12-17-2019

Analytic Non-adiabatic Derivative Coupling Terms for Spin-orbit MRCI Wavefunctions. I. Formalism

Lachlan T. Belcher
United States Air Force Academy

Gary S. Kedziora
Air Force Research Laboratory

David E. Weeks
Air Force Institute of Technology

Recommended Citation

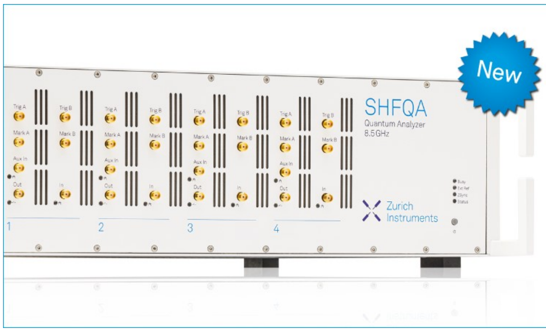
Belcher, L. T., Kedziora, G. S., & Weeks, D. E. (2019). Analytic non-adiabatic derivative coupling terms for spin-orbit MRCI wavefunctions. I. Formalism. Journal of Chemical Physics, 151(23), 234104. https://doi.org/10.1063/1.5126800

The Journal of Chemical Physics

Analytic non-adiabatic derivative coupling terms for spin-orbit MRCI wavefunctions. I. Formalism

Cite as: J. Chem. Phys. **151**, 234104 (2019); https://doi.org/10.1063/1.5126800
Submitted: 05 September 2019 . Accepted: 07 November 2019 . Published Online: 17 December 2019

Lachlan T. Belcher, Gary S. Kedziora, and David E. Weeks



The Journal of Chemical Physics

ARTICLE

scitation.org/journal/jcp

Analytic non-adiabatic derivative coupling terms for spin-orbit MRCI wavefunctions. I. Formalism

Cite as: J. Chem. Phys. 151, 234104 (2019); doi: 10.1063/1.5126800
Submitted: 5 September 2019 • Accepted: 7 November 2019 •
Published Online: 17 December 2019

Lachlan T. Belcher,[1,a)] **Gary S. Kedziora,**[2] **and David E. Weeks**[3]

AFFILIATIONS

[1] Laser and Optics Research Center, Department of Physics, US Air Force Academy, Colorado Springs, Colorado 80840, USA
[2] HPCMP PETTT/SAIC, Air Force Research Laboratory, Wright-Patterson AFB, Ohio 45433, USA
[3] Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson AFB, Ohio 45433, USA

[a)] lachlan.belcher@usafa.edu

ABSTRACT

Analytic gradients of electronic eigenvalues require one calculation per nuclear geometry, compared to at least 3n + 1 calculations for finite difference methods, where n is the number of nuclei. Analytic nonadiabatic derivative coupling terms (DCTs), which are calculated in a similar fashion, are used to remove nondiagonal contributions to the kinetic energy operator, leading to more accurate nuclear dynamics calculations than those that employ the Born-Oppenheimer approximation, i.e., that assume off-diagonal contributions are zero. The current methods and underpinnings for calculating both of these quantities, gradients and DCTs, for the State-Averaged MultiReference Configuration Interaction with Singles and Doubles (MRCI-SD) wavefunctions in COLUMBUS are reviewed. Before this work, these methods were not available for wavefunctions of a relativistic MRCI-SD Hamiltonian. Calculation of these terms is critical in successfully modeling the dynamics of systems that depend on transitions between potential energy surfaces split by the spin-orbit operator, such as diode-pumped alkali lasers. A formalism for calculating the transition density matrices and analytic derivative coupling terms for such systems is presented.

https://doi.org/10.1063/1.5126800

I. INTRODUCTION

Collisionally induced changes to states split by the spin-orbit interaction are of importance in calculating the dynamics of many systems, including Diode-Pumped Alkali Lasers (DPALs) in which alkali metals interact with noble gases to produce laser radiation.[1–5] In such cases, application of the Born-Oppenheimer approximation to separate the nuclear and electronic Hamiltonian is often insufficient to appropriately model system dynamics. The coupling between electronic and nuclear states is quantified by nonadiabatic derivative coupling terms (DCTs) and the resultant off-diagonal energy coupling surface.[6,7]

While robust methods have been in place for calculating DCTs for nonrelativistic multireference configuration interaction (MRCI) wavefunctions,[8–10] these implementations do not account for spin-orbit wavefunctions. DCTs for systems in which this coupling occurs strongly between states separated only by the spin-orbit energy, e.g., M + Ng, where M = K, Rb, or Cs and Ng = He, Ne, or Ar,[11,12] cannot be calculated by these methods. While alternative methods have been developed to approximate spin-orbit DCTs,[13–18] these have not been as robust as an MRCI calculation using spin-orbit wavefunctions.

In this article, we will generalize the method of calculating MRCI derivative coupling terms from Lischka *et al.*,[8] based on the method of calculating analytic energy gradients due to Shepard[19]

$$
\begin{aligned}
\Delta\varepsilon f_{JI}^{CI+CSFx} &= \mathrm{Tr}\Big(\mathbf{h}^{x[\chi]}\Big(\mathbf{D}_{tot}^{CI\,JI\,[\chi]} + \mathbf{D}_{tot}^{CSF\,JI[\chi]}\Big)\Big)\\
&\quad + \tfrac{1}{2}\mathrm{Tr}\Big(\mathbf{g}^{x[\chi]}\Big(\mathbf{d}_{tot}^{CI\,JI\,[\chi]} + \mathbf{d}_{tot}^{CSF\,JI\,[\chi]}\Big)\Big) - \mathrm{Tr}\Big(\mathbf{S}^{x[\chi]}\Big(\mathbf{F}_{tot}^{JI[\chi]}\Big)\Big)\\
&\quad + \Delta\varepsilon\mathrm{Tr}\Big(\mathbf{D}^{JI[\chi]a} f_{orb}^{CSF[\chi]x}\Big)
\end{aligned} \tag{1}
$$

(where we follow his shorthand notation using the superscript x to indicate a derivative with respect to a nuclear coordinate R_x; see below) to apply to spin-orbit MRCI wavefunctions. This is accomplished using the methods of calculating spin-orbit wavefunctions and energy eigenvalues due to Yabushita, Zhang, and Pitzer.[20]

II. FORMALISM

A. Origin of the spin-orbit DCT term

The form of the derivative coupling term (DCT) with respect to a nuclear coordinate R_x is[8–10]

$$f^{JI}(R)^x = \langle \psi_J(R)|\frac{\partial}{\partial R_x}|\psi_I(R)\rangle, \tag{2}$$

where $\psi_I(R)$ and $\psi_J(R)$ are the two MRCI wavefunctions of interest and $\frac{\partial}{\partial R_x}$ is shorthand notation for a derivative with respect to a nuclear coordinate in a Cartesian direction x, where x may be any of the three Cartesian directions for a given nucleus. In nonrelativistic MRCI, the wavefunctions are constructed as linear combinations of *configuration state functions* (CSFs) (which themselves are tensor products of the Gelf' and-Tsetlin basis, as introduced for N-electron systems by Paldus[21]) and real spin functions, $|S\ M\pm\rangle$, defined by Yabushita and co-workers,[20]

$$|\psi_I(R)\rangle = \sum_i C_i^I(R)|\varphi_i(R)\rangle, \tag{3}$$

where $|\varphi_i(R)\rangle = |(d)S\,M\pm\rangle$, the so-called real spherical spin functions, with d representing the step numbers defining the spatial part of the CSF[22] with total spin S. There are $2S + 1$ real spin functions with $|S\ M-\rangle$ defined for $M = 1$ to S and $|S\ M+\rangle$ defined for $M = 0$ to S. See Eqs. (46) and (47) of Ref. 20, which are valid for an even number of electrons. For an odd number of electrons, a noninteracting (ghost) electron is added to the system. Substituting Eq. (3) into Eq. (2), we find that the DCT is

$$\begin{aligned} f_{JI}(R)^x = \sum_j C_j^{J*}(R)\langle\varphi_j(R)|\Bigg[&\sum_i \frac{\partial}{\partial R_x}\big(C_i^I(R)\big)|\varphi_i(R)\rangle \\ &+ \sum_i C_i^I(R)\Big|\frac{\partial}{\partial R_x}\varphi_i(R)\Big\rangle\Bigg], \end{aligned} \tag{4}$$

which is separable into two distinct pieces,

$$f_{JI}(R)^x = \vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big) + \sum_{ji} C_j^{J*}(R)C_i^I(R)\Big\langle\varphi_j(R)\Big|\frac{\partial}{\partial R_x}\varphi_i(R)\Big\rangle. \tag{5}$$

The former piece, which captures the derivative of the CI coefficients, is called the Configuration Interaction Derivative Coupling Term (CI DCT) by Lischka *et al.*,[8] while the latter, which captures the derivative of the CSFs, is called the CSF DCT by the same group. As the coefficient vectors $\vec{C}^I(R)$ in the CI term and the CSFs in the CSF term are *not* analytic functions of the nuclear geometry, it will be necessary to manipulate the form of the DCT in Eq. (5) (to take into account the change in basis functions and parameters with respect to geometry) if we wish to evaluate it analytically.

Lengsfield, Saxe, and Yarkony have shown that the CSF DCT is equivalent to[9]

$$\begin{aligned} f_{JI}^{CSF}(R)^x &= \sum_{ji} C_j^{J*}(R)C_i^I(R)\Big\langle\varphi_j(R)\Big|\frac{\partial}{\partial R_x}\varphi_i(R)\Big\rangle \\ &= \sum_{kl}\mathbf{D}_{kl}^{JI}(R)\Big\langle\phi_k(R)\Big|\frac{\partial}{\partial R_x}\phi_l(R)\Big\rangle, \end{aligned} \tag{6}$$

where $\mathbf{D}_{kl}^{JI}(R)$ is the one-electron transition density matrix for $|\psi_I(R)\rangle$ and $|\psi_J(R)\rangle$, and $|\phi_k(R)\rangle$ are the molecular orbitals (MOs) from which the CSFs are constructed. Thus, the CSF DCT can be calculated analytically from gradients of MOs. In COLUMBUS, these MOs are fixed after the state-averaged MCSCF step but before the MRCI step in which spin-orbit effects are considered; thus, the CSF term will not require a rederivation for inclusion of spin-orbit effects.

The coefficient vectors $\vec{C}^I(R)$ in the CI DCT solve the Schrödinger eigenvalue equation

$$\mathbf{H}(R)\vec{C}^I(R) = E^I(R)\vec{C}^I(R). \tag{7}$$

We can take the derivative of this equation,

$$\begin{aligned} &\frac{\partial}{\partial R_x}\big(\mathbf{H}(R)\big)\vec{C}^I(R) + \mathbf{H}(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big) \\ &\quad = \frac{\partial}{\partial R_x}\big(E^I(R)\big)\vec{C}^I(R) + E^I(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big), \end{aligned} \tag{8}$$

and premultiply it by the row vector $\vec{C}^{J\dagger}(R)$,

$$\begin{aligned} &\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\mathbf{H}(R)\big)\vec{C}^I(R) + \vec{C}^{J\dagger}(R)\mathbf{H}(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big) \\ &\quad = \frac{\partial}{\partial R_x}\big(E^I(R)\big)\vec{C}^{J\dagger}(R)\vec{C}^I(R) + E^I(R)\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big), \end{aligned} \tag{9}$$

to reduce the equation to

$$\begin{aligned} &\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\mathbf{H}(R)\big)\vec{C}^I(R) + E^J(R)\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big) \\ &\quad = E^I(R)\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big). \end{aligned} \tag{10}$$

Rearranging this equation yields a form of the CI DCT,

$$\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\vec{C}^I(R)\big) = \big(E^I(R) - E^J(R)\big)^{-1}\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\mathbf{H}(R)\big)\vec{C}^I(R), \tag{11}$$

which may be computed analytically with additional assumptions described below.[8–10] The derivative operation has been removed from the CI coefficient vector, and only the Hamiltonian matrix is differentiated.

Now suppose that the Hamiltonian matrix $\mathbf{H}(R)$ includes both the nonrelativistic Hamiltonian $\mathbf{H}_0(R)$ and the spin-orbit Hamiltonian $\mathbf{H}_{so}(R)$. Then, the DCT from Eq. (5) includes an additional term

$$f_{JI}(R)^x = f_{JI}^{CI}(R)^x + f_{JI}^{CI\,so}(R)^x + f_{JI}^{CSF}(R)^x, \tag{12}$$

where

$$\begin{aligned} f_{JI}^{CI}(R)^x &= \big(E^I(R) - E^J(R)\big)^{-1}\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\mathbf{H}_0(R)\big)\vec{C}^I(R), \\ f_{JI}^{CI\,so}(R)^x &= \big(E^I(R) - E^J(R)\big)^{-1}\vec{C}^{J\dagger}(R)\frac{\partial}{\partial R_x}\big(\mathbf{H}_{so}(R)\big)\vec{C}^I(R), \\ f_{JI}^{CSF}(R)^x &= \sum_{ji} C_j^{J*}(R)C_i^I(R)\Big\langle\varphi_j(R)\Big|\frac{\partial}{\partial R_x}\varphi_i(R)\Big\rangle, \end{aligned} \tag{13}$$

and we thus introduce the spin-orbit CI DCT (SO CI DCT), $f_{JI}^{CI\,so}(R)^x$.

The calculation of the terms $f_{JI}^{CI}(R)^x$ and $f_{JI}^{CSF}(R)^x$ from Eq. (12) has been presented by Lischka *et al.*[8] The term $f_{JI}^{CI}(R)^x$, which involves the differentiation of the nonrelativistic

Hamiltonian, does not change form when the spin-orbit term is added to the Hamiltonian in our method and thus will require no rederivation for our implementation. This leaves the treatment of the $f_{JI}^{CI\,so}(R)^x$ term as the thrust of this paper, which will parallel Lischka, Dallos, Szalay, Yarkony, and Shepard's treatment of the $f_{JI}^{CI}(R)^x$ term.

B. The spin-orbit CI DCT $f_{JI}^{CI\,so}(R)^x$

1. Establishing the analytic basis

Here, we give an overview of the method used to construct analytic energy MRCI gradients introduced by Shepard[19] based on the connection matrix approach proposed by Helgaker and Almlöf,[23] which has been shown by Lengsfield, Saxe, and Yarkony,[9] Saxe, Lengsfield, and Yarkony,[10] and Lischka *et al.*,[8] to apply to analytic MRCI DCTs as well.

In order to create analytic gradients and DCTs, we need an orthonormal basis set that smoothly connects the basis set at nearby geometries R to the basis set at R_0, our reference geometry, maintaining orthonormality. This allows the use of the creation-annihilation operator algebra that assumes orthonormality for all geometries[23,24] (for a concise description of this formalism, see Secs. 2.3 and 2.4 of Ref. 25).

Suppose at a given nuclear geometry R_0, we have established an atom-centered set of basis functions, $|\chi_i(R_0)\rangle$, or atomic orbitals (AOs). Let us represent this set of nonorthogonal functions by the vector

$$\vec{\chi}(R_0) \equiv \big(|\chi_1(R_0)\rangle \; |\chi_2(R_0)\rangle \; \ldots \big). \tag{14}$$

Wavefunctions built from this basis will be indicated by a superscript bracketed χ. From this basis, we may form an orthogonal, optimized set of MOs,

$$\vec{\phi}(R_0) = \vec{\chi}(R_0)\mathbf{C}(R_0), \tag{15}$$

where $\mathbf{C}(R_0)$ is the coefficient matrix. In order to evaluate analytic derivatives, we must be able to define a basis within a neighborhood $R = R_0 + \delta$. Here, we follow the methodology of Helgaker[23–25] by allowing the AOs to vary with nuclear geometry but keeping the coefficient matrix constant,

$$\vec{\phi}^{[C]}(R) = \vec{\chi}(R)\mathbf{C}(R_0), \tag{16}$$

and fixing the coefficient matrix precludes the need to take derivatives of it with respect to nuclear geometry. Wavefunctions built from this basis will be indicated by the superscript bracketed C. This basis is geometry dependent but only orthogonal at R_0. By means of the overlap matrix,

$$S^{[\chi]}(R) \equiv \vec{\chi}^{\dagger}(R)\vec{\chi}(R), \tag{17}$$

we can define a third basis that is geometry-dependent and orthogonal everywhere using the *symmetric connection*,[23,25,26]

$$\begin{aligned}\vec{\phi}^{[S]}(R) &\equiv \Big[\mathbf{C}^{\dagger}(R_0)\mathbf{S}^{[\chi]}(R)\mathbf{C}(R_0)\Big]^{-1/2}\vec{\phi}^{[C]}(R)\\ &= \mathbf{S}^{[C]}(R)^{-1/2}\vec{\phi}^{[C]}(R).\end{aligned} \tag{18}$$

Wavefunctions built from this basis will be indicated by the superscript bracketed S. This basis will change by means of an energy optimization during the MCSCF procedure, which is accomplished by means of a rotation,[19]

$$\vec{\phi}^{[K]}(R) \equiv \exp\Big[\mathbf{K}^{mc[S]}\Big]\vec{\phi}^{[S]}(R), \tag{19}$$

where

$$\mathbf{K}^{mc[S]} = \sum_{rs} k_{rs}^{mc}\Big(\hat{E}_{rs}^{[S]} - \hat{E}_{sr}^{[S]}\Big), \tag{20}$$

and terms in this basis will be denoted by the superscript bracketed K. A final rotation resolves invariant orbital subspaces in the MRCI wavefunction, where any rotation of the orbitals will lead to the same energy when the CI coefficients are optimized (for example, complete active space orbital rotations can be made well defined by using natural orbitals). The superscript bracketed Z will denote terms that have undergone this rotation,[19]

$$\begin{aligned}\vec{\phi}^{[Z]}(R) &\equiv \exp\Big[\mathbf{Z}^{mc[K]}\Big]\vec{\phi}^{[K]}(R)\\ &= \exp\Big[\mathbf{Z}^{mc[K]}\Big]\exp\Big[\mathbf{K}^{mc[S]}\Big]\vec{\phi}^{[S]}(R),\end{aligned} \tag{21}$$

where

$$\mathbf{Z}^{mc[K]} = \sum_{rs} z_{rs}^{mc}\Big(\hat{E}_{rs}^{[K]} - \hat{E}_{sr}^{[K]}\Big), \tag{22}$$

where z_{rs}^{mc} are elements of the orbital resolution vector $\overrightarrow{z}$. The form of $\overrightarrow{z}$ depends on the method of resolution;[19] this will be discussed more in Sec. III. Equation (21) involves mixed [K] and [S] bases. In order to define $\vec{\phi}^{[Z]}(R)$ completely in the [S] basis, we effect the following transformation [compare Eqs. (38) and (39) from Ref. 19]:

$$\mathbf{Z}^{mc[K]} = \exp\Big[\mathbf{K}^{mc[S]}\Big]\mathbf{Z}^{mc[S]}\exp\Big[-\mathbf{K}^{mc[S]}\Big], \tag{23}$$

which gives us that

$$\vec{\phi}^{[Z]}(R) = \exp\Big[\mathbf{K}^{mc[S]}\Big]\exp\Big[\mathbf{Z}^{mc[S]}\Big]\vec{\phi}^{[S]}(R). \tag{24}$$

With this chain of bases traceable back to the analytic AOs, it is now possible to consider analytic differentiation of the Hamiltonian. We will assume that the rotation matrices are in the [S] basis unless otherwise noted.

2. Differentiation of the spin-orbit Hamiltonian

Continuing with Shepard's formalism,[19] a CI solution wavefunction in the resolved $[Z]$ basis can be expressed in the unresolved but orthogonal $[S]$ basis as

$$\Big|\psi_{CI}^{[Z]}(R)\Big\rangle = \exp\big(\hat{K}(R)\big)\exp\big(\hat{Z}(R)\big)\Big|\psi_{CI}^{[S]}(R_0)\Big\rangle. \tag{25}$$

We can use the commutator expansion and apply the Hellman-Feynman theorem to a differentiation with respect to nuclear displacement of this wavefunction at R. Evaluating the result at the reference geometry yields

$$\begin{aligned}&\Big\langle\psi_J^{[Z]}(R_0)\Big|\mathbf{H}_{so}^{[Z]}(R_0)^x\Big|\psi_I^{[Z]}(R_0)\Big\rangle\\ &\quad= \Big\langle\psi_J^{[S]}(R_0)\Big|\mathbf{H}_{so}^{[S]}(R_0)^x\Big|\psi_I^{[S]}(R_0)\Big\rangle\\ &\qquad+ \Big\langle\psi_J^{[S]}(R_0)\Big|\Big[\mathbf{H}_{so}^{[S]}(R_0), \mathbf{Z}^{mc}(R_0)^x\Big]\Big|\psi_I^{[S]}(R_0)\Big\rangle\\ &\qquad+ \Big\langle\psi_J^{[S]}(R_0)\Big|\Big[\mathbf{H}_{so}^{[S]}(R_0), \mathbf{K}^{mc}(R_0)^x\Big]\Big|\psi_I^{[S]}(R_0)\Big\rangle,\end{aligned} \tag{26}$$

where higher orders of commutators are zero at the reference geometry and the bra-ket notation indicates vector-matrix multiplication. Let us address the first term on the right-hand side of Eq. (26), the orthogonal basis derivative term, and then we shall address the final two terms, which are treated similarly to one another.

a. The first term: The orthogonal basis derivative term. The relativistic effects in the valence region can be approximated using a single-electron spin-orbit operator and a Relativistic Effective Core Potential (RECP),[27] which represent the repulsion of the core electrons, the spin-orbit interaction with the nucleus, the spin-orbit interaction with the core electrons, and the approximate multielectron spin-orbit interaction in the valence region.[20] As in Yabushita, Zhang, and Pitzer's approach,[20] we use the second-quantized form of the spin-orbit Hamiltonian,

$$\mathbf{H}_{so} = \sum_{r,\mu,s,\nu} h^{so}_{r\mu s\nu} E_{r\mu s\nu}, \tag{27}$$

where $E_{r\mu s\nu}$ is a one-body nonspin-averaged unitary group generator,[22] r and s are spatial molecular orbital indices, μ and ν are their respective spin variable indices, and the matrix $\mathbf{h}^{so}$ represents the operator $\hat{h}^{so}$, defined to be proportional to the single-electron spin-orbit operator,[20,28]

$$\hat{h}^{so} = \sum_{\gamma \in \{x,y,z\}} \Lambda_\gamma S_\gamma, \tag{28}$$

where

$$\vec{\Lambda} = -i\vec{q} = -i \sum_{A} \sum_{l_A}^{L_A} \xi_{A,l_A}(r_A) l_A \sum_{m=-l_A}^{l_A} |m l_A\rangle\langle l_A m|, \tag{29}$$

where $\xi_{A,lA}(r_A)$ contains the information from the spin-orbit potential for atom A.[28] The first term on the right-hand side of Eq. (26) can be reduced to

$$\begin{aligned}
&\Big\langle \psi_J^{[S]}(R_0) \Big| \mathbf{H}_{so}^{[S]}(R_0)^x \Big| \psi_I^{[S]}(R_0) \Big\rangle \\
&\quad = \sum_{r\mu s\nu} h^{so[S]x}_{r\mu s\nu} \Big\langle \psi_J^{[S]}(R_0) \Big| E_{r\mu s\nu} \Big| \psi_I^{[S]}(R_0) \Big\rangle \\
&\quad = \mathrm{Tr}\Big(\mathbf{h}^{so[S]x} \Big\langle \psi_J^{[S]}(R_0) \Big| \mathbf{E}_{\mu\nu} \Big| \psi_I^{[S]}(R_0) \Big\rangle \Big).
\end{aligned} \tag{30}$$

The derivative of the core potential integrals (including $\mathbf{h}^{so}$) is not in any integral program in the COLUMBUS suite; however, these terms are available in NWCHEM in C_1 symmetry.[29] When the matrix element in Eq. (30) is integrated over electronic coordinates between spin-orbitals, we see that[20]

$$h^{[S]so}_{r\mu s\nu} = \sum_{\gamma \in \{x,y,z\}} \Big\langle r^{[S]} \Big| \Lambda \Big| s^{[S]} \Big\rangle \langle \mu | s_\gamma | \nu \rangle, \tag{31}$$

where $r^{[S]}$ and $s^{[S]}$ indicate molecular orbitals in the [S] basis.

We can now rewrite the orthogonal basis derivative term

$$\Big\langle \psi_J^{[S]}(R_0) \Big| \mathbf{H}_{so}^{[S]}(R_0)^x \Big| \psi_I^{[S]}(R_0) \Big\rangle = \sum_{rs} \sum_{\gamma} \left[\begin{aligned} &\Big\langle r^{[S]}(r_e : R_0) \Big| \Lambda_\gamma^x \Big| s^{[S]}(r_e : R_0) \Big\rangle \\ &\quad \times \sum_{\mu\nu} \left(\langle \mu | s_\gamma | \nu \rangle \sum_{ij} \left(C_j^J C_i^I \Big\langle \varphi_j^{[S]}(r_e : R_0) \Big| E_{r\mu s\nu} \Big| \varphi_i^{[S]}(r_e : R_0) \Big\rangle \right) \right) \end{aligned} \right], \tag{32}$$

which we will separate into a spin-independent integral piece,

$$\Big(\Lambda_\gamma^{[S]}(R_0) \Big)^x_{rs} \equiv (-1)^\chi \Big\langle r^{[S]}(r_e : R_0) \Big| \Lambda_\gamma^x \Big| s^{[S]}(r_e : R_0) \Big\rangle, \tag{33}$$

and a spin-dependent density piece,

$$\Big(Z_\chi^{JI\,[S]}(R_0) \Big)_{rs} \equiv \sum_{\mu\nu} \langle \mu | \hat{s}_\chi | \nu \rangle \sum_{ij} C_j^J C_i^I \Big\langle \varphi_j^{[S]}(r_e : R_0) \Big| E_{r\mu s\nu} \Big| \varphi_i^{[S]}(r_e : R_0) \Big\rangle, \tag{34}$$

which is the *spin-dependent transition density matrix*. The spin functions are transformed to the x,y,z form. The elements in Eq. (34) are real when working in the real spherical N-electron basis, and the matrices in Eq. (33) are real analogous to the Cartesian core potential terms in Ref. 20. Thus, we see that the orthogonal basis derivative term [the first term in Eq. (26)] reduces to the trace of the matrices,

$$\Big\langle \psi_J^{[S]}(R_0) \Big| \mathbf{H}_{so}^{[S]}(R_0)^x \Big| \psi_I^{[S]}(R_0) \Big\rangle = Tr\Big(\mathbf{\Lambda}^{[S]}(R_0)^x \cdot \mathbf{Z}^{JI[S]}(R_0) \Big). \tag{35}$$

Following this formalism, the spin-dependent transition density matrices were coded into the program CIDEN in an experimental version of COLUMBUS at the Department of Defense Supercomputing Resource Center (DSRC) at Wright-Patterson AFB, OH,[30] and are traced with the derivatives of the spin-orbit potential integral matrices, $\mathbf{\Lambda}_\gamma$, in a modified version of NWCHEM at the same institution. (In NWCHEM, the core potential matrices and their accompanying analytic gradients are multiplied by i to force them to be real.)

b. The second and third terms. The nuclear dependence will now be dropped for brevity, and we are assuming that all quantities are evaluated at the reference geometry at which we are taking derivatives. Using Eqs. (20), (22), and (27), the second and third terms on the right-hand side of Eq. (26) can be rewritten as

$$\begin{aligned}
&\Big\langle \psi_J^{[S]} \Big| \Big[\mathbf{H}_{so}^{[S]}, \mathbf{Z}^{mcx} \Big] \Big| \psi_I^{[S]} \Big\rangle \\
&\quad = \sum_{rs} z^{mcx}_{rs} \Big\langle \psi_J^{[S]} \Big| \sum_{r'\mu s'\nu} h^{so[S]}_{r'\mu s'\nu} \big[\hat{E}_{r'\mu s'\nu}, \big(\hat{E}_{rs} - \hat{E}_{sr} \big) \big] \Big| \psi_I^{[S]} \Big\rangle
\end{aligned} \tag{36}$$

and

$$\left\langle \psi_J^{[S]} \middle| \left[\mathbf{H}_{so}^{[S]}, \mathbf{K}^{mcx} \right] \middle| \psi_I^{[S]} \right\rangle = \sum_{rs} k_{rs}^{mcx} \left\langle \psi_J^{[S]} \middle| \sum_{r'\mu s'\nu} h_{r'\mu s'\nu}^{so\,[S]} \left[\hat{E}_{r'\mu s'\nu}, \left(\hat{E}_{rs} - \hat{E}_{sr} \right) \right] \middle| \psi_I^{[S]} \right\rangle, \tag{37}$$

respectively. It has been shown by Belcher[12] that the term $\sum_{r'\mu s'\nu} h_{r'\mu s'\nu}^{so[S]} \left[\hat{E}_{r'\mu s'\nu}, \left(\hat{E}_{rs} - \hat{E}_{sr} \right) \right]$ appearing in both of these equations is equivalent to

$$\sum_{r'\mu s'\nu} h_{r'\mu s'\nu}^{so} \left[\hat{E}_{r'\mu s'\nu}, \left(\hat{E}_{rs} - \hat{E}_{sr} \right) \right] = 2 \sum_{t\mu\nu} h_{r\nu t\mu}^{so} \hat{E}_{t\mu s\nu} - 2 \sum_{t\mu\nu} h_{s\nu t\mu}^{so} \hat{E}_{t\mu r\nu}. \tag{38}$$

Each of the terms on the right-hand side of this equation is an element of a spin-contracted Fock matrix for the spin-orbit Hamiltonian. Using the same type of notation as Shepard,[19] let us define

$$\begin{aligned} \left(F_{so}^{JI[S]} \right)_{rs} &\equiv \sum_{t\mu\nu} h_{r\nu t\mu}^{so} \left\langle \psi_J^{[S]} \middle| \hat{E}_{t\mu s\nu} \middle| \psi_I^{[S]} \right\rangle \\ &= \sum_{t} \sum_{\gamma \in \{x,y,z\}} \left\langle r^{[S]} \middle| \Lambda_\gamma \middle| t^{[S]} \right\rangle \sum_{\nu\mu} \langle \nu | s_\gamma | \mu \rangle \left\langle \psi_J^{[S]} \middle| \hat{E}_{t\mu s\nu} \middle| \psi_I^{[S]} \right\rangle \\ &= \sum_{t} \sum_{\gamma \in \{x,y,z\}} \left(\Lambda_\gamma^{[S]} \right)_{rt} \left(Z_\gamma^{JI[S]} \right)_{ts} \end{aligned} \tag{39}$$

as the spin-orbit contribution to a generalized Fock matrix and also the *spin-orbit orbital gradient vector*

$$\left(f_{orb}^{JI\,so} \right)_{rs} \equiv 2 \left(\left(F_{so}^{JI[S]} \right)_{rs} - \left(F_{so}^{JI[S]} \right)_{sr} \right) \tag{40}$$

so that Eqs. (36) and (37) yield

$$\left\langle \psi_J^{[S]} \middle| \left[\mathbf{H}_{so}^{[S]}, \mathbf{Z}^{mcx} \right] \middle| \psi_I^{[S]} \right\rangle = \sum_{rs} z_{rs}^{mcx} \left(f_{orb}^{JI\,so} \right)_{rs} = \vec{z}^{\,mcx} \cdot \vec{f}_{orb}^{JI\,so} \tag{41}$$

and

$$\left\langle \psi_J^{[S]} \middle| \left[\mathbf{H}_{so}^{[S]}, \mathbf{K}^{mcx} \right] \middle| \psi_I^{[S]} \right\rangle = \sum_{rs} k_{rs}^{mcx} \left(f_{orb}^{JI\,so} \right)_{rs} = \vec{k}^{mcx} \cdot \vec{f}_{orb}^{JI\,so}, \tag{42}$$

respectively. Thus, Eq. (26) can be rewritten as

$$\begin{aligned} \left\langle \psi_J^{[Z]}(R_0) \middle| \mathbf{H}_{so}^{[Z]}(R_0)^x \middle| \psi_I^{[Z]}(R_0) \right\rangle = Tr\left(\mathbf{q}_\chi^{[S]}(R_0) \cdot \mathbf{Z}_\chi^{JI[S]}(R_0) \right) \\ + \vec{z}^{\,mcx} \cdot \vec{f}_{orb}^{JI\,so} + \vec{k}^{mcx} \cdot \vec{f}_{orb}^{JI\,so}. \end{aligned} \tag{43}$$

3. Orbital resolution vector

Two methods available in the COLUMBUS MCSCF program to specify $\vec{z}$ are natural orbital (NO) resolution and Q-Fock matrix resolution. Lischka *et al.* have shown that the derivatives of these orbital resolution parameters can be written in terms of the state-averaged MCSCF density matrix elements and their derivatives.[8,31] For NO resolution, we have

$$\vec{z}_{rs}^{\,NOx} = \frac{\bar{D}_{rs}^{[K]x}}{\bar{D}_{ss}^{[K]} - \bar{D}_{rr}^{[K]}}, \tag{44}$$

which uses the one-electron nonrelativistic MCSCF state-averaged density matrix, $\bar{\mathbf{D}}^{[K]}$, and for Q-Fock resolution, we have

$$\vec{z}_{rs}^{\,Qx} = \frac{\bar{Q}_{rs}^{[K]x}}{\bar{Q}_{ss}^{[K]} - \bar{Q}_{rr}^{[K]}}, \tag{45}$$

where the Q-Fock matrix is defined as

$$Q_{rs}^{[K]} \equiv 2h_{rs}^{[K]} + \sum_{tu} \left(2g_{rstu}^{[K]} - g_{rtsu}^{[K]} \right) \bar{D}_{tu}^{[K]}, \tag{46}$$

where $h_{rs}^{[K]}$ and $g_{rstu}^{[K]}$ are the one- and two-electron integrals in the $[K]$ basis.

a. The product $\vec{z}^{\,x} \cdot \vec{f}$. While the product of the orbital resolution vector gradient with the orbital gradient vector will remain the same for the nonrelativistic term (as in Ref. 8), the spin-orbit term from Eq. (41) will require a few modifications based on the results presented above. That product can be expressed as[19]

$$\vec{z}^{\,NOx} \cdot \vec{f}_{orb}^{JI\,so} = 2 \sum_{r>s} \bar{D}_{rs}^{[K]x} \left(\frac{\left(F_{so}^{JI} \right)_{rs} - \left(F_{so}^{JI} \right)_{sr}}{\bar{D}_{ss}^{[K]} - \bar{D}_{rr}^{[K]}} \right) \equiv \sum_{rs} \bar{D}_{rs}^{[K]x} \left(A_{so}^{D} \right)_{rs}, \tag{47}$$

$$\vec{z}^{\,Qx} \cdot \vec{f}_{orb}^{JI\,so} = 2 \sum_{r>s} Q_{rs}^{[K]x} \left(\frac{\left(F_{so}^{JI} \right)_{rs} - \left(F_{so}^{JI} \right)_{sr}}{Q_{ss}^{[K]} - Q_{rr}^{[K]}} \right) \equiv \sum_{rs} Q_{rs}^{[K]x} \left(A_{so}^{Q} \right)_{rs}, \tag{48}$$

where $\mathbf{F}_{\mathbf{so}}^{JI}$ was defined in Eq. (39). The result is that these terms are evaluated parallel to Shepard's formalism with the exception that the $\mathbf{A}_{so}^{X}$ matrices are substituted for the nonrelativistic variety.

The derivative of the Q-Fock matrix in Eq. (46) is

$$Q_{rs}^{[K]x} = 2h_{rs}^{[K]x} + \sum_{tu} \left(2g_{rstu}^{[K]x} - g_{rtsu}^{[K]x} \right) \bar{D}_{tu}^{[K]} + \sum_{tu} \left(2g_{rstu}^{[K]} - g_{rtsu}^{[K]} \right) \bar{D}_{tu}^{[K]x}. \tag{49}$$

When back transformed into the [S] basis, this derivative is[19,25]

$$\begin{aligned} Q_{rs}^{[K]x} = 2h_{rs}^{[S]x} &+ \sum_{tu} \left(2g_{rstu}^{[S]x} - g_{rtsu}^{[S]x} \right) \bar{D}_{tu}^{[S]} + 2\left\{ h^{[S]}; K^x \right\}_{rs} \\ &+ \sum_{tu} \left(2\left\{ g^{[S]}; K^x \right\}_{rstu} - \left\{ g^{[S]}; K^x \right\}_{rtsu} \right) \bar{D}_{tu}^{[S]} \\ &+ \sum_{tu} \left(2g_{rstu}^{[K]} - g_{rtsu}^{[K]} \right) \bar{D}_{tu}^{[K]x}, \end{aligned} \tag{50}$$

where $\{\mathbf{A};\mathbf{B}\} = \mathbf{AB} + \mathbf{B}^\dagger \mathbf{A}$. The following three types of terms exist in Eqs. (47) and (48):

1. terms involving derivatives of integral matrices,
2. terms involving derivatives of K, and
3. terms involving derivatives of the state-averaged MCSCF density matrices.

The natural orbital resolution will only involve the third type of term because it has no generalized Fock matrices.

b. Q-matrix terms, type 1. These terms have the form

$$\left(\vec{z}^{Qx}\cdot\vec{f}^{JI\,so}_{orb}\right)^{I} = \sum_{rs} 2h^{[S]x}_{rs}\left(A^{Q}_{so}\right)_{rs} + \sum_{rstu}\left(2g^{[S]x}_{rstu} - g^{[S]\,x}_{rtsu}\right)\bar{D}^{[S]}_{tu}\left(A^{Q}_{so}\right)_{rs}$$
$$= Tr\left(\mathbf{h}^{[S]x}\mathbf{D}^{JI\,Q}_{so}\right) + \tfrac{1}{2}Tr\left(\mathbf{g}^{[S]x}\mathbf{d}^{JI\,Q}_{so}\right) \tag{51}$$

with the definitions

$$\begin{aligned}\left(\mathbf{D}^{JI\,Q}_{so}\right)_{rs} &\equiv 2\left(A^{Q}_{so}\right)_{rs},\\ \left(\mathbf{d}^{JI\,Q}_{so}\right)_{rstu} &\equiv 2\left(A^{Q}_{so}\right)_{rs}\bar{D}^{[S]}_{tu} + 2\left(A^{Q}_{so}\right)_{tu}\bar{D}^{[S]}_{rs} - \tfrac{1}{2}\left(A^{Q}_{so}\right)_{rt}\bar{D}^{[S]}_{us}\\ &\quad - \tfrac{1}{2}\left(A^{Q}_{so}\right)_{ru}\bar{D}^{[S]}_{st} - \tfrac{1}{2}\left(A^{Q}_{so}\right)_{su}\bar{D}^{[S]}_{rt} - \tfrac{1}{2}\left(A^{Q}_{so}\right)_{st}\bar{D}^{[S]}_{ru}.\end{aligned} \tag{52}$$

c. Q-matrix terms, type 2. These terms have the form

$$\begin{aligned}\left(\vec{z}^{Qx}\cdot\vec{f}^{JI\,so}_{orb}\right)^{II} &= \sum_{rs} 2\left\{h^{[S]};K^{x}\right\}_{rs}\left(A^{Q}_{so}\right)_{rs} + \sum_{rstu}\Big(2\left\{g^{[S]};K^{x}\right\}_{rstu}\\ &\quad - \left\{g^{[S]};K^{x}\right\}_{rtsu}\Big)\bar{D}^{[S]}_{tu}\left(A^{Q}_{so}\right)_{rs}\\ &= Tr\left(\left\{h^{[S]};\mathbf{K}^{x}\right\}\mathbf{D}^{JI\,Q}_{so}\right) + \tfrac{1}{2}Tr\left(\left\{g^{[S]};\mathbf{K}^{x}\right\}\mathbf{d}^{JI\,Q}_{so}\right)\\ &= Tr\Big(\mathbf{K}^{x\dagger}\Big(\mathbf{h}^{[S]}\mathbf{D}^{JI\,Q}_{so} + \mathbf{D}^{Q\,JI}_{so}\mathbf{h}^{[S]} + \tfrac{1}{2}\mathbf{g}^{[S]}\mathbf{d}^{JI\,Q}_{so}\\ &\quad + \tfrac{1}{2}\mathbf{g}^{[S]}\mathbf{d}^{JI\,Q}_{so}\Big)\Big)\\ &= -2Tr\left(\mathbf{K}^{x}\mathbf{F}^{JI\,Q}_{so}\right)\\ &\equiv \vec{k}^{mc\,x}\cdot\vec{f}^{Q\,so}_{orb},\end{aligned} \tag{53}$$

where we have analogously defined

$$\mathbf{F}^{JI\,Q}_{so} \equiv \mathbf{h}^{[S]}\mathbf{D}^{JI\,Q}_{so} + \tfrac{1}{2}\mathbf{g}^{[S]}\mathbf{d}^{JI\,Q}_{so} \tag{54}$$

with definitions from Eq. (52).

d. Q-matrix terms, type 3. These terms have the form

$$\begin{aligned}\left(\vec{z}^{Qx}\cdot\vec{f}^{JI\,so}_{orb}\right)^{III} &= \sum_{rstu}\left(2g^{[K]}_{rstu} - g^{[K]}_{rtsu}\right)\bar{D}^{[K]x}_{tu}\left(A^{Q}_{so}\right)_{rs}\\ &= \sum_{tu}\left(Q^{A}_{so}\right)_{tu}\bar{D}^{[K]x}_{tu}\\ &= \sum_{n}\sum_{tu} p^{x}_{n}\left\langle n^{[K]}_{\perp}\middle|\left(Q^{A}_{so}\right)_{tu}\left(\hat{E}_{tu} + \hat{E}_{ut}\right)\middle|mc^{[K]}\right\rangle\\ &= \sum_{n} p^{x}_{n}\left\langle n^{[K]}_{\perp}\middle|2\mathbf{Q}^{A}_{so}\middle|mc^{[K]}\right\rangle\\ &\equiv \vec{p}^{x}\cdot\vec{f}^{JI\,Q\,so}_{csf},\end{aligned} \tag{55}$$

where $\left\langle n^{[K]}_{\perp}\right|$ is the complement space of the MCSCF solution vector $\left|mc^{[K]}\right\rangle$ and p^{x}_{n} are elements of the *CSF response vector* [see Eqs. (141) and (196) in Ref. 19 and Eq. (28) in Ref. 8 for full treatment], and we have defined

$$\left(\mathbf{Q}^{A}_{so}\right)_{rs} \equiv \sum_{tu}\left(2g^{[S]}_{rstu} - g^{[S]}_{rtsu}\right)\left(A^{Q}_{so}\right)_{rs}. \tag{56}$$

e. Natural orbital terms, type 3. These terms have the form

$$\begin{aligned}\left(\vec{z}^{NOx}\cdot\vec{f}^{JI\,so}_{orb}\right)^{III} &= \sum_{rs}\bar{D}^{[K]x}_{rs}\left(A_{so}\right)_{rs}\\ &= \sum_{n}\sum_{rs} p^{x}_{n}\left\langle n^{[K]}_{\perp}\middle|\left(A^{D}_{so}\right)_{rs}\left(\hat{E}_{rs} + \hat{E}_{sr}\right)\middle|mc^{[K]}\right\rangle\\ &= \sum_{n} p^{x}_{n}\left\langle n^{[K]}_{\perp}\middle|2\mathbf{A}^{D}_{so}\middle|mc^{[K]}\right\rangle\\ &\equiv \vec{p}^{x}_{n}\cdot\vec{f}^{JI\,D\,so}_{csf}.\end{aligned} \tag{57}$$

Combining Eqs. (51), (53), (55), and (57) into Eq. (43), we have the more refined form of the spin-orbit CI DCT,

$$\begin{aligned}\frac{\left\langle\psi^{[Z]}_{J}\middle|\mathbf{H}^{[Z]x}_{so}\middle|\psi^{[Z]}_{I}\right\rangle}{\Delta\varepsilon} &= \frac{1}{\Delta\varepsilon}\Bigg[\mathrm{Tr}\left(\mathbf{h}^{[S]x}\mathbf{D}^{JI\,Q}_{so}\right) + \tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{[S]x}\mathbf{d}^{JI\,Q}_{so}\right)\\ &\quad + \mathrm{Tr}\left(\mathbf{q}^{[S]x}_{\chi}\cdot\mathbf{Z}^{JI[S]}_{\chi}\right) + \left(\vec{k}^{x\,\dagger}\vec{p}^{x\,\dagger}\right)\begin{pmatrix}\vec{f}^{JI\,so}_{orb} + \vec{f}^{JI\,Q\,so}_{orb}\\ \vec{f}^{JI\,Qso}_{csf} + \vec{f}^{JI\,D\,so}_{csf}\end{pmatrix}\Bigg],\end{aligned} \tag{58}$$

which is analogous to Eq. (28) in Ref. 8 and Eq. (319) in Ref. 19.

4. Matrix turnover

We can simplify the final term in Eq. (58) by defining

$$\begin{aligned}\vec{\lambda}^{mc\,x} &\equiv \left(\vec{k}^{x\,\dagger}\vec{p}^{x\,\dagger}\right),\\ \vec{f}^{JI\,total}_{so} &\equiv \begin{pmatrix}\vec{f}^{JI\,so}_{orb} + \vec{f}^{JI\,Q\,so}_{orb}\\ \vec{f}^{JI\,Q\,so}_{csf} + \vec{f}^{JI\,D\,so}_{csf}\end{pmatrix}.\end{aligned} \tag{59}$$

$\vec{\lambda}^{mc\,x}$ is known as the *first-order response* of the MCSCF wavefunction and is shown by Shepard[19] following the method of Handy and Schaefer[32] to be equal to

$$\vec{\lambda}^{mc\,x} = -\vec{f}^{mc\,x}\left(\mathbf{G}^{mc}\right)^{-1};\vec{f}^{mc\,x} \equiv \begin{pmatrix}\vec{f}^{mc\,x}_{orb}\\ \vec{f}^{mc\,x}_{csf}\end{pmatrix} \tag{60}$$

at the reference geometry, where $\mathbf{G}^{mc}$ is the Hessian matrix, $\vec{f}^{mc}_{orb}$ is the orbital gradient vector, and $\vec{f}^{mc}_{csf}$ is the CSF gradient vector. Equivalent equations for the generalized coupled perturbed Hartree Fock (GCPHF) equations were derived by Balgaard and Jørgansen, who developed a quadratically convergent method (with respect to orbital variations) for MCSCF.[33] Thus, the last term in Eq. (58) is equal to

$$\left(\vec{k}^{x\,\dagger}\vec{p}^{x\,\dagger}\right)\begin{pmatrix}\vec{f}^{JI\,so}_{orb} + \vec{f}^{JI\,Q\,so}_{orb}\\ \vec{f}^{JI\,Qso}_{csf} + \vec{f}^{JI\,D\,so}_{csf}\end{pmatrix} = \vec{f}^{mc\,x}\left(\mathbf{G}^{mc}\right)^{-1}\vec{f}^{JI\,total}_{so}. \tag{61}$$

To the right-most matrix-vector product, we assign the symbol

$$\vec{\lambda}^{JI\,so} \equiv -\left(\mathbf{G}^{mc}\right)^{-1}\vec{f}^{JI\,total}_{so}, \tag{62}$$

which we separate into orbital and CSF pieces,

$$\vec{\lambda}^{mc\,x}\left(\mathbf{G}^{mc}\right)^{-1}\vec{f}^{JI\,total}_{so} = \vec{f}^{mc\,x}_{orb}\cdot\vec{\lambda}^{JI\,so}_{orb} + \vec{f}^{mc\,x}_{csf}\cdot\vec{\lambda}^{JI\,so}_{csf}, \tag{63}$$

where we have used the so-called *matrix turnover* rule where $\vec{\lambda}^{JI\,so}$ is defined in Ref. 32 in terms of the MCSCF GCPHF Hessian.

Analogous to Shepard's notation,[19] we assert that the orbital piece has the form

$$\vec{f}^{\,mcx}_{orb} \cdot \vec{\lambda}^{JI\,so}_{orb} = \mathrm{Tr}\left(\mathbf{h}^{[S]x}\mathbf{D}^{JI\,\Lambda}_{so}\right) + \tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{[S]x}\mathbf{d}^{JI\,\Lambda}_{so}\right), \tag{64}$$

where

$$\begin{aligned}\mathbf{D}^{JI\,\Lambda}_{so} &\equiv -\left\{\bar{\mathbf{D}}^{[S]};\boldsymbol{\Lambda}^{JI\,so}_{orb}\right\},\\ \mathbf{d}^{JI\,\Lambda}_{so} &\equiv -\left\{\bar{\mathbf{d}}^{[S]};\boldsymbol{\Lambda}^{JI\,so}_{orb}\right\},\end{aligned} \tag{65}$$

and $\boldsymbol{\Lambda}^{JI\,so}_{orb}$ is the matrix form of the vector $\vec{\lambda}^{JI\,so}_{orb}$. Similarly, we have

$$\vec{f}^{\,mc\,x}_{csf} \cdot \vec{\lambda}^{JI\,so}_{csf} = \mathrm{Tr}\left(\mathbf{h}^{[S]x}\mathbf{D}^{JI\,\lambda}_{so}\right) + \tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{[S]x}\mathbf{d}^{JI\,\lambda}_{so}\right), \tag{66}$$

where

$$\begin{aligned}\left(\mathbf{D}^{JI\,\lambda}_{so}\right)_{rs} &\equiv \sum_{n}\left(\lambda^{JI\,so}_{csf}\right)_{n}\langle n_{\perp}|\hat{E}_{rs}+\hat{E}_{sr}|mc\rangle,\\ \left(\mathbf{d}^{JI\,\lambda}_{so}\right)_{rstu} &\equiv \sum_{n}\left(\lambda^{JI\,so}_{csf}\right)_{n}\tfrac{1}{2}\langle n_{\perp}|\hat{e}_{rstu}+\hat{e}_{srtu}+\hat{e}_{rsut}+\hat{e}_{srut}|mc\rangle.\end{aligned} \tag{67}$$

Substituting the results from Eqs. (61), (63), (64), and (66) into Eq. (58), we find that the numerator of the spin-orbit CI DCT is

$$\begin{aligned}\Delta E f^{CI\,x}_{JI\,so} &= \left\langle \psi^{[Z]}_{J}\middle|\mathbf{H}^{[Z]x}_{so}\middle|\psi^{[Z]}_{I}\right\rangle\\ &= \mathrm{Tr}\left(\mathbf{h}^{[S]x}\left(\mathbf{D}^{JI\,Q}_{so}+\mathbf{D}^{JI\,\Lambda}_{so}+\mathbf{D}^{JI\,\lambda}_{so}\right)\right)\\ &\quad+\tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{[S]x}\left(\mathbf{d}^{JI\,Q}_{so}+\mathbf{d}^{JI\,\Lambda}_{so}+\mathbf{d}^{JI\,\lambda}_{so}\right)\right)+\mathrm{Tr}\left(\mathbf{q}^{[S]x}\cdot\mathbf{Z}^{JI\,[S]}\right),\end{aligned} \tag{68}$$

which we simplify as

$$\begin{aligned}\Delta E f^{CI\,x}_{JI\,so} &= \mathrm{Tr}\left(\mathbf{h}^{[S]x}\left(\mathbf{D}^{JI\,tot}_{so}\right)\right)+\tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{[S]x}\left(\mathbf{d}^{JI\,tot}_{so}\right)\right)\\ &\quad+\mathrm{Tr}\left(\mathbf{q}^{[S]x}\cdot\mathbf{Z}^{JI\,[S]}\right),\end{aligned} \tag{69}$$

where

$$\mathbf{D}^{JI\,tot}_{so} = \mathbf{D}^{JI\,Q}_{so}+\mathbf{D}^{JI\,\Lambda}_{so}+\mathbf{D}^{JI\,\lambda}_{so} \tag{70}$$

and

$$\mathbf{d}^{JI\,tot}_{so} = \mathbf{d}^{JI\,Q}_{so}+\mathbf{d}^{JI\,\Lambda}_{so}+\mathbf{d}^{JI\,\lambda}_{so}. \tag{71}$$

5. Transformation to the atomic basis

The three traces in Eq. (69) are in the $[S]$ basis and must be back-transformed to the atomic basis. First we evaluate them in the C basis at the reference geometry. The transition density matrices do not change; however, the integral matrices transform as[19,23]

$$\mathbf{h}^{[S]x} = \mathbf{h}^{[C]x} - \tfrac{1}{2}\left\{\mathbf{h}^{[C]};\mathbf{S}^{[C]x}\right\}, \tag{72}$$

leading to the transformation of Eq. (69),

$$\begin{aligned}\Delta E f^{CI\,x}_{JI\,so} &= \mathrm{Tr}\left(\mathbf{h}^{[C]x}\left(\mathbf{D}^{JI\,tot[C]}_{so}\right)\right)+\tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{[C]x}\left(\mathbf{d}^{JI\,tot[C]}_{so}\right)\right)\\ &\quad+\mathrm{Tr}\left(\mathbf{q}^{[C]x}\cdot\mathbf{Z}^{JI\,[C]}\right)-\tfrac{1}{2}\mathrm{Tr}\left(\left\{\mathbf{h}^{[C]},\mathbf{S}^{[C]x}\right\}\mathbf{D}^{JI\,tot[C]}_{so}\right)\\ &\quad-\tfrac{1}{4}\mathrm{Tr}\left(\left\{\mathbf{g}^{[C]},\mathbf{S}^{[C]x}\right\}\mathbf{d}^{JI\,tot\,[C]}_{so}\right)-\tfrac{1}{2}\mathrm{Tr}\left(\left\{\mathbf{q}^{[C]},\mathbf{S}^{[C]x}\right\}\cdot\mathbf{Z}^{JI\,[C]}\right).\end{aligned} \tag{73}$$

Shepard[19] has also shown that the fourth and fifth trace operations in Eq. (73) are equal to

$$\begin{aligned}\mathrm{Tr}\left(\left\{\mathbf{h}^{[C]};\mathbf{S}^{[C]x}\right\}\mathbf{D}^{JI\,tot\,[C]}_{so}\right) &= 2\mathrm{Tr}\left(\mathbf{S}^{[C]x}\mathbf{F}^{1\,JI\,[C]}_{so}\right),\\ \mathrm{Tr}\left(\left\{\mathbf{g}^{[C]};\mathbf{S}^{[C]x}\right\}\mathbf{d}^{JI\,tot\,[C]}_{so}\right) &= 4\mathrm{Tr}\left(\mathbf{S}^{[C]x}\mathbf{F}^{2\,JI\,[C]}_{so}\right),\end{aligned} \tag{74}$$

where $\mathbf{F}^{1\,JI\,[C]}_{so}$ and $\mathbf{F}^{2\,JI\,[C]}_{so}$ are effective Fock matrices defined as

$$\begin{aligned}\left(F^{1\,JI\,[C]}_{so}\right)_{rs} &\equiv \sum_{t} h^{[C]}_{rt}\left(D^{JI\,tot\,[C]}_{so}\right)_{ts},\\ \left(F^{2\,JI\,[C]}_{so}\right)_{rs} &\equiv \sum_{tuv} g^{[C]}_{rtuv}\left(d^{JI\,tot\,[C]}_{so}\right)_{stuv},\\ \left(F^{JI\,[C]}_{so}\right)_{rs} &\equiv \left(F^{1\,JI\,[C]}_{so}\right)_{rs}+\tfrac{1}{2}\left(F^{2\,JI\,[C]}_{so}\right)_{rs}.\end{aligned} \tag{75}$$

In a similar fashion, the last trace operation in Eq. (73) becomes

$$\mathrm{Tr}\left(\left\{\mathbf{q}^{[C]},\mathbf{S}^{x[C]}\right\}\cdot\mathbf{Z}^{JI\,[C]}\right) = 2\mathrm{Tr}\left(\mathbf{S}^{x[C]}\mathbf{F}^{JI\,[C]}_{so}\right) \tag{76}$$

using the Fock matrix defined in Eq. (39). Substituting Eqs. (74) and (76) into Eq. (73), the spin-orbit CI DCT is defined completely in terms of traces of products of integral and density matrices in the $[C]$ basis, whose form is equivalent in the atomic basis at the reference geometry. After the transformation of the matrices from the MCSCF molecular orbital basis to the AO basis, the spin-orbit CI DCT becomes

$$\begin{aligned}\Delta\varepsilon f^{CI\,x}_{JI\,so} &= \mathrm{Tr}\left(\mathbf{h}^{x[\chi]}\left(\mathbf{D}^{JI\,tot\,[\chi]}_{so}\right)\right)+\tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{x[\chi]}\left(\mathbf{d}^{JI\,tot\,[\chi]}_{so}\right)\right)\\ &\quad+\mathrm{Tr}\left(\mathbf{q}^{x[\chi]}\cdot\mathbf{Z}^{JI\,[\chi]}\right)-\mathrm{Tr}\left(\mathbf{S}^{x[\chi]}\left(\mathbf{F}^{JI\,tot\,[\chi]}_{so}+\mathbf{F}^{JI\,[\chi]}_{so}\right)\right).\end{aligned} \tag{77}$$

Liska *et al.* defined the nonrelativistic CI DCT with analogous nonrelativistic transition density and Fock matrices as[8]

$$\begin{aligned}\Delta\varepsilon f^{CI\,x}_{JI} &= \mathrm{Tr}\left(\mathbf{h}^{x[\chi]}\left(\mathbf{D}^{JI\,tot\,[\chi]}\right)\right)+\tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{x[\chi]}\left(\mathbf{d}^{JI\,tot\,[\chi]}\right)\right)\\ &\quad-\mathrm{Tr}\left(\mathbf{S}^{x[\chi]}\left(\mathbf{F}^{JI\,[\chi]}_{tot}\right)\right)\end{aligned} \tag{78}$$

and the nonrelativistic CSF DCT as

$$f^{CSF\,x}_{JI} = \mathrm{Tr}\left(\mathbf{D}^{JI[\chi]a}f^{CSF[\chi]x}_{orb}\right)+\mathrm{Tr}\left(\mathbf{h}^{[\chi]x}\mathbf{D}^{CSF\,JI}_{tot}\right)+\tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{[\chi]x}\mathbf{d}^{CSF\,JI}_{tot}\right), \tag{79}$$

to produce the full form of the nonrelativistic DCT,

$$\begin{aligned}\Delta\varepsilon f^{CI+CSF}_{JI} &= \mathrm{Tr}\left(\mathbf{h}^{x[\chi]}\left(\mathbf{D}^{JI\,[\chi]}_{tot}+\mathbf{D}^{CSF\,JI\,[\chi]}_{tot}\right)\right)\\ &\quad+\tfrac{1}{2}\mathrm{Tr}\left(\mathbf{g}^{x[\chi]}\left(\mathbf{d}^{JI\,[\chi]}_{tot}+\mathbf{d}^{CSF\,JI\,[\chi]}_{tot}\right)\right)\\ &\quad-\mathrm{Tr}\left(\mathbf{S}^{x[\chi]}\left(\mathbf{F}^{JI[\chi]}_{tot}\right)\right)+\Delta\varepsilon\mathrm{Tr}\left(\mathbf{D}^{JI[\chi]\,a}f^{CSF[\chi]x}_{orb}\right).\end{aligned} \tag{80}$$

Compare Eqs. (46)–(49) in Ref. 8; compare definitions of their effective transition density matrices to Eqs. (70) and (71) in this paper. To this, we add the new contribution from spin-orbit, Eq. (77),

$$\begin{aligned}\Delta\varepsilon f_{JI}^{CI+CSF} &= \mathrm{Tr}\Big(\mathbf{h}^{x[\chi]}\Big(\mathbf{D}_{tot}^{JI\,[\chi]} + \mathbf{D}_{tot}^{CSF\,JI\,[\chi]} + \mathbf{D}_{so}^{JI\,tot\,[\chi]}\Big)\Big)\\ &+ \mathrm{Tr}\Big(\mathbf{q}^{x[\chi]}\cdot\mathbf{Z}^{JI\,[\chi]}\Big)\\ &+ \tfrac{1}{2}\mathrm{Tr}\Big(\mathbf{g}^{x[\chi]}\Big(\mathbf{d}_{tot}^{JI\,[\chi]} + \mathbf{d}_{tot}^{CSF\,JI\,[\chi]} + \mathbf{d}_{so}^{JI\,tot\,[\chi]}\Big)\Big)\\ &- \mathrm{Tr}\Big(\mathbf{S}^{x[\chi]}\Big(\mathbf{F}_{tot}^{JI[\chi]} + \mathbf{F}_{so}^{JI\,tot\,[\chi]} + \mathbf{F}_{so}^{JI\,[\chi]}\Big)\Big)\\ &+ \Delta\varepsilon\mathrm{Tr}\Big(\mathbf{D}^{JI[\chi]\,a} f_{orb}^{CSF[\chi]x}\Big). \end{aligned} \tag{81}$$

For compactness of notation, let us add the new effective transition density matrices to the old such that

$$\begin{gathered}\mathbf{D}_{tot}^{JI[\chi]} + \mathbf{D}_{so}^{tot\,JI[\chi]} \to \mathbf{D}_{tot}^{JI[\chi]},\\ \mathbf{d}_{tot}^{JI[\chi]} + \mathbf{d}_{so}^{tot\,JI[\chi]} \to \mathbf{d}_{tot}^{JI[\chi]},\\ \mathbf{F}_{tot}^{JI[\chi]} + \mathbf{F}_{so}^{JI[\chi]} \to \mathbf{F}_{tot}^{JI[\chi]}\end{gathered} \tag{82}$$

to yield a cleaner formulation of the DCT,

$$\begin{aligned}\Delta f_{JI}^{CI+CSF+so\,x} &= \mathrm{Tr}\Big(\mathbf{h}^{x[\chi]}\Big(\mathbf{D}_{tot}^{JI\,[\chi]} + \mathbf{D}_{tot}^{CSF\,JI\,[\chi]}\Big)\Big) + \mathrm{Tr}\Big(\mathbf{q}^{x[\chi]}\cdot\mathbf{Z}^{JI\,[\chi]}\Big)\\ &+ \tfrac{1}{2}\mathrm{Tr}\Big(\mathbf{g}^{x[\chi]}\Big(\mathbf{d}_{tot}^{JI\,[\chi]} + \mathbf{d}_{tot}^{CSF\,JI\,[\chi]}\Big)\Big)\\ &- \mathrm{Tr}\Big(\mathbf{S}^{x[\chi]}\Big(\mathbf{F}_{tot}^{JI[\chi]} + \mathbf{F}_{so}^{JI[\chi]}\Big)\Big) + \Delta\varepsilon\mathrm{Tr}\Big(\mathbf{D}^{JI[\chi]\,a} f_{orb}^{CSF[\chi]x}\Big),\end{aligned} \tag{83}$$

where now inclusion of the spin-orbit effects is implied. It should be noted that this method, in setting $I = J$ and removing the last term, also calculates the analytic energy gradient for spin-orbit MRCI wavefunctions,

$$\begin{aligned}\varepsilon^x &= \mathrm{Tr}\Big(\mathbf{h}^{x[\chi]}\Big(\mathbf{D}_{tot}^{[\chi]} + \mathbf{D}_{tot}^{CSF[\chi]}\Big)\Big) + \mathrm{Tr}\Big(\mathbf{q}^{x[\chi]}\cdot\mathbf{Z}^{[\chi]}\Big)\\ &+ \tfrac{1}{2}\mathrm{Tr}\Big(\mathbf{g}^{x[\chi]}\Big(\mathbf{d}_{tot}^{[\chi]} + \mathbf{d}_{tot}^{CSF[\chi]}\Big)\Big) - \mathrm{Tr}\Big(\mathbf{S}^{x[\chi]}\Big(\mathbf{F}_{tot}^{[\chi]} + \mathbf{F}_{so}^{[\chi]}\Big)\Big).\end{aligned} \tag{84}$$

III. IMPLEMENTATION

In order to implement the formalism presented here, experimental versions of COLUMBUS and NWCHEM software suites were modified accordingly and tested with the KHe system. Results of that calculation will be presented in Paper II.[35] The outline of changes follows.

A. Atomic integrals

The calculation of spin-orbit DCTs requires derivatives of spin-orbit RECP integrals and potentials. In the current implementation in CIUDG, COLUMBUS typically uses one of the two integral programs: ARGOS, which is capable of handling spin-orbit potentials and integrals, or DALTON,[34] which can produce gradients of atomic integrals. ARGOS does not have RECP gradients and DALTON does not implement spin-orbit core potential integrals, so NWCHEM was leveraged to produce the spin-orbit integrals to be fed into COLUMBUS as well as to calculate the spin-orbit integral gradients used in the traces in Eq. (78). We used a modified version of NWCHEM to write the integrals, including RECP gradients, into the Standard Integral File System (SIFS) format used by all COLUMBUS programs. The disadvantage of using NWCHEM for integrals was that symmetry-adapted integrals were not available. This shortcoming required that all calculations be done in the C_1 symmetry group, thus increasing calculation time, memory, and space required.

B. MCSCF step

No change is needed for the MCSCF program, as this optimization takes place before spin-orbit effects are considered.

C. Diagonalization step

No change is made to the CIUDG program. The work of Yabushita, Zhang, and Pitzer[20] has already modified CIUDG to produce spin-orbit wavefunctions and eigenvalues.

D. Density matrices

Critical to the above formalism is the formation of transition density matrices. For nonspin-orbit calculations, this step is performed in the CIDEN program. Using the techniques implemented by Yabushita, Zhang, and Pitzer in CIUDG,[20] CIDEN has been modified to correctly interpret the multiheaded (multispin) spin-orbit distinct row tables (DRTs)[22] and to produce the (antisymmetric) spin-orbit transition density matrices, $\mathbf{Z}_{\chi}^{JI\,[Z]}(R_0)$, defined in Eq. (34). The algorithm for producing the nonrelativistic transition density matrices, $\mathbf{D}^{JI\,[Z]}(R_0)$ and $\mathbf{d}^{JI\,[Z]}(R_0)$, the one- and two-electron MRCI transition density matrices in the orbital resolved basis set,[8] has been modified to accept spin-orbit wavefunctions from CIUDG.

E. Effective density and Fock matrices

Effective density matrices and Fock matrices defined in Eqs. (52), (65), and (67) are computed in the CIGRD program. The spin-orbit Fock matrix, $\mathbf{F}_{so}^{JI[Z]}(R_0)$, as defined in Eq. (39) has been added to the output. The standard Fock matrices have been modified to include contributions from the spin-orbit integrals and density matrices early in the program. This inclusion effectively combines the spin-orbit effective density and Fock matrices, $\mathbf{D}_{so}^{tot\,JI[Z]}(R_0)$, $\mathbf{d}_{so}^{tot\,JI[Z]}(R_0)$, and $\mathbf{F}_{so}^{JI[Z]}(R_0)$, into their nonrelativistic counterparts, as these are built upon the Fock matrices [see, e.g., Eq. (47)].

F. Antisymmetric density matrices

The last term in Eq. (83) requires calculation of the antisymmetric portion of the one-electron transition density matrix, $\mathbf{D}^{JI\,[\chi]\,a}(R_0)$.[8] This is handled by the TRANSCI program. TRANSCI has been modified to correctly account for odd-electron spin-orbit systems.

Because DALTON could not, at the time of this work, calculate gradients of spin-orbit integrals, effective density and Fock matrices in the AO basis are passed back to NWCHEM to be traced with the appropriate integrals.

G. Antisymmetric DCT term

The final term in Eq. (83) is the trace of two antisymmetric matrices, $\mathbf{D}^{JI\,[\chi]\,a}(R_0)$ and $f_{orb}^{CSF[\chi]}(R_0)^x$. This term is unchanged from the nonrelativistic DCT, and thus, $f_{orb}^{CSF[\chi]}(R_0)^x$ can still be calculated in DALTON and traced with $\mathbf{D}^{JI[\chi]\ a}(R_0)$. At this time, integrating the calculation of $f_{orb}^{CSF[\chi]}(R_0)^x$ into NWCHEM is resource-prohibitive.

IV. CONCLUSION

We followed the formalism of Shepard, Lischka, and coworkers to derive formulas to analytically calculate DCTs of spin-orbit wavefunctions at the MRCI level, which are easily adapted to calculate the analytic energy gradients as well. An experimental implementation of this formalism shows that such a method is possible with small changes to the MRCI, DCT, and spin-orbit methods already in place in COLUMBUS. This new method combines the method of calculating nonrelativistic MRCI DCTs developed by Lischka *et al.* with the method of calculating spin-orbit wavefunctions of Yabushita, Zhang, and Pitzer. This implementation generalizes the current method for calculating MRCI DCTs with COLUMBUS to include wavefunctions with significant spin-orbit contributions.

With this formalism in place, spin-orbit energy gradients and DCTs can now be analytically calculated for large-atom systems where spin-orbit contributions to the Hamiltonian are non-negligible, such as open-shell systems like the alkali-noble-gas mixtures that may be used in DPALs. While the energy gradients will be useful in geometry optimization problems, the DCTs will provide diabatic potential energy surfaces for nuclear dynamics calculations. Our experimental implementation has been run using the KHe system, the results of which will be presented in Paper II.[35]

ACKNOWLEDGMENTS

We would like to acknowledge the High-Energy Laser Joint Technology Office, Albuquerque, NM, for their financial support of this effort. We would also like to thank the AFRL DoD Supercomputing Resource Center for computer resources. This material is based on the work supported by, or in part by, the Department of Defense High Performance Computing Modernization Program (HPCMP) under User Productivity Enhancement Technology Transfer, and Training (PETTT) Contract No. GS04T09DBC0017. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the DoD HPCMP, the Air Force, the Department of Defense, or the United States Government.

REFERENCES

[1] W. Krupke, R. Beach, V. Kanz, and S. Payne, Opt. Lett. **28**, 2336 (2003).
[2] B. V. Zhdanov, J. Sell, and R. J. Knize, Electron. Lett. **44**, 582 (2008).
[3] B. V. Zhsanov, T. Ehrenreich, and R. J. Knize, Opt. Commun. **260**, 696 (2006).
[4] R. H. Page, R. J. Beach, V. K. Kanz, and W. F. Krupke, Opt. Lett. **31**, 353 (2006).
[5] R. J. Beach, W. F. Krupke, V. K. Kanz, and S. A. Payne, J. Opt. Soc. Am. B **21**, 2151 (2004).
[6] T. Pascher, L. S. Cederbaum, and H. Köppel, Adv. Chem. Phys. **84**, 293 (1993).
[7] H. Köppel, Adv. Ser. Phys. Chem. **15**, 175 (2004).
[8] H. Lischka, M. Dallos, P. G. Szalay, D. R. Yarkony, and R. Shepard, J. Chem. Phys. **120**, 7322 (2004).
[9] B. H. Lengsfield III, P. Saxe, and D. R. Yarkony, J. Chem. Phys. **81**, 4549 (1984).
[10] P. Saxe, B. H. Lengsfield, and D. R. Yarkony, Chem. Phys. Lett. **113**, 159 (1985).
[11] L. Blank, D. E. Weeks, and G. S. Kedziora, J. Chem. Phys. **136**, 124315 (2012).
[12] L. T. Belcher, "Gradients and non-adiabatic derivative coupling terms for spin-orbit wavefunctions," Ph.D. dissertation (Air Force Institute of Technology, 2011).
[13] S. Matsika and D. R. Yarkony, J. Chem. Phys. **115**, 2038 (2001).
[14] S. Matsika and D. R. Yarkony, J. Chem. Phys. **116**, 2825 (2002).
[15] S. Matsika and D. R. Yarkony, J. Chem. Phys. **106**, 8108 (2002).
[16] M. R. Manaa and D. R. Yarkony, J. Chem. Phys. **100**, 8204 (1994).
[17] G. Parlant, J. Rostas, G. Taieb, and D. R. Yarkony, J. Chem. Phys. **93**, 6403 (1990).
[18] J. J. Dillon and D. R. Yarkony, J. Chem. Phys. **130**, 154312-1 (2009).
[19] R. Shepard, Mod. Eletron. Struct. Theory **1**, 345 (1995).
[20] S. Yabushita, Z. Zhang, and R. M. Pitzer, J. Chem. Phys. **103**, 5791 (1999).
[21] J. Paldus, J. Chem. Phys. **61**, 5321 (1974).
[22] I. Shavitt, in *The Unitary Group for the Evaluation of Electronic Energy Matrix Elements*, Lecture Notes in Chemistry Vol. 22, edited by J. Hinze (Springer, 1981), pp. 51–99.
[23] T. U. Helgaker and J. Almlöf, Int. J. Quantum Chem. **26**, 275 (1984).
[24] T. U. Helgaker, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, edited by P. Jørgensen and J. Simons (Clarendon Press, 1986), pp. 1–16.
[25] T. Helgaker, S. Coriani, P. Jørgensen, K. Kristensen, J. Olsen, and K. Rudd, Chem. Rev. **112**, 543 (2012).
[26] J. Olsen, K. L. Bak, K. Ruud, T. Helgaker, and P. Jørgensen, Theor. Chim. Acta **90**, 421 (1995).
[27] R. M. Pitzer and N. W. Winter, Int. J. Quantum Chem. **40**, 773 (1991).
[28] R. M. Pitzer and N. W. Winter, J. Phys. Chem. **92**, 3061 (1991).
[29] M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, and W. A. de Jong, Comput. Phys. Commun. **181**, 1477 (2010).
[30] AFRL DSRC, online at http://www.afrl.hpc.mil/.
[31] H. Lischka, M. Dallos, and R. Shepard, Mol. Phys. **100**, 1647 (2002).
[32] N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984).
[33] E. Dalgaard and P. Jørgensen, J. Chem. Phys. **69**, 3833 (1978).
[34] T. Helgaker, H. J. A. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Agren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Kock, K. V. Mikkelsen, P. Norman, M. J. Packer, T. Saue, P. R. Taylor, and O. Vahtras, DALTON, an *ab initio* electronic structure program, Release 1.0, 1997.
[35] L. T. Belcher, C. D. Lewis III, G. S. Kedziora, and D. E. Weeks, J. Chem. Phys. **151**, 234109 (2019).