A CASE STUDY OF STATE-SPECIFIC AND STATE-AVERAGED BRUECKNER EQUATION-OF-MOTION COUPLED-CLUSTER THEORY: THE IONIC-COVALENT AVOIDED CROSSING IN LITHIUM FLUORIDE

Marcel NOOIJEN[1,*] and K. R. SHAMASUNDAR[2]

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada;
e-mail: [1] nooijen@uwaterloo.ca, [2] krsham@uwaterloo.ca

Received April 5, 2005
Acepted June 24, 2005

Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

State-specific Brueckner equation-of-motion coupled-cluster theory (SS-B-EOMCC) is summarized, which can be considered an internally contracted version of a state-selective multireference coupled-cluster theory, which, however, is not entirely size-consistent. The method is applicable to general multireference problems, adheres to the space and spin symmetries of the molecular system, is straightforwardly extended to a state-averaged version, and has an associated perturbative variant which yields results close to the full coupled-cluster treatment. A key strength is that Brueckner orbitals are used, such that orbitals are optimized in the presence of dynamic correlation. A number of variations on the theme of SS-EOMCC is applied to study the ionic-covalent avoided crossing in LiF in a 6-311++G(3df,3pd) basis set. While reasonable results are obtained at the state-averaged level, the iterative solution process does not consistently converge for SS-EOMCC, due to the non-Hermiticity of the transformed Hamiltonian which may yield complex eigenvalues upon truncated diagonalization. This leads to an irrevocable breakdown of the state-specific EOMCC approach. We indicate some future directions that can resolve some of the problems with the SS-EOMCC methodology, as revealed by the demanding test case of the LiF potential energy curves.

Keywords: Coupled clusters; Multireference methods; Quantum chemistry; Hamiltonian; CCSD; *Ab initio* calculations.

In recent years coupled-cluster theory has seen an increasing number of applications to open-shell problems. This is true in particular for applications to electronically excited states, which are usually accurately described by coupled-cluster linear response theory[1–6], or equivalently for most purposes, equation of motion coupled-cluster theory[7–13]. Likewise, Fock space coupled-cluster theory[14–21], in particular in the intermediate Hamiltonian formulation of Meissner et al.[22–25], which has been used extensively by

doi:10.1135/cccc20051082

Kaldor et al.[26–29], and closely related, similarity transformed equation of motion coupled-cluster theory[30–36], are applicable to sizeable molecular systems. For EOMCC in its IP/EE/EA variants[37–39] and for STEOM in the DIP/EE/DEA variants[40–42] analytical energy gradients are available, testifying to the routine usage of these methodologies, e.g.[43,44] At the current forefront of excited state calculations is the simulation of spectra, including the effects of nuclear motion. Both Franck–Condon approaches[45–47] and non-adiabatic vibronic models[47–51] are currently in use, and often very nice agreement with experiment is reported. The description of electronically excited states is straightforward using coupled-cluster methods if the ground state (or parent state) is well described at the single-reference level. These methods have to large extent a black box character, which makes these calculations user-friendly for experts and novices alike.

The description of potential energy surfaces at the coupled-cluster level, or the description of molecules without a well-behaved parent state is far more cumbersome. Single-reference techniques continue to have their appeal, and the spin-flip approach by Krylov et al.[52–57] and the renormalized CC methods by Piecuch and Kowalski[58–60] have been applied successfully to a variety of problems. It is likely in our opinion that these approaches will be limited to certain classes of problems, which are however of great interest to chemistry. There is in addition a need for generally applicable multireference coupled-cluster (MRCC) methods. There is consensus in the literature that state-specific methods are preferable, as multistate or effective Hamiltonian methods are likely prone to intruders at some region of nuclear configuration space. In order to ensure continuous potential energy surfaces one should ideally use a single parametrization for the wave function across the complete region of interest. Several methods, notably the state-selective MRCC method by Mukherjee et al.[61–68], the multireference Brillouin–Wigner method by Pittner et al.[69–72] and the unitary group based approaches by Paldus and Li[73–75] have witnessed promising progress in recent years. One practical limitation of these methods is that they are built upon the Jeziorski–Monkhorst parametrization[76], implying that the number of cluster amplitudes grows linearly with the number of reference configurations, which limits the applicability of this class of methods. Another type of approach is the single-reference inspired state-selective MRCC work by Adamowicz et al.[77–81], and relatedly the CCSDt and CCSDtq approaches by Piecuch et al.[82,83] The number of amplitudes in these methods likewise shows an unfavourable scaling with the size of the active space. A method that behaves quite differently in this respect is the reduced multireference CCSD method by Li and Paldus[84–88], which is based upon the same number of CCSD amplitudes as in the single-reference case and a generally small number of higher-order amplitudes, which are obtained from an external calculation, typically MRCI in a limited orbital/reference space. Meissner et al. have presented cluster corrections to MR-CISD calculations which are non-iterative analogs of the RMR-CCSD approach by Li and Paldus[89,90].

The importance of the computational scaling of multireference coupled-cluster approaches with the size of the reference space may be surmised from the literature on multiconfigurational perturbation theory[91–96]. MRPT is applied to a great variety of problems and the number of reference states can be very large (on the order of a hundred thousand perhaps). Such large reference spaces will almost certainly be needed frequently to provide meaningful descriptions of compounds involving transition metal atoms, for example. With this type of applications in mind, in our group we have been working on MRCC theories of the internal contracted variety[30,97–99]. In effect we define a similarity transform of the Hamiltonian, of a single-reference format $\bar{\hat{H}} = \mathrm{e}^{-\hat{T}} \hat{H}\mathrm{e}^{\hat{T}}$, which is diagonalized over a large set of configurations. We are interested in only one or very few eigenstates of the transformed Hamiltonian, and the *t*-amplitudes that enter the transformation, as well as the orbitals, are optimized for precisely the states of interest. The formulation appears similar to EOMCC theory, but the methodology is state-specific. Our current preliminary implementation of the theory is closely related to the DIP-EOMCCSD method[41], in which the CCSD equations are solved for a reference state that contains two more electrons than the states of interest. The transformed Hamiltonian $\bar{\hat{H}} = \mathrm{e}^{-\hat{T}} \hat{H}\mathrm{e}^{\hat{T}}$ is subsequently diagonalized over the 2h and 3h1p configurations to access the states of interest. This allows the description of a number of multiconfigurational situations, in particular the breaking of single bonds, and the description of biradicals. However, orbital relaxation effects (to describe the change from N+2 to N-electron systems) can be important and these are not very well treated in the DIP-EOMCCSD method. Moreover, results may be unphysical using large diffuse basis sets if the parent state is a dianion, as occurs for example in the DIP-EOMCCSD description of the neutral states of ozone. Similar difficulties face the DIP-STEOM and DIP-FSCC approaches, although very good results can be obtained in smaller basis sets, e.g. ref.[33] The present state-selective EOMCC approach alleviates these problems as both orbitals and cluster amplitudes are optimized for the states of interest. Moreover, the theory applies directly to systems in which the vacuum state in the many-body theory has many more electrons than the states of interest. For example, to treat the Mn dimer we would envision a vacuum state with 10 more electrons to completely fill the d-shell. In the final diagonalization step based on the transformed Hamiltonian we would remove 10 electrons from an active space and in addition include single excitations. It will be clear that the vacuum state only serves as a formal device in the theory, and the theory is conceptually removed from equation-of-motion coupled-cluster theory, and certainly from coupled-cluster linear response theory, as the vacuum state in our theory does not carry a physical significance. In many respects the theory should be viewed as an internally contracted multireference method, however the formulation we employ is not exactly size-consistent. For this reason we refer to the methodology as a state-selective EOMCC method. Very few applications of the method have appeared to date, as we are still working to resolve a number of technical difficulties, as will be discussed here.

In this paper we focus on the application of the state-selective equation-of-motion coupled-cluster method to the ionic-covalent curve crossing of LiF. This problem is a crucial test case for multireference methods as it involves a narrow avoided crossing between two states which have a very different orbital character. Moreover, the curve crossing is located at a completely different internuclear distance if dynamic correlation is included, than when it is based on a mean-field description. The orbitals that describe the two states of interest are for this reason obtained from Brueckner type of calculations[100–103]. The fact that each state requires a different set of orbitals means that one in principle should not use a state-averaged calculation. Rather, both states should be described in separate state-specific calculations. This makes it hard to describe a smooth avoided crossing, as the calculations cannot benefit from a joint diagonalization which would lead naturally to an avoided crossing as in a 2 × 2 eigenvalue problem. These interesting features of ionic-covalent curve crossing problem were described by Spiegelmann and Malrieu[104,105] for the similar case of NaCl. The LiF molecule has been a test case of multistate CASPT2 studies[106,107] and quasi degenerate perturbation theory studies by Nakano et al.[94,108] An extensive study employing the multistate CASPT2 approach to a number of alkali halide molecules was presented recently[109]. In all of the multireference perturbation theory calculations best results are obtained using an interacting state model that assumes a common set of orbitals for both states. This strategy provides a smooth curve crossing, but is not ideal as the optimal orbitals for each of the two states can be expected to be very different. By a careful inspection of the potential energy curves presented by Finley et al.[106] it is seen that the avoidance exhibited by the potential energy curves is actually too strong and for large R the ground state curve bends downwards, clearly indicating too strong of a mixing in the multistate treatment.

The LiF curve crossing has also been studied using the density matrix renormalization group[110], and the advantages of this methodology which is not biased by orbital selection were convincingly demonstrated. Nevertheless, pure DMRG is not necessarily a very effective approach to include dynamic correlation effects in large basis sets.

In this paper we will describe the SS-EOMCC methodology in some detail and investigate its applications to the LiF ionic-covalent curve crossing problem in a 6-311++G(3df,3pd) basis set[111]. Even though our results will clearly show much to be desired, we think we can indicate some promising aspects of our approach. Even more importantly, the calculations reported in this paper clearly point to some alternative directions which will have to be pursued in the future.

THEORY

Parametrization of the Wave Function

Following our previous work[99] we use the following parametrization for the wave function

$$|\Psi\rangle = \mathrm{e}^{\hat{T}}\hat{C}|0\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a \hat{E}_i^a + \frac{1}{2}\sum_{i,j,a,b} t_{ij}^{ab}\hat{E}_i^a\hat{E}_j^b \tag{1}$$

$$\hat{C} = \hat{C}_1 + \hat{C}_2 = \sum_{i,j} c_{ij}\hat{a}_i\hat{a}_j + \sum_{i,j,k,a} c_{ijk}^a \hat{a}_i\hat{a}_j\hat{a}_a^\dagger\hat{a}_k\ .$$

The closed-shell vacuum state $|0\rangle$ contains two more electrons than the states we are interested in, and this defines a set of occupied orbitals, labelled *i*, *j*, *k*, ... and virtual orbitals, denoted *a*, *b*, *c*. The precise definition of the vacuum state is critical to the approach, and we will consider a few variations to define this state, to be discussed below. The cluster operator $\hat{T}$ has precisely the same form as the single-reference, spin-adapted cluster operator for a closed shell system, but the equations that define the amplitudes will be different. The elementary excitation operators are the generators of the unitary group $\hat{E}_p^q = \hat{a}_{q\alpha}^\dagger\hat{a}_{p\alpha} + \hat{a}_{q\beta}^\dagger\hat{a}_{p\beta}$, where α, β indicate the spin part of the orbital. Above we use the same notation for spatial orbitals and spin-orbitals, while the distinction is made by the operators: $\hat{E}_q^p$ indicates spatial orbitals are used, while $\hat{a}_q^\dagger, \hat{a}_p$ refer to spin-orbitals. The operator $\hat{C}$ has the same form as in the DIP-EOMCC method[41,112]. It consists of 2h and 3h1p excitation operators. The equations that define the operator $\hat{C}$ are the same as in the DIP-EOMCC equations, but based on a vacuum state and cluster amplitudes that are defined precisely for the states of interest. They are not determined by an underlying closed-shell CCSD calculation, and for this reason we refer to the approach as state-specific. To obtain the amplitudes for the operator $\hat{C}$, as well as the final energies, the transformed Hamiltonian $\overline{\hat{H}} = \mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}$ is diagonalized over the 2h and 3h1p determinants $\hat{a}_i\hat{a}_j|0\rangle, \hat{a}_i\hat{a}_j\hat{a}_a^\dagger\hat{a}_k|0\rangle$. This diagonalization step is quite compact and, moreover, for the diagonalization step we do not require the numerous $\overline{\hat{H}}$ two-electron operators that have 3 or more virtual indices. The final states will have the proper spin symmetry properties as the transformed Hamiltonian is expressed in terms of generators of the unitary group, while the diagonalization manifold is also spin-adapted. Regarding spatial symmetry the issue is similar, although we may have to use state-averaging over degenerate states (Π states for example) to preserve spatial symmetry while solving for the *t*-amplitudes. The vacuum state is always chosen to be closed-shell, both with respect to spin and spatial symmetry.

The equations that define the cluster amplitudes use a reference state that provides a qualitatively correct description of the wave function. The reference state is parametrized as

$$|R\rangle = \hat{R}|0\rangle, \quad \hat{R} = r_{ij}\hat{a}_i\hat{a}_j \tag{2}$$

but the precise definition of the reference state (subject to the above parametrization) is again somewhat flexible. We will discuss a small number of variations below. In terms of the reference state the equations for the cluster amplitudes read

$$\langle 0|\hat{R}^\dagger \hat{E}_a^i \mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}\hat{R}|0\rangle \equiv Q_i^a = 0$$

$$\langle 0|\hat{R}^\dagger \hat{E}_a^i \hat{E}_b^j \mathrm{e}^{-\hat{T}}\hat{H}\mathrm{e}^{\hat{T}}\hat{R}|0\rangle \equiv Q_{ij}^{ab} = 0\,.$$

It is important to note that the above equations are not projections of the Schrödinger equation, which would involve $\hat{H}\mathrm{e}^{\hat{T}}\hat{C}|0\rangle$ instead. In ref.[99] we investigated both of these variants, and we concluded that the use of

$\hat{H}e^{\hat{T}}\hat{R}|0\rangle$ was the more promising and more straightforward approach. This approach was denoted RSS-EOMCCSD ("restricted or R-based" state-selective EOMCC) before[99]. Here we will simply denote the approach as SS-EOMCCSD. The exactness of the approach in the limit follows from using a complete diagonalization manifold, and this is independent of the equations satisfied by $\hat{T}$. This reflects the basic difficulty in "deriving" multireference coupled-cluster methods: there is no strict requirement for the cluster amplitudes, and we must be guided by practical results in truncated diagonalization spaces.

If we have defined a reference state, we can in principle solve for the t-amplitudes, obtain the required matrix-elements of the transformed Hamiltonian, and diagonalize to obtain the final eigenvector **C** and energy E.

The scheme can easily be adjusted to calculate a number of states in a state-averaged fashion. If we have a number of reference states $|R_\lambda\rangle$, and weights w_λ satisfying: $0 \le w_\lambda \le 1$, $\sum_\lambda w_\lambda = 1$, the state-averaged CC equations are defined by

$$\sum_\lambda w_\lambda \langle R_\lambda | \hat{E}_a^i e^{-\hat{T}} \hat{H} e^{\hat{T}} | R_\lambda \rangle \equiv Q_i^a = 0$$

$$\sum_\lambda w_\lambda \langle R_\lambda | \hat{E}_a^i \hat{E}_b^j e^{-\hat{T}} \hat{H} e^{\hat{T}} | R_\lambda \rangle \equiv Q_{ij}^{ab} = 0\,. \tag{3}$$

In practice the detailed amplitude equations are phrased in terms of the spin-summed state-averaged density matrices

$$D_i^k = \sum_\lambda w_\lambda \langle R_\lambda | \hat{E}_i^k | R_\lambda \rangle$$

$$D_{ij}^{kl} = \sum_\lambda w_\lambda \langle R_\lambda | \hat{E}_i^k \hat{E}_j^l | R_\lambda \rangle \tag{4}$$

and the only change in the algorithm is the appropriate definition of the reference density matrices.

Solution of CC Equations and Definition of Zeroth-Order Hamiltonian

The solution of the nonlinear equations for the t-amplitudes is nontrivial and deserves some discussion. To update the t-amplitudes we calculate a correction vector ΔT, by solving

$$-\sum_{\lambda} w_{\lambda} \langle R_{\lambda} | \hat{E}^i_a [\hat{H}_0, \Delta\hat{T}_1] | R_{\lambda} \rangle = Q^a_i = \sum_{\lambda} w_{\lambda} \langle R_{\lambda} | \hat{E}^i_a \hat{X}_1] | R_{\lambda} \rangle$$

$$-\sum_{\lambda} w_{\lambda} \langle R_{\lambda} | \hat{E}^i_a \hat{E}^j_b [\hat{H}_0, \Delta\hat{T}_2] | R_{\lambda} \rangle = Q^{ab}_{ij} = \sum_{\lambda} w_{\lambda} \langle R_{\lambda} | \hat{E}^i_a \hat{E}^j_b \hat{X}_2] | R_{\lambda} \rangle \qquad (5)$$

where $\hat{H}_0 = \sum_p \varepsilon_p \{\hat{p}^\dagger \hat{p}\}$ is a diagonal zeroth-order Hamiltonian (to be discussed below), while $\hat{X}_i = -[\hat{H}_0, \Delta T_i]$, $i = 1, 2$. The residual amplitudes $\mathbf{Q}$ are calculated as in Eq. (3). If the operator $\hat{X}$ is known, it is trivial to solve for the correction vector ΔT and a standard DIIS procedure can be used to accelerate convergence[113]. The equations for the amplitudes of $\hat{X}$ are linear and, moreover, they are diagonal in the virtual indices, as each of the reference states $|R_\lambda\rangle$ is expressed purely in terms of occupied orbitals in the vacuum state $|0\rangle$. The update equations can be written as

$$\sum_k A_{ik} X^a_k = Q^a_i$$

$$\sum_{k,l} A_{ij,kl} X_{kl,ab} = Q^{ab}_{ij} \qquad (6)$$

where the matrices A can be expressed in terms the one- and two-particle reduced density matrices corresponding to the reference state(s). The matrices A can be singular or nearly singular, but their dimensions are not very large. Hence we solve the equations by diagonalizing these matrices and only keeping those eigenvalues/eigenvectors in the inverse, which are smaller than a predetermined threshold. Unfortunately, this can easily lead to small discontinuities if a potential energy surface is evaluated. These problems are reduced if some kind of state-averaging is used, such that we do not have to discard any eigenvectors from the inverse. In practice we include multiple states therefore, even in a purely state-selective procedure. Typically we would add 0.05 times the average density over all included states plus 0.95 times the density of the true state of interest. This type of mixing will hardly affect the final result, but the stability of the approach is increased, certainly if the interest is a continuous potential energy surface. In the calculations on LiF below we have always included the two lowest states of $^1\Sigma$ symmetry and the two degenerate $^1\Pi$ states in the calculation, adjusting the weights that define the density matrices according to the specifics of the calculation and state of interest.

The definition of the canonical orbitals and diagonal orbital energies in $\hat{H}_0$ also poses an interesting problem. In principle we have two requirements. First of all we would like to achieve a smooth convergence of the CC iterations. Secondly, we would like to obtain reasonable results from the first iteration of the equations, which can be used to define a lowest order perturbation theory. Hence we define a perturbative variant by solving the cluster amplitudes from the first iteration to yield $\hat{T}^{(1)}$. The final energies are obtained by diagonalizing $\hat{H}^{[1]} = \mathrm{e}^{-\hat{T}(1)}\hat{H}\mathrm{e}^{\hat{T}(1)}$ over the usual set of configurations. Furthermore we realize that the occupied orbitals in $\hat{T}$ or $\hat{C}$ always correspond to annihilation operators, even while the orbitals have partial occupation numbers in the reference state. For this reason the occupied orbital energies should refer to an ionization process. This can be achieved by defining the orbitals and orbital energies following the extended Koopmans' theorem (EKT), which has an interesting history in quantum chemistry[114–121]. In the extended Koopmans' formulation one defines a non-orthogonal set of basis states $|\Phi_i\rangle = \hat{a}_i|R\rangle$ and solves for variationally optimal ionized states through

$$\sum_i \langle R|a_j^\dagger(\hat{H} - E_0)\hat{a}_i|R\rangle c_{i\mu} = \sum_i \langle R|a_j^\dagger \hat{a}_i|R\rangle c_{i\mu}(E_\mu^{\mathrm{IP}} - E_0) \tag{7}$$

which we approximate as

$$\sum_i \langle R|a_j^\dagger[\hat{H},\hat{a}_i]|R\rangle c_{i\mu} = \sum_i D_i^j c_{i\mu}\varepsilon_\mu^{\mathrm{IP}} \tag{8}$$

where $\varepsilon_\mu^{\mathrm{IP}} = E_\mu^{\mathrm{IP}} - E_0$. Moreover, we symmetrize the matrix on the left-hand side before solving the generalized eigenvalue problem. The coefficients $\mathbf{c}$ satisfy the normalization $\mathbf{c}^\dagger\mathbf{D}\mathbf{c} = 1$. After solving for the EKT eigenstates and eigenvalues, a set of orthonormal orbitals is obtained by symmetric orthogonalization of $\mathbf{c}$. The orbital energies are defined as the EKT ionization potentials corresponding to the reference state. For the virtual orbitals we follow the same procedure, using basis states $|\Phi_a\rangle = \hat{a}_a^\dagger|R\rangle$. In this case the procedure is equivalent to diagonalizing the virtual–virtual block of the Fock matrix corresponding to the one-particle reduced density matrix of the reference state, since the reference state has zero occupation of virtual orbitals by definition. Both the IP and EA EKT equations are easily expressed in terms of the one- and two-particle reduced density matrices of the reference state and hence can be generalized into a state-averaged version (with a less straightforward interpretation).

Let us emphasize that the orbital energies for the (partially) occupied orbitals are very different from a diagonalization of the Fock matrix. A clear example would be provided by a multireference treatment of the H_2 molecule, taking the σ and σ^* orbitals to form the vacuum state $|0\rangle$, containing 4 electrons. If the eigenvalues of the Fock matrix are used, the σ^* orbital would have a positive orbital energy, and it would be embedded in a set of diffuse Rydberg orbitals. The σ^* orbital energy would correspond to the electron affinity of neutral H_2. The Rydberg virtual orbitals would have similar energies as the formally occupied σ^* orbital and the corresponding energy denominators might be very small. The first-order amplitudes might easily have the wrong sign (compared to converged CC amplitudes). In our EKT picture the orbital energy of the σ^* would be the difference between the energy of ground state of the neutral H_2 molecule and the H_2 cation in the σ^* orbital/state. The shift in energy between these two definitions could be as large as 15 eV, from +5 eV for the Fock matrix variant to –10 eV for EKT. In practice, our equations converge smoothly, while also first-order perturbative corrections are generally of high quality, as will be demonstrated in the Results. This testifies that the physical ideas that underly the EKT inspired definition of $\hat{H}_0$ are correct. Using the EKT form of the zeroth-order Hamiltonian the SS-EOMCC equations can be solved even in very diffuse basis sets, which previously used to present severe problems. We no longer experience convergence problems that we can attribute to solving the CC equations (there are others though).

Brueckner Optimization of Orbitals and Definition of the Reference State

We still require a precise definition of the reference states $|R_\lambda\rangle = \hat{R}_\lambda|0\rangle$, and a definition of the orbitals that define the vacuum state. The most satisfactory approach for a system like LiF obtains if both the reference state and the orbitals are defined in the presence of dynamic correlation. This is possible if we define the reference state to be precisely the 2h component of the final correlated state $|\Psi\rangle = e^{\hat{T}}\hat{C}|0\rangle$, or $\hat{R} = \hat{C}_1$. The t-amplitudes are defined in conjunction with the vacuum state and the reference state, following Eq. (*3*). The coefficients t_i^a can be used to define a set of rotated orbitals $|\tilde{i}\rangle = |i\rangle + \sum_a |a\rangle t_i^a$. These orbitals are not orthogonal, but they are easily orthonormalized and this defines the new set of orbitals that defines the new vacuum state $|0\rangle$. This procedure is analogous to the use of Brueckner orbitals in single-reference coupled-cluster methods[100–103]. Taking the t_1-amplitudes as the orbital rotation parameters, we iterate until convergence as in conventional Brueckner calculations. This B-SS-EOM-CCSD approach has the advantage that all parameters are optimized for the precise state of interest and in the presence of dynamic correlation effects.

Unfortunately, the present Brueckner approach has a drawback in practice. The transformed Hamiltonian $\bar{\hat{H}}$ is non-Hermitian, and near the avoided crossing in LiF the energies obtained from a truncated diagonalization can become complex. This problem tends to be worse as we are in the process of trying to converge the equations and we acquire some large t-amplitudes in the iterative cycling. If we obtain a complex eigenvector, even if it is only during the process of converging the equation, it is impossible to extract a meaningful state and we are forced to terminate the state-selective iteration process. We think this is a very serious drawback of the scheme, and we think that we will have to go back to the drawing board and ultimately design a method in which the transformed Hamiltonian is Hermitian. It should be the goal of multireference methods to describe close-lying states and conical intersections, and non-Hermitian Hamiltonians can be expected to lead to insurmountable difficulties in such situations.

In this paper we follow an alternate track and consider the use of an MCSCF reference state. This will also allow us to compare the results between B-SS-EOM-CCSD and SS-EOM-CCSD based on an MCSCF reference state in the regions of the PES where all calculations can be converged. The MCSCF state $\hat{R}|0\rangle$ is defined by a CI over the 2h configurations, following our usual prescription. We use a particular implementation of MCSCF and optimize the orbitals using a CC singles approach, solving:

$$\sum_\lambda w_\lambda \langle R_\lambda | \hat{E}_a^i \mathrm{e}^{-\hat{T}_1} \hat{H} \mathrm{e}^{\hat{T}_1} | R_\lambda \rangle \equiv Q_i^a = 0 . \qquad (9)$$

These equations, which apply equally to state-specific and state-averaged approaches, can be converged in the usual Brueckner fashion. This results in conventional variational MCSCF results, but we denote the approach as Brueckner-MCSCF or B-MCSCF in short to reflect the particulars of the computational procedure. Unfortunately, converging state-specific MCSCF calculations is also troublesome for the case of LiF. Near the avoided crossing in LiF it is very hard to converge the B-MCSCF equations, due to so-called root-flipping problems: it is very hard to keep track of the proper state to optimize. This is true in particular for the excited state. If the orbitals are optimized for the excited state this state becomes the ground state in the limited CI, and moreover the 2h-CI coefficients (transformed to the AO basis to facilitate tracking of the state) vary wildly during the orbital optimization process. In our experience it is very hard to keep track of the state, and in the literature this is referred to as a root-flipping problem.

For this reason we developed yet another approach to define the orbitals and reference state, in an approach we denote as Brueckner-CI. In B-CI the reference state is taken to be the 2h component of the full vector **C** obtained by diagonalizing the bare Hamiltonian over 2h and 3h1p configurations. This has the advantage that the bare Hamiltonian matrix is Hermitian and the eigenvalues and eigenvectors are always real. Following a similar recipe as in the B-SS-EOM-CCSD scheme the reference state is taken to be the 2h component of the full vector **C**, $\hat{R} = \hat{C}_1$, and we use Eq. (*9*) to define the orbital optimization process, just as in B-MCSCF. While in B-MCSCF, the orbitals and reference state would be determined fully variationally, this is not true for B-CI. In B-CI we diagonalize over a larger space and from this extract the reference state. The subsequent orbital rotation is determined with respect to a reference state therefore, which is not itself variationally optimal.

Even though the results of converged B-CI and B-MCSCF calculations are expected to be very similar, the convergence behaviour of these methods is quite different. Interestingly, we experienced no convergence issues (root-flipping problems) using the B-CI method, and it is easy to track states through the crossing. This is due to the fact that relaxation effects are treated in an approximate fashion in the CI, which includes single excitations, and therefore the states are not so critically dependent on the orbitals, and they can easily be tracked. In particular the true excited state typically remains the excited state in the CI calculation, independent of the orbitals. The state of interest, for which the orbitals are optimized, has very little single excitation (i.e. 3h1p) character, as there is little need for inclusion of orbital relaxation effects in the CI as the orbitals are nearly optimal. This serves as a useful consistency check during the calculation. States for which the orbitals are not explicitly optimized in the B-CI scheme have a significantly higher 3p1h character. It is likely that the final B-CI states are not very different from the MCSCF states, and they might even serve as a starting point to optimize the true MCSCF states if so desired. We think the B-CI procedure might be of value in other procedures that require a CASSCF or MCSCF solution without resorting to a state averaging procedure.

Unfortunately, as discussed before, for the LiF potential energy curve the B-CI and B-MCSCF orbitals are far from ideal. Near the avoided crossing the states of interest acquire an arbitrary mixture of ionic and covalent configurations. The degree of mixing will depend greatly on dynamic correlation effects, and this is included in neither the B-CI nor the B-MCSCF treatment. Moreover, the optimal orbitals for these states will strongly depend on their precise character. It would be far more satisfactory if the orbitals and the reference state would be optimized in the presence of dynamic correlation. But this requires a Hermitian transformed Hamiltonian as discussed before, to avoid complex eigenvalues. In summary, at present we do not have a satisfactory solution to this problem yet.

For all of these orbital/reference optimization approaches, which we term B-MCSCF, B-CI, and B-EOMCC, we can define state-averaged and state-selective approaches. Even for the state-selective approaches we use only a weight of 0.95 for the state of interest, in order to alleviate problems with near-singularities of the reduced density matrices of the reference state, and to preserve continuous energy profiles.

RESULTS AND DISCUSSION

All of the calculations are using the 6-311++G(3df,3pd) basis set[111] and all orbitals are correlated. The SS-EOMCC calculations are of the DIP-SS-EOMCC variety, meaning we have one more spatial orbital (2 additional electrons) in the vacuum compared to the actual states of interest as described in the previous Section.

In Fig. 1 the results from a state-averaged SA-EOMCC calculation show a qualitatively correct behaviour of the potential energy curves. The covalent $^1\Sigma$ state is nearly degenerate with the doubly degenerate $^1\Pi$ states in the asymptotic region of large *R*. For decreasing internuclear distance this state very rapidly changes character around 6 Å and turns into the ionic state. Asymptotically, the ionic $^1\Sigma$ state is higher in energy and has a characteristic Coulombic tail at large *R*. In the avoided crossing region this state rapidly evolves into the covalent excited state. The orbitals required to describe the covalent and ionic states are quite different. This is not only true for the highest lying valence orbitals but also for the deeper lying orbitals, which are different for neutral and charged atoms. The effect can be expected to be more pronounced in larger basis sets. For this reason we expect the state-averaged EOMCC calculations to be deficient in some respects, and this will be confirmed below, although the behaviour close to the avoided crossing region might be acceptable (see the detail in Fig. 2).

Unfortunately, we do not have a fully accurate result in the 6-311++G(3df,3pd) basis set to compare with. Hence we will make comparisons with results from different types of approximate calculations. Many of our results are sufficiently poor that it is not difficult to draw conclusions even in the absence of good reference data. Let us emphasize here that a balanced description of both $^1\Sigma$ states of LiF over the entire range of internuclear distance is a challenging problem for multireference methods. We think that a proper description of these states is an important requirement of a generally applicable multireference method. Our results will show clearly we have not reached our goals yet, but they also point clearly towards possible improvements.

In Fig. 3 we focus on the ionic state in the asymptotic region, which diabatically connects to the ground state near the equilibrium geometry. The single-reference CCSD curve shows a discontinuity near the avoided crossing at around 6 Å. At the Hartree–Fock level the ionic state is lowest in energy, even in the asymptotic region of large *R*. Up to around 6 Å the CCSD solution follows the true ground state and acquires large single excitation amplitudes in order to follow the transition to the covalent solution. After the discontinuity CCSD follows the Hartree–Fock solution and converges to the ionic state, which is an excited state at these distances, result-

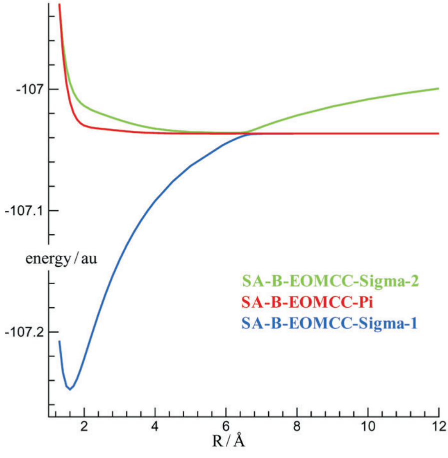

FIG. 1
State-averaged Brueckner EOMCC (SA-B-EOMCC) results for the ionic and covalent $^1\Sigma$ states and the doubly degenerate $^1\Pi$ states in the 6-311++G(3df,3pd) basis set

ing in small singles amplitudes again. This example clearly illustrates potential pitfalls in using single-reference methods to describe multireference situations. Following the solution of interest is tricky, and the calculated potential energy surface can exhibit discontinuities.

The behaviour of CCSD is exacerbated at the CCSD(T) level. The large singles amplitudes in conjunction with the perturbative correction in (T)

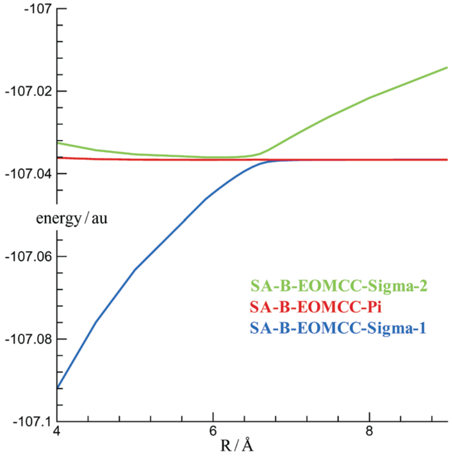

FIG. 2
Detail of the crossing region. Same SA-B-EOMCC calculations as in Fig. 1

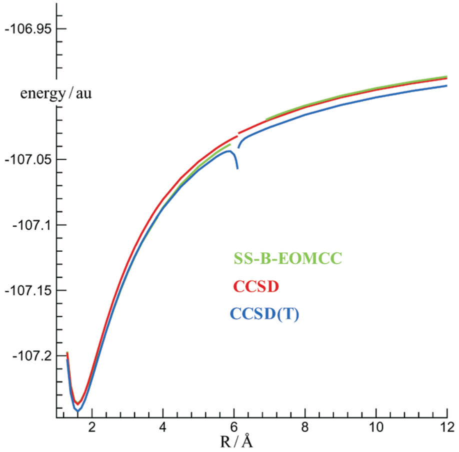

FIG. 3
A comparison of the ground state/ionic $^1\Sigma$ potential energy curve calculated at the CCSD, CCSD(T) and SS-B-EOMCC level of theory in the 6-311++G(3df,3pd) basis set

give rise to a weird “cusp-like” behaviour near the crossing point and a large discontinuity in the potential energy curve. The discontinuity in the CCSD(T) energy is a direct consequence of the discontinuity in the CCSD solution. Let us note here that it may be possible to solve for the covalent CCSD solution towards the asymptote. It does appear to be a nontrivial matter though, and it certainly does not seem to be the “black box” procedure, which we have come to expect from CC methodology.

Next, we compare the single-reference curve to the state-selective Brueckner EOMCC (SS-B-EOMCC) approach, which fares even worse. Near the crossing point, between 6 and 7.5 Å we cannot converge the equations. In our algorithm we start from orbitals from a previous geometry, but this is insufficient to find the solution. In the crossing region the orbitals change rapidly, and it appears impossible to find a good starting guess. During the iteration process we find large t_1-amplitudes. Moreover, the non-Hermitian Hamiltonian in the truncated diagonalization space easily leads to complex eigenvalues when two states are very close in energy. If this happens it is impossible to continue the calculations as there is no meaningful way to extract one state of interest from a pair of complex conjugate eigenvectors. We think this is a very severe drawback of the current methodology. We cannot expect to overcome these issues unless we resort to a Hermitian transformed Hamiltonian, which in turn implies using a unitary CC formalism or similar strategy. Let us note that we cannot actually conclude from the present calculations that (real) state-selective solutions do not exist at the troublesome geometries. Perhaps the state-average results even suggest they do exist, but they are certainly hard to find. It is evident that the non-Hermiticity of the transformed Hamiltonian is a clear danger when tracking for example conical intersections, and it serves little purpose in our opinion to try to solve the convergence problem for this particular case (if it is even possible). Moreover, the problem might show up in a similar fashion for state-averaged approaches, for which the transformed Hamiltonian is also non-Hermitian, although the iteration process is more friendly in these cases as the average density matrix does not change rapidly as one moves through a region with a crossing. The only robust solution appears to be the use of an explicitly Hermitian transformed Hamiltonian.

In Fig. 3 and also in Figs. 4 and 5 which focus on the details of the PES around the equilibrium distance and at large internuclear distance respectively, we observe another interesting behaviour. If the state is well described by Hartree–Fock the SS-B-EOMCCSD approach yields results that are quite close to SR-CCSD, which is to be expected. However, as the state becomes multiconfigurational SS-B-EOMCCSD starts to capture a significant portion of connected triples effects and the curve moves much closer to the CCSD(T) result. As a consequence SS-B-EOMCCSD is typically not well balanced across a potential energy surface. As we do not wish to enlarge the active space to capture the effects from connected triples, as is customary in high-accuracy MR-CISD calculations, it appears vital to include a connected

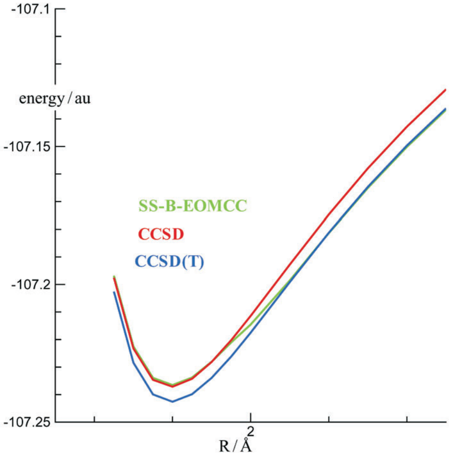

FIG. 4
Detailed potential energy curves around equilibrium geometry. Same calculations as in Fig. 3

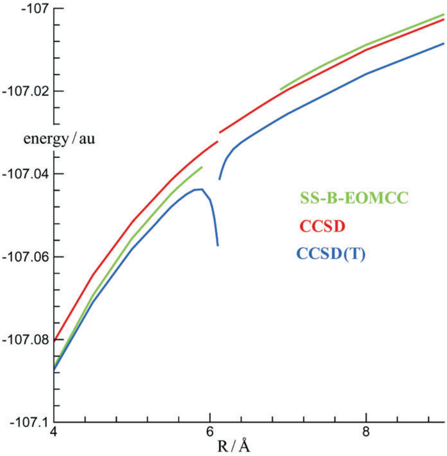

FIG. 5
Detailed ionic state potential energy curves in crossing region. Same calculations as in Fig. 3

triples correction in our methodology. In summary, from this simple comparison and results that are poor in many respects we learned two important things: (i) SS-EOMCCSD has to be reformulated to be based on a Hermitian transformed Hamiltonian; (ii) SS-EOMCCSD requires a connected triples correction in order to become a useful approach in conjunction with large basis sets, where effects from triples are particularly pronounced.

In Fig. 6 we compare the state-selective SS-B-EOMCCSD results against state-averaged SA-B-EOMCCSD results (discussed previously in conjunction with Figs. 1 and 2) which comprise the two $^1\Sigma$ and two degenerate $^1\Pi$ states. In the state-averaged calculations both the orbitals and the cluster amplitudes are optimized based on the averaged density matrix. In both the state-selective and the state-averaged calculations we use the Brueckner scheme to optimize the orbitals, which are hence optimized in the presence of dynamic correlation. Interestingly, in the SA-B-EOMCC scheme there are no problems with complex eigenvalues and we find continuous curves that show a nice avoided crossing. Moreover, the covalent/excited potential energy curve in SA-B-EOMCC is very close to the SS-B-EOMCC curve throughout (where available). This is likely because there is a 3 to 1 bias to this state in the state-averaged calculation as the $^1\Pi$ states require a similar set of orbitals and *t*-amplitudes as the covalent $^1\Sigma$. Also the ionic state is reasonably well described, but the energy at large *R* is too low, and this is likely

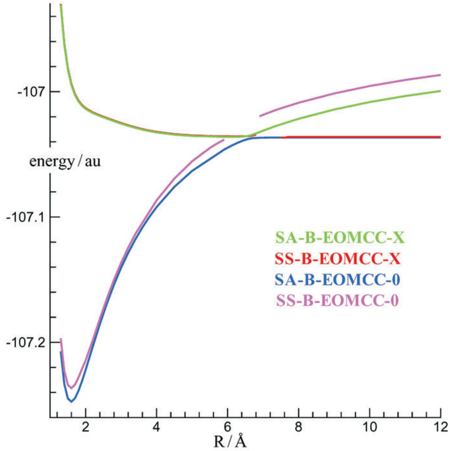

FIG. 6

Comparison of state-averaged and state-selective Brueckner EOMCC calculations for the ionic and covalent $^1\Sigma$ states. The designation -X indicates the excited state at the ground state geometry, -0 indicates the ground state at R_e

due to the fact that the orbitals are compromised. We should expect the correct solution to be close to the single-reference CCSD result, but the SA-B-EOMCC result is even lower than CCSD(T). It is important to point out here that the appropriate benchmark for the methodology in this region is CCSD, not full CI. A similar behaviour is seen near the equilibrium distance and a calculated ground state energy that is clearly too low testifies to the non-variational nature of the methodology: worse orbitals/amplitudes leading to lower energies (and perhaps erroneous better comparison to full CI). Overall we think (or perhaps better, we assume, for lack of accurate reference data) that the state-averaged method describes the crossing region itself rather well. The use of a common set of orbitals for states that have a very different character yields resonable results in this region of the PES. The common set of orbitals/amplitudes does deteriorate results away from the crossing. For greater clarity the details around the crossing are shown in Fig. 7.

In Fig. 8 we compare SS-B-CI-EOMPT calculations against SS-B-EOMCC. In the B-CI orbital optimization we use the MCSCF+singles CI space (i.e. 2h and 3h1p configurations) and optimize the orbitals using a similar approach as in the Brueckner CC schemes. It is worth noting that we found it impossible to converge the MCSCF (2h configuration space) equations themselves throughout the crossing region. Using the B-CI scheme we experienced no difficulties and we expect this scheme to be useful in general where root-flipping problems occur in MCSCF or CASSCF calculations. As a

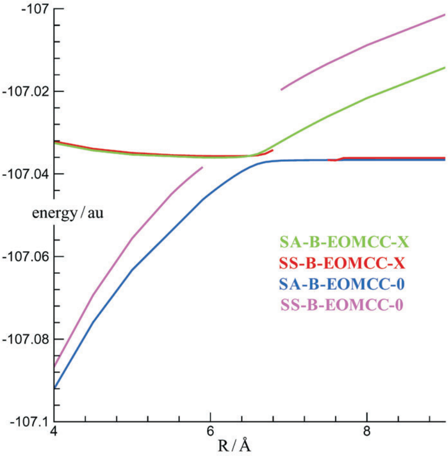

FIG. 7
Detail of the crossing region. Same calculations as in Fig. 6

useful diagnostic to home in on a particular root we found that the single CI (i.e. 3h1p) coefficients are always very small for the state of interest as they describe primarily orbital relaxation effects. Both states can therefore be easily characterized during the orbital optimization and this is clearly beneficial. It is clear from Fig. 8 that the behaviour of the B-CI energies itself is very different from the SS-B-CI-EOMPT curves, which include dynamic correlation. The B-CI energies show a strange 'discontinuous' behaviour, although our impression is we can follow the energies along the depicted curves, and there are no true discontinuities. Moreover, the curve crossing in B-CI occurs around 4 Å, far from the actual avoided crossing. We did not get meaningful results solving for the SS-B-CI-EOMCC solutions based on the B-CI orbitals, as we get very large t_1-amplitudes and associated problems in diagonalizing the transformed Hamiltonian. The perturbative variant SS-B-CI-EOMPT shows a smooth behaviour, locating the curve crossing around 6 Å, and following fairly closely the SS-B-EOMCC curve for the lower state. It is important to note that the SS-B-CI-EOMPT curves simply cross and do not show an avoided crossing type of behaviour. Moreover, it is evident that the curves are somewhat irregular as they go through the crossing region. One might think of these two states as 'diabatic' states showing a real, not avoided, crossing. We anticipate this will be typical behaviour in state-selective approaches based on MCSCF quality orbitals,

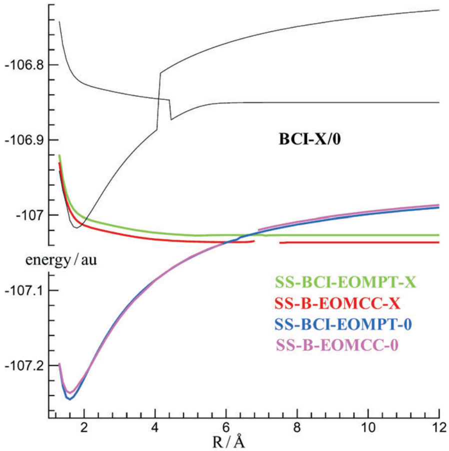

FIG. 8

Comparsion of Brueckner CI curves, and BCI-EOMPT and SS-B-EOMCC for the ionic and covalent $^1\Sigma$ states. The designation -X indicates the excited state at the ground state geometry, -0 indicates the ground state at R_e

when states are weakly interacting and show a very weakly (i.e. sharp) avoided crossing.

The upper state is calculated to have too high energy in SS-B-CI-EOMPT and this is quite irrespective of the orbitals used. While the comparison of SS-B-CI-EOMPT and SS-B-EOMCC is not bad it also clearly shows that it is not reasonable to expect a method that is based on B-CI (or MCSCF orbitals) to correctly describe the details of the crossing.

To gain some further insight into the potential of the perturbative variant we compare the state-averaged SA-EOMCC and SA-EOMPT results in Fig. 9 and find an almost uniform shift across the nuclear distance range for both curves. This result is quite promising as the relative energies between the CC and PT approaches are fully comparable across the curves. All curves in Fig. 9 are based on the same type of orbitals for all states, which have been optimized in a state-averaged fashion, but in presence of dynamic correlation. It is gratifying that these methods do capture the transition region in which the states change character. It is not unlikely that the true transition is yet somewhat sharper than observed in these calculations as the states are forced to be based on the same orbitals, increasing their potential for interaction. Improved methodology and presumably a full CI benchmark are needed to confirm this speculation.

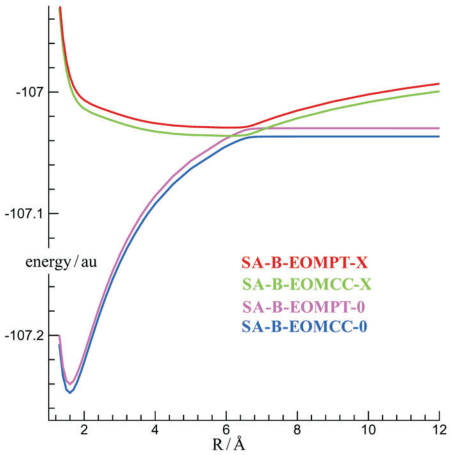

FIG. 9
Comparison of perturbative and coupled-cluster type state-averaged Brueckner EOM approaches. The designation -X indicates the excited state at the ground state geometry, -0 indicates the ground state at R_e

CONCLUSIONS

The LiF potential energy curves corresponding to the two lowest "ionic" and "covalent" $^1\Sigma$ states provide a wonderful test case to benchmark multireference methodologies. It is important to use sufficiently large basis sets to capture the full complexity of the problem. We think it is quite illustrative of the richness of this problem that, while none of our calculations gave correct results, we can draw clear conclusions regarding desirable and lacking aspects of our various approaches. This is perhaps even more remarkable in light of the fact that in order to draw these conclusions no "across the board accurate" reference data were needed. A comparison of resulting potential energy curves in different regions and simple logic suffice. Moreover, not all our conclusions are negative. Let us start with positive and semipositive conclusions.

1) The use of Brueckner orbitals in connection with state-selective multireference treatments allows one to optimize orbitals in the presence of dynamic correlation. Since surfaces may intersect at completely different geometries at correlated and mean-field levels of theory this is likely to be an important component of future multireference theories.

2) The definition of a zeroth-order Hamiltonian based on EKT yields first-order amplitudes and energies in close agreement with the full EOMCC results. Moreover the energy difference between CC- and PT-based approaches is nearly constant as a function of nuclear geometry, which is most important in practical applications. The use of the corresponding denominators in the CC iterative procedure leads to rapid convergence of the equations, similar to closed-shell CC theory. These denominators are in accord with the physical processes described by the *t*-amplitudes, e.g. ionization from orbitals lying in the active space. The fact that active orbitals are uniquely associated with annihilation operators is special to the present multireference formulation, which uses the antisymmetrized product of all active/occupied orbitals as the vacuum. The present theory is very simple in this respect.

3) The use of an average density matrix, even in state-specific calculations, comprised of 95% of the state of interest and 5% other states, to enlarge small eigenvalues in the density matrix yields a stable procedure to solve the SS-EOMCC equations. It is possible to achieve convergence by simply discarding "large eigenvalues" from the inverse, but this leads to (small) discontinuities in the potential energy surfaces in particular in regions where the MCSCF state of interest is essentially a single configuration and near-zero eigenvalues of the density matrix are to be expected.

4) SS-EOMCC is close to an internally contracted MRCC theory, and it is computationally quite effective. The theory is not completely size-extensive/size-consistent however, which is why we do not call it a MRCC theory. If Brueckner type orbitals are used, the deviations from size-consistency are very small in those cases we examined (less than 0.01 kcal/mol), implying that the size-consistency error might not have a practical importance. Let us note here that if the method is not based on Brueckner orbitals the size-consistency error is significantly larger, due to the increased importance of the 3h1p configurations to describe orbital relaxation effects.

5) State-averaged EOMCC procedures can be expected to yield smooth potential energy surfaces, and they are likely qualitatively correct, certainly close to the intersection. This conclusion is not very robust and it will depend on the degree of accuracy one expects from the calculations. We were surprised that SA-EOMCC does yield such reasonably looking potential energy curves for LiF, which is clearly a "worse case" scenario. The catch is that by design the curves look reasonable, smooth and so forth, but this does not guarantee their accuracy. We think these reservations apply with equal force to multistate perturbation theory calculations reported in the literature[94,106–109]. Nonetheless, qualitative insights are often of paramount importance in difficult cases, and we think the simple SA-approach has its appeal. In a way the state-averaged procedures are the black box procedures in the multireference world. This is the more true in relation to MRCC methods, where the choice of active orbital space is not so important, and it is relatively straightforward to select the active space. However, it is also clear that a state-averaged procedure cannot be expected to work across complete potential energy surfaces, and hence erroneous potential energy surfaces are a likely result of a too steadfast pursuit of this strategy. This is evident in the asymptotic region for LiF, where the ionic state is invariably found to be too low in energy in state-averaged calculations.

6) We used a Brueckner MCSCF+singles approach (coined Brueckner CI or B-CI by us) to calculate states at essentially MCSCF level of accuracy, and in this fashion resolved convergence issues in the pure MCSCF calculations related to root-flipping. We think this is a viable procedure that may be of general interest.

7) We developed some powerful state tracking algorithms that home in on a state while optimizing both orbital and cluster coefficients. In addition we can follow a state diabatically through a region of intersection, which can be useful in practical applications.

We also learned some very valuable lessons from clear-cut failures of our formally best SS-B-EOMCCSD approach.

8) The results from SS-EOMCCSD calculations approach single-reference CCSD accuracy in regions where Hartree–Fock is a good qualitative description, while it tends to be closer to CCSD(T) when the multireference character of the state is more pronounced. As a result complete potential energy curves can be rather poorly described, certainly in larger basis sets. The most promising remedy appears to be to add a connected triples correction to the SS-EOMCC approach. The details of this are yet to be worked out.

9) There is a great danger in using non-Hermitian transformed Hamiltonians in conjunction with (severely) truncated diagonalization spaces. If eigenvalues and eigenstates become complex it is impossible to define a meaningful single state and continue the iterative procedure in the state-selective approaches. These problems can show up in regular EOMCC approaches to calculate excited states, and they even more easily arise in STEOM, certainly when conical intersections are sought in a geometry optimization[41]. We think that unitary coupled-cluster theory in a Brueckner variant, or closely related, the strongly connected coupled-cluster theory proposed by Szalay, Nooijen and Bartlett[122] may provide a more promising avenue to solving this problem. Our experience with B-CI indicates that the convergence of the orbital optimization equations, and tracking a particular state of interest, is not itself a big issue. We are hopeful therefore that remaining convergence problems that occurred in this work are associated with complex roots of the transformed Hamiltonian.

10) We have learned once again during the course of this work to be cautious to call any individual problem the last hurdle to victory.

It is a pleasure to present this work in this issue dedicated to the celebration of the seventieth birthday of Professor Josef Paldus. We as authors both hope to grow older following Joe's example, resigning to the comforting fact that nature posed us with some problems that were just too hard to crack. We do hope that the multireference problem in electronic structure theory will lose some more of its formidable fangs as time progresses. This research was sponsored by an innovation grant from the National Science and Engineering Research Council (Canada).

REFERENCES

1. Monkhorst H. J.: *Int. J. Quantum Chem., Quantum Chem. Symp*. **1977**, *11*, 421.
2. Mukherjee D., Mukherjee P. K.: *Chem. Phys.* **1979**, *39*, 325.
3. Mukhopadhyay D., Mukhopadhyay S., Chauduri R., Mukherjee D.: *Theor. Chim. Acta* **1991**, *80*, 441.
4. Koch H., Jensen H. J., Jorgensen P., Helgaker T.: *J. Chem. Phys.* **1990**, *93*, 3345.

5. Christiansen O., Koch H., Halkier A., Jorgensen P., Helgaker T., deMeras A. S.: *J. Chem. Phys.* **1996**, *105*, 6921.
6. Koch H., Christiansen O., Jorgensen P., deMeras A. M. S., Helgaker T.: *J. Chem. Phys.* **1997**, *106*, 1808.
7. Stanton J. F., Bartlett R. J.: *J. Chem. Phys.* **1993**, *98*, 7029.
8. Bartlett R. J., Stanton J. F.: *Rev. Comp. Chem.* **1994**, *5*, 65.
9. Saeh J. C., Stanton J. F.: *J. Chem. Phys.* **1999**, *111*, 8275.
10. Hodges J. A., McMahon R. J., Sattelmeyer K. W., Stanton J. F.: *Astrophys. J.* **2000**, *544*, 838.
11. Nooijen M., Snijders J. G.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1992**, *26*, 55.
12. Nooijen M., Snijders J. G.: *Int. J. Quantum Chem.* **1993**, *48*, 15.
13. Nooijen M., Bartlett R. J.: *J. Chem. Phys.* **1995**, *102*, 3629.
14. Lindgren I.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1978**, *12*, 33.
15. Lindgren I., Mukherjee D.: *Phys. Rep.* **1987**, *151*, 93.
16. Mukherjee D., Pal S.: *Adv. Quantum Chem.* **1989**, *20*, 291.
17. Mukherjee D.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1986**, *20*, 409.
18. Mukherjee D.: *Chem. Phys. Lett.* **1986**, *125*, 207.
19. Stolarczyk L., Monkhorst H. J.: *Phys. Rev. A* **1985**, *32*, 725.
20. Kaldor U.: *Theor. Chim. Acta* **1991**, *80*, 427.
21. Hughes S. R., Kaldor U.: *J. Chem. Phys.* **1993**, *99*, 6773.
22. Meissner L.: *Chem. Phys. Lett.* **1996**, *255*, 244.
23. Meissner L., Malinowski P.: *Phys. Rev. A* **2000**, *61*, 062510.
24. Meissner L. Gryniakow J.: *Collect. Czech. Chem. Commun.* **2003**, *68*, 105.
25. Meissner L.: *J. Chem. Phys.* **1998**, *108*, 9227.
26. Landau A., Eliav E., Kaldor U.: *Chem. Phys. Lett.* **1999**, *313*, 399.
27. Landau A., Eliav E., Ishikawa Y., Kaldor U.: *J. Chem. Phys.* **2000**, *113*, 9905.
28. Landau A., Eliav E., Kaldor U.: *Int. J. Mod. Phys. B* **2003**, *17*, 5335.
29. Landau A., Eliav E., Ishikawa Y., Kaldor U.: *J. Chem. Phys.* **2004**, *121*, 6634.
30. Nooijen M.: *J. Chem. Phys.* **1996**, *104*, 2638.
31. Nooijen M., Bartlett R. J.: *J. Chem. Phys.* **1997**, *106*, 6441.
32. Nooijen M., Bartlett R. J.: *J. Chem. Phys.* **1997**, *106*, 6449.
33. Nooijen M., Bartlett R. J.: *J. Chem. Phys.* **1997**, *107*, 6812.
34. Nooijen M.: *Spectrochim. Acta, Part A* **1999**, *55*, 539.
35. Nooijen M., Lotrich V.: *J. Chem. Phys.* **2000**, *113*, 494.
36. Nooijen M.: *J. Phys. Chem. A* **2000**, *104*, 4553.
37. Stanton J. F., Gauss J.: *Theor. Chim. Acta* **1995**, *91*, 267.
38. Stanton J. F., Gauss J.: *J. Chem. Phys.* **1994**, *101*, 8938.
39. Stanton J. F., Gauss J.: *J. Chem. Phys.* **1994**, *100*, 4695.
40. Gwaltney S. R., Bartlett R. J., Nooijen M.: *J. Chem. Phys.* **1999**, *111*, 58.
41. Wladyslawski M., Nooijen M. in: *Low-Lying Potential Energy Surfaces*, ACS Symposium Series 828 (M. R. Hoffmann and K. G. Dyall, Eds), p. 65. ACS, Washington 2002.
42. Wladyslawski M., Nooijen M.: *Adv. Quantum Chem.* **2005**, in press.
43. Christiansen O., Gauss J., Stanton J. F., Jorgensen P.: *J. Chem. Phys.* **1999**, *111*, 525.
44. Tobita M., Perera S. A., Musial M., Bartlett R. J., Nooijen M., Lee J. S.: *J. Chem. Phys.* **2003**, *119*, 10713.
45. Hazra A., Nooijen M.: *Int. J. Quantum Chem.* **2003**, *95*, 643.
46. Hazra A., Chang H. H., Nooijen M.: *J. Chem. Phys.* **2004**, *121*, 2125.

47. Hazra A., Nooijen M.: *Phys. Chem. Chem. Phys.* **2005**, *7*, 1759.
48. Stanton J. F., Sattelmeyer K. W., Gauss J., Allan M., Skalicky T., Bally T.: *J. Chem. Phys.* **2001**, *115*, 1.
49. Bomble Y. J., Sattelmeyer K. W., Stanton J. F., Gauss J.: *J. Chem. Phys.* **2004**, *121*, 5236.
50. Nooijen M.: *Int. J. Quantum Chem.* **2003**, *95*, 768.
51. Hazra A., Nooijen M.: *J. Chem. Phys.* **2005**, accepted.
52. Krylov A. I.: *Chem. Phys. Lett.* **2001**, *350*, 522.
53. Krylov A. I.: *Chem. Phys. Lett.* **2001**, *338*, 375.
54. Krylov A. I., Sherrill C. D.: *J. Chem. Phys.* **2002**, *116*, 3194.
55. Slipchenko L. V., Krylov A. I.: *J. Chem. Phys.* **2003**, *118*, 9614.
56. Levchenko S. V., Krylov A. I.: *J. Chem. Phys.* **2004**, *120*, 175.
57. Cristian A. M. C., Shao Y., Krylov A. I.: *J. Phys. Chem. A* **2004**, *108*, 6581.
58. Kowalski K., Piecuch P.: *J. Chem. Phys.* **2000**, *113*, 5644.
59. Kowalski K., Piecuch P.: *J. Chem. Phys.* **2000**, *113*, 18.
60. Piecuch P., Kowalski K., Pimienta I. S. O., McGuire M. J.: *Int. Rev. Phys. Chem.* **2002**, *21*, 527.
61. Mahapatra U. S., Datta B., Mukherjee D.: *J. Chem. Phys.* **1998**, *110*, 6171.
62. Mahapatra U. S., Datta B., Bandyopadhyay B., Mukherjee D.: *Adv. Quantum Chem.* **1998**, *30*, 163.
63. Mahapatra U. S., Datta B., Mukherjee D.: *Mol. Phys.* **1998**, *94*, 157.
64. Mahapatra U. S., Datta B., Mukherjee D.: *J. Phys. Chem. A* **1999**, *103*, 1822.
65. Mahapatra U. S., Datta B., Mukherjee D.: *J. Chem. Phys.* **1999**, *110*, 6171.
66. Chattopadhyay S., Mahapatra U. S., Ghosh P., Mukherjee D. in: *Low-Lying Potential Energy Surfaces*, ACS Symposium Series 828 (M. R. Hoffmann and K. G. Dyall, Eds), p. 109. ACS, Washington 2002.
67. Chattopadhyay S., Mahapatra U. S., Datta B., Mukherjee D.: *Chem. Phys. Lett.* **2002**, *357*, 426.
68. Chattopadhyay S., Pahari D., Mukherjee D., Mahapatra U. S.: *J. Chem. Phys.* **2004**, *120*, 5968.
69. Hubač I., Pittner J., Čársky P.: *J. Chem. Phys.* **2000**, *112*, 8779.
70. Pittner J., Nachtigall P., Čársky P., Hubač I.: *J. Phys. Chem. A* **2001**, *105*, 1354.
71. Pittner J., Šmydke J., Čársky P., Hubač I.: *J. Mol. Struct. (THEOCHEM)* **2001**, *547*, 239.
72. Pittner J.: *J. Chem. Phys.* **2003**, *118*, 10876.
73. Li X. Z., Paldus J.: *J. Chem. Phys.* **1994**, *101*, 8812.
74. Li X. Z., Paldus J.: *J. Chem. Phys.* **1995**, *102*, 8059.
75. Li X. Z., Paldus J.: *Int. J. Quantum Chem.* **1998**, *70*, 65.
76. Jeziorski B., Monkhorst H. J.: *Phys. Rev. A* **1981**, *24*, 1668.
77. Oliphant N., Adamowicz L.: *J. Chem. Phys.* **1991**, *94*, 1229.
78. Oliphant N., Adamowicz L.: *Int. Rev. Phys. Chem.* **1993**, *12*, 339.
79. Piecuch P., Oliphant N., Adamowicz L.: *J. Chem. Phys.* **1993**, *99*, 1875.
80. Adamowicz L., Malrieu J. P., Ivanov V. V.: *J. Chem. Phys.* **2000**, *112*, 10075.
81. Lyakh D. I., Ivanov V. V., Adamowicz L.: *J. Chem. Phys.* **2005**, *122*, 024108.
82. Piecuch P., Kucharski S. A., Bartlett R. J.: *J. Chem. Phys.* **1999**, *110*, 6103.
83. Kowalski K., Piecuch P.: *Chem. Phys. Lett.* **2001**, *344*, 165.
84. Li X. Z., Paldus J.: *J. Chem. Phys.* **1997**, *107*, 6257.
85. Li X. Z., Paldus J.: *J. Chem. Phys.* **1998**, *108*, 637.
86. Li X. Z., Paldus J.: *J. Chem. Phys.* **1999**, *110*, 2844.

87. Li X. Z., Paldus J.: *J. Chem. Phys.* **2000**, *113*, 9966.
88. Li X. Z., Paldus J.: *Mol. Phys.* **2000**, *98*, 1185.
89. Meissner L., Grabowski I.: *Chem. Phys. Lett.* **1999**, *300*, 53.
90. Meissner L., Nooijen M.: *Chem. Phys. Lett.* **2000**, *316*, 501.
91. Fulscher M. P., Andersson K., Roos B. O.: *J. Phys. Chem.* **1992**, *96*, 9204.
92. Andersson K., Malmqvist P. A., Roos B. O.: *J. Chem. Phys.* **1992**, *96*, 1218.
93. Roos B. O., Andersson K., Fulscher M. P., Malmqvist P. A., Serrano-Andres L., Pierloot K., Merchan M.: *Adv. Chem. Phys.* **1996**, *93*, 219.
94. Nakano H., Uchiyama R., Hirao K.: *J. Comput. Chem.* **2002**, *23*, 1166.
95. Kawashima Y., Hashimoto T., Nakano H., Hirao K.: *Theor. Chem. Acc.* **1999**, *102*, 49.
96. Choe Y. K., Hashimoto T., Nakano H., Hirao K.: *Chem. Phys. Lett.* **1998**, *295*, 380.
97. Nooijen M., Bartlett R. J.: *J. Chem. Phys.* **1996**, *104*, 2652.
98. Nooijen M., Lotrich V.: *J. Mol. Struct. (THEOCHEM)* **2001**, *547*, 253.
99. Nooijen M.: *Int. J. Mol. Sci.* **2002**, *3*, 656.
100. Chiles R. A., Dykstra C. E.: *J. Chem. Phys.* **1981**, *74*, 4544.
101. Handy N. C., Pople J. A., Headgordon M., Raghavachari K., Trucks G. W.: *Chem. Phys. Lett.* **1989**, *164*, 185.
102. Koch H., Kobayashi R., Jorgensen P.: *Int. J. Quantum Chem.* **1994**, *49*, 835.
103. Nooijen M., Lotrich V.: *J. Chem. Phys.* **2000**, *113*, 4549.
104. Spiegelmann F., Malrieu J. P.: *J. Phys. B* **1984**, *17*, 1235.
105. Spiegelmann F., Malrieu J. P.: *J. Phys. B* **1984**, *17*, 1259.
106. Finley J., Malmqvist P. A., Roos B. O., Serrano-Andres L.: *Chem. Phys. Lett.* **1998**, *288*, 299.
107. Finley J. P., Witek H. A.: *J. Chem. Phys.* **2000**, *112*, 3958.
108. Nakano H., Nakatani J., Hirao K.: *J. Chem. Phys.* **2001**, *114*, 1133.
109. Sousa C., Dominguez-Ariza D., deGraaf C., Illas F.: *J. Chem. Phys.* **2000**, *113*, 9940.
110. Legeza O., Roder J., Hess B. A.: *Mol. Phys.* **2003**, *101*, 2019.
111. Krishnan R., Binkley J. S., Seeger R., Pople J. A.: *J. Chem. Phys.* **1980**, *72*, 650.
112. Sattelmeyer K. W., Schaefer H. F., Stanton J. F.: *Chem. Phys. Lett.* **2003**, *378*, 42.
113. Császár P., Pulay P.: *J. Mol. Struct. (THEOCHEM)* **1984**, *114*, 31.
114. Katriel J., Davidson E. R.: *Proc. Natl. Acad. Sci. U.S.A., Phys. Sci.* **1980**, *77*, 4403.
115. Pickup B. T., Snijders J. G.: *Chem. Phys. Lett.* **1988**, *153*, 69.
116. Matos J. M. O., Day O. W.: *Int. J. Quantum Chem.* **1987**, *31*, 871.
117. Morrison R. C.: *J. Chem. Phys.* **1992**, *96*, 3718.
118. Morrison R. C.: *Int. J. Quantum Chem.* **1994**, *49*, 649.
119. Sundholm D., Olsen J.: *J. Chem. Phys.* **1993**, *98*, 3999.
120. Olsen J., Sundholm D.: *Chem. Phys. Lett.* **1998**, *288*, 282.
121. Nooijen M. J.: *Chem. Phys.* **1999**, *111*, 8356.
122. Szalay P. G., Nooijen M., Bartlett R. J.: *J. Chem. Phys.* **1995**, *103*, 281.