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SOME COMMENTS ON DIFFERENT-ORBITALS-FOR-DIFFERENT-SPINS DETERMINANTS

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ABSTRACT

We have recently implemented the capability to compute the spin-density matrix within the COLUMBUS Program System[1]. This is currently for MCSCF wave functions, with plans to extend it to MRCI and MR-AQCC in the future. The COLUMBUS codes are based on the graphical unitary group approach (GUGA), a spin-free formulation, so the usual simple spin-orbital expression for the spin-density matrix elements,

$$D_{qp}^{[1,0;M]} = \langle \psi; S, M \left| \hat{a}_{p\alpha}^{\dagger} \hat{a}_{q\alpha} - \hat{a}_{p\beta}^{\dagger} \hat{a}_{q\beta} \right| \psi; S, M \rangle,$$

cannot be used directly. Instead, we compute the matrix elements from linear combinations of 1-RDM and 2-RDM elements that are already available within the MCSCF procedure. In this poster, I will discuss some of the details of this formulation, and I will show some results from our initial implementation. From the spin-density matrix the spatial spin-distribution may be computed.

$$\rho^{[-;M]}(\mathbf{r}) = \sum_{p,q} \varphi_q(\mathbf{r}) D_{qp}^{[1,0;M]} \varphi_p(\mathbf{r})^*$$

While comparing our results to previous calculations, we observed that most spin-density and spin-distribution calculations are formulated with unrestricted Hartree-Fock (UHF) and unrestricted Kohn-Sham (UKS) methods which are based on different-orbitals-for-different-spins (DODS) determinants. In these approaches, the spin-polarization, which contributes to the nonzero spin-density, is intrinsically associated with spin-contamination. Our GUGA results are done entirely with spin-eigenfunctions. This led to further investigation of what exactly is computed with these spin-contaminated formulations and how do those results relate to our spin-eigenfunction formulation. A new relationship was discovered between the cosine-sine decomposition (CSD) of an orthogonal matrix and the full spin-decomposition of spin-contaminated wave functions[2]. The CSD facilitates this spin-decomposition in three ways: 1) sparsity is introduced into the spin operators $\hat{S}_{+}$, $\hat{S}_{-}$, and $\hat{S}^2$, 2) the CSD allows the identification of frozen core and frozen virtual orbitals, effectively reducing the orbital dimension, and 3) it allows the spin-eigenfunction expansion space to be truncated. The poster will include additional details of the CSD, of the spin-decomposition procedure, and of the spin-density for DODS wave functions.

[1] "Spin-Density Calculation via the Graphical Unitary Group Approach," R. F. K. Spada, M. P. Franco, R. Nieman, A. J. A. Aquino, R. Shepard, F. Plasser, and H. Lischka, *Mol. Phys.* (submitted, 2022).

[2] "The Cosine-Sine Decomposition with Different-Orbitals-for-Different-Spins Determinants," R. Shepard, *Mol. Phys.* (2022). DOI: 10.1080/00268976.2022.2077853.

COLUMBUS SPIN-DENSITY

R. F. K. Spada, M. P. Franco, R. Shepard, F. Plasser, R. Nieman, A. J. A. Aquino, and H. Lischka, *Mol. Phys.* (submitted, 2022).

- Spin-density arises when computing spin-dependent properties ($\langle\hat{A}\rangle = Tr\left(\mathbf{D}^{(1,0;M)}\mathbf{A}^{(1,0)}\right)$, ESR and NMR spectra).
- The COLUMBUS MCSCF and MRCI codes are based on the Graphical Unitary Group Approach (GUGA).
- In GUGA, the spin-orbital occupation information is suppressed, and the wave function is represented entirely in terms of spatial orbitals.
- This makes quantities such as the spin-density difficult to formulate.

$$D_{qp}^{(1,0;M)} = \left\langle \psi; S, M \middle| \hat{a}_{p\alpha}^{\dagger}\hat{a}_{q\alpha} - \hat{a}_{p\beta}^{\dagger}\hat{a}_{q\beta} \middle| \psi; S, M \right\rangle$$

- The *S*=*M* multiplet member can be computed with spin-independent quantities:

$$D_{qp}^{(1,0;S)} = \frac{(2 - ½N)}{S+1} D_{qp}^{(0,0)} - \frac{1}{S+1}\sum_{k} d_{qkkp}$$

- Other *M* multiplet members are given by: $D_{qp}^{(1,0;M)} = \frac{M}{S} D_{qp}^{(1,0;S)}$

MCSCF SPIN-DENSITY

- The 1-RDM and 2-RDM elements $D_{qp}^{(0,0)}$ and d_{qkkp} are already available within the MCSCF procedure.
- We have now implemented spin-density computation in the COLUMBUS MCSCF program.
- If the orbitals are chosen to diagonalize $\mathbf{D}^{(1,0;S)}$, then the wave function is formulated in terms of the natural spin-density orbitals. These are the orbitals that display the most extreme spin-density values.

MCSCF SPIN-DENSITY

- The spin-distribution is the spatial representation of the spin-density.

$$\rho(\mathbf{r})^{(-;M)} = \boldsymbol{\varphi}(\mathbf{r})\mathbf{D}^{(1,0;M)}\boldsymbol{\varphi}(\mathbf{r})^{\dagger} = \sum_{pq} \varphi_q(\mathbf{r}) D_{qp}^{(1,0;M)} \varphi_p^*(\mathbf{r})$$

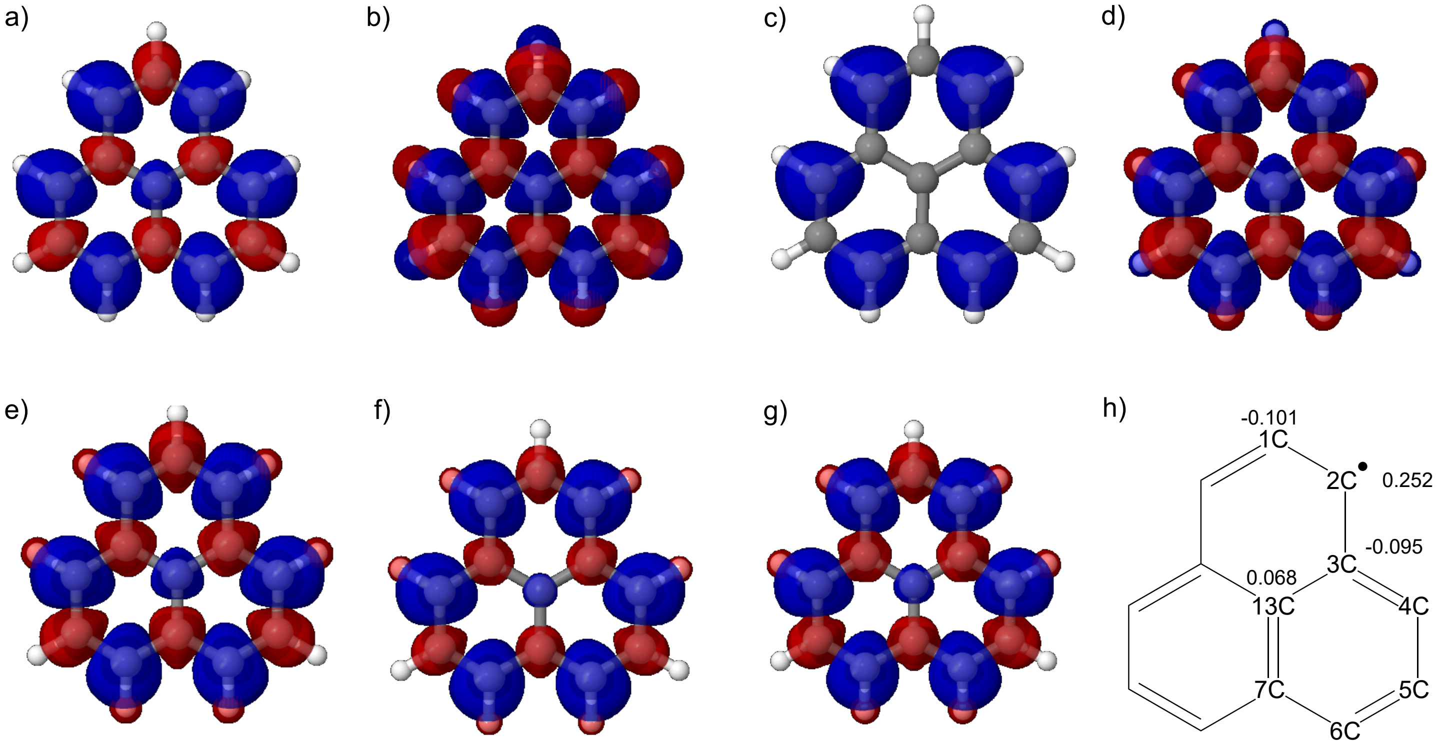
- Positive regions are α-rich, and negative regions are β-rich.
- Most studies involving spin-density are with UHF or UDFT based methods.
- In these methods, spin-polarization of the orbitals is closely associated with spin-contamination of the wave function.
- Our COLUMBUS implementation is with correlated spin-eigenfunctions.

MCSCF SPIN-DENSITY

Z.D. Levey, B.A. Laws, S.P. Sundar, K. Nauta, S.H. Kable, G. da Silva, J.F. Stanton, and T.W. Schmidt, J. Phys. Chem. A 126 (1), 101–108 (2022).

- Spin-distribution of the Phenalenyl radical $C_{13}H_9$, $S=M=½$, $^2A''_1/^2A_2$.

PAH Soot Precursor, Interstellar Grains, Global Warming, Solar Energy Conversion, Energy Storage, Organic Electronics, Quantum Computing.



a) MCSCF; b) UHF; c) RHF; d-g) UDFT with varying amount of HFX.

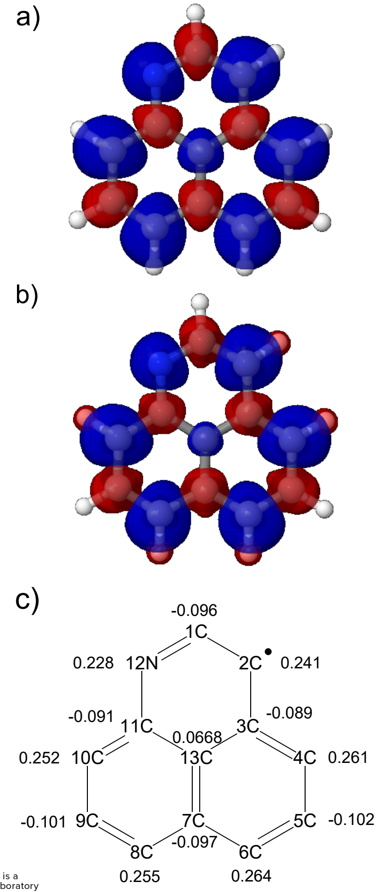
UHF and UDFT results are from Q-Chem

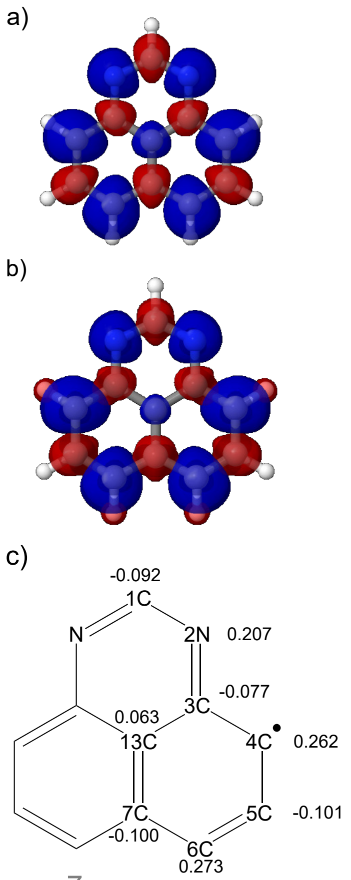
MCSCF SPIN-DENSITY

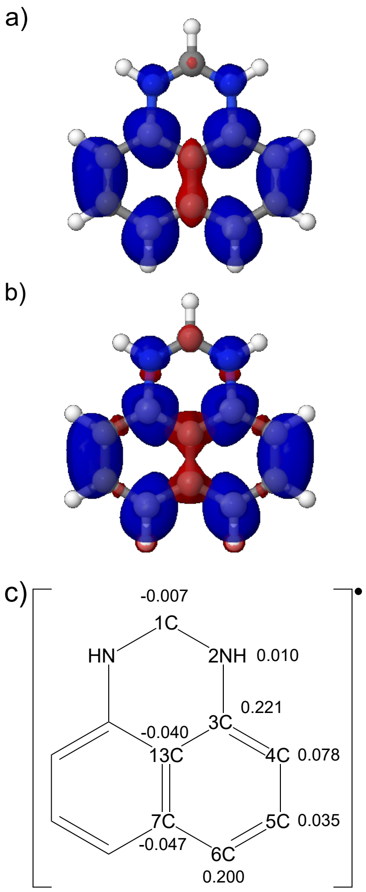
Substitutions: $C_{12}NH_8$ $C_{11}N_2H_7$ $C_{11}N_2H_9$

MCSCF:

UDFT:







MCSCF SPIN-DENSITY

- We also define spin-promotion distributions and a spin-promotion numbers (F. Plasser).
- Similar to the electronic excitation analysis in: M. Head-Gordon, A. M. Grafia, D. Maurice, and C. A. White, J. Phys. Chem. 99, 14261 (1995).

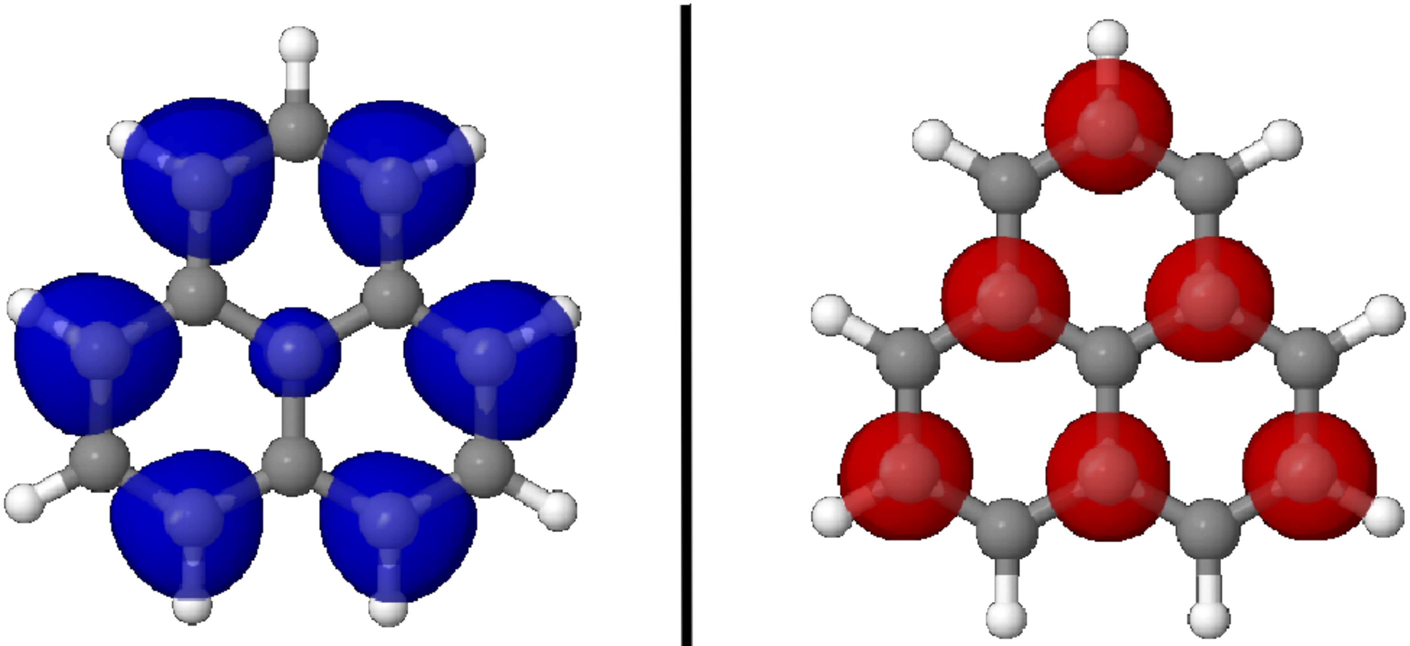
$$
\begin{aligned}
\rho(\mathbf{r})^{(-;S)} &= \boldsymbol{\varphi}(\mathbf{r})\mathbf{D}^{(1,0;S)}\boldsymbol{\varphi}(\mathbf{r})^{\dagger} \\
&= (\boldsymbol{\varphi}(\mathbf{r})\mathbf{U})\left(\mathbf{U}^{\dagger}\mathbf{D}^{(1,0;S)}\mathbf{U}\right)\left(\mathbf{U}^{\dagger}\boldsymbol{\varphi}(\mathbf{r})^{\dagger}\right) \\
&= \boldsymbol{\varphi}'^{(\mathbf{r})}\boldsymbol{\mu}^{(S)}\boldsymbol{\varphi}'(\mathbf{r})^{\dagger} = \sum_{p}\left|\varphi'_{p}(\mathbf{r})\right|^{2}\mu_{p}^{(S)} \\
&= \sum_{p}^{(\in\boldsymbol{\mu}^{(+;S)})}\left|\varphi'_{p}(\mathbf{r})\right|^{2}\mu_{p}^{(S)} + \sum_{q}^{(\in\boldsymbol{\mu}^{(-;S)})}\left|\varphi'_{q}(\mathbf{r})\right|^{2}\mu_{q}^{(S)} \\
&= \rho_{+}^{(-;S)}(\mathbf{r}) + \rho_{-}^{(-;S)}(\mathbf{r})
\end{aligned}
$$

- Integration of the spin-promotion distributions over space gives the spin-promotion numbers:

$$
p_{\pm}^{(S)} = \sum_{q}^{(\in\boldsymbol{\mu}^{(\pm;S)})}\mu_{q}^{(S)}
$$

MCSCF SPIN-DENSITY

- Spin-promotion distributions and numbers for the Phenalenyl radical:



$p_{+}^{(1/2)} = 1.564\ e$

$p_{-}^{(1/2)} = -\ 0.564\ e$

UHF SPIN-DENSITY

- Within a spin multiplet, the MCSCF spin-density matrix satisfies:

$$D_{qp}^{(1,0;M)} = \frac{M}{S} D_{qp}^{(1,0;S)}.$$

- This means that $\mathbf{D}^{(1,0;0)} = \mathbf{0}$. The corresponding spin-distribution is

$$\rho(\mathbf{r})^{(-;0)} = \boldsymbol{\varphi}(\mathbf{r})\mathbf{D}^{(1,0;0)}\boldsymbol{\varphi}(\mathbf{r})^{\dagger} = 0.$$

- A spin-contaminated wave function can be decomposed as

$$|\psi;*,M\rangle = \sum_{S=S_{\min}}^{S_{\max}} x_S |\psi;S,M\rangle$$

with $S_{\min} = |M|$ and $S_{\max} = \min(½N, n - ½N)$.

UHF SPIN-DENSITY

- For *M*=0, a spin-contaminated wave function can have a nonzero spin-density. Consider a UHF determinant:

$$\uparrow \mathrm{H} - \mathrm{R} - \mathrm{H} \downarrow$$

- How does this nonzero spin-density arise in the DODS spin-eigenfunction expansion?

- In the DODS basis, the spin-density operator has the form

$$\hat{D}^{1,0}_{qp} = \hat{a}^{\dagger}_{p\alpha}\hat{a}_{q\alpha} - \sum_{rs} X_{pr}X_{qs}\hat{a}^{\dagger}_{r\beta}\hat{a}_{s\beta}$$

UHF SPIN-DENSITY

$$D_{qp}^{(1,0;M)} = \langle \psi;*,M | \widehat{D}_{qp}^{1,0} | \psi;*,M \rangle = \sum_{S=S_{\min}}^{S_{\max}} \sum_{S'=S_{\min}}^{S_{\max}} x_S x_{S'} \langle \psi;S,M | \widehat{D}_{qp}^{1,0} | \psi;S',M \rangle$$

$$= \sum_{S=S_{\min}}^{S_{\max}} x_S^2 \langle \psi;S,M | \widehat{D}_{qp}^{1,0} | \psi;S,M \rangle + \sum_{S=S_{\min}}^{S_{\max}-1} x_S x_{S+1} \langle \psi;S,M | \widehat{D}_{qp}^{1,0} | \psi;S+1,M \rangle$$
$$+ \sum_{S=S_{\min}+1}^{S_{\max}} x_S x_{S-1} \langle \psi;S,M | \widehat{D}_{qp}^{1,0} | \psi;S-1,M \rangle$$

- The summation simplifies because the triple $(S,1,S')$ must satisfy the triangle inequality.
- The S=$|M|$ term in the first summation is the correct matrix element; everything else is due to spin-contamination of the wave function.

UHF SPIN-DENSITY

- For *M*=0, the first summation vanishes.

$$D_{qp}^{(1,0;0)} = \sum_{S=S_{\min}}^{S_{\max}-1} x_S x_{S+1} \left\langle \psi; S, 0 \middle| \widehat{D}_{qp}^{1,0} + \widehat{D}_{pq}^{1,0} \middle| \psi; S+1,0 \right\rangle$$

- The entire contribution is due to the off-diagonal spin-contamination terms.
- Integration of the DODS spin-distribution over space gives

$$\int \rho^{(-)}(\mathbf{r}) d\mathbf{r} = N_\alpha - N_\beta = 2M = 0$$

- For a spin-eigenfunction with *M*=0, the spin-distribution is zero at each point in space; for a spin-contaminated wave function, it is only the integral over all space that is zero.

COSINE-SINE DECOMPOSITION

- The previous spin-density work revealed a new relation between the Cosine-Sine Decomposition (CSD) and Spin-Projection of wave functions with different-orbitals-for-different-spins (DODS) determinants.
  R. Shepard, *Mol. Phys.* (2022). DOI: 10.1080/00268976.2022.2077853.
- The full spin-decomposition may be performed as

$$|\psi;*,M\rangle = \sum_{S=S_{\min}}^{S_{\max}} x_S|\psi;S,M\rangle = \sum_{S=S_{\min}}^{S_{\max}} \hat{P}_S|\psi;*,M\rangle$$

- with

$$\hat{P}_S = \prod_{S'=S_{\min}}^{S_{\max}(S'\neq S)} \frac{\hat{S}^2 - S'(S'+1)}{S(S+1) - S'(S'+1)} = \Lambda_0 + \Lambda_1\hat{S}^2 + \Lambda_2\left(\hat{S}^2\right)^2 + \cdots$$

COSINE-SINE DECOMPOSITION

- The effort required for Krylov space generation

$$\left(\hat{S}^2\right)^k |\psi;*,M\rangle = \hat{S}^2\left(\left(\hat{S}^2\right)^{k-1}|\psi;*,M\rangle\right)$$

- depends on the sparsity of the matrix $\mathbf{X}$ where $\boldsymbol{\varphi}^{[\beta]} = \boldsymbol{\varphi}^{[\alpha]}\mathbf{X}$.

$$\hat{S}_+ = \hat{S}_-^\dagger = \sum_{pq} X_{pq}\hat{a}_{p\alpha}^\dagger \hat{a}_{q\beta} \qquad \hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z(\hat{S}_z+1)$$

- A UHF wave function is invariant to orthogonal orbital transformations of the form:

$$\boldsymbol{\varphi}'^{[\alpha]} = \boldsymbol{\varphi}^{[\alpha]}\begin{pmatrix}\mathbf{U}_{oo} & 0 \\ 0 & \mathbf{U}_{vv}\end{pmatrix}$$

$$\boldsymbol{\varphi}'^{[\beta]} = \boldsymbol{\varphi}^{[\beta]}\begin{pmatrix}\mathbf{V}_{oo} & 0 \\ 0 & \mathbf{V}_{vv}\end{pmatrix}$$

COSINE-SINE DECOMPOSITION

- When this transformation is applied to the orbitals, the matrix $\mathbf{X}$ transforms as:

$$\begin{pmatrix} \mathbf{X'}_{oo} & \mathbf{X'}_{ov} \\ \mathbf{X'}_{vo} & \mathbf{X'}_{vv} \end{pmatrix} = \begin{pmatrix} \mathbf{U}^T_{oo} & 0 \\ 0 & \mathbf{U}^T_{vv} \end{pmatrix} \begin{pmatrix} \mathbf{X}_{oo} & \mathbf{X}_{ov} \\ \mathbf{X}_{vo} & \mathbf{X}_{vv} \end{pmatrix} \begin{pmatrix} \mathbf{V}_{oo} & 0 \\ 0 & \mathbf{V}_{vv} \end{pmatrix}.$$

- If the blocks of $\mathbf{U}$ and $\mathbf{V}$ are chosen according to the CSD procedure, then $\mathbf{X}'$ takes a sparse form in which each row or column has only 1 or 2 nonzero elements.

$$\begin{array}{cc} & \begin{array}{cc} \overbrace{n_1 \quad n_\theta \quad n_2}^{N_\beta} & \overbrace{n_3 \quad n_\theta \quad n_4}^{n_v^\beta} \end{array} \\ \begin{array}{c} N_\alpha \left\{ \begin{array}{c} n_1 \\ n_\theta \\ n_4 \end{array} \right. \\ n_v^\alpha \left\{ \begin{array}{c} n_3 \\ n_\theta \\ n_2 \end{array} \right. \end{array} & \left(\begin{array}{ccc|ccc} \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{C} & \mathbf{0} & \mathbf{0} & -\mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{1} \\ \hline \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} & \mathbf{0} & \mathbf{0} & \mathbf{C} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \end{array} \right) \end{array}$$

COSINE-SINE DECOMPOSITION

- The CSD simplifies the spin-decomposition procedure in three ways:

  1) The sparse $\mathbf{X}'$ reduces the storage and the number of floating point operations;

  2) The CSD identifies frozen core and frozen virtual orbitals, which may be ignored during the spin-decomposition process, reducing the effective N' and n';

  3) The upper range of the spin expansion may be reduced due to the frozen orbitals:

$$S'_{\mathrm{max}} = min(½N', n' - ½N').$$

SUMMARY

- The MCSCF spin-density computation provides interesting insights into electronic wave functions.
- The spin-density computation will be extended to MRCI and MR-AQCC within COLUMBUS. With these accurate wave functions, we can explore the role of spin-density in chemical reactivity in radical-radical and radical-ion reactions.
- The spin-promotion densities, spin-promotion distributions, and spin-promotion numbers provide useful analysis tools that will be studied further.
- The spin-decomposition process provides insight into the nature of UHF, UDFT, and DODS wave functions and associated molecular properties.
- The Cosine-Sine Decomposition simplifies the application of DODS spin operators and the computation of other related properties.

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