Evaluation of the Spin−Orbit Interaction within the Graphically Contracted Function Method[†]

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The graphically contracted function (GCF) method is extended to include an effective one-electron spin−orbit (SO) operator in the Hamiltonian matrix construction. Our initial implementation is based on a multiheaded Shavitt graph approach that allows for the efficient simultaneous computation of entire blocks of Hamiltonian matrix elements. Two algorithms are implemented. The SO-GCF method expands the spin−orbit wave function in the basis of GCFs and results in a Hamiltonian matrix of dimension $N_{\text{dim}}=N_\alpha((S_{\text{max}}+1)^2-S_{\text{min}}^2)$. N_α is the number of sets of nonlinear arc factor parameters, and S_{min} and S_{max} are respectively the minimum and maximum values of an allowed spin range in the wave function expansion. The SO-SCGCF (SO spin contracted GCF) method expands the wave function in a basis of spin contracted functions and results in a Hamiltonian matrix of dimension $N_{\text{dim}}=N_\alpha$. For a given N_α and spin range, the number of parameters defining the wave function is the same in the two methods after accounting for normalization. The full Hamiltonian matrix construction with both approaches scales formally as $O(N_\alpha^2\omega n^4)$ for n molecular orbitals. The ω factor depends on the complexity of the Shavitt graph and includes factors such as the number of electrons, N, and the number of interacting spin states. Timings are given for Hamiltonian matrix construction for both algorithms for a range of wave functions with up to $N = n = 128$ and that correspond to an underlying linear full-CI CSF expansion dimension of over 10^{75} CSFs, many orders of magnitude larger than can be considered using traditional CSF-based spin−orbit CI approaches. For Hamiltonian matrix construction, the SO-SCGCF method is slightly faster than the SO-GCF method for a given N_α and spin range. The SO-GCF method may be more suitable for describing multiple states, whereas the SO-SCGCF method may be more suitable for describing single states.

1. Introduction

In the graphically contracted function (GCF) method,[1−4] the configuration interaction (CI) wave function is expanded as a linear combination of GCFs

$$|\psi\rangle = \sum_{P=1}^{N_\alpha} c_P|P\rangle \quad (1)$$

where the GCF basis functions $|P\rangle$ in turn are linear combinations over the configuration state function (CSF) basis of dimension N_{CSF}

$$|P\rangle = \sum_{m=1}^{N_{\text{CSF}}} x_m^P|\tilde{m}\rangle \quad (2)$$

The method is formulated in terms of spin-eigenfunctions using the Graphical Unitary Group Approach (GUGA).[5,6] The expansion coefficients x_m^P are products of arc factors associated with the Shavitt graph

$$x_m^P = \prod_{r=1}^{n} \alpha_{\mu(r;m)}^P \quad (3)$$

Each GCF basis function $|P\rangle$ corresponds to a particular set of arc factors $\boldsymbol{\alpha}^P$. N_α is the number of sets of arc factors. The arc factor $\alpha_{\mu(q;m)}^P$ is associated with the arc μ in the directed walk connecting orbital levels $(q-1)$ to q in the CSF $|\tilde{m}\rangle$. There are n orbitals in the Shavitt graph, so each CSF coefficient in a particular GCF consists of a product of n arc factors. Consequently, the wave function depends on the linear coefficients c_P and on the nonlinear arc factor parameters. The expansion form is appropriate for both ground and excited states and to closed- and open-shell molecules. N_α dimensions in the range 10−20 have been shown sufficient[4] to achieve chemical accuracy for small molecules.

Efficient recursive algorithms have been developed to compute reduced density matrices, scalar products $S_{PQ}=\langle P|Q\rangle$, and Hamiltonian matrix elements $H_{PQ} = \langle P|\hat{H}|Q\rangle$ in this basis. In the non-spin−orbit case, the effort required to construct an individual Hamiltonian matrix element between two GCF basis functions H_{PQ} scales as $O(\omega n^4)$ for a wave function expanded in n molecular orbitals. The prefactor ω itself scales between N^0 and N^2, for N electrons, depending on the complexity of the underlying Shavitt graph. The corresponding metric matrix element $S_{PQ} = \langle P|Q\rangle$ requires effort that scales as $O(\omega n)$, the transition reduced density matrix $\mathbf{D}^{MN}$ requires $O(\omega n^2)$ effort, and the two-particle density $\mathbf{d}^{MN}$ requires $O(\omega n^4)$ effort. There is no component of the effort or storage for matrix element computation that scales as N_{CSF}.

In this work, we extend the GCF method to include the spin−orbit (SO) interaction into the Hamiltonian matrix element construction within a relativistic effective core potential (RECP) formalism,[7] and we present timing results for our initial implementations. When the spin−orbit interaction is incorporated, the wave function expansion basis must include several possible interacting spin states.[8] Two paradigms have been explored previously: the straightforward idea of computing interactions between separate Shavitt graphs, and the idea of

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merging several such graphs together to form a single multiheaded Shavitt graph. This latter paradigm appears to be particularly promising because it allows the interactions to be computed for all of the interacting spin states simultaneously, with only minimal additional effort compared to the non-spin−orbit, single-headed graph case. Particularly when applied to ground and excited states of molecules containing transition metals, lanthanides, and actinides, which are characterized by large spin−orbit interactions involving many valence electrons with sometimes large numbers of interacting spin states,[9] the multiheaded Shavitt graph paradigm appears to have significant computational advantages. Closed-form expressions have been derived[8] for the number of nodes and arcs in full-CI multiheaded Shavitt graphs and also for the number of nodes in the corresponding auxiliary pair graphs; it is these parameters that determine the efficiency and scaling properties of the reduced density matrix and Hamiltonian matrix element construction. As discussed in more detail in the following sections, for a multiheaded Shavitt graph each set of arc factors results in several graphically contracted wave functions associated with the different graph heads which, in turn, are associated with the interacting spin states.

2. Method

Yabushita, Zhang, and Pitzer[10] have formulated the inclusion of a one-electron spin−orbit operator into the GUGA CI Hamiltonian in the traditional CSF basis. We briefly review that work since our methods are based on it. The total Hamiltonian operator is defined as the sum of the non-spin−orbit operator and the spin−orbit operator

$$\hat{H}^{\mathrm{total}} = \hat{H}^{0} + \hat{H}^{\mathrm{SO}} \tag{4}$$

The non-spin−orbit Hamiltonian is defined in the usual way

$$\hat{H}^{0} = \sum_{pr} h_{pr}\hat{E}_{pr} + \frac{1}{2}\sum_{prst} g_{prst}\hat{e}_{prst} \tag{5}$$

with $\hat{E}_{pr} = a^{\dagger}_{p\alpha}a_{r\alpha} + a^{\dagger}_{p\beta}a_{r\beta}$ and $\hat{e}_{prst} = \hat{E}_{pr}\hat{E}_{st} - \delta_{sr}\hat{E}_{pt}$. The array **h** includes the usual one-electron kinetic energy and nuclear attractions, and the array **g** includes the two-electron repulsions. The spin−orbital creation and annihilation operators $a^{\dagger}_{p\sigma}$ and $a_{p\sigma}$ correspond to spatial orbital $\varphi_p(\mathbf{r})$ and spin function $\sigma \in \{\alpha, \beta\}$. Matrix elements of $\hat{H}^0$ are computed in the usual way within the GUGA formalism in which Abelian point group symmetry is utilized.

A one-electron spin−orbit operator

$$\hat{H}^{\mathrm{SO}} = \sum_{pr}\sum_{\sigma\sigma'} h^{\mathrm{so}}_{p\sigma,r\sigma'} a^{\dagger}_{p\sigma}a_{r\sigma'} \tag{6}$$

is defined with the matrix elements[10]

$$h^{\mathrm{SO}}_{p\sigma,r\sigma'} = \int\int \phi^{*}(\mathbf{r})_{p\sigma}\Big(\sum_{A}\sum_{l_A=1}^{L_A} \xi_{Al_A}(\mathbf{r}_A)\vec{l}_A\cdot\vec{s}\,\hat{O}_{l_A}\Big)\phi(\mathbf{r})_{r\sigma'}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\tau \tag{7}$$

The index A includes all nuclear centers, and the index l_A is the (truncated) spherical harmonic expansion index for nuclear center A. The spin−orbit coupling functions $\xi_{Al_A}(\mathbf{r}_A)$, the orbital angular momentum $\vec{l}_A$, and the projection operator $\hat{O}_{l_A}$ are all defined with respect to nuclear center A. Averaged relativistic effective core potentials and effective spin−orbit operators are used to define the above one-election $\mathbf{h}^{\mathrm{SO}}$ matrix elements and also to modify the above **h** matrix elements. In this manner, only the noncore electrons and orbitals are treated explicitly. The scalar part of this RECP approach is simple to incorporate into software for nonrelativistic computations; the principal complication arises from the symmetry properties of the spin−orbit operator.[11,12]

The linear expansion space for the spin−orbit wave function is the union of the $|\tilde{m};S,M\rangle$ CSFs corresponding to $\hat{S}^2$eigenvalues $S(S + 1)$ and to $\hat{S}_Z$ eigenvalues $M = -S, -S + 1, ..., +S$. In general, the wave function transforms according to double group symmetry. However, the formalism is developed specifically for even-electron wave functions corresponding to integral S and M values, in which case the irreducible representations correspond to those of normal point groups.[13] Odd-electron wave functions are computed by formally adding a fictitious noninteracting electron in a fictitious orbital to result in a formal even-electron system, and by treating this extra electron and orbital implicitly. In this basis, a spin−orbit Hamiltonian matrix element takes the form

$$\begin{aligned}\langle\tilde{m}';S',M'|\hat{H}^{\mathrm{SO}}|\tilde{m};S,M\rangle = \sum_{pr}\sum_{\gamma=-1}^{1}(-1)^{\gamma}q_{-\gamma,pr}\times \\ \sum_{\sigma\sigma'} s_{\gamma,\sigma\sigma'}\langle\tilde{m}';S',M'|a^{\dagger}_{p\sigma}a_{r\sigma'}|\tilde{m}';S,M\rangle\end{aligned} \tag{8}$$

where $q_{\gamma,pr}$ is a matrix element of the spherical tensor form of the orbital angular momentum operator and $s_{\gamma,\sigma\sigma'}$ is a matrix element of the spherical tensor form of the Pauli spin matrices. Equation 8 is simplified further following McWeeny[14,15] using the Wigner−Eckart theorem.[16−18]

$$\begin{aligned}\sum_{\sigma\sigma'} s_{\gamma,\sigma\sigma'}\langle\tilde{m}';S',M'|a^{\dagger}_{p\sigma}a_{r\sigma'}|\tilde{m}';S,M\rangle = \\ (-1)^{S'-M'}\begin{pmatrix} S' & 1 & S \\ -M' & \gamma & M \end{pmatrix}\langle\tilde{m}';S'||\hat{Z}_{pr}||\tilde{m}';S\rangle\end{aligned} \tag{9}$$

In this manner, the computation of a single reduced coupling coefficient $\langle\tilde{m}';S'||\hat{Z}_{pq}||\tilde{m};S\rangle$ is sufficient to compute all of the nonzero elements within the spin block indexed by the $2S' + 1$ values of M' and by the $2S + 1$ values of M.

Depending on the molecular symmetry, this could result in a complex, hermitian, Hamiltonian matrix with complex eigenvectors. Instead, the "real spherical" basis used in ref 10 is denoted $|m;S,M_{\pm}\rangle$ and consists of linear combinations of the spin eigenfunction basis functions.

$$\begin{aligned}|m;S,M_{-}\rangle &= \frac{i^{S+1}}{\sqrt{2}}(|\tilde{m};S,-M\rangle - (-1)^{M}|\tilde{m};S,M\rangle) \\ &\qquad M = 1, ..., S \\ |m;S,M_{+}\rangle &= \frac{i^{S}}{\sqrt{2+2\delta_{M0}}}(|\tilde{m};S,-M\rangle + (-1)^{M}|\tilde{m};S,M\rangle) \\ &\qquad M = 0, ..., S\end{aligned} \tag{10}$$

These basis functions are normalized and are individually either purely real or purely imaginary (assuming real orbital basis functions), and for all molecular symmetries this basis choice results in a real, symmetric, Hamiltonian matrix which in turn has real eigenvectors.

In this basis, the nonzero spin−orbit Hamiltonian matrix elements correspond to $|S - S'| \leq 1$ and to $|M_\pm - M_\pm'| \leq 1$ (except that if $S = S'$ and $M_\pm = M_\pm' = 0$ then the matrix elements are zero). All possible nonzero elements are enumerated in eqs 50−57 of ref 10. In general, a spin−orbit Hamiltonian matrix element in the CSF basis is a product of an S- and M-dependent factor from the $3j$ symbols and from eq 10, a single Cartesian spin−orbit integral, and a Shavitt loop value of type 8*b*.

Our present work uses the same approach described above, except that the bra and ket functions are GCFs $|P;S,M_\pm\rangle$ rather than individual CSFs $|m;S,M_\pm\rangle$. The reduced coupling coefficient $\langle \tilde{m}';S'||\hat{Z}_{pr}||\tilde{m};S\rangle$ in eq 9 is replaced with the reduced transition density matrix element $\langle P;S'||\hat{Z}_{pr}||Q;S\rangle$ for GCFs constructed from arc factor sets P and Q. These transition density matrix elements are, in turn, computed recursively from products of segment factor matrices, the elements of which are denoted $D_{pr}^{S'S,PQ}$. The selection rules, i.e., the combinations of S, $M_\pm$, and S', $M_\pm'$ that correspond to nonzero matrix elements, are the same as for individual CSFs. Consequently, a single reduced transition density matrix element computation step is sufficient to determine all of the nonzero spin−orbit Hamiltonian matrix element contributions arising within an entire spin block. This is demonstrated in the following matrix element expression which corresponds to eq 50 in ref 10.

$$\begin{aligned}\langle P;S,(M+1)_\mp|\hat{H}^{\mathrm{SO}}|Q;S,M_\pm\rangle &= -\langle P;S,M_\pm|\hat{H}^{\mathrm{SO}}|Q;S,(M+1)_\mp\rangle \\ &= \sqrt{\pm\frac{(1 \pm \delta_{M0})(S - M)(S + M + 1)}{8S(S + 1)}}\, h_x^{SS,PQ}\end{aligned} \tag{11}$$

with

$$h_t^{S'S,PQ} = \sum_{pr} \Lambda_{t,pr}(D_{pr}^{S'S,PQ}) \qquad t \in \{x, y, z\} \tag{12}$$

This summation actually reduces to a single term in the CSF basis as discussed in ref 10, but the full summation contributes to the GCF basis expression since, in principle, all expansion CSFs are included in the expression. In eq 12, $\Lambda_{t,pr} = -\Lambda_{t,rp} = -\mathrm{i}q_{t,pr}$ is an element of the real, skew-symmetric representation of the spin−orbit integral[12] associated with the Cartesian orbital angular momentum axis $t \in \{x, y, z\}$. Thus all Hamiltonian matrix elements are computed using only real arithmetic.

In previous work with the GCF method[8] we extended the DRT generation program to create Shavitt graphs with multiple heads, and we extended the Hamiltonian matrix element program to create auxiliary pair graphs with node pairs for the multiple heads. For the current work, we have continued extending the latter program to create auxiliary pair graphs with edges for the spin−orbit 8*b* loops. The RL^1 and the $R\underline{L}^1$ segment value types do not occur at the top level n for normal Shavitt loops. However, these segments are used at the top via the spin−orbit virtual loop head(s) at level $n + 1$; the 8*b* loop head $\overline{RL}^1$ segment values are incorporated into the S- and M-dependent terms in the formulas for the spin−orbit matrix elements. This is the only change to the auxiliary pair graph edge construction needed for the spin−orbit loops.

The final augmentations for the spin−orbit matrix elements occur in the recursive construction of the transition density matrix elements. This procedure begins at the graph tail and propagates to the top level. The spin−orbit 8*b* loops use the non-spin−orbit 8*b* node pair value array and results from the normal "initiation" and "propagation" steps without modification. In our initial implementation, the spin−orbit loops always "terminate" at the top level n, and a special termination process was added to return the reduced transition density elements for all spin blocks that correspond to interacting heads of the Shavitt graph. It is necessary to identify the bra and ket nodes of the node pair at level n; these node pairs identify the GCF spin block within the given P and Q pair of arc factors. An alternative implementation, which we intend to investigate in future work, consists of precomputing the $\overline{RL}^1$ and $\overline{RL}^1$ segment factor products from the top down, and "terminating" the 8*b* loops at level r within the graph with $R\underline{L}^1$ segment factors. As discussed in ref 19, in the context of spin-density matrix computations, we expect this to result in a more efficient algorithm if the transition density matrices $\mathbf{D}^{SS',PQ}$ are computed in a separate step from the other one- and two-particle density matrices. However, as discussed below, we find this to be minor in our current implementation in which the elements of all density matrices are computed simultaneously. Once the reduced transition density matrix elements are available, the S- and M-dependent factors and the spin−orbit Cartesian integrals are combined, and the corresponding Hamiltonian matrix elements are updated. In our current implementation, type 9 loops are not computed separately because they are equivalent to the bra-ket interchange of type 8*b* loops; this equivalence holds also for the spin−orbit type 9 loops.

Once spin−orbit matrix elements have been computed, the next step concerns their employment. In the multiheaded Shavitt graph paradigm being pursued here, two alternative approaches exist for the wave function expansion, a direct expansion in the GCF spin basis

$$|\psi\rangle = \sum_{P=1}^{N_\alpha} \sum_{S=S_{\min}}^{S_{\max}} \sum_{M=-S}^{S} c_{PSM}|P;S,M\rangle \tag{13}$$

or an expansion in a spin contracted basis

$$|\psi\rangle = \sum_{P=1}^{N_\alpha} c_P|P\rangle; \qquad |P\rangle = \sum_{S=S_{\min}}^{S_{\max}} \sum_{M=-S}^{S} \alpha^{P;SM}|P;S,M\rangle \tag{14}$$

In these expressions it is assumed for simplicity that all possible interacting spin states are included from a chosen minimum $S_{\min}$ to maximum $S_{\max}$ range; in addition, for notational simplicity the M terms are written in the spin eigenfunction basis instead of the real spherical basis. In the latter approach, denoted SO-SCGCF (spin−orbit spin contracted GCF), additional arc-factor-like parameters $\alpha^{P;SM}$ associated with each GCF $|P;S,M\rangle$ are introduced as linear contraction coefficients to form a new basis, and the wave function is expanded as a linear combination of these SO-SCGCFs. One set of arc factors $\boldsymbol{\alpha}^P$ along with one set of the additional parameters $\alpha^{P;SM}$, called spin contraction coefficients, generates one SO-SCGCF basis function, and the Hamiltonian matrix dimension is $N_{\mathrm{dim}} = N_\alpha$. For a single $\langle P|\hat{H}^{\mathrm{total}}|Q\rangle$ matrix element, the implementation of this approach is particularly simple because the spin contraction coefficients are utilized in an analogous manner to the arc factors and only in the termination steps for the $\langle P|\hat{H}^{\mathrm{SO}}|Q\rangle$ matrix elements and in the computation of the $\bar{\gamma}^{PQ}$ array used in the computation of $\langle P|\hat{H}^0|Q\rangle$. These spin contraction coefficients are optimized with the nonlinear arc-factors and allow the various components of the wave function to mix optimally for a single state. In analogy to single-headed Shavitt graphs, a single SO-SCGCF from a multiheaded Shavitt graph with a set of arc factors and spin contraction coefficients can represent any individual CSF $|m;S,M_\pm\rangle$. But a single set of spin contraction coefficients does not allow for the changes of mixings that would be associated with the description of multiple states; additional SO-SCGCF basis functions, increasing the value of N_α, would be required for this flexibility. Note that for a given N_α, the number of parameters introduced into the procedures are the same in the two approaches after accounting for wave function normalization; the primary difference is the dimension of the Hamiltonian matrix.

The direct expansion in the GCF basis approach in eq 13, denoted SO-GCF (spin−orbit GCF), consists of explicit diagonalization of the Hamiltonian matrix over the individual GCFs to determine the expansion coefficients c_{PSM}. That is, all matrix elements of the form $\langle P;S',M'|\hat{H}^{\mathrm{total}}|Q;S,M\rangle$ are computed. For an even-electron system, the b values of the graph heads are even integers. Suppose these heads have the range of values $b = 0, 2, ..., b_{\max}$ corresponding to spin states $S = 0, 1, ..., S_{\max}$ with $b_{\max} = 2S_{\max}$. Each set of arc factors $\boldsymbol{\alpha}^P$ results in a set of GCFs, the singlet GCF $|P;0,0\rangle$, the three components of the triplet GCFs $|P;1,-1\rangle$, $|P;1,0\rangle$, and $|P;1,+1\rangle$, and so on, up to the $(2S_{\max} + 1)$ components of the maximum spin GCFs $|P;S_{\max},-S_{\max}\rangle$, $|P;S_{\max},-S_{\max}+1\rangle$, ..., $|P;S_{\max},S_{\max}\rangle$. Each set of arc factors thereby contributes $(S_{\max} + 1)^2$ total SO-GCF basis functions, and the total dimension of the Hamiltonian matrix is $N_{\dim} = N_\alpha(S_{\max} + 1)^2$. In the more general expansion corresponding to eqs 13−14, $N_{\dim} = N_\alpha((S_{\max} + 1)^2 - S_{\min}{}^2)$. As discussed above, the actual basis functions used in our implementation are the $|P;S,M_\pm\rangle$ combinations, but $N_{\dim}$ is the same in either case. Diagonalization of this Hamiltonian matrix results in up to $N_{\dim}$ eigenvalues and associated eigenvectors. Thus both ground and excited electronic states can be described with this approach in a straightforward manner, with the possibility of describing several states simultaneously.

Two issues are important in comparing the two multiheaded spin−orbit approaches. One is the desired number of states. The SO-SCGCF approach is well suited to single state calculations due to the flexibility introduced via the spin contraction coefficients and to the relatively simple termination steps. Although both approaches will probably require additional sets of arc factors to describe multiple states, for a given N_α the SO-GCF approach describes more states due to its greater Hamiltonian matrix dimension. If the N_α sets of arc factors are flexible enough to accurately describe more states via the expansion coefficients c_{PSM}, then SO-GCF will be more computationally effective than SO-SCGCF for multistate calculations. We expect this to be an important feature for molecules containing, for example, lanthanide or actinide atoms, but it remains to be seen how well multiple states are described with limited numbers of arc factor sets. The second issue is the variational computation of the wave function. In both spin−orbit approaches there is a matrix diagonalization to determine linear coefficients and a nonlinear optimization to determine the other parameters. In general, SO-GCF has a larger diagonalization dimension than SO-SCGCF: $N_{\dim} = N_\alpha((S_{\max} + 1)^2 - S_{\min}{}^2)$ versus N_α. However SO-GCF has a smaller number of nonlinear optimization parameters than SO-SCGCF: $N_\alpha N_\phi$ versus $N_\alpha(N_\phi + ((S_{\max} + 1)^2 - S_{\min}{}^2) - 1)$, where N_ϕ is the number of essential variables[1] for each arc factor set $\boldsymbol{\alpha}^P$ and each set of spin contraction coefficients has $((S_{\max} + 1)^2 - S_{\min}{}^2) - 1$ degrees of freedom after normalization. In previous work to date,[3,4] the dominant computational bottleneck has been the nonlinear arc-factor optimization, and the diagonalization has been relatively insignificant. It remains to be seen how the relative optimization costs affect the performance of the two spin−orbit methods.

The computation of the matrix elements of the SO-GCF Hamiltonian matrix of dimension $N_{\dim}$ is done by blocks indexed by pairs of arc factor sets, P and Q. Each PQ block, denoted $\mathbf{H}^{PQ}$ is square and has dimension $((S_{\max}+1)^2 - S_{\min}{}^2)$, and within each of these blocks there are rectangular subblocks associated with the individual interacting GCFs denoted $\mathbf{H}^{S'S,PQ}$. Only the unique $P \geq Q$ blocks of the real, symmetric Hamiltonian matrix are computed explicitly. The $\hat{H}^0$ operator is diagonal with respect to the spin labels S and $M_\pm$, and for a given S value, all the $\langle P;S,M_\pm|\hat{H}^0|Q;S,M_\pm\rangle$ elements are the same. These $H^{0,S}_{PQ} = \langle P;S|\hat{H}^0|Q;S\rangle$ matrix elements are computed simultaneously for all S using the recursive procedure described in ref 2. Inspection of this procedure reveals that the initiation and propagation steps do not explicitly depend on the multiple S values, and that only the termination steps do, in part, directly depend on the multiple heads of the graph. Termination involves a $\bar{\gamma}^{PQ,S}$array associated with the graph head that corresponds to spin S. The computation and storage of the $\bar{\gamma}^{PQ,S}$ array is proportional to the product of the number of head nodes and the total number of nodes (N_{row}) in the Shavitt graph. For a multiheaded Shavitt graph, the $\bar{\gamma}^{PQ,S}$ related termination effort increases by a factor of the number of head nodes $(S_{\max} - S_{\min} + 1)$ compared to a single-headed graph. In the next section we examine the relative costs of these termination steps compared to the propagation costs. The effort to compute the transition density matrix elements that terminate at level t is approximately proportional to $N_{\mathrm{row}}(t)$ the number of nodes of the Shavitt graph at that level. The number of nodes in multiheaded full-CI graphs is larger than for single headed full-CI graphs. Thus the simultaneous computation of all $H^{0,S}_{PQ}$ elements for $S = S_{\min} ... S_{\max}$ for a given PQ pair is expected to scale as $O(\omega n^4)$, the same as for a single Hamiltonian element of a single-headed Shavitt graph, but with a larger factor ω appropriate for the larger $N_{\mathrm{row}}(t)$ values and for the $(S_{\max} - S_{\min} + 1)$ multiple heads.

In contrast, the $\langle P|\hat{H}^0|Q\rangle$ construction in the SO-SCGCF approach consists of single terminations involving a single $\bar{\gamma}^{PQ}$ array. For a given PQ pair, this effort is expected to scale also as $O(\omega n^4)$, analogous to the single-headed Shavitt graph case, but with a larger factor ω appropriate for the larger $N_{\mathrm{row}}(t)$ values of the multiheaded graph. The termination effort for the SO-SCGCF method should require a factor of $(S_{\max} - S_{\min} + 1)$ less effort than the SO-GCF approach due to the different treatment of the multiple graph heads. All other things being equal, we would expect generally this Hamiltonian construction effort for a single-headed graph to be less than for the SO-SCGCF approach which, in turn, would be less than for the SO-GCF approach.

The spin−orbit Hamiltonian elements $\langle P;S',M'_\pm|\hat{H}^{\mathrm{SO}}|Q;S,M_\pm\rangle$ discussed above are also computed by P and Q blocks in the SO-GCF approach. A square $\mathbf{H}^{SS,PQ}$ subblock is symmetric of dimension $(2S + 1)$, and only the upper triangular subblock is explicitly computed; the other elements are simply copied afterward as necessary. The total number of nonzero matrix elements from the upper triangular portions of all these subblocks is $(S_{\max}(5S_{\max} + 1) - S_{\min}(5S_{\min} + 1))/2$. For the rectangular $\mathbf{H}^{S'S,PQ}$ and $\mathbf{H}^{SS',PQ}$ subblocks the total number of nonzero matrix elements from all these upper subblocks is $2((5S_{\max}{}^2 - 4S_{\max} + 2) - (5S_{\min}{}^2 - 4S_{\min} + 2))$. The upper triangular portion of a $\mathbf{H}^{SS,PQ}$ subblock and the $\mathbf{H}^{S'S,PQ}$ and $\mathbf{H}^{SS',PQ}$ subblocks have internal structures that might be exploited in a future implementation to reduce the number of explicitly computed elements. For a given PQ pair, the transition density computation and spin−orbit Hamiltonian matrix construction employs three nested do-loops in the following simplified form.

```
DO $p = 1, n$
    Initiate with $\underline{R}$ segment factors at level $p$.
    DO $r = (p+1), n$
        Propagate with $R\underline{L}^1$ segment factors at level $r$.
        DO $s = (r+1), n$
            Propagate with $RL^1$ segment factors at level $s$.
        ENDDO $s$
        Terminate at level $n$ to form all $D_{pr}^{S'S,PQ}$ and combine
            with $\Lambda_{t,pr}$ to update all $h_t^{SS',PQ}$ matrix elements.
        Propagate with $R$ segment factors at level $r$.
    ENDDO $r$
ENDDO $p$
Update all $\mathbf{H}^{PQ}$ matrix elements from the $h_t^{SS',PQ}$ elements.
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The above $O(\omega n^3)$ algorithm is implemented within the $O(\omega n^4)$ algorithm to compute the non-spin−orbit Hamiltonian contributions, and consequently, the initiation and propagation effort for the spin−orbit Hamiltonian is actually shared between the two steps. The actual *additional* effort to compute the spin−orbit contributions consists of the $h_t^{SS',PQ}$ update step, which requires only $O(\omega n^2)$ effort, being within the p and r nested do-loops, and the final combination of these elements with the S- and M-dependent factors (as in eq 11) to update the $\mathbf{H}^{PQ}$ elements. This latter step is outside of the nested do-loop structure and scales as $O(n^0)$.

In the SO-SCGCF approach, the above procedure is followed except that the single H_{PQ} matrix element is updated in the final step rather than the individual elements of the $\mathbf{H}^{PQ}$ block. We are currently implementing several additional optimizations within our initial implementation of the above approaches. These will be reported separately. As shown in the following section, the actual spin−orbit computation effort is minor compared to the larger non-spin−orbit Hamiltonian computation effort.

Although both of the spin−orbit approaches described here employ highly (graphically) contracted expansions of the individual expansion CSFs, during the optimization of the wave function the parameters for each GCF (arc factors in SO-GCF, and arc factors and spin contraction coefficients in SO-SCGCF) are varied to minimize the energy computed from a Hamiltonian that includes the spin−orbit operators. Thus, both approaches lead to variational methods in which the ultimate CSF coefficients are relaxed to account for the spin−orbit interaction. In particular, the spin−orbit interaction is not treated as a perturbation to frozen spin-specific wave functions. However, even though both approaches are, in this sense, one-step spin−orbit (SO) CI methods, where spin−orbit and electron correlation are computed simultaneously,[13] due to the nature of the implementation of the SO-GCF approach, it would be simple to also produce two-step GCF wave functions like those of the variation-perturbation methods of Marian, Hess, et al.[20−22] or the Λ−S contracted SO−CI method of Alekseyev et al.[23] In those methods a spin−orbit matrix over a set of spin-specific, well correlated wave functions is diagonalized to produce an approximate spin−orbit wave function. By performing only a single terminal diagonalization over the spin basis, we could produce an analogous GCF wave function. Finally, we emphasize that since the GCF method is a full-CI approach (which converges toward the full-CI wave function with increasing N_α), both SO-GCF and SO-SCGCF are full two-component methods in the sense of both orbital and CSF coefficient optimization.

3. Results and Discussion

Table 1 shows timings for N electron, n orbital, full-CI Shavitt graphs with $N = n$, where n is even, for non-spin−orbit and for both spin−orbit approaches. All times are in seconds on a 2.6 GHz AMD Opteron CPU. The non-spin−orbit wave functions have singlet multiplicity $b = 0$ and triplet multiplicity $b = 2$, and the spin−orbit ones have the full multiplicity range $b_{\min} = 0$ to $b_{\max} = n$. A single $\langle P|\hat{H}|Q\rangle$ matrix element between two basis functions $|P\rangle$ and $|Q\rangle$ was computed for the singlet GCF, the triplet GCF, and the SO-SCGCF expansions; and all the matrix elements in a $\mathbf{H}^{PQ}$ block of dimension $(S_{\max} + 1)^2$ with $S_{\max} = n/2$ were computed for the SO-GCF expansions. Since our initial implementation is not yet able to efficiently optimize arc factors, an arbitrary set of nonzero arc factors and spin contraction coefficients were used to generate the timing data. The timings do not depend on the actual arc factor values and are therefore indicative of the efficiency of the method, but the computed energies and wave functions do not correspond to observable eigenstates. The smallest spin−orbit calculation was performed with arc factor optimization and compared with the results from the determinant based SOCI[11] and the traditional (CSF-based) GUGA SOCI[10] programs from the COLUMBUS Program System[24−27] for validation.

In a multiheaded Shavitt graph, each walk contributes $2S + 1$ expansion terms to the spin−orbit wave function basis according to the multiplicity of its head node.[8] Thus, the number of CSFs increases substantially faster with the spin−orbit interaction than for any single multiplicity. For example, in the sequence of wave functions in Table 1, the singlet non-spin−orbit expansion spaces have $N_{\mathrm{CSF}}^{\mathrm{singlet}} = 1/(n + 1)\binom{n+1}{n/2}^2$, and the spin−orbit expansion spaces have $N_{\mathrm{CSF}}^{\mathrm{SO}} = \binom{2n}{n}$. Using Stirling's approximation, the ratio $N_{\mathrm{CSF}}^{\mathrm{SO}}/N_{\mathrm{CSF}}^{\mathrm{singlet}}$ of these two values is $(\pi^{1/2}/8)n^{3/2}$ in the limit of large n. The actual ratio is shown in column 3 of Table 1, and it is seen to range from 2 to over 300, consistent with this approximation. In addition, N_{row} the total number of nodes in a Shavitt graph, N_{pair} the total number of pairs of nodes in a Shavitt graph (that contribute to upper-triangular Shavitt loops), which is also the number of vertices in the auxiliary pair graph, and N_{value} the total number of segment values are all significantly larger for multiheaded than for single-headed graphs.[8] For these $N = n$ full-CI wave function expansions, the spin−orbit to non-spin−orbit ratios of the analytical expressions[4,8] for N_{row} and N_{pair} are both two in the limit of large n. The determination of the analytical expressions for N_{value} is in progress, but it is clear that the large n limit of the spin−orbit to non-spin−orbit ratio is also two which is consistent with the data in Table 1.

In comparing the timings in Table 1, the dominant factor is the general shape of the graphs. The single-headed graphs begin with a single node at the tail, build up to some maximum value at level $n/2$ for singlets or level $n/2 + 1$ for triplets, and then taper down from this value to a single node at level n. In contrast, the multiheaded graphs begin with a single node at the tail, build up to some maximum value well above level $n/2$ in general, and then taper down more slowly to $(S_{\max} + 1)$ nodes

TABLE 1: Statistics for Singlet, Triplet and Spin−Orbit Full-CI Shavitt Graphs

$n = N$	N_{CSF}	N_{CSF} ratio	N_{row}	N_{pair}[a]	N_{value}[b]	time[c]	
			Singlet				
2	3	1	5	10	26	0.00	
4	20	1	14	43	278	0.00	
8	1764	1	55	261	2682	0.00	
16	3.476×10^{7}	1	285	1865	23938	0.04	
32	4.126×10^{16}	1	1785	14225	203026	1.74	
40	1.767×10^{21}	1	3311	27541	401306	6.31	
48	8.153×10^{25}	1	5525	47321	699042	17.93	
64	2.005×10^{35}	1	12529	111393	1673778	95.86	
128	1.752×10^{73}	1	93665	882241	13595762	4917.36	
			Triplet				
2	1	0.33	3	3	6	0.00	
4	15	0.75	13	40	276	0.00	
8	2352	1.3	62	330	3686	0.00	
16	6.675×10^{7}	1.9	332	2318	30762	0.05	
32	9.779×10^{16}	2.4	2008	16406	236658	2.31	
40	4.380×10^{21}	2.5	3670	31006	455926	7.92	
48	2.084×10^{26}	2.6	6052	52510	779706	21.77	
64	5.327×10^{35}	2.7	13488	120870	1821698	112.82	
128	4.941×10^{73}	2.8	97632	921670	14214946	5508.83	
		Spin−Orbit				SO-SCGCF	SO-GCF
2	6	2.0	6	13	36	0.00	0.00
4	70	3.5	19	69	471	0.00	0.00
8	12870	7.3	85	473	5053	0.00	0.00
16	6.011×10^{8}	17.3	489	3569	46777	0.11	0.12
32	1.833×10^{18}	44.4	3281	27873	402033	6.57	7.85
40	1.075×10^{23}	60.9	6181	54201	796461	23.62	24.98
48	6.435×10^{27}	78.9	10425	93393	1389353	67.25	71.43
64	2.395×10^{37}	119.5	23969	220609	3332321	357.76	366.91
128	5.769×10^{75}	329.4	183105	1756033	27132353	19496.34	28315.56

[a] N_{pair} is the total number of pairs of nodes in the Shavitt graph (that contribute to upper-triangular Shavitt loops) and the number of vertices in the auxiliary pair graph. [b] N_{value} is the total number of segment values. [c] Times are in seconds on a 2.6 GHz AMD Opteron CPU to construct a single $\langle P|\hat{H}|Q\rangle$ matrix element involving two basis functions $|P\rangle$ and $|Q\rangle$ for the singlet and the triplet GCF expansions and for the SO-SCGCF expansions, and to construct all the matrix elements in a $\mathbf{H}^{PQ}$ block of dimension $(S_{\max} + 1)^2$ in the SO-GCF expansions with $S_{\max} = n/2$.

at level n. The critical difference in the graphs is in the $N_{\mathrm{row}}(t)$ values for the higher orbital levels t. The termination effort for the two-particle transition density elements used to compute $\langle P|\hat{H}|Q\rangle$ in the SO-SCGCF and non-spin−orbit approaches may be modeled by

$$T(n) = \sum_{p=1}^{n} \sum_{r=p+1}^{n} \sum_{s=r+1}^{n} \sum_{t=s+1}^{n} N_{\mathrm{row}}(t) \qquad (15)$$

In this expression, the higher orbital levels t are sampled more often than the lower levels, and consequently graphs with larger $N_{\mathrm{row}}(t)$ values at the higher orbital levels are more computationally demanding. Table 2 displays the computed ratios $T(n)^{\mathrm{SO}}/T(n)^{\text{non-SO}}$ and $T(n)^{\mathrm{triplet}}/T(n)^{\mathrm{singlet}}$ along with the corresponding ratios of the measured Hamiltonian matrix construction times for the graphs with $N = n = 32$ through $N = n = 128$. There is good agreement between the computed and the measured ratios for the SO-SCGCF and non-spin−orbit GCF wave functions.

TABLE 2: Performance Modeling for Singlet, Triplet, and Spin-Orbit Full-CI Shavitt Graphs[a,b]

$n = N$	$T(n)^{\mathrm{SO}}/T(n)^{\mathrm{singlet}}$	$\mathrm{time}^{\mathrm{SO}}/\mathrm{time}^{\mathrm{singlet}}$	$T(n)^{\mathrm{SO}}/T(n)^{\mathrm{triplet}}$	$\mathrm{time}^{\mathrm{SO}}/\mathrm{time}^{\mathrm{triplet}}$	$T(n)^{\mathrm{triplet}}/T(n)^{\mathrm{singlet}}$	$\mathrm{time}^{\mathrm{triplet}}/\mathrm{time}^{\mathrm{singlet}}$
32	3.50	3.77	2.78	2.84	1.26	1.33
40	3.54	3.74	2.90	2.98	1.22	1.26
48	3.58	3.75	3.00	3.09	1.19	1.21
64	3.62	3.73	3.13	3.17	1.15	1.18
128	3.69	3.96	3.40	3.54	1.09	1.12

[a] $T(n)$ is a model of the termination effort for the two-particle transition density elements used to compute $\langle P|\hat{H}|Q\rangle$. See eq 15. [b] Times are in seconds on a 2.6 GHz AMD Opteron CPU to construct a single $\langle P|\hat{H}|Q\rangle$ matrix element involving two basis functions $|P\rangle$ and $|Q\rangle$ for the single state expansions and for the SO-SCGCF expansions.

As seen in Table 1, SO-SCGCF has a small computational advantage over SO-GCF which increases with $S_{\max}$ as expected. As discussed in the previous section, this is due primarily to the fact that terminations in the SO-SCGCF approach involve only a single contraction with the $\bar{\gamma}^{PQ}$ elements whereas terminations in the SO-GCF approach require $(S_{\max} - S_{\min} + 1)$ terminations with the $\bar{\gamma}^{PQ,S}$ elements for the range of S values. It is these terminations for the two-particle transition density matrix elements in the $\langle P|\hat{H}^0|Q\rangle$ and $\langle P;S|\hat{H}^0|Q;S\rangle$ contributions that dominate the difference in the timings rather than the smaller $O(n^2)$ termination effort required for the $\langle P|\hat{H}^{\mathrm{SO}}|Q\rangle$ and $\langle P;S',M'_{\pm}|\hat{H}^{\mathrm{SO}}|Q;S,M_{\pm}\rangle$ elements. As seen in Table 3, the spin−orbit termination times relative to the entire Hamiltonian matrix element construction times are small percentages which decrease with n and are similar for the two methods. Propagation and non-spin−orbit termination account for almost all of the construction time. In the limit of large n and $S_{\max}$, SO-GCF should have a lower fraction of spin−orbit termination time relative to the entire construction time than SO-SCGCF because of the former's relative increasing cost for non-spin−orbit terminations. It is not clear whether the larger fractions for SO-SCGCF compared to SO-GCF at large n are due to this effect

TABLE 3: Spin−Orbit Termination Costs[a,b]

$n = N$	SO-SCGCF	SO-GCF
2	10.2	8.1
4	10.1	9.2
8	6.8	7.3
16	3.8	3.7
32	2.7	2.7
40	2.4	2.5
48	2.1	2.1
64	2.8	1.7
128	1.9	1.6

[a] Percentage of time for the spin−orbit termination steps compared to the full Hamiltonian matrix element construction for the two spin−orbit algorithms. [b] Profiling on a 2.6 GHz AMD Opteron CPU to construct a single $\langle P|\hat{H}|Q\rangle$ matrix element involving two sets of arc factors $\boldsymbol{\alpha}^{\mathbf{P}}$ and $\boldsymbol{\alpha}^{\mathbf{Q}}$ for the SO-SCGCF expansions, and to construct all matrix elements in a $\mathbf{H}^{PQ}$ block of dimension $(S_{\max} + 1)^2$ in the SO-GCF expansions with $S_{\max} = n/2$.

or are anomalous, perhaps because of memory cache effects. Our planned improvements to this initial implementation are expected to clarify and affect these relative timings.

In our current implementation, the Hamiltonian matrix is diagonalized directly using standard LAPACK routines at a cost of $O(N_{\dim}^3)$. For larger values of $N_{\dim}$, it may prove more efficient to adopt an iterative diagonalization approach based on the Davidson procedure with an expected cost of $O(N_{\text{root}}N_{\dim}^2)$. This would have the potential advantages of exploiting the sparseness of the Hamiltonian matrix in the SO-GCF basis (reducing the $N_{\dim}^2$ factor accordingly) and possibly even computing the required matrix-vector products directly from the $H_{PQ}^{0,S}$ and $h_t^{SS',PQ}$ reduced matrix elements. This will be examined in future work.

4. Conclusions

The GCF method has been extended to include an effective one-electron spin−orbit operator in the Hamiltonian matrix construction. Our approach uses RECP methodology and is entirely analogous to previous spin−orbit CI approaches using CSFs based on GUGA. Two possible approaches have been discussed, one based on multiple single-headed Shavitt graphs, each of which corresponds to an interacting spin state, and the other based on the use of single, multiheaded Shavitt graphs in which the graph heads correspond to the interacting spin states. Our initial implementation is based on the latter multiheaded graph approach which allows for the efficient simultaneous computation of entire blocks of Hamiltonian matrix elements. Two algorithms have been implemented. The SO-GCF method expands the spin−orbit wave function in the basis of GCFs and results in a Hamiltonian matrix of dimension $N_{\dim} = N_\alpha((S_{\max} + 1)^2 - S_{\min}^2)$. The SO-SCGCF method expands the wave function in a basis of spin contracted functions and results in a Hamiltonian matrix of dimension $N_{\dim} = N_\alpha$. The full Hamiltonian matrix construction with both approaches scales formally as $O(N_\alpha^2\omega n^4)$. Timings have been given for Hamiltonian matrix construction for both algorithms for a range of wave functions with up to $N = n = 128$ and that correspond to an underlying linear full-CI CSF expansion dimension of over 10^{75} CSFs, many orders of magnitude larger than can be considered using traditional CSF-based spin−orbit CI approaches. We find that the SO-SCGCF method is slightly faster than the SO-GCF method for a given N_α and spin range. The SO-GCF method may be more suitable for describing multiple states, whereas the SO-SCGCF method may be more suitable for describing single states.

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References and Notes

(1) Shepard, R. *J. Phys. Chem. A* **2005**, *109*, 11629.
(2) Shepard, R. *J. Phys. Chem. A* **2006**, *110*, 8880.
(3) Shepard, R.; Minkoff, M. *Int. J. Quantum Chem.* **2006**, *106*, 3190.
(4) Shepard, R.; Minkoff, M.; Brozell, S. R. *Int. J. Quantum Chem.* **2007**, *107*, 3203.
(5) Shavitt, I. In *The Unitary Group for the Evaluation of Electronic Energy Matrix Elements*; Hinze, J., Ed.; Lecture Notes in Chemistry 22; Springer-Verlag: Berlin, 1981; pp 51−99.
(6) Shavitt, I. *Int. J. Quantum Chem.* **1977**, *S11*, 131.
(7) Christiansen, P. A.; Ermler, W. C.; Pitzer, K. S. *Annu. Rev. Phys. Chem.* **1985**, *36*, 407.
(8) Brozell, S. R.; Shepard, R.; Zhang, Z. *Int. J. Quantum Chem.* **2007**, *107*, 3191.
(9) Dolg, M.; Cao, X. In *Recent Advances in Relativistic Molecular Theory*; Hirao, K., Ishikawa, Y., Eds.; Recent Advances in Computational Chemistry 5; World Scientific: River Edge, NJ, 2004; pp 1−35.
(10) Yabushita, S.; Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*, 5791.
(11) Pitzer, R. M.; Winter, N. W. *J. Phys. Chem.* **1988**, *92*, 3061.
(12) Pitzer, R. M.; Winter, N. W. *Int. J. Quantum Chem.* **1991**, *40*, 773.
(13) Marian, C. M. In *Reviews of Computational Chemistry 17*; Kipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 2001; pp 99−204.
(14) McWeeny, R. *J. Chem. Phys.* **1965**, *42*, 1717.
(15) Kleinschmidt, M.; Marian, C. M. *Chem. Phys.* **2005**, *311*, 71.
(16) Wigner, E. P. *Z. Phys.* **1927**, *43*, 624.
(17) Eckart, C. *Rev. Mod. Phys.* **1930**, *2*, 305.
(18) Wigner, E. P. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*; Academic Press: New York, 1959.
(19) Gidofalvi, G.; Shepard, R. *Int. J. Quantum Chem.*, in press. DOI: 10.1002/qua.22320.
(20) Hess, B. A.; Marian, C. M.; Peyerimhoff, S. D. In *Modern Electronic Structure Theory Part I*; Yarkony, D. R., Ed.; Advanced Series in Physical Chemistry 2; World Scientific: River Edge, NJ, 1995; pp 152−278.
(21) Rakowitz, F.; Marian, C. M. *Chem. Phys. Lett.* **1996**, *257*, 105.
(22) Kleinschmidt, M.; Tatchen, J.; Marian, C. M. *J. Chem. Phys.* **2006**, *124*, 124101.
(23) Alekseyev, A. B.; Liebermann, H.-P.; Buenker, R. J. In *Recent Advances in Relativistic Molecular Theory (Recent Advances in Computational Chemistry 5)*; Hirao, K. Ishikawa, Y. Eds.; World Scientific: River Edge NJ, 2004; pp 65−105.
(24) Lischka, H.; Shepard, R.; Brown, F. B.; Shavitt, I. *Int. J. Quantum Chem.* **1981**, *S15*, 91.
(25) Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J.-G. *Int. J. Quantum Chem.* **1988**, *22*, 149.
(26) Lischka, H.; Shepard, R.; Pitzer, R. M.; Shavitt, I.; Dallos, M.; Mueller, T.; Szalay, P. G.; Seth, M.; Kedziora, G. S.; Yabushita, S.; Zhang, Z. *Phys. Chem. Chem. Phys.* **2001**, *3*, 664.
(27) Lischka, H.; Shepard, R.; Shavitt, I.; Pitzer, R. M.; Dallos, M.; Mueller, T.; Szalay, P. G.; Brown, F. B.; Ahlrichs, R.; Boehm, H. J.; Chang, A.; Comeau, D. C.; Gdanitz, R.; Dachsel, H.; Ehrhardt, C.; Ernzerhof, E.; Hoechtl, P.; Irle, S.; Kedziora, G. S.; Kovar, T.; Parasuk, V.; Pepper, M. J. M.; Scharf, P.; Schiffer, H.; Schindler, M.; Schueler, M.; Seth, M.; Stahlberg, E. A.; Zhao, J.-G.; Yabushita, S.; Zhang, Z.; Barbatti, M.; Matsika, S.; Schuurmann, M.; Yarkony, D. R.; Brozell, S. R.; Beck, E. V.; Blaudeau, J.-P. COLUMBUS, An Ab Initio Electronic Structure Program, Releases 5.9 and 6.0beta, 2006.

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