of the small size of the employed basis set.

Compared to the theoretical reference values, the absolute mean errors are reduced from 0.061 to 0.023 a.u. for the dipole moments and from 0.146 to 0.068 a.u. for the quadrupole moments. When compared to experimental values, the absolute mean errors are decreased from 0.074 to 0.016 and from 0.150 to 0.068 a.u. for dipole and quadrupole moments, respectively. The present study shows that the proposed corrected procedures work in the correct direction.

The reported results are size-consistent and improved in relation to the SDCI ones. However, an important test remains to be performed in relation to these results, as they should be compared with the corresponding property values obtained by means of a derivative approach (e.g., by differentiation of the energy with respect to an external perturbation).

5 Conclusions

The $(SC)^2$-SR-SDCI procedure can yield as many vectors as roots are found for the dressed SDCI matrix. These vectors can be used to calculate size-consistent one-electron properties of the molecule as mean values of the corresponding operators, but some caution is required. Given the single-reference nature of the intermediate hamiltonian, and the intermediate normalisation of the correlation method implicit to the $(SC)^2$ approach, the coefficient expansions must be unnormalised. But this is not enough to assure a size-consistent behaviour of the property values, because the mean value calculation of a property whose operator has not been explicitly dressed (as the hamiltonian was) would involve the overcorrection of high order effects that had not been partially included in the wave function. We propose the approach shown in Eq. (10) as a procedure for calculating size-consistent first order one-electron properties from converged $(SC)^2$-SR-SDCI vector coefficients. The application of this procedure to a number of test systems indicates that the values obtained from the corrected method behave as size-consistent property values to the limits of the numerical accuracy. Deviations from this condition can occur that are associated to significant deviations in the energy separability condition itself. These deviations are related, in turn, to the property of the $(SC)^2$ method of behaving as strictly separable only if the one-electron basis is localised in the fragments. The results in the present work show also that the correction procedure is well founded in the formal properties of the dressing approach and makes sense only if it is applied to the $(SC)^2$ vectors.

The procedure can be generalized to $(SC)^2$-MR-CI calculations by means of Eq. (17). The result of the tests shows that the size-consistent errors are significantly smaller than those occurring when the procedure is not applied, and, as it can be expected, smaller than those obtained with the undressed MR-SDCI method.

Finally, we have verified that the corrected $(SC)^2$-SR-SDCI properties are in better agreement with theoretical and experimental reference values than those obtained with the bare SR-SDCI method.

References

1. Shavitt I (1998) Mol Phys 94:3
2. Shavitt I (1977) In: Schaeffer HF (ed) Methods of electronic structure theory. Plenum Press, New York
3. Klessinger M, Michl J (1995) Excited states and photochemistry of organic molecules. VHC Publishers, New York
4. Langhoff SR, Davidson ER (1974) Int J Quantum Chem 8:61
5. Davidson ER, Silver DW (1977) Chem Phys Lett 52:403
6. Siegbahn PEM (1978) Chem Phys Lett 55:386
7. Kutzelnigg W (1992) The many-body perturbation theory of Brueckner and Goldstone. In: Mukherjee D (ed) Applied many-body methods in spectroscopy and electronic structure. Plenum Press. New York, p 1
8. Bueckner KA (1955) Phys Rev 97:1353
9. Bueckner KA (1955) Phys Rev 100:36
10. Goldstone J (1957) Proc Roy Soc Lond A 240:263
11. Lindgren I, Morrison J (1986) Atomic many-body theory: Springer, Berlin Heidelberg New York
12. Heully JL, Malrieu JP (1982) Chem Phys Lett 199:545
13. Malrieu JP, Durand Ph, Daudey JP (1985) J Phys A 18:809
14. Daudey JP, Heully JL, Malrieu JP (1993) J Chem Phys 99:1240
15. Durand Ph, Malrieu JP (1986) In: Lawley KP (ed) Ab initio methods in quantum chemistry, vol 1. Wiley, New York, p 321
16. Durand Ph. Malrieu JP (1987) Adv Chem Phys 57:321
17. Evangelisti S, Daudey JP, Malrieu JP (1987) Phys Rev A 35:4930
18. Sánchez-Marín J, Nebot-Gil I, Malrieu JP, Heully JL, Maynau D (1997) Theor Chim Acta 95:215
19. Meyer W (1973) J Chem Phys 58:1017
20. Meyer W (1974) Theor Chim Acta 35:277
21. Pitarch-Ruiz J, Sánchez-Marín J, Maynau D (2000) J Chem Phys 112:1655
22. Reinhardt P (2000) Theor Chem Acc 104:426
23. Meller J, Malrieu JP, Caballol R (1996) J Chem Phys 104:4068
24. Chattopadhyay S, Mahapatra US, Datta B, Mukherjee D (2002) Chem Phys Lett 357:426
25. Chattopadhyay S, Pahari D, Mukherjee D, Mahapatra US (2004) J Chem Phys 120:5968
26. Chattopadhyay S (2004) J Phys B At Mol Opt Phys 37:1783
27. Meller J, Malrieu JP, Heully JL (2003) Mol Phys 101:2029
28. Pitarch-Ruiz J, Sánchez-Marin J, Maynau D (2002) J Comput Chem 23:1157
29. Ahlrichs R, Scharf P, Ehrhardt C (1985) J Chem Phys 82:890
30. Gdanitz RJ, Ahlrichs R (1988) Chem Phys Lett 143:413
31. Szalay PG, Müller T, Lischka H (2000) Phys Chem Chem Phys 2:2067
32. Widmark PO, Malmqvist PA, Roos BO (1990) Theor Chim Acta 77:291
33. Widmark PO, Persson BJ, Roos BO (1991) Theor Chim Acta 97:491
34. Halkier A, Coriani S (1999) Chem Phys Lett 303:408
35. Woon DE, Dunning TH (1994) J Chem Phys 100:2975
36. Maroulis G, Makris C, Xenides D, Karamanis P (2000) Mol Phys 98:481
37. Buckingham AD (1967) Adv Chem Phys 12:107
38. Lide DR (ed) (1999) CRC handbook of chemistry and physics 80th ed. CRC Press, London
39. Olsen J, Sánchez de Merás AM, Jensen HJAa, Jorgensen P (1989) Chem Phys Lett 154:380
40. Junquera-Hernández JM, Sánchez-Marín J, Maynau D (2002) Chem Phys Lett 359:343
41. Piecuch P, Spirko V, Paldus J (1996) J Chem Phys 105:11068
42. Halkier A, Larsen H, Olsen J, Jorgensen P, Gauss J (1999) J Chem Phys 110:734
43. Maroulis G (2000) J Chem Phys 113:1813
44. Mérawa M, Dargelos A (2000) J Mol Struct Theochem 528:37
45. Junquera-Hernández JM, Sánchez-Marín J, Bendazzoli GL, Evangelisti S (2004) J Chem Phys 120:8405
46. Halkier A, Coriani S, Jorgensen P (1998) Chem Phys Lett 294:292
47. Rizzo A, Coriani S, Halkier A, Hattig C (2000) J Chem Phys 113:3077
48. Coriani S, Halkier A, Rizzo A, Ruud K (2000) Chem Phys Lett 326:269
49. Junquera-Hernández JM, Sánchez-Marín J, Pérez-Mondéjar V, Sánchez de Merás A (2003) Chem Phys Lett 378:211
50. Muentner JS, Klemperer W, (1970) J Chem Phys 52:6033
51. Halkier A, Koch H, Christiansen O, Jorgensen P, Helgaker T (1997) J Chem Phys 107:849
52. Kukolich SG (1970) Chem Phys Lett 5:401
53. Kukolich SG (1971) Chem Phys Lett 12:216

54. Höfinger S, Wendland M (2002) J Quantum Chem 86:199
55. Verhoeven J, Dymanus A (1970) J Chem Phys 52:3222
56. Leeuw FH, Dymanus A (1973) J Mol Spectrosc 48:427
57. Ellenbroek WA, Dymanus A (1976) Chem Phys Lett 42:42
58. Coriani S, Halkier A, Rizzo A, Ruud K (2000) Chem Phys Lett 326:269