High-level multireference methods in the quantum-chemistry program system COLUMBUS: Analytic MR-CISD and MR-AQCC gradients and MR-AQCC-LRT for excited states, GUGA spin–orbit CI and parallel CI density†

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Development of several new computational approaches within the framework of multi-reference \textit{ab initio} molecular electronic structure methodology and their implementation in the COLUMBUS program system are reported. These new features are: calculation of the analytical MR-CI gradient for excited states based on state-averaged MCSCF orbitals, the extension of the MR-ACPF/AQCC methods to excited states in the framework of linear-response theory, spin–orbit CI for molecules containing heavy atoms and the development of a massively-parallel code for the computation of the one- and two-particle density matrix elements. Illustrative examples are given for each of these cases.

1. Introduction

The popularity of quantum chemistry \textit{ab initio} methods in computational chemistry has increased rapidly in recent years due to the development of new methods and of corresponding efficient computer programs that take advantage of modern computer technology. The most popular methods by far have been of the single-reference (SR) type, including approaches such as the Hartree–Fock self-consistent field (SCF) method, Muller–Plesset perturbation theory, coupled-cluster theory and density-functional theory (DFT). However, the SR approaches often fail when nondynamical electron correlation (near-degeneracy effects) is important, as usually happens in the description of bond stretching and dissociation, electronically excited states and many open-shell cases. Multi-reference (MR) methods can deal effectively with such problems, but their successful application requires significantly more careful planning and understanding of the details of a calculation as compared to the SR case, especially in the selection of appropriate reference spaces.

An MR treatment usually starts with a multiconfiguration SCF (MCSCF) calculation, which describes the nondynamical electron correlation by including the nearly degenerate electron configurations (and often many others) in the MCSCF wavefunction. Dynamical electron correlation can then be included in several ways. The classical method for that purpose is configuration interaction\(^1\)-\(^2\) (CI), using the Ritz variation principle. The most common form of this approach is MR-CI singles and doubles (MR-CISD), in which the expansion space for the wavefunction is constructed from single and double substitutions of occupied orbitals by virtual orbitals in the individual configuration state functions (CSFs) of the reference wavefunction. The truncation of the expansion space to single and double substitutions, while physically motivated, is usually mandated by the very steep increase in the number of CSFs, and the consequent computational effort, with increases in the substitution level.

The CI method is very flexible and robust, but the greatest disadvantage of truncated CI is its lack of extensivity, \textit{i.e.}, its...
incorrect scaling with the size of the system. A variety of correction methods have been developed for the approximate treatment of this problem, but the use of extensivity corrections is by no means straightforward in MR-CI as in the SR case. We shall mention just a few of the many extensivity correction approaches. The simplest and most commonly used are the Davidson correction\(^2\)–\(^7\) and its MR extension,\(^8\)–\(^9\) which provide a correction to the computed energy, but not to the wavefunction or to computed properties. These corrections are obtained as relatively cheap byproducts of SR-CISD and MR-CISD calculations, respectively, but are of limited reliability.\(^10\) In order to address the previously mentioned single reference limitations, multireference extensions of coupled cluster theory (see, e.g., ref. 11–15) and perturbation methods (see, e.g., ref. 16 and 17) have also been developed. However, there is still no widely applicable and generally available MR-coupled-cluster procedure. Various approximations have been introduced, mostly as modifications to the MR-CISD procedure, to deal with this problem. Of these methods we shall mention MR-LCCM\(^12\) (linearized coupled cluster), MR-ACPF\(^18\) (averaged coupled-pair functional) and MC-CEPA\(^19\) (coupled electron-pair approximation). In many applications the MR-ACPF approach has been quite successful, but it tends to overestimate the effect of the omitted higher excitations, sometimes producing anomalous results.\(^20\) The MR-AQCC (averaged quadratic coupled-cluster) method,\(^20\)\(^,\)\(^21\) which is closely related to MR-ACPF, was formulated in an attempt to overcome these problems, and usually produces more reliable results. The usefulness and effectiveness of MR-ACPF\(^2\) and MR-AQCC\(^4\) are due to a good balance of simplicity and satisfactory treatment of the basic size-extensivity effect. The availability of analytic gradients for these models (see below) is another important point in their favor. For a review of these and related methods see, e.g., ref. 22.

The availability of analytic gradient methods is crucial for the geometry optimization of molecules. Analytic gradient methods are often unavailable for MR calculations because of the much greater complexity of the formalisms\(^23\)–\(^27\) compared to the SR case. The situation becomes particularly complicated if the invariance properties of the wavefunction with respect to orbital transformations differ in the MCSCF and MR-CI wavefunctions. Such situations will arise, for example, if orbitals are frozen at the CI stage or if the MR-CI reference wavefunction includes only a selected subset of the CSFs in the original MCSCF wavefunction. Additional requirements arise in calculations of electronically excited states. For a balanced description of a series of states, state-averaged MCSCF calculations are very useful in order to provide a common set of orbitals for all states of interest. Such orbitals are not optimal for any one electronic state, introducing further complications in the gradient formalism. Moreover, it is highly desirable that the availability of analytic gradients should extend beyond truncated CI to include methods that try to correct for extensivity effects. The MR-CI, MR-ACPF and MR-AQCC implementations in the COLUMBUS system of programs\(^28\)–\(^29\) deal with all the complications discussed above, and provide the analytic gradients for these models.\(^24\)\(^,\)\(^25\)\(^,\)\(^30\)

In calculations on molecules that include heavy atoms relativistic effects are important, and many methods have been developed to deal with them, ranging from full four-component wavefunctions to semiempirical methods.\(^31\) The most widely used approaches have been those based on relativistic effective core potentials (RECP) and valence spin–orbit operators. In the context of MR-CI and related methods, including RECPs is straightforward, and the major additional aspect to be dealt with is the inclusion of the spin–orbit interactions of the valence electrons. Spin–orbit interactions were implemented in an early (unreleased) version of COLUMBUS by S. Yabushita\(^2\)\(^,\)\(^23\) starting in 1989. An updated version\(^2\)\(^6\) of this implementation has been included in the current version of COLUMBUS,\(^35\) and has been applied to a number of systems containing very heavy atoms.

The COLUMBUS program project\(^28\)–\(^29\)\(^,\)\(^33\) was started in 1980 with the aim of developing an efficient and flexible tool for MR-CISD calculations, with emphasis on the multireference character of the computational approaches. An early version included MR-LCCM, and the MR-ACPF and MR-AQCC methods were added as soon as they became available. The implementation was constructed as a set of individual programs for the computation of AO integrals and for the various stages of the SCF, MCSCF and CI procedures. These programs communicated with each other through files. The modular and open structure facilitated the implementation of new methods and features and interaction with other program systems. It is the purpose of this work to present new methodological developments, their implementation in COLUMBUS, and illustrative applications. An important aspect of the current version concerns excited state calculations, including implementation of analytic gradients for MR-CISD and MR-AQCC calculations based on state-averaged MCSCF orbitals and the treatment of extensivity corrections by means of MR-AQCC and MR-AQCC-LRT (linear-response theory).\(^36\) These features significantly increase the capabilities for accurate geometry optimizations of excited states. The other major new development is the spin–orbit CI implementation, which opens the way for completely new applications. In addition, the effort to develop a version of COLUMBUS for massively parallel computers has continued, adding an efficient parallel version of the one- and two-particle density-matrix program to the previously available parallel modules. This feature is very important for efficient analytic gradient calculations.

2. Synopsis of COLUMBUS

The MCSCF and CI wavefunctions are specified using the graphical unitary group approach (GUGA).\(^37\)–\(^40\) This allows the treatment of any pure spin state with no practical restriction with respect to the number of open shells in the individual CSF expansion terms. Mixing of different spin states through the spin–orbit interaction is included in the spin–orbit capability. The reference space and CI expansion space are defined by means of a distinct row table (DRT), which is a tabular representation of a distinct row graph.\(^39\)\(^,\)\(^40\) The graph comprises two parts: the internal part describes the occupations and spin couplings of the internal orbitals (the orbitals occupied in at least one of the reference configurations), and the external part, which has the same simple structure in all CISD expansions, treats the external (virtual) orbitals. Only the internal part of the graph (and of the DRT) needs to be constructed and processed in the CI program. Each CSF (Gelfand state) is described as a walk on the graph. The CI wave functions are optimized in a direct-CI iterative approach,\(^41\)\(^,\)\(^42\) employing the Davidson diagonalization method.\(^43\) The coupling coefficients needed in this approach are split into internal and external contributions. The internal coefficients are generated from the internal DRT are either stored in a file (“formula file”) at the beginning of the calculation or, alternatively, are recomputed on the fly during the diagonalization iterations. The external contributions, which are always of the same simple form, are built into the computational algorithms in the program. The most expensive computational step is the generation of the matrix–vector product in each iteration. This product, which involves the sparse Hamiltonian matrix and the current trial vector, is separated in the GUGA formalism into dense matrix operations over dimensions of symmetry-blocked sections of the external orbital space. The process is organized in terms of the

internal orbitals that index blocks of the one- and two-electron integrals. One- and two-particle density-matrix elements are computed by an analogous, index-driven method. For more details see ref. 28, 29, 39, 40.

The implementation of the MR-ACPF and MR-AQCC models is accomplished at the level of the subspace matrices by means of a diagonal-shift technique.\textsuperscript{25,36} The spin–orbit CI treatment requires an extension of the standard GUGA formalism,\textsuperscript{34} which can be easily combined with the standard, nonrelativistic approach into one code. The computation of the MR-CISD gradient requires additional computational steps (see ref. 24), including the computation of effective density matrices in the MO basis, their back-transformation to the AO basis, and their contraction with the AO gradient integrals. More information about methods and implementations can be found below in the respective sections.

Two AO integral programs are currently available in COLUMBUS: ARGOS\textsuperscript{44} and the AO integrals sections of DALTON.\textsuperscript{65} Both of these programs support generally contracted basis sets. The ARGOS program includes the treatment of effective core potentials and spin-orbit operators, but does not provide AO gradient integrals. The gradient integrals are available in DALTON, but that program currently does not handle effective core potentials. Input to the individual computational sections of COLUMBUS are managed by an interactive Perl script, and the programs are executed by means of another Perl script.

3. Analytic MR-CISD gradient for excited states

3.1. Methodological overview

The basic formalism for the analytic gradient method used in this work can be found in ref. 23–25. In the evaluation of the analytic gradient the following computational procedure is implied: (i) an MCSCF calculation is carried out as the first step, (ii) reference configurations are selected from the MCSCF wavefunction, and (iii) an MR-CI calculation is carried out. The CI gradient can be written as the sum of two terms: one is the trace of the one- and two-particle density matrices with the respective one- and two-electron gradient integrals. The second term describes the response of the MOs with respect to a geometrical displacement. The latter term is given by the essential and redundant orbital rotations defined for the MCSCF wavefunction (see, e.g., ref. 46) and an orbital force determined at the CI level. The resolution of redundant orbital rotations must be taken into account if the respective invariant orbital subspaces differ in the MCSCF and the subsequent CI calculation. Such cases arise frequently, for example when a general subset of the MCSCF configurations is chosen as reference space for the MR-CISD expansion or when a subset of the MCSCF inactive orbitals is frozen in the MRCI wavefunction while the remaining MCSCF inactive orbitals are correlated. The analysis and program implementation have been carried out for two resolution methods, Fock operator resolution and natural orbital resolution. Thus, a large variety of reference-selection schemes can be used in conjunction with the gradient calculation as well. For a detailed description of the respective procedures see ref. 24. In addition to the flexibility with respect to reference-selection schemes, the gradient formalism is also very open to the way the MCSCF calculation is carried out. In fact, a close relationship between the MCSCF and MRCI wavefunctions is not required. For example, the MCSCF orbitals can be determined for a different state, a weighted average of states, a different spin or spatial symmetry, or even for a state with a different number of electrons, than the MRCI wavefunction. In the original implementation of the CI gradient, the case of MCSCF state-averaging had not been available. In recent work\textsuperscript{30} this feature has been implemented as well, and is crucial for gradient calculations of excited states.

With the aid of the coupled perturbed MCSCF equations and the use of the matrix turnover proposed by Handy and Schaefer,\textsuperscript{47} the CI gradient can be written exactly as in the MCSCF case with the only difference being that effective one- and two-particle density matrices are used. It has also been shown\textsuperscript{24} that the computer time needed for the gradient calculation amounts only to a fraction of the time required for the energy calculation.

The same analytic gradient formalism can be used in connection with the MR-ACPF/MR-AQCC methods.\textsuperscript{24,25} In total, a very flexible and efficient tool for multi-reference geometry optimizations is available. This has been demonstrated recently in calculations on the valence-excited states of formaldehyde.\textsuperscript{48} In the present paper another interesting example has been chosen, the predissociation of ammonia in the 3s Rydberg excited state.

3.2. Geometry optimization of the S\textsubscript{1} equilibrium structure and the predissociative transition state of NH\textsubscript{3}\textsuperscript{50}

The lowest excited singlet state of ammonia is very well characterized experimentally.\textsuperscript{49} This state is of great interest because of its importance for the photodissociation of NH\textsubscript{3} into NH\textsubscript{2}(4\textsuperscript{1}B\textsubscript{1}) and H(\textsuperscript{1}S\textsuperscript{2}). The theoretical study of this excited state of ammonia is a challenging task due to the remarkable changes in the character of this state. Near the planar equilibrium structure ($D_{\text{3h}}$ symmetry) the S\textsubscript{1} state is a $1\text{A}_{\text{g}}$ (1a\textsuperscript{1}-3s) Rydberg state.\textsuperscript{50} However, the state becomes more compact under dissociation of one hydrogen atom. Near the $1\text{B}_{\text{3g}}$ dissociation saddle point the S\textsubscript{1} state shows significant valence character.\textsuperscript{50,51} The $\tilde{A}(\text{S})$ state and the photodissociation have been investigated by Runau et al.\textsuperscript{50} using the MRD-CI method, and later by Rosmus et al.\textsuperscript{52} and McCarthy et al.\textsuperscript{53} using extensive grid searches of the energy hypersurface by means of CASSCF calculations and additional CEPA calculations for selected points. Analytic gradient EOM-CCSD calculations\textsuperscript{34} have been reported for the S\textsubscript{1} minimum structure and the $1\text{B}_{\text{3g}}$ saddle point.

In this work we report geometry optimizations based on the MR-CISD and MR-AQCC analytical gradient methods described in the preceding section for the determination of the $1\text{A}_{\text{g}}$ minimum structure and the $1\text{B}_{\text{3g}}$ dissociation saddle point. Harmonic vibrational frequencies are computed from harmonic force constants calculated by means of finite differences of analytic gradients. Two basis sets were used. Basis set DZPP consists of an aug-cc-pVDZ basis,\textsuperscript{55,56} supplemented by a diffuse $s$-function from the d-augmented basis set.\textsuperscript{57} A d-(doubly) augmented basis set contains two diffuse basis functions where the exponents are chosen according to the prescriptions given in ref. 57. In basis set TZPP the aug-cc-pVTZ basis\textsuperscript{55,56} (the augmented d-function on H was omitted) is supplemented by a diffuse d-augmented $s$-function.\textsuperscript{57} All calculations were performed in $C_{\text{2v}}$ symmetry. Thus, the actual symmetry used for the S\textsubscript{1} minimum structure is $1\text{B}_{\text{3g}}$ rather than $1\text{A}_{\text{g}}$.

State-averaged MCSCF calculations with equal weights for the $1\text{A}_{\text{g}}$ ground state and the $1\text{A}_{\text{g}}$ (4\textsuperscript{1}B\textsubscript{1}) S\textsubscript{1} state were carried out in the first step. For the ground state a valence CAS (complete active space) of 8 electrons in the 2-5a\textsubscript{1}, 1b\textsubscript{1} and 1-2b\textsubscript{2} orbitals was chosen. For the $1\text{B}_{\text{3g}}$ state this orbital set was augmented by the 6a\textsubscript{1} (3s Rydberg) orbital and in addition to the valence CAS all single excitations from the active valence orbitals into the 3s (6a\textsubscript{1}) orbital were allowed. The reference space for the subsequent MR-CISD and MR-AQCC calculations was identical to the MCSCF active space with the exception that the 2a\textsubscript{1} orbital has been kept doubly occupied in all reference configurations. All single- and double-excitation contributions to the virtual orbitals based on these reference...
configurations constituted the final expansion space for MR-CISD and MR-AQCC calculations. The 1s orbital of N was kept frozen in all post-MCSCF calculations.

The results obtained for the minimum structure of the ^1A_1 (1B_1) state, including the harmonic frequencies, are collected in Table 1. Experimental\(^{18}\) and previous theoretical results\(^ {52,54}\) are given for comparison. The NH bond distance calculated in the present work is in very good agreement with the experimental, CEPA and EOM-CCSD values. The MR-AQCC method affects frequencies by about 10 to 40 cm^{-1} compared to MR-CISD. Agreement with the experimental harmonic frequencies and EOM-CCSD results (see Table 1) is acceptable. Notable discrepancies are observed for \(\omega_4\) with respect to the experimental value and for \(\omega_6\) with respect to the EOM-CCSD result.

The excitation energies \(\Delta E_{\text{planar}}\) given in Table 1 were computed as the energy difference of the optimized ^1A_1 structure and the optimized planar ground-state structure. Term values \(\Delta E\) were computed by adding the inversion barrier (1975 cm^{-1} taken from ref. 52) of ground state NH to \(\Delta E_{\text{planar}}\). The excitation energy is increased when going from the DZPP to the TZPP basis. Size-extensivity corrections computed by means of the Davidson correction (MR-CISD + Q) or MR-AQCC increase this value further by about 0.05–0.1 eV. As in several other cases (see e.g. ref. 59), the Davidson correction gives larger effects than MR-AQCC. An inverse power fit of the \(\omega\) values (where \(\omega\) is the cardinal number of the basis set) was used\(^ {60,61}\) to extrapolate the DZPP and TZPP total energies to the basis set limit. Respective extrapolated \(\Delta E_{\text{planar}}\) and \(T_e\) values can be found in Table 1 under the heading (DT). This extrapolation scheme has also been used quite successfully for the energy extrapolation of a large number of excited states of diatomic molecules.\(^ {39}\) The (DT) value for MR-AQCC of 47 703 cm^{-1} is in very good agreement with the experimental value of 48.070 ± 200 cm^{-1}.\(^ {38}\)

Results for the dissociation saddle point are collected in Table 2. The dissociating H atom is indicated by H*, and the dissociation energy is increased when going from the DZPP to the TZPP basis. Size-extensivity corrections computed by means of the Davidson correction (MR-CISD + Q) or MR-AQCC increase this value further by about 0.05–0.1 eV. As in several other cases (see e.g. ref. 59), the Davidson correction gives larger effects than MR-AQCC. An inverse power fit of the \(\omega\) values (where \(\omega\) is the cardinal number of the basis set) was used\(^ {60,61}\) to extrapolate the DZPP and TZPP total energies to the basis set limit. Respective extrapolated \(\Delta E_{\text{planar}}\) and \(T_e\) values can be found in Table 1 under the heading (DT). This extrapolation scheme has also been used quite successfully for the energy extrapolation of a large number of excited states of diatomic molecules.\(^ {39}\) The (DT) value for MR-AQCC of 47 703 cm^{-1} is in very good agreement with the experimental value of 48.070 ± 200 cm^{-1}.\(^ {38}\)

Table 1

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Table 2

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<td>2056</td>
<td>2000</td>
<td>2152</td>
<td>1570</td>
<td>3226</td>
<td>2663</td>
</tr>
<tr>
<td>height((^\circ))</td>
<td>(1949)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

| a       | Ref. 53. |   |   | Ref. 54. |   |   |
| b       | Ref. 54. |   |   | NH bond leading to dissociation. |   |   |
| c       | MR-CISD + Q value in parentheses. |   |   | Experimental estimate: 2075 cm^{-1} (ref. 62). |   |   |

the valence character along the reaction path. The dipole moment is significantly reduced by the MR-AQCC method compared to MR-CISD. The former value is in good agreement with the EOM-CCSD result. The barrier height to NH bond dissociation is computed to be between 1570 and 2022 cm\(^{-1}\) (MR-AQCC and MR-CISD + Q values in Table 2). A model potential has been determined by Henck et al.\(^{52}\) in order to fit the experimentally observed dissociation rate. In their work a barrier of 2075 cm\(^{-1}\) has been determined, which is in better agreement with the range of present results than with the previous MCSCF or EOM-CCSD values of 3226 and 2663 cm\(^{-1}\), respectively.

4. MR-AQCC calculations for excited states

As mentioned in the Introduction, MR-AQCC is closely related to, and has its roots in, the MR-ACPF method of Gdanitz and Ahlrichs.\(^{18}\) Therefore, it is possible to treat the two methods in the same framework. In both methods, the following functional of the correlation energy \(\Delta E_n\) is made stationary with respect to the wavefunction parameters \((\epsilon_i)\) of state \(n\):

\[
F_n(\epsilon) = \sum_{i \in \text{int}} c_i \left( \hat{H} - E_0 - \sum_{i \in \text{int}} c_i \phi_i \right),
\]

where the factor \(G\) is equal to \(2n_s\) for ACPF and to \(1 - \left( n_a - 3(n_e - 2) \right) / (n_a - 1)\) for AQCC. \(n_s\) is the number of electrons being correlated and ‘int’ stands for the set of configurations having the same orbital occupancy as at least one of the reference configurations. This functional was originally formulated to calculate the energy of the ground state, but it can be generalized for excited states, as well.\(^{22,36}\) In practice, this is most conveniently done if the method is formulated in terms of the eigenvalue equation of a diagonally shifted Hamiltonian,\(^{63}\)

\[
\phi_i^* \left( \hat{H} - E_0 + \Delta_s \sum_{i \in \text{int}} c_i \phi_i \right) = \Delta E_n c_i^2,
\]

where the diagonal shift is defined by

\[
\Delta_s = \sum_{k \in \text{int}} (1 - G) \Delta E_n |\phi_k \rangle \langle \phi_k |.
\]

This equation looks like a matrix eigenvalue equation, and therefore the energies of the excited states can be calculated as the higher roots. Note, however, that the shift depends on the correlation energy \(\Delta E_n\) of the state \(n\), i.e., a different matrix is to be diagonalized for each state. For further reference we choose to call this the state-specific formulation.

Theoretically there is no limit to obtaining any excited state by the state-specific MR-AQCC/MR-ACPF method. Technically, two problems have to be considered. First, since the diagonal shift depends on the correlation energy itself, an iterative solution must be implemented. Since the eigenvalue problem of large CI matrices is usually solved iteratively, such a procedure can readily be used for MR-AQCC/MR-ACPF with the correlation energy approximated by the current iterate. Making use of this fact, as in the COLUMBUS code, the implementation of AQCC/ACPF requires only a minor modification in the subspace manipulation part, where the current energy is used to calculate the diagonal shift and modify the subspace Hamiltonian:

\[
\hat{H}_{\text{MN}} = \hat{H}_{\text{MN}} + (1 - G) \Delta E_n S_{\text{MN}}.
\]

Here \(\hat{H}_{\text{MN}}\) is the subspace matrix as in the CI calculation, and

\[
S_{\text{MN}} = \sum_{k \in \text{int}} c_k^{(n)} c_k^{(\text{MN})},
\]

is the overlap over the non-internal configurations, with \(\epsilon^{(M)}\) being the \(M\)th expansion vector.

The second problem is that the order of the roots of the shifted Hamiltonian may differ from that of the CI matrix or that in the reference space, and therefore the correct vector has to be selected in each iteration. In COLUMBUS we have implemented a root-following scheme: in each subspace iteration that root is selected for which the eigenvector has the maximum overlap with the respective reference vector.

To characterize excitation spectra, the other key quantity beside the excitation energy is the transition moment. Traditional formulation of transition properties requires the knowledge of the ground and excited state wavefunctions. Since these are not defined in the framework of the AQCC/ACPF methods, linear response theory (LRT) can be used as an alternative tool. For a recent review of LRT of variational methods see ref. 64. In LRT the excited states are obtained by perturbation theory from the ground state. In a recent paper\(^{36}\) we have examined whether the excited states obtained by the state-specific AQCC/ACPF approach can be obtained by LRT from the AQCC/ACPF ground state. It turned out that this is not the case. Since theoretically this property is essential for the derivation of transition properties, we have developed an LRT version of AQCC/ACPF excitation energies. The new equations are very similar to the original formulation, with the diagonal shift given by

\[
\Delta_s = \sum_{k \in \text{int}} (1 - G) \Delta E_n |\phi_k \rangle \langle \phi_k |,
\]

i.e., the correlation energy of the excited state is simply replaced by the correlation energy of the ground state. We refer to this new method as MR-AQCC-LRT.\(^{36}\) The very convenient property of this modified formula is that this shift is the same for all states, i.e., the same matrix has to be diagonalized for all excited states. If the reference spaces are of similar quality for the ground and excited states, we expect the correlation energy to be close, and therefore MR-AQCC and MR-AQCC-LRT will give similar results. This has been well demonstrated by numerical test in ref. 36 and an example will also be given below.

The calculation of transition properties is straightforward in AQCC/ACPF-LRT. The detailed derivation of the transition density between the ground state (0) and the excited state (2) can be found in ref. 36, and here we only give the final equation,

\[
\Gamma_{0a} = \alpha^0 \Gamma_{0a}^0 + (1 - \alpha) \Gamma_{0a}^\text{ref},
\]

where \(\text{ref}\) \(\Gamma_{0a}^\text{ref}\) is the transition density matrix corresponding to the reference wavefunction and \(\Gamma_{0a}^0\) is a CI-type transition density calculated with the AQCC/ACPF coefficients. The parameter \(\alpha\) is given as \(^{18}\)

\[
\alpha = \frac{\sum_i (c_i)^2}{\sum_i (c_i)^2 + G \sum_i (c_i)^2},
\]

which is to be calculated with the ground-state coefficients. Two notes are in order: First, this equation is very similar to the corresponding expression for the density itself, as first given by Gdanitz and Ahlrichs.\(^{18}\) Second, calculation of the transition density requires only the corresponding CI-like quantity and that corresponding to the reference states. Thus, the calculation of the AQCC/ACPF transition density can be implemented in any CI code where these quantities are obtained.

It has been shown\(^{36}\) that for calculation of the transition moments the MR-AQCC-LRT method is superior to MR-CISD and MR-ACPF-LRT. While for large valence-CAS reference functions all three methods gave very good agreement with full CI, for a smaller reference space the MR-CISD

transition moments were too large and MR-ACPF-LRT seemed to overestimate the effect of higher excitations, giving values which were too small, but MR-AQCC-LRT was still in good agreement with the full CI results.

To demonstrate the applicability of the procedure outlined above, we describe here the electronic transition corresponding to the so-called Phillips band in the C$_2$ molecule, which includes the $^1\Sigma^+_u \rightarrow ^1\Pi_u$ excitation. For a recent review of the available experiments and theoretical calculations see ref. 65. The equilibrium geometries of the states are rather different, and the description of the transition requires knowledge of the potential energy and transition moment surfaces over a wide range of internuclear distance. The situation is further complicated by the fact that an avoided crossing takes place between the $^1\Sigma^+_u$ and the excited $^2\Sigma^+_u$ states at about 3.2 $\sigma_0$. An adequate description of such a situation certainly requires a multireference treatment and inclusion of both dynamic and static correlation. Therefore this system is well suited for the MR-AQCC-LRT method.

Previously, accurate calculations have been performed by Chabalowski et al. and by O'Neil et al., but the calculated lifetime of the $^1\Pi_u$ state has been found to be considerably lower than the experimental value. After a careful analysis, O'Neil et al. determined that their results were converged with respect to basis set and that the MR-CISD model was adequate for the description of the system. They concluded that the results might be improved by using a full-valence CAS reference space, which could give better orbitals as well as increase the flexibility of the MR-CI wavefunction. Therefore we have decided to reinvestigate this problem by the MR-AQCC-LRT method using the valence CAS reference space. The basis set was aug-cc-pVTZ which is of similar quality as the basis used by O'Neil et al.

Fig. 1 shows the potential energy surfaces calculated by the MR-AQCC-LRT method for the three states in question. The same calculations have also been performed by the state specific MR-AQCC method, but the results are so close to the MR-AQCC-LRT results that the differences could hardly be seen in the figure, so they were left out. The figure shows that the avoided crossing between the two $^1\Sigma^+_u$ states is nicely described by the MR-AQCC methods. Fig. 2 plots the transition moments between the two $^2\Sigma_u^+$ states and the $^1\Pi_u$ state. The exchange of character between the two $^2\Sigma_u^+$ states can be clearly observed in the sharp changes in the transition moments: the value corresponding to the $^1\Sigma^+_u$ state decreases while that corresponding to the $^2\Sigma_u^+$ state increases.

The present results are in good agreement with those of O'Neil et al. The calculated spectroscopic constants also agree well with the experimental values. Our set of transition moments calculated at the different distances differ by less than 1% from those obtained by O'Neil et al. This means that the increased flexibility of the present calculations does not resolve the discrepancy between theory and experiment. Since these results have been obtained with a more flexible wavefunction than that of O'Neil et al., we conclude that the electronic wavefunction is well converged, and the discrepancy between theory and experiment must have a different origin. This question is presently being investigated in a new study, which includes the calculation of additional states and detailed dynamics of the nuclear motion. The accuracy of the MR-AQCC-LRT method gives good hopes for a resolution of this discrepancy in the near future.

5. GUGA spin–orbit CI

Relativistic effects can be included in quantum chemical calculations in a number of ways, with varying levels of approximation and varying levels of computational complexity. We have chosen to use the RECP method and to incorporate it into the GUGA CI formalism. A detailed description of this work has been published recently, so we only describe the general features here.

There are two important types of relativistic effects: (1) those involving the fastest moving electrons, which are in the core shells of atoms, and (2) those involving additional interactions, principally the spin–orbit interaction, in the valence shells of atoms and molecules. If only processes and properties that do not involve core electrons are of interest, then the core shells of atoms can be replaced by RECPs which incorporate the core–shell relativistic effects as well as remove a number of electrons from the calculation. Each RECP may be written as a sum of a spin-independent operator (averaged relativistic effective potential, AREP) and a spin–dependent operator (effective valence spin–orbit operator).

Atomic-orbital basis sets for use with RECPs are still being developed. These basis sets differ from all-electron basis sets in being smaller, since they have no primitive or contracted functions for the core orbitals and the contracted valence orbitals must all go smoothly to zero in the core regions both of the atom in question and of neighboring atoms. MOs for use in the CI calculations are usually obtained from SCF or MCSCF calculations. If several electronic states are to be studied, the SCF or MCSCF calculations are usually done with state-averaged energy expressions in order to obtain MOs of approximately equal quality for all the states. Use of a single set of MOs is required for transition-moment calculations. The SCF and MCSCF programs do not include the spin–orbit interaction, but energy-averaged calculations tend to average out the spin–orbit effects.

Beginning with standard non-relativistic methods, the addition of the AREPs, including the evaluation of their additional
AO integrals, and limiting the treatment to the valence electrons only, causes only minor changes in the formulation. However, the addition of the spin-orbit operators results in qualitatively new types of matrix elements, and therefore causes major changes in the computational formulation. Some workers have chosen to do the calculations in two steps, a first step which omits the spin-orbit operator, and a second step that includes the spin-orbit interaction in some way that uses the results from the first step. We have chosen, however, to include the spin-orbit interaction from the beginning and to carry out the calculations in a single step. This choice avoids any explicit or implicit assumptions about the size of the spin-orbit interaction compared to the other interactions, but requires the consideration of a larger configuration space. The spin angular momentum quantum numbers $S$ and $M_S$ can no longer be used to subdivide the configuration space; only the less restrictive double-group symmetry can be used instead. Configuration interaction is chosen to treat electron correlation because so many heavy-element electronic states require a multireference treatment. Since the spin-orbit interaction is mostly a one-electron effect, the electron correlation treatment is always the convergence-limiting aspect of these calculations in high-accuracy work.

The introduction of this spin-orbit operator in the simplest formulation leads to a new type of AO integral and to pure imaginary or complex matrix elements. It is computationally prudent to avoid complex arithmetic if a simple way can be found to do so. For the case of an even number of electrons there are several strategies to accomplish this. We use a transformation of the spin functions to “real spherical harmonic” form. For the case of an odd number of electrons the situation is more complicated, so we use the strategy of adding a fictitious electron which always occupies a unique fictitious MO and then applying the even-number formulation.

Several aspects of the GUGA algorithms need to be general-
alized to accommodate spin-orbit matrix elements. The dis-
tinct row graphs, which normally have a single head, now have several heads, corresponding to the number of $S$ values that must be included. Each head of the graph, instead of having the usual weight of one, now receives a weight of $2S + 1$. The derivation of the formulae for the spin-orbit matrix elements is mostly guided by the expression for the matrix element of products of unitary group operators (the resulting simplest form is in eqn. (44) and (45) in ref. 34). The GUGA distinct row table (CIDRT), sorting (CISRT), formula file (CIUFT), and diagonalization (CIUDG) programs are all modified, partly with a few additional subroutines and partly with small numbers of lines of additional code in previously existing subroutines. The spin-orbit generalization of the expressions for transition densities has been made and coded for the calculation of electric and magnetic dipole transition moments, and will be included in a future released version once additional testing is carried out.

The spin–orbit GUGA programs can be applied to light-
atom systems when spin–orbit effects are being studied, such as in the MgAr complex, but these systems can also be studied with methods based on perturbation theory. Examples of applications to heavy-atom complexes are to the actinyl ions and their complexes. The fluorescence of the uranyl ion has been studied since the 1840s and now additional understand-
ing of the uranyl excited states has been obtained from the use of the spin–orbit GUGA programs. Calculations on other actinyl ions and complexes have led to a better understanding of their solution absorption spectra and to an understanding of the pattern of their electronic states in terms of a weak-crystal-field description using only part of the $f$ orbital space.

An example of a calculation on an actinyl complex is one that was done recently on UO$_2$F$_2$(H$_2$O)$_4$. Uranyl fluoride (UO$_2$F$_2$) is a product of the reaction of UF$_6$ with water. The luminescence properties of uranyl ions complexed with various numbers of fluoride ions have been studied, and UO$_2$F$_2$ has the most intense emission. UO$_2$F$_2$ was used with the LDA exchange correlation functional to optimize the structure of UO$_2$F$_2$(H$_2$O)$_4$, the most probable species in aqueous solution. The structure found has $D_3$ symmetry with all six ligands in or near the equatorial plane of the uranyl ion (Fig. 3). In the spin–orbit calculation 84 electrons of this complex were replaced by RECPs, leaving 82 electrons to be treated explicitly. The basis sets were of approximately polarized double-zeta size. The ground state has 41 doubly occupied MOs; the excited states of interest involve excitation to 4 of the 132 virtual MOs. The MOs were chosen by an average SCF calculation on the ground state and all of these excited states. In the spin–orbit CI calculations, 76 electrons were frozen in their 38 MOs, and 6 electrons were correlated by including all single and double excitations from the five reference electron configurations. No virtual orbitals were left out. The number of CSFs for each of the four double-group irreducible representations was close to 1.2 million. Either three or four roots were converged per calculation. Each of the four calculations required 10.5 CPU hours and twice that amount of wall clock time on a Sun Ultra 1 Model 200E workstation. All other steps (integrals, SCF, transformation, transition moments, etc.) required much smaller amounts of time. The results included excitation energies, splittings due to the ligands, and oscillator strengths due to ligand interactions.

Thus the COLUMBUS programs can be used to do calcula-
tions of quite useful accuracy on moderate-sized systems containing heavy atoms. So far such calculations have mainly been used to study spectroscopic properties. Structural inform-
ation can also be obtained, but doing so will be of more practical efficiency once energy gradient calculations are available. Another important improvement would be a parallel version of the spin–orbit CI code. It is gratifying that the unitary group, which is closely related to the properties of electron spin, can be used efficiently to treat a spin-dependent interaction, spin–orbit coupling.

6. Geometry optimization of ethylene using analytic energy gradients and massively parallel electronic structure codes

A comparison study of computed molecular geometries has been undertaken. This comparison includes several closed-shell molecules, and the main thrust is to quantify the errors in computed equilibrium geometries using several electronic structure methods, ranging from simple SCF and other single-
reference methods to the more flexible MCSCF and multireference CI methods. The ground state of ethylene, C₂H₄, is one of the molecules included in this larger comparison. The MCSCF wavefunction used in this study is denoted pictorially in the form

Each solid line denotes a 2-electron-2-orbital subspace, and the total wavefunction consists of the direct product of all possible orbital occupations consistent with these subspace-occupation restrictions; this wavefunction can be described symbolically by the notation \( \psi[\sigma_1 \sigma_2 \sigma_3 \sigma_4]^2 \sigma_5 \sigma_6 \sigma_7 \sigma_8]^2 \sigma_9 \sigma_10 \sigma_11 \sigma_12] \). The first two orbitals are doubly occupied and are, essentially, the 1s orbitals on each of the carbon atoms. All of the remaining valence orbitals are correlated in the active space. Unlike a single-reference SCF wavefunction, this flexible multi-configuration wavefunction is sufficiently general to allow dissociation to the correct spin states of the various fragments H, C₂H₃, and CH₃ without artifactual ionic charge contamination.

It is well known that spin- and charge-contamination limit the accuracy and convergence rate of single-reference methods, and this study is intended to quantify these errors by using more flexible wavefunctions that eliminate these two sources of error. The large-scale CI wavefunctions used in this comparison are generated, in the case of C₂H₄, by using the above flexible MCSCF wavefunction as a reference space in order to generate, with single- and double-excitations, a much larger MR-CISD wavefunction expansion. While the reference wavefunction is sufficiently flexible to eliminate spurious spin- and charge-contamination, this larger wavefunction expansion accounts for the more subtle dynamical electron-correlation effects. So far, two different atomic basis sets have been used in this study, the cc-pV(DZ and the cc-pVTZ basis sets of Dunning. Larger cc-pVQZ basis set calculations are in progress. As can be seen in Table 3, these basis sets lead to very large MR-CISD wavefunction expansions.

Such large wavefunction expansions cannot be geometry-optimized practically with normal sequential electronic structure codes, but become practical with the use of parallel computers. A parallel MR-CISD code was available previously for the wavefunction optimization itself, but geometry optimizations using analytic energy-gradient methods require the electron density as well. A parallel electron-density code has been developed recently using the same general approach and programming methodology as that used previously in the parallel CI code. B Briefly, a single-program multiple data (SPMD) programming model based on distributed memory with message passing is used. This is appropriate for both shared-memory and distributed-memory computers. In the parallel environment, some data sets (e.g., the distinct row table and the smaller indexing arrays) are replicated on the nodes and others (e.g., the large CI expansion vector and the two-particle density matrix elements) are distributed among the nodes using the Global Array library. The compute tasks are determined by segmentation of the expansion vectors and partitioning of the density matrix indices.

The parallel performance of this code is shown in Fig. 4. In this figure, ideal parallel behavior would be characterized by a straight line with slope of -1. As seen, the actual wall-time performance deviates from this ideal behavior for 64 or more CPUs. Inspection of detailed timing shows that the bottleneck is in the setup step, which involves some calculations of the optimal segmentation of the CI expansion vectors, distribution of the converged CI vector, and distribution of the two-particle density matrix. Removal of the timings for this initial setup, as shown in Fig. 4, reveals that the remaining parts of the process, the actual parallel calculation of the electron density, scales linearly with number of nodes used.

**Table 3** Summary of C₂H₄ results

<table>
<thead>
<tr>
<th>Method</th>
<th>cc-pVDZ</th>
<th>cc-pVTZ</th>
<th>cc-pVQZ</th>
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</thead>
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<td>MCSCF Expansion size</td>
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<td>3012</td>
<td>3012</td>
<td>3012</td>
<td></td>
</tr>
<tr>
<td>( R_{CC} )</td>
<td>1.1035</td>
<td>1.0923</td>
<td>1.0918</td>
<td>1.0917</td>
<td>1.081(2)</td>
</tr>
<tr>
<td>( R_{CC} )</td>
<td>1.3553</td>
<td>1.3477</td>
<td>1.3470</td>
<td>1.3470</td>
<td>1.334(2)</td>
</tr>
<tr>
<td>MR-CISD Expansion size</td>
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<td>197655128</td>
<td>857810264</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_{CC} )</td>
<td>1.0986</td>
<td>1.0834</td>
<td>—</td>
<td>1.0770</td>
<td>1.081(2)</td>
</tr>
<tr>
<td>( R_{CC} )</td>
<td>1.3527</td>
<td>1.3384</td>
<td>—</td>
<td>1.3325</td>
<td>1.334(2)</td>
</tr>
</tbody>
</table>

*All bond lengths are in Å. b The three-point MCSCF basis set extrapolation is based on the exponential model, \( R_a = R_{ab} + an^{-3} \). c Ref. 89.

![Parallel Performance C₂H₄ Density Construction](image)
density, scales very well even up to 128 CPUs. Future efforts will be directed towards eliminating this computational setup bottleneck.

Eventually, the molecular geometry with three basis sets, cc-pVDZ, cc-pVTZ, and cc-pVQZ,55 will be used to extrapolate to the infinite basis set limit. Because the spurious spin-and charge-contamination are treated qualitatively correctly with our multireference approach, we find that the convergence of energies and other molecular properties with increasingly flexible basis sets is almost always smooth and predictable. This is in contrast with single-reference approaches, for which convergence of properties is sometimes irregular and nonuniform. The cc-pVQZ MR-CISD calculation for C$_{6}$H$_{6}$ has not been completed at this time, so a preliminary two-point extrapolation using just the available DZ and TZ results is given in Table 3. However, even with the cc-pVDZ and cc-pVTZ bases, these calculations represent the largest wavefunction expansions that have ever been used in a full geometry optimization using analytic energy gradients. As seen in Table 3, the extrapolated MCSCF bond lengths are slightly longer than experiment. This is consistent with the fact that the spurious ionic contamination, which tends to shorten the computed bond lengths artificially, has successfully been eliminated from the reference wavefunction. The more flexible orbital basis sets and the more flexible treatment of electron correlation both tend to shorten the computed bond lengths, as shown by the MR-CISD results in Table 3. Comparison with the accepted experimental results shows quite small errors for the cc-pVTZ MR-CISD calculations, suggesting that the preliminary two-point extrapolation may be slightly overshooting. This will be resolved when the cc-pVQZ calculations are completed.

7. Conclusions

The development of several new computational methods within the framework of ab initio electronic structure theory and their implementations within the COLUMBUS program system have been reported, and illustrative examples have been given. These new features extend the available quantum chemical tools, on the one hand, in the direction of extended investigations of excited states and, on the other hand, by opening new possibilities for reliable calculations of spin–orbit effects for molecules containing heavy atoms. The parallelization efforts for COLUMBUS have been extended, removing an important bottleneck for the MR-CI gradient calculation. Interactive scripts have been written in order to improve the management of the complex steps of input generation encountered in multi-reference calculations.

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