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Internally contracted multiconfiguration-reference configuration interaction calculations for excited states*

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Summary. The calculation of electronically excited states with the internally contracted multiconfiguration-reference configuration interaction (CMRCI) method is discussed. A straightforward method, in which contracted functions for all states are included in the basis, is shown to be very accurate and stable even in cases of narrow avoided crossings. However, the expense strongly increases with the number of states. A new method is proposed, which employs different contracted basis sets for each state, and in which eigensolutions of the Hamiltonian are found using an approximate projection operator technique. The computational effort for this method scales only linearly with the number of states. The two methods are compared for various applications.

Key words: Quantum chemistry – Configuration interaction – Excited states

1 Introduction

Today, the multiconfiguration-reference configuration interaction method [1–13] (MRCI) is considered to be one of the most accurate approximations used in quantum chemistry. The main advantage of this method is that it is not restricted to specific choices of the zeroth order wavefunction and can therefore be used to compute potential energy functions and other molecular properties for ground and excited electronic states and for any nuclear geometry. A particularly efficient variant is the internally contracted MRCI method [8–13]. In this method the number of variational parameters is strongly reduced by contracting subsets of the CSFs with fixed coefficients. For a given basis set, the number of variational parameters only depends on the number of correlated orbitals in the reference wavefunction, and is independent of the number of reference configurations which are constructed from this orbital set. It has been demonstrated [11, 13–15] that in most cases this contraction leads to only very small errors.

The price one has to pay for the reduction of the number of variational parameters is the complicated structure of the contracted N-electron basis functions. In the direct CI procedure, this complicates the evaluation of the

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*Dedicated in honor of Prof. Klaus Ruedenberg residual vector $\boldsymbol{g} = \boldsymbol{H} \cdot \boldsymbol{c}$. However, we have recently developed very efficient new techniques [11, 12] which now enable us to perform internally contracted MRCI calculations with very large reference spaces and very large basis sets. Some of our previous calculations [11, 13–15] included more than 3000 reference configurations and basis sets of more than 200 orbitals.

A particular difficulty with the internally contracted MRCI method is the calculation of excited states. Since the contracted configurations depend on the expansion coefficients of the reference configurations, different contracted configuration sets are required for each state. Therefore, if several states are computed simultaneously in a straightforward manner as outlined in Sect. 2, the number of external pair functions which must be included increases linearly in the number of states. This leads to a quadratic to cubic dependence of the computational effort on the number of states and reduces or even eliminates the advantage of the internally contracted MRCI method. However, in Sect. 3, we present a new approximate method for which the effort depends only linearly on the number of states. The efficiency and accuracy of this method will be demonstrated in Sect. 4.

2 Internally contracted MRCI for excited states

In the standard uncontracted MRCI method, the N particle basis set depends only on the structure of the reference space and not directly on the reference wavefunction Ψ_0. In the calculation of excited states, one typically uses the same reference space for all states of interest, and so in turn the same basis of configurations is used in the CI calculation, with the first, second, third, . . . state wavefunctions appearing as the first, second, third, . . . eigensolutions of the common Hamiltonian matrix. MacDonald's theorem [16] holds, and gives some justification to the calculation of excitation properties (transition moments and excitation energies) from the resulting wavefunctions. For the case of the internally contracted MRCI wavefunction [8–11], however, the situation is somewhat more complicated. In this case the configurations for state n are generated by applying two-electron excitation operators to the corresponding MCSCF reference function

$$\Psi_0^{(n)} = \sum_R a_R^{(n)} \Phi_R. \tag{1}$$

In the following we use the short-hand notation $|n\rangle \equiv \Psi_0^{(n)}$. In our present approach only the configurations with two electrons in the external orbital space are internally contracted, while the internal configurations Φ_I and the singly external configuration Φ_S^a are standard configuration state functions [11, 12]. The internal configuration space $\{\Phi_I\}$ includes the reference space $\{\Phi_R\}$. The internally contracted configurations are defined as:

$$\Phi_{ijp,n}^{ab} = (\hat{E}_{ai}\hat{E}_{bj} + p\hat{E}_{bi}\hat{E}_{aj})\,|n\rangle \quad (i \geqslant j \text{ internal, } a \geqslant b \text{ external, } p = \pm 1), \tag{2}$$

where $\hat{E}_{ai}$ are the usual one-electron excitation operators:

$$\hat{E}_{ai} = \eta_a^{\alpha\dagger}\eta_i^{\alpha} + \eta_a^{\beta\dagger}\eta_i^{\beta}. \tag{3}$$

For a given internal orbital space, the number of contracted configurations $\Phi_{ijp,n}^{ab}$ is independent of the number of reference configurations. However, the functions $\Phi_{ijp,n}^{ab}$ depend on the numerical values of the reference coefficients $a_R^{(n)}$, and so are inherently specific to the one particular state n which is well approximated by the reference wavefunction $\Psi_0^{(n)}$. A straightforward method, which has been in routine use since the development of the internally contracted CI approach [8], is to use a basis which is the union of all contracted configurations formed from separate reference functions for each state up to, and including, the state k of interest. The wavefunction then takes the form:

$$\Psi^{(n)} = \sum_I c_I^{(n)} \Phi_I + \sum_S \sum_a [c_S^{(n)}]_a \Phi_S^a + \sum_{m=1}^{k} \sum_{i \geqslant j} \sum_p \sum_{ab} [C_{ijp,m}^{(n)}]_{ab} \Phi_{ijp,m}^{ab} \tag{4}$$

with

$$[C_{ijp,m}^{(n)}]_{ab} = p[C_{ijp,m}^{(n)}]_{ba} \quad (p = \pm 1). \tag{5}$$

In general, the functions $\Phi_{ijp,m}^{ab}$ are not orthonormal and may be linearly dependent. In order to orthonormalize them and to eliminate redundant functions, we need their overlap matrix:

$$\langle \Phi_{ijp,m}^{ab} | \Phi_{klq,n}^{cd} \rangle = \tfrac{1}{2}\delta_{pq}(\delta_{ac}\delta_{bd} + \delta_{ad}\delta_{bc})(\langle m | \hat{E}_{ik,jl} | n \rangle + p \langle m | \hat{E}_{il,jk} | n \rangle), \tag{6}$$

which is obtained in terms of the elements of the second-order reduced transition density matrices of the reference wavefunctions. Similarly, the coupling coefficients needed to compute Hamiltonian matrix elements between the contracted functions are transition density matrices up to order four. For details we refer to Ref. [11].

If one is interested in the kth state, then the first k eigensolutions of the Hamiltonian matrix in this compound contracted basis must be computed. We have found this approach to be rather robust, giving potential energy and property surfaces which are nearly identical to those obtainable from uncontracted calculations, even in cases with strongly interacting states as LiF (*X* and *A* states) and CN (*X* and *B* states) (cf. Sect. 4). The main disadvantage of the approach is its cost. To a fair approximation, the size of the basis increases linearly with the number of states k, and there is usually no additional Hamiltonian sparsity associated with the increase in basis size. The cost of computing the pair-pair interactions then scales as k^2, and the effort for the interactions of the pair functions with the singly external functions Ψ_S^a, which often dominates the whole calculation, scales as k. Since the number of times the action of Hamiltonian on a trial vector is required for diagonalization also scales linearly with the number of eigenvalues required, the cost of the whole calculation scales as k^2 to k^3. This becomes a serious consideration when one is interested in four or five states of a given symmetry.

3 A projection method for excited states

The unfavourable scaling of effort with the number of states discussed in Sect. 2 could be avoided if it were possible to calculate one state at a time, and to use a contracted basis generated from one appropriate reference function (usually, for the kth state, the kth eigensolution of the Hamiltonian in the reference space). The excited state eigenvector can be found by solving in each iteration of the direct CI procedure a smaller eigenvalue problem for a wavefunction of the form

$$\Psi^{(n)} = \sum_I c_I^{(n)} \Phi_I + \sum_\lambda \alpha_\lambda^{(n)} \, \Delta\Psi_\lambda^{(n)} \tag{7}$$

where

$$\Delta\Psi_{\lambda}^{(n)} = \sum_{S}\sum_{a}[\Delta c_{S}^{(n,\lambda)}]_a \Phi_S^a + \sum_{i\geqslant j}\sum_{p}\sum_{ab}[\Delta C_{ijp}^{(n,\lambda)}]_{ab}\Phi_{ijp,n}^{ab} \tag{8}$$

are external expansion functions, which are obtained in subsequent iterations λ. Note that these functions are specific to state n, since only contracted functions for this state are included. For the kth state, usually the lowest k eigensolutions $\Psi^{(n)}$, $n = 1, k$ are calculated, and then the root which is most similar in character to the reference state is selected. The external expansion functions $\Delta\Psi_{\lambda}^{(n)}$ and the corresponding residuals $\hat{H}\,\Delta\Psi_{\lambda}^{(n)}$ are finally linearly combined using the appropriate expansion coefficient $\alpha_{\lambda}^{(n)}$. Then, as usual, the next expansion vector is found by first order perturbation theory.

However, there are two significant and distinct problems which can arise in such an approach. Firstly, we recognise that valence correlation energies are of the same order of magnitude as, and often larger than, electronic excitation energies. Since the contracted configurations for the kth state correlate the lower states poorly, this has the effect that as iterative diagonalization proceeds, the desired root, for example for the first excited state, switches from being the second lowest to the lowest root of the reduced eigenvalue problem. This root flipping often causes a completely non-physical mixing of ground and excited states as well as introducing convergence problems. The second, more severe, problem that can occur is in situations of near degeneracy, where the reference states might have an incorrect energy ordering. Such a situation occurs, for instance, for a part of the potential energy curves for LiF, where the MCSCF predicts the ionic-covalent crossing at much too short a bond length. In these circumstances, even ground state calculations in a contracted basis built from the ground reference state only give very poor results. However, with a compound contracted basis constructed from two reference states one obtains very accurate results even in the region of the avoided crossing.

The root flipping problem discussed above can be avoided by the following new procedure. We suggest to diagonalise a modified Hamiltonian matrix in which the required state appears as the lowest root, with the lower eigensolutions shifted away. For the kth state, we define a projection matrix:

$$\boldsymbol{P}^{(k)} = \mathbf{1} - \sum_{n=1}^{k-1}\boldsymbol{c}^{(n)}\boldsymbol{c}^{(n)\dagger} \tag{9}$$

and the corresponding projected Hamiltonian matrix:

$$\boldsymbol{H}^{(k)} = \boldsymbol{P}^{(k)}\boldsymbol{H}\boldsymbol{P}^{(k)}. \tag{10}$$

In the above, $\boldsymbol{c}^{(n)}$ represents the eigenvector for the nth state, i.e., the lowest eigenvector of $\boldsymbol{H}^{(n)}$, and so we proceed through a sequence of calculations, finding in turn the lowest eigensolutions of $\boldsymbol{H}^{(1)} \equiv \boldsymbol{H}$, $\boldsymbol{H}^{(2)}, \ldots, \boldsymbol{H}^{(k)}$. The computational effort is clearly linear in k.

If $\boldsymbol{H}$ were the full CI Hamiltonian matrix, then this sequence would be exactly equivalent to finding the lowest k eigensolutions of the Schrödinger equation with $\boldsymbol{P}^{(k)}$ being an exact projection operator whose only effect is to shift the lower $k - 1$ eigenvalues to zero. In the context of contracted CI calculations, the basis used for each state is different, and direct construction of the full projector becomes difficult. It is, however, perfectly feasible to form an approximate projector, where only such configurations are included in the $\boldsymbol{c}^{(n)}$ vector in Eq. (9) which lie in the configuration set for both the nth and kth state calculations. As noted in Sect. 2, in our implementation of the internally contracted MRCI, we use a basis of uncontracted CSFs Φ_I for the internal part of the wavefunction, and so it is natural to restrict the projector to include only internal CSFs which are common to the nth and kth state bases. For a properly designed calculation, the internal space should represent the dominant part of the wavefunction, and so the approximate projection operators should be effective in shifting away the unwanted lower roots of the Hamiltonian. Since the projection operator does not extend over the singly and doubly external configurations, the additional matrix elements require trivial computational effort.

However, because the projector is only approximate, it is no longer true that the lowest eigenvalue of $\boldsymbol{H}^{(k)}$ is the exact kth eigenvalue of $\boldsymbol{H}$; not even MacDonald's theorem holds, and one must interpret the computed excited state properties with some caution. A remedy for this problem is described below.

In a slightly different context, it has been shown [17] that when CI wavefunctions are obtained in different bases for different states, much more reliable transition properties are obtained by constructing final wavefunctions which are those linear combinations of the (non-orthogonal) wavefunctions which bring the Hamiltonian between themselves into diagonal form. We have implemented this approach in our contracted CI program. After solving for the lowest eigenvector of $\boldsymbol{H}^{(n)}$, we form all $H_{mn} = \langle \Psi^{(n)} | \hat{H} | \Psi^{(m)} \rangle$, $S_{mn} = \langle \Psi^{(n)} | \Psi^{(m)} \rangle$ $(m \leqslant n)$, in what is effectively $n - 1$ further iterations of the CI procedure. Note that the procedures used for calculating Hamiltonian matrix elements have to allow for the possibility that bra and ket wavefunctions are in different linear spaces. After the calculation of all k state wavefunctions, the $k \times k$ Hamiltonian matrix is diagonalised. In fact, this is a non-orthogonal eigenvalue problem. The final states are linear combinations of those obtained in the approximate projector calculation. Properties are also easily obtained as linear transformations of the property matrix elements computed between the original states. We found that in most cases this procedure gives almost identical results to the computationally more demanding multi-state procedure described in Sect. 2. Some examples are presented in Sect. 4.

4 Applications

As a first example, we discuss some calculations for the two lowest $^2\Sigma^+$ states of the CN radical. Results of a calculation in which the basis for both states included the union of all contracted pair functions generated from two CASSCF reference states are shown in the first column of Table 1. Using separate contracted basis sets for each state with the projection technique suggested in Sect. 3, we obtain the results in the second column of Table 1. We see significant differences between both calculations, particularly in the dipole moments. This can be understood in that the two approximate wavefunctions are not orthogonal and there is a sizeable remaining Hamiltonian interaction between them, as also shown in Table 1. After solving the 2×2 eigenvalue problem in the basis of these wavefunctions and transforming the properties correspondingly, we obtain the values in the third column of Table 1. These results are seen to come very close to those from the more expensive two-state basis calculation, in particular for the dipole moments.

In Table 2, we present results of calculations for the first four $^1A'$ states of HCO^+. The calculation was performed near the ground state equilibrium

Table 1. Comparison of excited state calculations$^{(a)}$ for CN, $X^2\Sigma^+$, $B^2\Sigma^+$

	Two-state basis	One-state basis (projected)	One-state basis (transformed)
E_X	−92.571955	−92.571667	−92.571673
E_B	−92.458143	−92.457763	−92.457758
ΔE/eV	3.0970	3.0995	3.0998
$\langle\Psi_B\|\hat{H}\|\Psi_X\rangle$	0.0	−0.009049	0.0
$\langle\Psi_B\|\Psi_X\rangle$	0.0	0.000106	0.0
μ_X	−0.5631	−0.5725	−0.5632
μ_B	0.5372	0.5473	0.5381
μ_{BX}	0.6914	0.6898	0.6972

[a] $R = 2.1$ bohr. Basis: [5*s*4*p*3*d*2*f*1*g*] valence quadruple zeta correlation consistent basis set of Dunning [20]; method see text

Table 2. Comparison of CI calculations[a] for the lowest four $^1A'$ states of HCO^+

	Two-state basis	Three-state basis	Four-state basis	Projected & transformed
E_1[b]	−113.322323	−113.322600	−113.322860	−113.322021
E_2	−113.057684	−113.058049	−113.058350	−113.056935
E_3		−113.006982	−113.007325	−113.005364
E_4			−112.885245	−112.882904
ΔE_{12}[c]	7.212	7.199	7.198	7.213
ΔE_{13}		8.588	8.586	8.617
ΔE_{14}			11.908	11.949
μ_1[d]	1.6666	1.6655	1.6638	1.6647
μ_2	1.9572	1.9540	1.9523	1.9519
μ_3		1.8219	1.8234	1.8202
μ_4			1.7863	1.7952
μ_{12}	0.2548	0.2568	0.2572	0.2583
μ_{13}		0.1269	0.1269	0.1318
μ_{14}			0.6343	0.6139

[a] Geometry: $R_{CH} = 1.08$ Å, $R_{CO} = 1.198$ Å, $H\hat{C}O = 119.5°$
Basis set: [4*s*3*p*2*d*1*f*] (C, O), [3*s*2*p*1*d*] (H) valence triple zeta correlation consistent functions of Dunning [20]. For methods used, see text

[b] State energies in hartrees

[c] Excitation energies in eV

[d] Expectation and transition dipole moments in atomic units

geometry of HCO using a valence triple zeta basis set. Molecular orbitals were determined through a CASSCF calculation, with the orbitals $3a' - 8a'$, $1a'' - 2a''$ active. This CAS expansion was also used as the reference space for the contracted MRCI computations, in which the ten valence electrons were correlated. The calculations were performed using the new approach, as well as with full two, three and four state bases. We observe that the excitation energies and dipole properties obtained with the projection & transformation method are extremely close to those from the full multistate calculations, with significantly reduced computational effort; to obtain the results for all four states using the new method requires 1541 seconds of CRAY-XMP CPU time, whilst the full four state calculation used 5253 sec, with increased memory requirements also.

It might be expected that our method gives less accurate results near avoided crossings, where electron correlation may significantly change the mixing of the states. As an example for such a case we present some calculations for the lowest two $^2\Pi$ and $^2\Sigma^+$ states of $AlCl^+$. The two $^2\Pi$ states form an avoided crossing at short internuclear distances. In a diabatic picture, the two states involved can be characterized as $Al^{++}Cl^-$ ("ionic") and Al^+Cl ("neutral"). The change of the electronic structure in the region of the avoided crossing is reflected by strong variations of the electric dipole moments and the electronic transition moment. Figure 1 shows the potential energy functions of both states, computed both with the two-state basis and the new projection method. On the scale of this figure, the differences of the potentials obtained with both methods can hardly be detected. Figures 2 and 3 show the same comparison for the dipole and

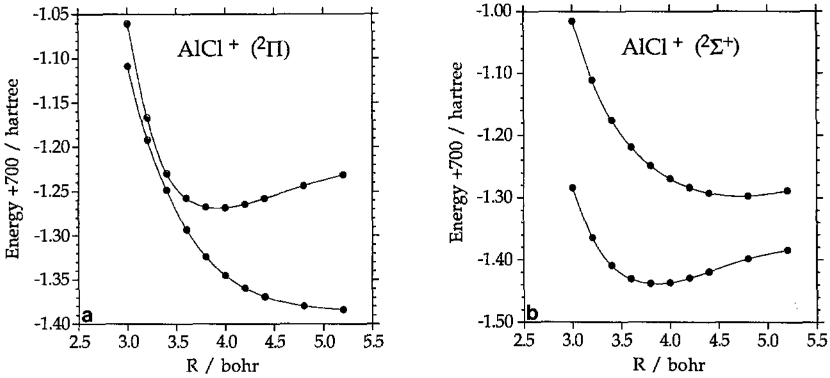

Fig. 1. Calculated potential energy functions for the lowest two $^2\Pi$ (**a**) and $^2\Sigma^+$ (**b**) states of $AlCl^+$. The difference of the one-state projection/transformation and the two-state calculations is hardly visible on this scale

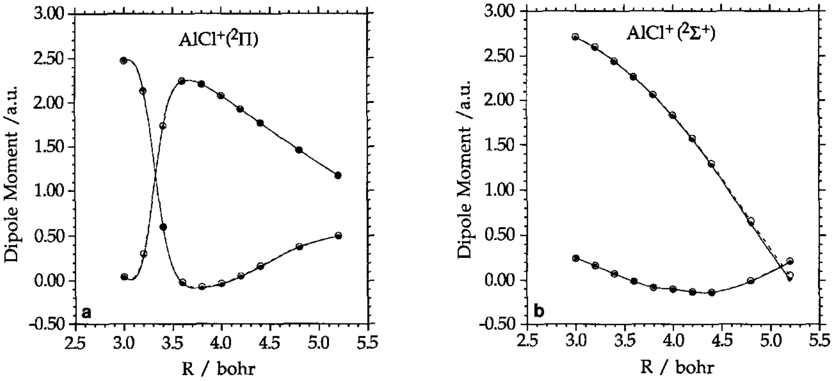

Fig. 2. Calculated dipole moment functions for the lowest two $^2\Pi$ (**a**) and $^2\Sigma^+$ (**b**) states of $AlCl^+$. *Open circles*: One-state calculation with projection and transformation. *Full circles*: Two-state calculation

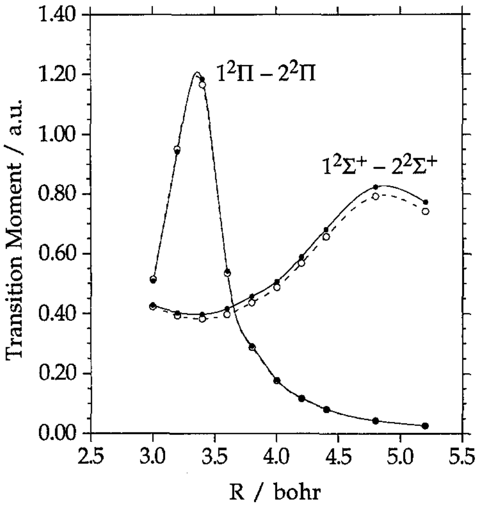

Fig. 3. Calculated transition moment functions for the lowest two $^2\Pi$ and $^2\Sigma^+$ states of $AlCl^+$. *Open circles*: One-state calculation with projection and transformation. *Full circles*: Two-state calculation

transition moment functions. Again, the differences between the more accurate two-state calculation and the projected calculations are extremely small. A more complete presentation of our calculations for $AlCl^+$ and AlF^+ can be found in Ref. [18].

Another example is shown in Fig. 4 for the symmetric stretching potentials ($D_{\infty h}$) of the lowest two $^1\Pi_u$ and $^3\Pi_u$ states of CO_2. Again these states form narrow avoided crossings, but this time one state has Rydberg and one state has valence character. For most geometries, we have only used the projected method with subsequent solution of the 2×2 eigenvalue problem. Figure 4 shows a comparison of the (non-variational) projected results with the variational results obtained in the final diagonalization. The energy differences are found to be very small for all considered geometries. At one geometry ($R = 2.4$ bohr) in the region

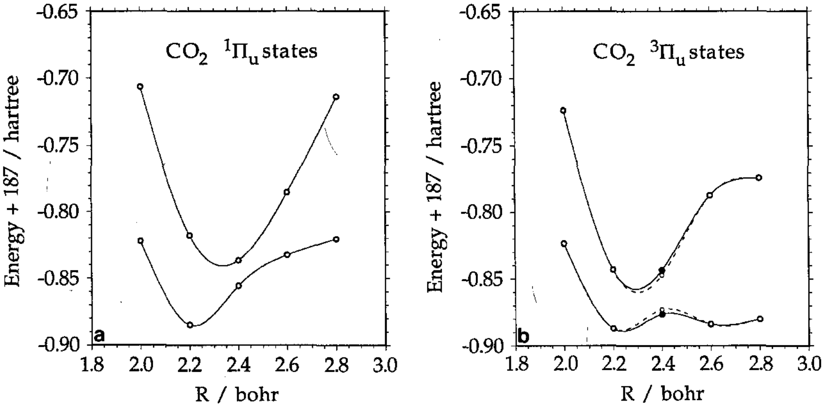

Fig. 4. Calculated symmetric stretching potentials ($D_{\infty h}$) for the lowest two $^1\Pi_u$ (**a**) and $^3\Pi_u$ (**b**) states of CO_2. *Open circles*: One-state calculation with projection. *Full circles*: One-state calculation with projection and transformation

Table 3. Comparison of MRCI calculations[a] for the lowest two $^1\Pi_u$ states of CO_2

Method	E_1/a.u.	E_2/a.u.	ΔE/eV
Projected	−187.855614	−187.836616	0.517
Projected & transformed	−187.855686	−187.836543	0.521
Two-state	−187.855752	−187.836848	0.514

[a] $D_{\infty h}$, $R = 2.4$ bohr. Basis set: 13*s*,9*p*,3*d*,1*f*, 70 reference CSFs. For details see Ref. [19]

of the avoided crossing, we have compared the results from a calculation with a two-state basis with the projected and transformed results. These data are presented in Table 3. It is seen that the energy differences between the two-state and the projected & transformed cases are less than 0.1 mH for the lower state and 0.3 mH for the upper state. For more details of these calculations we refer to Ref. [19].

These examples clearly demonstrate that our new method is efficient and accurate in many different situations. Nevertheless, it cannot be excluded that under certain circumstances the one-state basis N-electron basis sets used are inappropriate, in particular in the region of avoided crossings. This can be detected by consideration of the mixing coefficients in the final CI in the basis of the projected wavefunctions. If there are strong mixings, it is recommended to perform the more accurate but more expensive calculations in a composite multi-state N-electron basis set.

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