# CC2 excitation energy calculations on large molecules using the resolution of the identity approximation

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A new implementation of the approximate coupled cluster singles and doubles method CC2 is reported, which is suitable for large scale integral-direct calculations. It employs the resolution of the identity (RI) approximation for two-electron integrals to reduce the CPU time needed for calculation and I/O of these integrals. We use a partitioned form of the CC2 equations which eliminates the need to store double excitation cluster amplitudes. In combination with the RI approximation this formulation of the CC2 equations leads to a reduced scaling of memory and disk space requirements with the number of correlated electrons ($n$) and basis functions ($N$) to, respectively, $\mathcal{O}(N^2)$ and $\mathcal{O}(nN^2)$, compared to $\mathcal{O}(n^2N^2)$ in previous implementations. The reduced CPU, memory and disk space requirements make it possible to perform CC2 calculations with accurate basis sets on large molecules, which would not be accessible with conventional implementations of the CC2 method. We present an application to vertical excitation energies of alkenes $C_{2n}H_{2n+2}$, for $n=1-12$, and report results for the lowest lying dipole-allowed transitions for the TZVPP basis sets, which for $n=12$ contain 1108 basis functions. Comparison with conventional CC2 results for the smaller alkenes show that for CC2 ground state energies and for excitation energies of valence states, the error due to the RI approximation is negligible compared to the usual basis set error, if auxiliary basis sets are used, which have been optimized for MP2 energy calculations. © *2000 American Institute of Physics.* [S0021-9606(00)31237-5]

## I. INTRODUCTION

Since the first implementations of excitation energies within the framework of coupled cluster response theory were reported[1–4] between 1984 and 1990 for the coupled cluster singles and doubles (CCSD) model, the coupled cluster response approach has gained increasing popularity and has been applied to many different properties. Today it can be considered one of the most important standard approaches for the calculation of accurate excitation energies and frequency-dependent molecular properties for small and medium sized molecules. Implementations for excitation energies have now been reported for a broad spectrum of methods covering coupled cluster singles (CCS, for excitation energies also known as configuration interaction singles, CIS, or Tamm–Dancoff approximation, TDA), the approximate coupled cluster singles and doubles method CC2,[5] the CCSD model, and numerous methods with iterative or noniterative approximations for the contributions of connected triples (CCSDT-1a,[6,7] CCSDT-1b,[8] CCSDT-3,[9] EOM-CCSD(T),[10] CC3,[11,12] CCSDR(3),[13] CCSDR(1a),[13] CCSDR(1b)[13] ...). With increasing complexity and computational costs, these methods give increasingly accurate results for excitation energies. In particular the sequence CCS, CC2, CCSD and CC3 has been shown to form a systematic hierarchy for excitation energy calculations with average and maximum errors decreasing approximately by a factor of 3 at each new level.[14]

Recently, integral-direct implementations have been reported[15,16] for some of these methods which extended in particular the applicability of the CC2 and the CCSD model to large scale calculations on molecules with up to 10–15 atoms and 400–600 basis functions, provided that molecular point group symmetry can be employed to reduce computational efforts. Applications to larger systems are hampered for the CCSD model by the steep increase of the computational costs (in terms of CPU time), which for the most expensive contributions scale as $n^2N^4$ and $n^3N^3$, where $n$ is the number of correlated electrons and $N$ the size of the basis set. For integral-direct CC2 calculations[16] the most severe bottlenecks are, beside the computational costs for calculation ($\propto N^4$), I/O ($\propto N^4$) and transformation of the two-electron integrals ($\propto nN^4$), the large memory and disk space demands scaling as $n^2N^2$. In particular the latter demands restrict today the applicability of the implementation to systems with less than $4\times10^8$ double excitation amplitudes (e.g., $\approx40$ occupied orbitals and $\approx500$ basis functions in $C_1$ symmetry).

A number of different approaches have been proposed in the last years to reduce the computational costs of electron correlated methods. For example the local correlation ansatz developed by Pulay and Sæbo[17,18] and Schütz and Werner,[19] or the Laplace transformation proposed by Almlöf and Häser[20–22] for MP2 and the perturbative triples correction included in CCSD(T) or the resolution of the identity (RI) approximation[23,24] implemented, e.g., for MP2[25–28] and CCSD.[29] Despite their unquestionable advantages all of these approaches still have some weaknesses. The local correlation methods neglect about 1%–5% of the correlation energy and

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rely on the use of small, compact basis sets to obtain efficient screening ratios. Also the efficiency of the Laplace transformation methods depends on screening ratios and thus on the use of compact basis sets, and in practice significant savings in the computational costs can first be expected for relatively large molecules. The resolution of the identity (RI) approximation reduces for electron correlated methods enormously the pre-factor but not the scaling of the computational costs with the size of the system.

However, since the efficiency of the RI approximation does not depend on screening ratios and thereby on localization or compact basis sets, it is well suited for correlated methods for excitation energies, which usually require basis sets of at least polarized triple zeta quality in order to provide results with a balanced accuracy, i.e., with a basis set error small compared to the error inherent to the method. As we will show in the following, for the approximate coupled cluster singles and doubles model CC2 the RI approximation leads immediately to significant reductions for all bottlenecks present in a conventional AO integral-direct implementation. The computational costs for calculation and transformation of two-electron integrals are reduced by about one order of magnitude, and the memory and disk space demands are reduced from $\mathcal{O}(n^2N^2)$ to, respectively, $\mathcal{O}(N^2)$ and $\mathcal{O}(nN^2)$. Thereby, the RI approximation extends the applicability of the CC2 method to systems which are 2–3 times larger than those that can be handled with a conventional AO integral-direct implementation.

## II. THEORY

The equations for the approximated coupled cluster singles and doubles model CC2 in absence of external perturbations have been introduced by Christiansen *et al.* in Ref. 5 as:

$$\Omega_{\mu_1}=\langle\mu_1|\hat{H}+[\hat{H},T_2]|\mathrm{HF}\rangle=0, \tag{1}$$

$$\Omega_{\mu_2}=\langle\mu_2|\hat{H}+[F,T_2]|\mathrm{HF}\rangle=0, \tag{2}$$

where $\{\langle\mu_1|,\langle\mu_2|\}$ denote the single and double excitation manifolds and $T_2=\Sigma_{\mu_2}t_{\mu_2}\tau_{\mu_2}$ is the double excitation cluster operator. The residual $\Omega$ is also called coupled cluster vector function. $\langle\mathrm{HF}|$ is the SCF wave function and $F$ the SCF Fock operator. $\hat{H}$ is the Hamiltonian, similarity transformed with the exponential function of the single excitation cluster operator $\exp(T_1)$ with $T_1=\Sigma_{\mu_1}t_{\mu_1}\tau_{\mu_1}$:

$$\hat{H}=\exp(-T_1)H\exp(T_1). \tag{3}$$

Using the modified two-electron MO integrals:[30]

$$(pq\hat{|}rs)=\sum_{\alpha\beta\gamma\delta}\Lambda^p_{\alpha p}\Lambda^h_{\beta q}\Lambda^p_{\gamma r}\Lambda^h_{\delta s}(\alpha\beta|\gamma\delta), \tag{4}$$

$$\Lambda^p=C(\mathbf{1}-t_1^T), \tag{5}$$

$$\Lambda^h=C(\mathbf{1}+t_1), \tag{6}$$

TABLE I. Explicit expressions for the CC2 vector functions and for a trial vector linear transformed with the effective Jacobian [Eqs. (1), (2) and (13)]. The single and double excitation parts of the vector function are written respectively as $\Omega_{ai}=\Omega^G_{ai}+\Omega^H_{ai}+\Omega^I_{ai}+\Omega^J_{ai}$ and $\Omega_{aibj}=(1/1+\delta_{ij}\delta_{ab})\{\Omega^E_{aibj}+\Omega^F_{aibj}\}$, where $\hat{F}$ is a Fock matrix calculated from the similarity transformed Hamiltonian $\hat{H}$ and $\hat{t}^{ab}_{ij}=(1+\delta_{ij}\delta_{ab})\{2t^{ab}_{ij}-t^{ba}_{ij}\}$. The transformed vector is written as $\sigma_{ai}(\omega,b_1)=\sigma^0_{ai}+\sigma^G_{ai}+\sigma^H_{ai}+\sigma^I_{ai}+\sigma^J_{ai}$. For the definition of $\hat{b}^{ab}_{ij}$ see Eq. (14).

| | |
|---|---|
| | $\sigma^0_{ai}=\Sigma_b E^{(1)}_{ab}b_{bi}-\Sigma_j b_{aj}E^{(2)}_{ji}$ |
| $\Omega^G_{ai}=+\Sigma_{dlc}\hat{t}^{cd}_{il}\,(ld\hat{|}ac)$ | $\sigma^G_{ai}=+\Sigma_{dlc}\hat{b}^{cd}_{il}\,(ld\hat{|}ac)$ |
| $\Omega^H_{ai}=-\Sigma_{dlk}\hat{t}^{ad}_{kl}(ld\hat{|}ki)$ | $\sigma^H_{ai}=-\Sigma_{dlk}\hat{b}^{ad}_{kl}(ld\hat{|}ki)$ |
| $\Omega^I_{ai}=\Sigma_{dl}\hat{t}^{ad}_{il}\hat{F}_{ld}$ | $\sigma^I_{ai}=\Sigma_{dl}(\hat{b}^{ad}_{il}\hat{F}_{ld}+\hat{t}^{ad}_{il}\overline{F}_{ld})$ |
| $\Omega^J_{ai}=\hat{F}_{ai}$ | $\sigma^J_{ai}=\overline{F}'_{ai}$ |
| $\Omega^E_{aibj}=(\epsilon_a-\epsilon_i+\epsilon_b-\epsilon_j)t^{ab}_{ij}$ | $E^{(1)}_{ab}=\hat{F}_{ab}-\Sigma_{dlk}\hat{t}^{ad}_{kl}(ld\hat{|}kb)$ |
| $\Omega^F_{aibj}=(ai\hat{|}bj)$ | $E^{(2)}_{ij}=\hat{F}_{ij}+\Sigma_{dlc}\hat{t}^{cd}_{il}(ld\hat{|}jc)$ |
| | $\overline{F}_{ld}=\Sigma_{ck}[2(ld\hat{|}kc)-(lc\hat{|}kd)]b_{ck}$ |
| | $\overline{F}'_{ai}=\Sigma_{ck}[2(ai\hat{|}kc)-(ac\hat{|}ki)]b_{ck}$ |

where $C$ is the usual SCF MO coefficient matrix, the explicit expressions for the single and double excitation vector functions $\Omega_{\mu_1}$ and $\Omega_{\mu_2}$ can be cast into the form listed in Table I.

The double excitation part of the CC2 equations has a particularly simple form, which, apart from the modification of the MO two-electron integrals, is identical to the form of the MP2 equations. For a known set of single excitation amplitudes $t_{\mu_1}$, they can thus be solved explicitly for the double excitation amplitudes:

$$t_{aibj}=\frac{1}{1+\delta_{ij}\delta_{ab}}\,\frac{(ai\hat{|}bj)}{\epsilon_i-\epsilon_a+\epsilon_j-\epsilon_b}. \tag{7}$$

Substituting Eq. (7) into the expressions for $\Omega_{\mu_1}$ results in an effective equation for the single excitation amplitudes $t_{\mu_1}$, which references the double excitation amplitudes $t_{\mu_2}$ only as intermediates, calculated and contracted with two-electron integrals ''on-the-fly,'' without need to store a complete set of $t_{\mu_2}$. The effective equations for $t_{\mu_1}$ can be solved using the same algorithms as employed to solve the usual CC2 or CCSD equations, e.g., a simple DIIS algorithm, and require about the same number of iterations to converge.

Eliminating the double excitation part of the CC2 equations alone would not reduce the scaling of the memory and disk space requirements, because an efficient on-the-fly calculation of $t_{aibj}$ from four-index AO integrals $(\alpha\beta|\gamma\delta)$ followed by a contraction with the integrals $(ld\hat{|}ac)$ requires storage of a complete set of either the half-transformed integrals $(\alpha i\hat{|}\gamma j)$, or the three-quarter-transformed integrals $(\alpha i\hat{|}bj)$, scaling with $\sim n^2N^2$. A reduction in the scaling of disk space requirements to $\sim nN^2$ and significant savings in the demands for memory and I/O are obtained with the resolution of the identity (RI) approximation for the two-electron integrals. In the RI approximation the four-index two-electron integrals are expanded in an auxiliary basis $\{P\}$ as

$$(\alpha\beta|\gamma\delta)=\sum_{PQ}(\alpha\beta|P)V_{PQ}^{-1}(Q|\gamma\delta), \tag{8}$$

$$V_{PQ}=(P|Q), \tag{9}$$

where $(\alpha\beta|P)$ are three-index two-electron integrals and $(P|Q)$ two-index two-electron integrals. This allows to perform the AO to MO transformation and some of the contractions with three-index integrals instead of four-index integrals and removes the need to save any four-index integrals on disk. The contractions needed for the calculation of the CC2 vectors resemble some of the contractions needed for the calculation of the MP2 density matrices. Thus, we can for the formulation of an algorithm for the RI-CC2 method follow the same strategies as outlined by Weigend and Häser[28] for the RI-MP2 method. A scheme of the algorithm for the calculation of the CC2 vector function is shown in Fig. 1. The three most important steps are:

- calculation of the three-index RI-integrals and the AO to MO transformation (step 2). This step needs $\mathcal{O}(nN^3)$ CPU time and the subsequent storage of the transformed integrals $\hat{B}_{pi}^{Q}$ on file requires $\sim nN^2$ disk space.
- formation of the four-index MO integrals $(\hat{ai}|\hat{bj})$, calculation of the amplitudes $\hat{t}_{ij}^{ab}$ and contraction with $B_{jb}^{P}$ and $\hat{F}_{jb}$ to $Y_{ia}^{P}$ and $\Omega_{ai}^{I}$ (step 4). This is the most expensive step in terms of CPU time, since the formation of the four-index integrals from the $\hat{B}_{ai}^{Q}$ intermediates and the contraction of the amplitudes with $B_{jb}^{P}$ to $Y_{ai}^{P}$ both need $\mathcal{O}(n^2N^3)$ operations. The memory requirements for arrays keeping the three-index integrals, $(\hat{ai}|\hat{bj})$, $\hat{t}_{ij}^{ab}$ and $Y_{ia}^{P}$ scale with $\sim mNN_{\mathrm{aux}}$, where $m$ is the size of the subsets of occupied orbitals $I$ and $J$ and $N_{\mathrm{aux}}$ the dimension of the auxiliary basis set (typically $N_{\mathrm{aux}}\approx 2.5\times N$). The I/O scales with $nN^2n_I$, where $n_I$ is the number of subsets $I$.
- formation of the intermediate $\Gamma_{i\beta}^{P}$, recalculation of the three-index RI-integrals and contraction with $\Gamma_{i\beta}^{P}$ to $\Omega_{\alpha i}^{G}$ (step 5). This step requires $\mathcal{O}(nN^3n_\Xi)$ operations and $\mathcal{O}(nN^2n_\Xi)$ I/O for the $Y_{ai}^{Q}$ intermediate, where $n_\Xi$ is the number of subsets of basis functions $\Xi$.

The integrals $B_{jb}^{Q}$ are due to the structure of the $\Lambda^p$ and $\Lambda^h$ matrices independent of the cluster amplitudes $t_{\mu_1}$ and can be pre-calculated and stored on disk once at the beginning.

A similar technique as outlined above for the CC2 vector function can be used to reformulate the CC2 eigenvalue problem for excitation energies such that no complete double excitation amplitude vector needs to be stored in memory or on disk. In coupled cluster response theory excitation energies are obtained as eigenvalues of the Jacobian matrix, which is defined as derivative of the vector function with respect to the cluster amplitudes:[3]

$$\mathbf{A}_{\mu_i\nu_j}=\frac{\partial\Omega_{\mu_i}}{\partial t_{\nu_j}}=\begin{pmatrix}\langle\mu_1|[\hat{H},\tau_{\nu_1}]+[[\hat{H},\tau_{\nu_1}],T_2]|\mathrm{HF}\rangle & \langle\mu_1|[\hat{H},\tau_{\nu_2}]|\mathrm{HF}\rangle\\ \langle\mu_2|[\hat{H},\tau_{\nu_1}]|\mathrm{HF}\rangle & \delta_{\mu_2\nu_2}\epsilon_{\mu_2}\end{pmatrix}. \tag{10}$$

The doubles–doubles block $\mathbf{A}_{\mu_2\nu_2}$ is diagonal with diagonal elements $\epsilon_{aibj}=\epsilon_a-\epsilon_i+\epsilon_b-\epsilon_j$. This can be employed to partition the CC2 eigenvalue problem as:

$$\left[\mathbf{A}_{\mu_1\nu_1}-\frac{\mathbf{A}_{\mu_1\gamma_2}\mathbf{A}_{\gamma_2\nu_1}}{\epsilon_{\gamma_2}-\omega}\right]E_{\nu_1}=\omega E_{\mu_1}, \tag{11}$$

$$E_{\mu_2}=-\frac{\mathbf{A}_{\mu_2\nu_1}E_{\nu_1}}{\epsilon_{\mu_2}-\omega}. \tag{12}$$

Equation (11) is an effective, but now nonlinear, eigenvalue equation which has only the dimension of the single excitation manifold. Since the double excitation part of the eigenvector $E_{\mu_2}$ is related in a simple way to the single excitation part $E_{\mu_1}$ via Eq. (12), the complete information which can be obtained from the CC2 model about the excited states is contained in the single excitation part of the eigenvectors and in the excitation energies.

To solve Eq. (11) by iterative techniques, we need the capability to transform for a given guess for $\omega$ a trial vector $b_{\mu_1}$ with the effective matrix appearing on the left hand side of Eq. (11):

$$\sigma_{\mu_1}(\omega,b_1)=\mathbf{A}^{\mathrm{eff}}_{\mu_1\nu_1}(\omega)b_{\nu_1}=\left[\mathbf{A}_{\mu_1\nu_1}-\frac{\mathbf{A}_{\mu_1\gamma_2}\mathbf{A}_{\gamma_2\nu_1}}{\epsilon_{\gamma_2}-\omega}\right]b_{\nu_1}. \tag{13}$$

Like the single excitation part of the vector function $\Omega_{\mu_1}$ the transformed vector $\sigma_{\mu_1}(\omega,R)$ can be computed without storing a complete set of double excitation amplitudes, neither in memory nor on disk. Required is only the capability to calculate and contract on-the-fly with other intermediates the double excitation cluster amplitudes $t_{ij}^{ab}$ and an auxiliary vector $\hat{b}_{ij}^{ab}$,

$$\hat{b}_{ij}^{ab}=\frac{2(\overline{ai}|\overline{bj})-(\overline{bi}|\overline{aj})}{\epsilon_i-\epsilon_a+\epsilon_j-\epsilon_b+\omega} \tag{14}$$

calculated from the modified two-electron MO integrals

$$(\overline{ai}|\overline{bj})=\hat{P}_{ij}^{ab}\sum_{\alpha\beta\gamma\delta}(\overline{\Lambda}_{\alpha a}^{p}\Lambda_{\beta i}^{h}+\Lambda_{\alpha a}^{p}\overline{\Lambda}_{\beta i}^{h})\Lambda_{\gamma b}^{p}\Lambda_{\delta i}^{h}(\alpha\beta|\gamma\delta). \tag{15}$$

1. calculate $\Lambda^p_{\alpha p}$, $\Lambda^h_{\alpha p}$
2. loop I (where I is a subset of active occupied orbitals i)

   calculate $(\alpha\beta|P)$ for all $\alpha$, $\beta$, $P$

   $\hat{B}^Q_{pi} \leftarrow \Lambda^p_{\alpha p}\Lambda^h_{\beta i}(\alpha\beta|P)V^{-1/2}_{PQ}$ for $i \in I$

   store $\hat{B}^Q_{pi}$ on disc

   end loop I
3. form $i^Q = B^Q_{kc}t_{kc}$ and $\hat{F}_{ia} = B^Q_{ia}\, i^Q - B^Q_{ja}\, B^Q_{ib}\, t_{jb}$
4. loop I

   read $\hat{B}^Q_{ai}$ for $i \in I$

   loop J

   – read $\hat{B}^Q_{bj}$ and $B^Q_{jb}$ for $j \in J$

   – $(ai\hat{|}bj) \leftarrow \hat{B}^Q_{ai}\hat{B}^Q_{bj}$

   – $\hat{t}^{ab}_{ij} \leftarrow \{2(ai\hat{|}bj) - (aj\hat{|}bi)\}/\{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b\}$

   – $Y^P_{ai} \leftarrow \hat{t}^{ab}_{ij}\, B^P_{jb}$ and $\Omega^I_{ai} \leftarrow \hat{t}^{ab}_{ij}\, \hat{F}_{jb}$

   end loop J

   store $Y^P_{ai}$ on disc

   end loop I
5. loop $\Xi$ (where $\Xi$ is a subset of basis functions $\beta$)

   loop I

   – read $B^P_{ki}$ and $Y^P_{ai}$ for $i \in I$

   – $\Gamma^P_{i\beta} \leftarrow \{Y^Q_{ai}\Lambda^h_{\beta a} + 2\Lambda^h_{\beta i}\, i^P - \Lambda^h_{\beta c}t_{ck}B^P_{ki}\}V^{-1/2}_{PQ}$

   end loop I

   calculate $(P|\alpha\beta)$ for $\beta \in \Xi$

   $\Omega^{JG}_{\alpha i} \leftarrow \Gamma^P_{i\beta}(P|\alpha\beta)$

   end loop $\Xi$
6. $\Omega_{ai} \leftarrow (\epsilon_a - \epsilon_i)t^a_i + \Omega^I_{ai} + \Lambda^p_{\alpha a}\Omega^{JG}_{\alpha i} - Y^P_{ak}B^P_{ki}$

FIG. 1. Algorithm for a RI-CC2 vector function calculation.

In the last equation, the operator $\hat{P}^{ab}_{ij}$ symmetrizes a function $f_{ai,bj}$ in the index pairs $(ai)$ and $(bj)$ as $\hat{P}^{ab}_{ij}f_{ai,bj} = f_{ai,bj} + f_{bj,ai}$. The transformation matrices $\overline{\Lambda^p}$ and $\overline{\Lambda^h}$ are defined as $\overline{\Lambda^p} = -C\,b_1^T$ and $\overline{\Lambda^h} = C\,b_1$. Explicit formulas for $\sigma_{\mu_1}(\omega,b_1)$ are given in Table I. The intermediates $E^{(1)}_{ab}$ and $E^{(1)}_{ij}$ are independent of the trial vector $b_1$ and can be precalculated and kept on file once the equations for cluster amplitudes $t_{\mu_1}$ have been solved.[15] The contractions required for the individual contributions to $\sigma_{\mu_1}(\omega,b_1)$ have the same structure as the contraction needed for the calculation of the CC2 vector function. The algorithm for calculating $\sigma_{\mu_q}(\omega,b_1)$ is thus obtained straightforwardly by generalizing the algorithm for $\Omega_{\mu_1}$.

A nontrivial complication introduced by the partitioning of the CC2 eigenvalue problem is the nonlinearity of the resulting effective eigenproblem, which stems from the dependence of the effective Jacobian $\mathbf{A}^{\text{eff}}_{\mu_1\nu_1}(\omega)$ on the excitation energy $\omega$. As a consequence the transformed trial vectors $\sigma_{\mu_1}(\omega,b_1)$ depend on $\omega$ and it is no longer possible to use, e.g., the Davidson algorithm to solve simultaneously for several eigenvalues and eigenvectors using a common set of orthonormal trial vectors $b_{\mu_1}$ and the corresponding transformed vectors $\sigma_{\mu_1}(\omega,b_1)$, at least not without modification of the algorithm.

We have found that in practice a combination of two algorithms leads to a sufficiently stable and efficient convergence: If an initial guess is available for the eigenvectors and eigenvalues, which is close enough to the final results, an obvious choice for the solution of the nonlinear problem is a DIIS algorithm similar to the one usually applied to solve the nonlinear coupled cluster equations for the ground state:

(1) In iteration $i$, the transformed vector $\sigma^{(i)}_{\mu_1} = \sigma_{\mu_1}(\omega^{(i)},b^{(i)}_1)$ is constructed for the present approximate eigenvalue $\omega^{(i)}$ and eigenvector $b^{(i)}_{\mu_1}$. A new approximation for $\omega$ is obtained as $\omega^{(i+1)} = (\sigma^{(i)}_{\mu_1}b^{(i)}_{\mu_1})/||b^{(i)}_1||^2$ and the residual is calculated according to $r^{(i)}_{\mu_1} = (\sigma^{(i)}_{\mu_1} - \omega^{(i+1)}\, b^{(i)}_{\mu_1})/||b^{(i)}_1||$.

(2) If the norm of the residual vector $||r^{(i)}_{\mu_1}||$ has become smaller than a predefined threshold the procedure is converged, else a perturbational estimate for an update of the trial vector is calculated as $u^{(i)}_{ai} = r^{(i)}_{ai}/(\epsilon_i - \epsilon_a)$. In the first iteration $u^{(1)}_{\mu_1}$ is used without modification to calculate the next trial vector as $b^{(i+1)}_{\mu_1} = (b^{(i)}_{\mu_1} + u^{(i)}_{\mu_1})/||b^{(i)}_1||$. In all subsequent iterations an improved update vector $u^{(i)'}_{\mu_1}$ is calculated by solving the DIIS problem for the series of $u^{(i)}_{\mu_1}$ vectors. Then the procedure continues with step 1.

The DIIS procedure turned out to be a stable and rapidly convergent algorithm for the solution of the partitioned CC2 eigenvalue problem, provided the initial guesses for eigenvalues and eigenvectors are close enough to the final CC2 results. It has the additional advantage of being a single root algorithm, i.e., it is possible to solve for high lying excitation energies without converging all lower lying states. An initial guess for the CC2 excitation energies and eigenvectors can be obtained, e.g., from the coupled cluster singles (CCS) method. However, often the CCS eigenvalues and eigenvectors or the results of other initial guesses are far from the converged CC2 results and then the DIIS procedure converges only slowly or may even diverge. In this case, the eigenvalues and eigenvectors must be pre-optimized using an alternative algorithm before the DIIS procedure can be applied. For this purpose we use a modification of the Davidson algorithm, which employs that a set of converged eigenvalues and eigenvectors will fulfill the linear generalized eigenproblem

$$\mathbf{A}^{\text{red}} = \mathbf{S}^{\text{red}}\mathbf{\Omega}^{\text{red}}, \tag{16}$$

with

$$A^{\text{red}}_{ij} = E^{(i)}_{\mu_1}A^{\text{eff}}_{\mu_1\nu_1}(\omega^{(j)})E^{(j)}_{\nu_1} = E^{(i)}_{\mu_1}\sigma_{\mu_1}(\omega^{(j)},E^{(j)}), \tag{17}$$

TABLE II. Vertical excitation energies (in eV) for the lowest singlet excited states in ethene $C_2H_4$, obtained with the TZVPP basis sets at the RI-MP2 equilibrium geometry. $\|T_1\|$ is the norm of the single excitation part of the CC3 (right) eigenvectors, $\Delta$ RI is the error (in eV) in the RI-CC2 excitation energies due to the RI approximation.

| Symmetry | B3-LYP | RPA | CCS | RI-CC2 | CCSD | CC3 | $\|T_1\|$ | $\Delta$ RI |
|---|---|---|---|---|---|---|---|---|
| $B_{1u}$ | 7.72 | 7.58 | 8.01 | 8.27 | 8.34 | 8.22 | 0.96 | $-0.78\times10^{-3}$ |
| $B_{1g}$ | 8.09 | 9.14 | 9.19 | 8.73 | 8.65 | 8.59 | 0.93 | $-0.97\times10^{-3}$ |
| $B_{3u}$ | 8.11 | 8.69 | 8.71 | 8.84 | 8.83 | 8.75 | 0.94 | $-2.95\times10^{-3}$ |
| $B_{1g}$ | 8.71 | 9.39 | 9.44 | 9.59 | 9.58 | 9.51 | 0.95 | $-1.17\times10^{-3}$ |
| $B_{2g}$ | 8.96 | 9.81 | 9.84 | 9.81 | 9.78 | 9.68 | 0.93 | $-0.70\times10^{-3}$ |
| $B_{2g}$ | 9.56 | 10.24 | 10.36 | 10.20 | 10.18 | 10.11 | 0.95 | $-1.04\times10^{-3}$ |
| $B_{3g}$ | 10.40 | 11.90 | 11.91 | 11.12 | 11.19 | 11.10 | 0.94 | $-1.37\times10^{-3}$ |
| $A_u$ | 10.52 | 11.43 | 11.46 | 11.53 | 11.49 | 11.32 | 0.86 | $-0.83\times10^{-3}$ |
| $A_u$ | 11.08 | 12.57 | 12.61 | 11.97 | 11.76 | 11.58 | 0.89 | $-0.62\times10^{-3}$ |
| $B_{3u}$ | 11.39 | 12.11 | 12.13 | 12.23 | 12.20 | 12.11 | 0.94 | $-1.09\times10^{-3}$ |
| $B_{2u}$ | 11.28 | 12.85 | 12.88 | 12.15 | 12.23 | 12.14 | 0.94 | $-0.57\times10^{-3}$ |
| $B_{1u}$ | 11.28 | 13.07 | 13.13 | 12.21 | 12.31 | 12.22 | 0.94 | $-0.89\times10^{-3}$ |
| $A_g$ | 12.08 | 12.61 | 12.66 | 12.75 | 12.60 | 12.44 | 0.86 | $-0.94\times10^{-3}$ |
| $B_{3u}$ | 12.23 | 12.48 | 12.56 | 12.81 | 12.75 | 12.64 | 0.93 | $+0.85\times10^{-3}$ |
| $B_{2g}$ | 12.23 | 13.10 | 13.13 | 13.13 | 13.10 | 13.00 | 0.93 | $-1.08\times10^{-3}$ |

and $S_{ij}^{\text{red}}=E_{\mu_1}^{(i)}E_{\mu_1}^{(j)}$ and $\Omega_{ij}^{\text{red}}=\delta_{ij}\omega^j$. Starting from an initial set of approximate eigenvalues and trial vectors the Davidson algorithm and Eq. (16) are used to obtain an improved set of eigenvalues and eigenvectors, ignoring the dependence of $\sigma_{\mu_1}$ on $\omega^{(j)}$. When the results for the norm of the residual vectors become comparable to or smaller than the difference between the present solutions for the eigenvalues and the initial guess, the procedure is restarted using the present optimum solution as new initial guess. These macro cycles are iterated until self-consistency is obtained:

(1) For the new trial vectors $b^{(i)}$ and frequencies $\omega^{(i)}$ the sigma vectors $\sigma^{(i)}=\mathbf{A}^{\text{eff}}(\omega^{(i)})b^{(i)}$ are computed.
(2) The reduced space matrices $\mathbf{A}^{\text{red}}$ and $\mathbf{S}^{\text{red}}$ are set up for the present set of trial vectors and the generalized eigenproblem Eq. (16) is solved to obtain new approximate eigenvalues $\omega^{(j)}$ and eigenvectors $E^{(j)}=\Sigma_i c_{ji}b^{(i)}$.
(3) For each required eigenvalue/eigenvector the residual vector is calculated as $r_{\mu_1}^{(j)}=\Sigma_i c_{ji}\,\sigma^{(i)}-\omega^{(j)}E^{(j)}$. If the norm of the residual vectors has become smaller than the changes in the eigenvalues since the beginning of the macro-iteration, the present macro-iteration is stopped and the procedure is restarted from the present optimal solutions with step 1, discarding all $b^{(i)}$ and $\sigma^{(i)}$ vectors. Otherwise the macro-iteration is continued by extending the reduced space $\{b^{(i)}\}$ for each nonconverged solution $E^{(j)}$ by a new trial vector generated from the residual as $b_{ai}^{(i)}=r_{ai}^{(j)}/(\epsilon_i-\epsilon_a)$. Provided that not all eigenvalues/eigenvectors are converged, the procedure continues with step 1.

## III. EXCITATION ENERGIES FOR THE ALKENES $C_{2n}H_{2n+2}$ FOR $n=1,\ldots,12$

To test the performance of the RI-CC2 method we applied it to the calculation of excitation energies for the lowest singlet excited states in the all-trans alkenes $C_{2n}H_{2n+2}$ with $n=1,\ldots,12$, to investigate in particular two questions:

- How large are the errors in the excitation energies due to the resolution of the identity (RI) approximation?

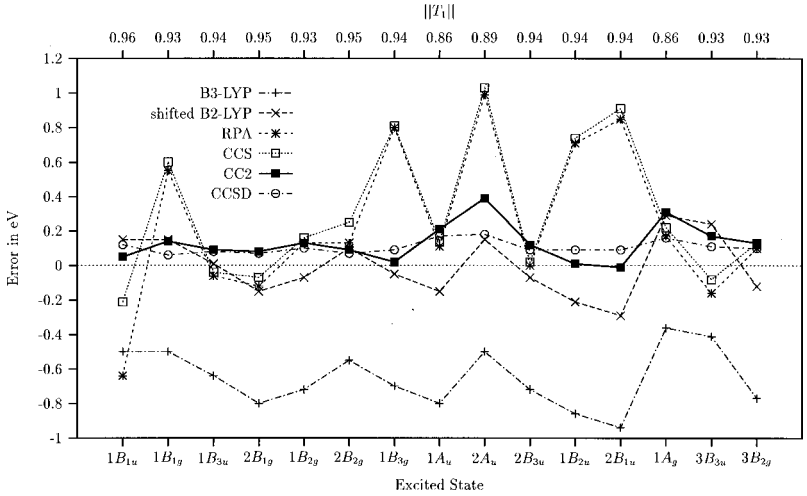



FIG. 2. Performance of different response methods for the lowest 15 excited singlet states of ethane. The plot shows the deviation (in eV) of the B3-LYP, shifted B3-LYP, RPA, CCS, CC2, and CCSD excitation energies from the corresponding CC3 results which are used as benchmark. (For geometry and basis set see text.)

TABLE III. Vertical excitation energies (in eV) for the lowest singlet excited states in *trans*-butadiene $C_4H_6$, obtained with the TZVPP basis sets at the RI-MP2 equilibrium geometry. $\|T_1\|$ is the norm of the single excitation part of the CCSD (right) eigenvectors, Δ RI is the error (in eV) in the RI-CC2 excitation energies due to the RI approximation.

| Symmetry | B3-LYP | RPA | CCS | RI-CC2 | CCSD | $\|T_1\|$ | Δ RI |
|---|---|---|---|---|---|---|---|
| $B_u$ | 5.75 | 6.07 | 6.42 | 6.37 | 6.57 | 0.95 | $-1.20 \times 10^{-3}$ |
| $A_g$ | 6.84 | 8.00 | 8.33 | 7.57 | 7.47 | 0.88 | $-2.11 \times 10^{-3}$ |
| $A_u$ | 7.15 | 8.03 | 8.05 | 7.90 | 7.92 | 0.94 | $-2.82 \times 10^{-3}$ |
| $A_u$ | 7.20 | 8.49 | 8.51 | 8.04 | 8.09 | 0.95 | $-4.01 \times 10^{-3}$ |
| $B_g$ | 7.38 | 8.20 | 8.22 | 8.18 | 8.22 | 0.95 | $-6.88 \times 10^{-3}$ |
| $A_u$ | 7.61 | 8.77 | 8.84 | 8.44 | 8.49 | 0.95 | $-8.08 \times 10^{-3}$ |
| $A_g$ | 8.06 | 9.12 | 9.25 | 8.59 | 8.61 | 0.95 | $-0.23 \times 10^{-3}$ |
| $A_u$ | 8.23 | 9.40 | 9.50 | 8.98 | 9.04 | 0.95 | $+2.53 \times 10^{-3}$ |
| $B_g$ | 8.24 | 9.46 | 9.52 | 9.07 | 9.05 | 0.94 | $+2.41 \times 10^{-3}$ |
| $B_g$ | 8.73 | 9.76 | 9.83 | 9.64 | 9.65 | 0.95 | $-5.36 \times 10^{-3}$ |

- How efficient is the implementation for large molecules?

An additional point is that the CC2 method never before could be applied to molecules with large systems of conjugated double bonds. It is therefore not known how well the CC2 method will perform for such molecules, where the HOMO-LUMO gap between the SCF orbital energies decreases continuously and second-order perturbation theory is expected to break eventually down.

For the calculations on the alkenes we employed the TZVPP basis sets[31,32] from the Turbomole basis set library,[33] consisting of a $[5s2p1d]/(3s2p1d)$ contracted set for H and of a $(11s6p2d1f)/[5s3p2d1f]$ contracted set for C, and for the auxiliary basis for hydrogen of a $(4s3p2d1f)$ and for carbon of a $(8s6p5d3f1g)$ primitive set. This basis is not sufficient to give accurate results for the excited states of the shortest polyenes, in particular of ethene, since for these molecules even the lowest excited states are rather diffuse and have partially Rydberg character. With increasing chain length, however, the character of the lowest dipole allowed transition becomes dominantly $\pi \rightarrow \pi^\star$, and the TZVPP basis sets can be expected to give accurate results for this transition. The geometries used for the CC2 calculations were obtained by optimizing the structures at the RI-MP2 level employing the same basis sets.

In Table II we have listed the lowest 15 excitation energies of ethene as obtained with RI-CC2 compared with CCS, RPA, TDDFT (B3-LYP), CCSD and CC3 results obtained at the same geometry and with the same basis set. The RPA and TDDFT calculations were performed with the ESCF program of the Turbomole package,[34–36] the CCS (non-RI), CC2, CCSD, and CC3 calculation were done with the Coupled Cluster response program of Koch *et al.*[15,30,37] which is interfaced with Dalton, release 1.0.[38] In the last column of Table II the errors of the RI-CC2 excitation energies due to the RI approximation are given. For all states investigated, these errors are of the order of meV, and thus completely negligible compared to the remaining correlation error inherent to the CC2 method which is typically of the order of 0.2–0.3 eV,[14,39] i.e., two orders of magnitudes larger than the RI error.

Since for $C_2H_4$ in the TZVPP basis set full CI calculations are not feasible, we use in the following the CC3 results, which typically deviate by less than 0.1 eV from the corresponding full CI numbers,[14,39] as benchmark to assess the correlation errors inherent to the less accurate methods. Figure 2 shows the deviation of the RPA, CCS, TDDFT, CC2 and CCSD results from the corresponding excitation energies obtained at the CC3 level for the 15 lowest excited states of ethylene. We find the usual pattern: RPA and CCS give similar results with errors as large as 1 eV. For most excitations the RPA and CCS results are blue shifted compared to the CC3 results, but the errors show no correlation with the contributions of double and higher excitations to the excited state, which can approximately be measured as $(1-||T_1||)$, where $||T_1||$ is the norm of the single excitation part of the CC3 eigenvectors. TDDFT with the B3-LYP functional yields excitation energies, which are systematically red shifted by about 0.7 eV. If this systematic error is corrected by shifting the TDDFT results such that the average deviation from the CC3 results becomes zero, the remaining errors in the TDDFT excitation energies are of similar magnitude as the errors in the (uncorrected) CC2 results, i.e., about 0.15–0.2 eV. At the CCSD level the deviations from the CC3 results are reduced to about 0.1 eV. For CC2 and CCSD the remaining correlation error is correlated with the measure for the contribution of double and higher excitation levels, $1-||T_1||$, as obtained at the CC3 level. (This correlation is less good with the $||T_1||$ norm obtained at the CC2 or CCSD level.)

A similar comparison for the lowest 10 excitations in *trans*-butadiene is presented in Table III. Because for this molecule CC3 calculations in the TZVPP basis were no

TABLE IV. Vertical excitation energies for the $1\ ^1B_u$ state for the all-trans polyenes $C_{2n}H_{2n+2}$ in eV, calculated in the TZVPP basis sets at the MP2 equilibrium geometries.

| $n$ | RPA | CCS | TDDFT | CC2 |
|---|---|---|---|---|
| 2 | 6.07 | 6.42 | 5.75 | 6.37 |
| 3 | 5.14 | 5.44 | 4.69 | 5.30 |
| 4 | 4.52 | 4.79 | 4.01 | 4.60 |
| 5 | 4.08 | 4.32 | 3.53 | 4.11 |
| 6 | 3.75 | 3.98 | 3.18 | 3.75 |
| 7 | 3.50 | 3.72 | 2.90 | 3.47 |
| 8 | 3.30 | 3.51 | 2.67 | 3.24 |
| 9 | 3.13 | 3.34 | 2.49 | 3.07 |
| 10 | 3.00 | 3.21 | 2.33 | 2.92 |
| 11 | 2.89 | 3.10 | 2.20 | 2.80 |
| 12 | 2.80 | 3.01 | 2.09 | 2.70 |

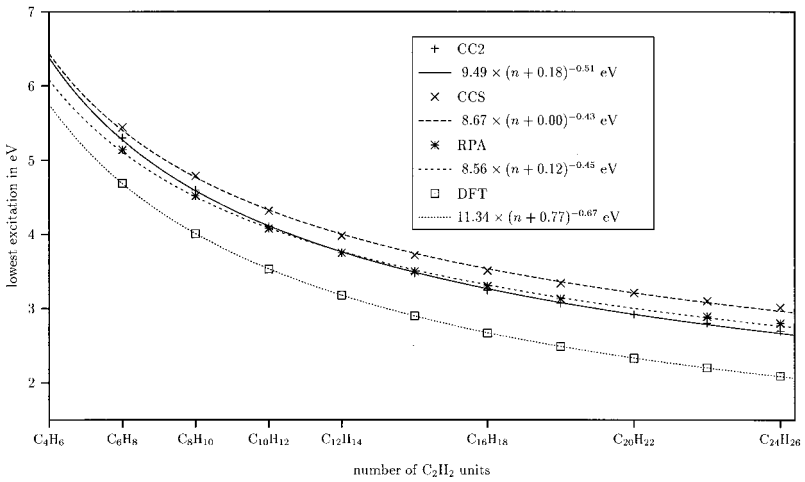



FIG. 3. The lowest singlet excitation energies in the *all-trans* polyenes $C_{2n}H_{2n+2}$ as function of the chain length. Fit of the CC2, CCS, RPA, and DFT (B3-LYP) results (in eV) to a power law of the form $a\times(n+b)^c$, where $n$ is the number of $C_2H_2$ units. (For geometries and basis set see text.)

longer feasible with acceptable costs, we can only compare the results of the lower-order methods with the CCSD numbers. We find the same trends as for ethylene results: for most states the difference between the CC2 and CCSD results is less than 0.1 eV; only for the lowest ($1\,^1B_u$) state the CC2 and CCSD results differ by 0.2 eV. RPA and CCS give again very similar results, for all but the $1\,^1B_u$ state blue shifted compared to the CCSD excitation energies. The deviations between the CCSD results and the RPA and CCS numbers are unsystematic and as large as 0.5 eV (RPA) and 0.8 eV (CCS). Again, TDDFT with the B3-LYP functional yields excitation energies, which are systematically red shifted, compared to the CCSD results by about 0.8 eV. If this systematic deviation is corrected by shifting the TDDFT results such that the average deviation from the CCSD results becomes zero, the remaining deviations are of similar magnitude as deviations between CCSD and the (uncorrected) CC2 results. The errors introduced by the RI approximation ($\Delta$ RI) are for *trans*-butadiene somewhat larger than for ethylene, but still between one and two orders of magnitude smaller than the remaining correlation error inherent in the CC2 method and much smaller than the expected remaining basis set error.

Table IV lists the vertical excitation energies for the lowest dipole allowed transition, $1\,^1B_u \leftarrow 1\,^1A_g$, for the polyenes $C_{2n}H_{2n+2}$ for $n=2,\ldots,12$ for RPA, CCS, B3-LYP and CC2. As shown in Fig. 3, the results fit for all four methods nicely to a power law of the form $\Delta E_{1\,^1B_u \leftarrow 1\,^1A_u}(n) \approx a\times(n+b)^c$. Again, we find that CCS and RPA behave very similar, in particular the exponent $c$ found by least squares fit to the results for $n=2,\ldots,12$, are with $-0.43$ (CCS) and $-0.45$ (RPA) very similar. The excitation energies obtained with CC2 decrease significantly more rapid with increasing carbon chain length $n$ ($c=-0.51$) and the fastest decrease of $\Delta E_{1\,^1B_u \leftarrow 1\,^1A_u}(n)$ is found for B3-LYP with $c=-0.67$.

Figure 4 shows the CPU timings for the calculation of the CC2 vector function $\Omega_{\mu_1}$ and a transformation of a trial vector with the effective Jacobian $A^{\text{eff}}_{\mu_1\nu_1}(\omega)\,b_{\nu_1}$ for the polyenes $C_{2n}H_{2n+2}$ as a function of the chain length $n$ on an IBM Power 3 225 MHz processor, which has a peak performance of 880 MFlops. No molecular point group symmetry was exploited in these calculations. For the lower oligomers ($n \leqslant 6$) a significant fraction of the total CPU time is spent for integral evaluation and transformations and for computing

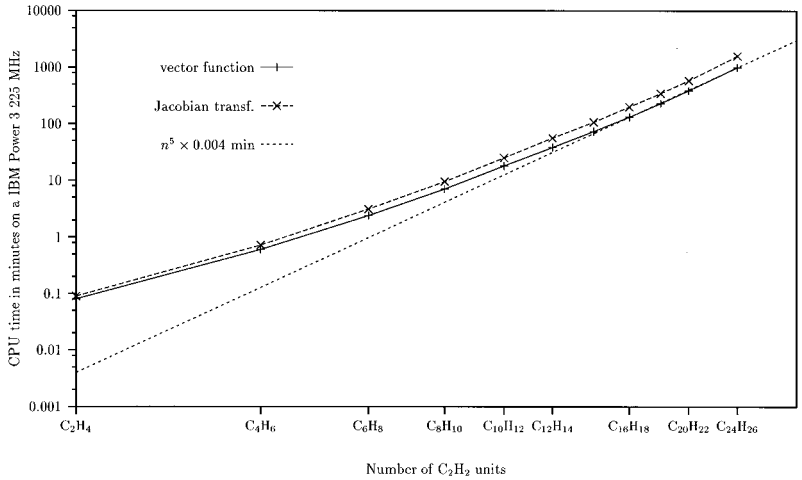



FIG. 4. Scaling of the CPU timings for RI-CC2 calculations with the system size. Shown are the CPU timing in minutes on a 225 MHz IBM Power 3 processor for a single vector function calculation and for the transformation of a single trial vector with the Jacobian matrix for the *all-trans* polyenes as function of the chain length. (For geometries and basis set see text.)

the $\Omega^{JG}$ intermediate, which leads for this range of molecules to an effective scaling between $n^3$ and $n^5$. But for $n>6$ the $\mathcal{O}(n^5)$ steps clearly dominate the operation count and the CPU timings for a vector function calculation increases asymptotically as $n^5\times 0.004$ min. The transformation of a trial vector with the Jacobian matrix takes about 60% longer, which is due to two additional $\mathcal{O}(n^5)$ operations required for the calculation of a $\sigma$ vector compared to the calculation of $\Omega$. For the largest polyene investigated, $C_{24}H_{26}$ with 122 correlated electrons and 1108 basis functions, a vector function calculation takes about 16.7 h and a Jacobian transformation 26.3 h. In the present study we have not employed the molecular point group symmetry to reduce the computational effort, but it can be shown that for the $\mathcal{O}(n^5)$ steps this will lead to a reduction of the operation count by a factor between $1/g^2$ and $1/g$, where $g$ is the group order.[40] Since for large molecules or basis sets more than 90% of the CPU time is spent in matrix–matrix multiplications, the RI-CC2 method is perfectly suited for parallelization on shared memory computers and in particular on symmetric multiprocessor (SMP) systems. For example, on an IBM SP Power 3 SMP machine with nodes which each have eight processors we obtained just by linking with an SMP version of the BLAS library a reduction of the execution time by a factor of 3–4. Parallelization of the routines for computing the AO RI-integrals using OpenMP[41] increased the speed up to 4–6. Taking this into account, one can expect that RI-CC2 calculations with 1500–2000 basis functions and 150–200 correlated electrons will be soon become routine.

## IV. CONCLUSIONS

A new implementation of the approximate coupled cluster singles and doubles method CC2 is reported, which exploits the resolution of the identity (RI) approximation for two-electron integrals and a partitioned form of the CC2 equations, which makes it possible to avoid the storage of double excitation amplitudes. We obtain thereby a major reduction of the computational costs and the scaling of the memory and disk space requirements are reduced from $\mathcal{O}(n^2N^2)$ to, respectively, $\mathcal{O}(N^2)$ and $\mathcal{O}(nN^2)$, which extends the applicability of the CC2 method to molecules 2–3 times larger than can be handled with a conventional integral-direct implementation using four-index integrals. We find that with auxiliary basis sets optimized for MP2 energy calculations the errors in excitation energies caused by the RI approximation are negligible compared to the remaining correlation error inherent in the CC2 method.


[1] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem. **S18**, 255 (1984).
[2] J. Geertsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989).
[3] H. Koch and P. Jørgensen, J. Chem. Phys. **93**, 3333 (1990).
[4] H. Koch, H. J. A. Jensen, P. Jørgensen, and T. Helgaker, J. Chem. Phys. **93**, 3345 (1990).
[5] O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **243**, 409 (1995).
[6] Y. S. Lee and R. J. Bartlett, J. Chem. Phys. **80**, 4371 (1984).
[7] Y. S. Lee, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **81**, 5906 (1984).
[8] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).
[9] J. Noga, R. J. Bartlett, and M. Urban, Chem. Phys. Lett. **134**, 126 (1987).
[10] J. D. Watts and R. J. Bartlett, Chem. Phys. Lett. **233**, 81 (1995).
[11] O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **103**, 7429 (1995).
[12] H. Koch, O. Christiansen, P. Jørgensen, T. Helgaker, and A. S. de Merás, J. Chem. Phys. **106**, 1808 (1997).
[13] O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **105**, 1451 (1996).
[14] H. Koch, O. Christiansen, P. Jørgensen, and J. Olsen, Chem. Phys. Lett. **244**, 75 (1995).
[15] O. Christiansen, H. Koch, A. Halkier, P. Jørgensen, T. Helgaker, and A. M. Sanchez de Meras, J. Chem. Phys. **105**, 6921 (1996).
[16] O. Christiansen, H. Koch, P. Jørgensen, and T. Helgaker, Chem. Phys. Lett. **263**, 530 (1996).
[17] P. Pulay and S. Sæbo, Theor. Chim. Acta **69**, 357 (1986).
[18] S. Sæbo and P. Pulay, J. Chem. Phys. **86**, 914 (1987).
[19] M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999).
[20] J. Almlöf, Chem. Phys. Lett. **181**, 319 (1991).
[21] M. Häser and J. Almlöf, J. Chem. Phys. **96**, 489 (1992).
[22] M. Häser, Theor. Chim. Acta **87**, 147 (1993).
[23] O. Vahtras, J. E. Almlöf, and M. W. Feyereisen, Chem. Phys. Lett. **213**, 514 (1993).
[24] M. W. Feyereisen, G. Fitzgerald, and A. Komornicki, Chem. Phys. Lett. **208**, 359 (1993).
[25] D. Feller, E. D. Glendening, D. E. Woon, and M. W. Feyereisen, J. Chem. Phys. **103**, 3526 (1995).
[26] M. W. Feyereisen, D. Feller, and D. A. Dixon, J. Phys. Chem. **100**, 2993 (1996).
[27] D. E. Bernholdt and R. J. Harrison, Chem. Phys. Lett. **250**, 477 (1996).
[28] F. Weigend and M. Häser, Theor. Chem. Acc. **97**, 331 (1997).
[29] A. P. Rendell and T. J. Lee, J. Chem. Phys. **101**, 400 (1994).
[30] H. Koch, A. S. de Merás, O. Christiansen, and T. Helgaker, J. Chem. Phys. **14**, 4157 (1996).
[31] A. Schäfer, C. Huber, and R. Ahlrichs, J. Chem. Phys. **100**, 5829 (1994).
[32] F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, Chem. Phys. Lett. **294**, 143 (1998).
[33] The turbomole basis set library is available by ftp from ftp://ftp.chemie.unikarlsruhe.de/pub/basen.
[34] H. Weiss, R. Ahlrichs, and M. Haeser, J. Chem. Phys. **99**, 1262 (1993).
[35] O. Treutler and R. Ahlrichs, J. Chem. Phys. **102**, 346 (1995).
[36] R. Bauernschmitt and R. Ahlrichs, J. Chem. Phys. **104**, 9047 (1996).
[37] H. Koch, O. Christiansen, R. Kobayashi, P. Jørgensen, and T. Helgaker, Chem. Phys. Lett. **228**, 233 (1994).
[38] T. Helgaker, H. J. A. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. Saue, P. R. Taylor, and O. Vahtras, Dalton—An electronic structure program, release 1.0, 1997.
[39] O. Christiansen, H. Koch, P. Jørgensen, and J. Olsen, Chem. Phys. Lett. **256**, 185 (1996).
[40] A reduction by $1/g^2$ is obtained for abelian groups, for non-Abelian groups the factor varies between $1/g^2$ and $1/g$ depending on the number of direct products of irreducible representations that contain the totally symmetric representation.
[41] OpenMP Fortran Application Program Interface, Version 1.0, October 1997.